ISEC'88

INTERNATIONAL
SOLVENT EXTRACTION
CONFERENCE

Moscow, USSR
July 18-24, 1988

Conference Papers
Volume I

USSR Academy of Sciences

International Committee for Solvent Extraction
Chemistry and Technology

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INTERNATIONAL SOLVENT EXTRACTION CONFERENCE (ISEC'88).
Conference Papers:

Volume I
             Plenary Lectures
         1. Fundamentals
         2. Extractants

Volume II
         3. Interphase Phenomena, Mass Transfer
            and Kinetics
         4. Equipment
         5. Modelling and Control

Volume III
         6. Liquid Membranes
         7. Metal Extraction
         8. Organic and Bioorganic Processes

Volume IV
         9. Analytical Chemistry
        10. Nuclear Processes
        11. Hydrometallurgy

PREFACE

Liquid-liquid extraction is one of the most important methods of separation, it plays an essential part in nuclear technology, hydrometallurgy, oil processing, analytical chemistry. The theory of solvent extraction processes is a highly interesting field of research, which is connected with many branches of science. A great number of first class scientists and engineers work in the field of solvent extraction.

The problems of the development of the method are regularly discussed at International Solvent Extraction Conferences(ISEC). The Conferences are sponsored by the International Committee for Solvent Extraction Chemistry and Technology, which is based on national organizations. The previous two conferences took place in Denver, Colorado, USA, in 1983 and in Munich, FRG, in 1986. A great part in the organization of many conferences and in the activities of the International Committee was played by late Karl Hanson, Professor of Bradford University, UK.

The present book contains extended abstracts of the presentations, contributed to the Conference of 1988 (Moscow, July 18-24, 1988). According to the tradition, the materials are rather detailed, the book actually combines laconic scientific papers. The ISEC'88 papers are published not after the Conference, as its conclusion, but before the event, thus serving mainly as an auxiliary source of information for the participants. However, when the Conference is finished, this three-volume publication gains the statute of a usual scientific book. The circulation of the book is sufficient for being available in large libraries of many countries.

The papers are arranged in a certain logical sequence, corresponding to their scientific contents. The No of a presentation corresponds to its number in the program of the Conference, thus enabling the participants to find easily the desired paper.

Almost all the papers are reproduced in the original form, as presented by the authors. Only in some cases, when the materials were prepared in poor English or badly typed, the Editorial Board of the Conference Committee edited and retyped the manuscripts. We were not able to discuss the new texts with the authors because of the lack of time, so we apologize for probable mistakes.

3

The choice of papers was done by the Program Commission of the Conference Committee, which included Prof. G.V.Korpusov, Prof. A.M.Rozen, and others. The Editorial Board included E.P.Shumilova, N.G.Vanifatova and other collaborators from Vernadsky Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences, which took over the functions of the base institution of the Conference. We take the chance to extend our gratutude to the administration of the Institute (Prof.V.L.Barsukov, Prof.B.F.Myasoedov) and all the above mentioned and not mentioned here colleagues.

Professor Yu.A.Zolotov,
Conference Chairman

Doctor B.Ya.Spivakov,
Scientific Secretary

PLENARY
LECTURES

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Studies in the field of liquid-liquid extraction are being carried out in the USSR during a long period of time, on a large scale and, perhaps, with not so bad results. Practical applications of the extraction are also quite significant, first, in nuclear technology and radiochemistry, analytical chemistry, technology of rare metals, petrochemistry and some other fields.

History. Russian works in the field of extraction have a history beginning in the last century. A.A.Yakovkin defended his Master's thesis "On the distribution of substances between solvents" in 1895. The main results of the work were published a year later [1]. K.V. Kharichkov used the extraction as a method in the petroleum investigations at the beginning of this century. In twenties, to follow up Bertelot-Nernst-Yakovkin line, N.A.Shilov and his co-worker Lidia K. Lepin' have studied theoretical aspects of substance distribution between two liquid phases.

In thirties, extraction-photometric methods using dithizone penetrated into analytical chemistry. The first Soviet publications in this field belonged to I.B. Suprunovich who worked in Dnepropetrovsk. Before the World War II several papers on dithizone have been published in Russian and Ukrainian. Just after the war, the number of publications on the extraction of dithizonates significantly increased; among them a series of papers by A.K.Babko and A.T.Pilipenko are worth mentioning [2].

At the beginning of fifties, solvent extraction was considered to be a very effective and perspective method. This was greatly promoted by its successful and very important application in nuclear technology. The first Soviet open publications in this field refer to the period of the First Geneva Conference on Peaceful Use of Atomic Energy (1955). For instance, the theoretical paper by A.M.Rozen [3] should be mentioned as well as the series of papers by V.V.Fomin and co-workers, pacticularly on the study of complex formation using solvent extraction [4], works of Radium Institute in Leningrad headed by V.M.Vdovenko and, of course, presentations at the Geneva Conference itself. The first books on the extraction in Russian were published in the end of fifties and at the beginning of sixties:the collection of papers "Solvent Extraction" edited by A.G.Kasatkin (1958), the monograph by V.V.Fomin "Chemistry of Extraction Processes" (1960), the translation of the book by G.Morrison and H.Freiser "Solvent Extraction in Analytical Chemistry" (1960). Then a broad flow of books appeared.

Scientific directions and main achievements. The solvent extrac-
tion is being developed in the USSR in various directions: chemical
theoretical bases of the method, new extractants, mass transfer and
kinetics; mathematical modelling; membrane techniques; equipment;
extraction of metals; organic substances and biomaterials; extrac-
tion methods in analytical chemistry; radiochemistry and nuclear
technology; in hydrometallurgy of nonferrous and rare metals.

However, various directions are presented differently. This co-
untry seems to have the leading positions in some aspects: chemical
theoretical fundamentals of the method, new extractants, extraction
kinetics, metal extraction, application in analytical chemistry,
nuclear technology and hydrometallurgy of several rare metals. There
are fields that are presented in a smaller degree: mathematical mo-
delling, membrane extraction, application in hydrometallurgy of com-
mon nonferrous metals.

A great material has been accumulated in the field of chemical
fundamentals of extraction, a series of important generalizations
has been made, many problems have been successfully solved. A great
deal of publications has been devoted to this field, including mono-
graphs. Examples of certain achievements: the study of extraction
ability of phosphoryl-containig compounds, amines and other extrac-
tants as a function of molecule structure and diluent nature; in-
vestigation of the mutual influence of elements; so called binary
extraction; new extraction systems including two-phase aqueous ones
should be mentioned.

Broad investigations in the field of chemical theoretical bases
of the solvent extraction are carried out in All-Union Scientific-
Research Institute of Inorganic Materials (IIM,Moscow), Moscow Men-
deleev Institute of Chemical Technology (MICT), Vernadsky Institute
of Geochemistry and Analytical Chemistry (Moscow), All-Union Insti-
tute of Chemical Technology (ICT,Moscow), Leningrad Technological
Institute, Institute of Inorganic Chemistry in Novosibirsk (IIC),
Institute of Chemistry and Chemical Technology in Krasnoyarsk (ICCT),
Lomonosov Moscow State University (MSU) and in many other institu-
tions.

New extractants are being discovered continiously. Sulfides and
sulfoxides have been proposed and thoroughly investigated in the
Institute of Chemistry in Ufa and in IIC in Novosibirsk. Organome-
tal extractants, particullaly organotin compounds have been sug-
gested in Vernadsky Institute. Recently, IIC in Novosibirsk has
contributed to the study of unsaturated organic compounds as extrac-
tants forming $\mathcal{K}$-complexes with metals. Much has been done in IIM
and ICT in the field of extractants on the basis of phosphoric
acids. New effective macrocyclic extractants have been suggested
in Vernadsky Institute and MSU. Extractants of the phenolic type

9

are studied in Moscow Institute of Fine Chemical Technology (MIFCT). An interesting series of investigations of 8-mercaptoquinoline and many of its derivatives has been carried out in the Institute of Inorganic Chemistry of the AS of Latvian SSR (IIC in Riga).

Wide and original investigations have been carried out in the field of extraction kinetics and interphase phenomena under leadership of G.A.Yagodin in MICT (at the first stage - in Vernadsky Institute). Specialists in Karpov Research Physico-Chemical Institute deal with mathematical modelling of extraction processes (M.G. Slinko et al.). A.M.Rozen in IIM has proposed a new approach for the scale-up calculations. Studies in MICT (V.V.Kafarov et al.) in chemical cybernetics should be noted.

There are two centers of membrane extraction: IIC in Riga (B.A. Purin et al.) and MICT (S.Yu.Ivakhno et al.). Emulsion membranes are mainly used in MICT while supported membranes or traditional three-chamber version with liquid ones - in Riga. So called electroextraction is also utilised in IIC, that is separation through membranes in electrical field. Electrodialysis is developed in Leningrad (L.N.Moskvin).

Great is the volume of investigations in the field of metal extraction. An extraction method of rare earth element separation, developed in the Institute of Physical Chemistry of AS of the USSR (IPC, Moscow) in the end of fifties was one of the first used on an industrial scale. At present investigations in this field are carried out most intensively in IPC and State Scientific-Research and Design Institute of Rare Metal Industry (Moscow). Extraction of niobium, tantalum, gallium, indium, thallium, rhenium and many other elements has been thoroughly investigated. Thousands of papers have been published in this field, in particular by higher school specialists.

Considerably moderate are the successes achieved in solvent extraction of organic substances. It is worth to mention the works on phenols (IIC in Novosibirsk, Voronezh Technological Institute), alkaloids (MICT), extraction of organic substances from biological materials (MICT).

The Soviet Union seems to have a leading position in application of solvent extraction in analytical chemistry. Important investigations have been carried out on extraction-photometric determination of elements (and similar approaches), for example, with basic dyes. Methodology of extraction concentration has been developed. New extractants for analytical purposes and new extraction systems, for instance, threephase ones, and systems with fusible extractants have been suggested. These works have been carried out in Vernadsky Institute, MSU, Kiev University, Institute of Colloid and Water Chemistry (Kiev) and in a number of other institutions.

Important are the applications of solvent extraction in nuclear processes and corresponding investigations. Liquid-liquid extraction makes it possible to solve actual practical problems. Extraction of uranium, transuranium elements and various fission products has been studied in detailes. Methods for extraction of carrier-free radioisotopes have been developed.

Finally, the application of solvent extraction in hydrometallurgy of nonferrous and rare metals should be considered. The extraction is used for production of indium, thallium, niobium, tantalum, rare-earth elements, zirconium and a number of other rare elements. Extraction with carboxylic acids is utilized for high-purity cobalt production. However, extraction is not used on industrial scale in the Soviet Union for production of cheap and common metals such as copper, zinc, nickel. However, there appeared a new thing: a solvent extraction process in ferrous metallurgy (for purification of pickling solutions of iron).

Development of extraction equipment is usually carried out in the Soviet Union by the institutions taking direct part in the investigation of new technological processes of separation.

Research and development in the field of extraction equipment envelops all types of apparatus: gravitate columns and mixer-settlers, as well as centrifugal extractors.

Increase of capacity and efficiency of mass transfer, decrease of energy consumption, rise of reliability, improvement of safe working conditions are the main purposes.

The important means of the capacity and efficiency increasing lie in the creation of such hydrodynamic situation that allows to get a certain optimal drop-size of disperse phase and the most favourable emulsion type, as well as flows organization bringing their character nearer to the ideal ousting regime.

Methods of extractors calculation and scaling-up have been developed, enabling to design industrial apparatus on the basis of laboratory experiments, process kinetics and statics data and physicochemical properties of reagents.

Important contributions to the development of Soviet extractors were made by I.Ya.Gorodetzky, S.V.Dilman, E.I.Zaharov, S.M.Karpacheva, G.I.Kuznetsov, G.V.Korpusov, V.M.Muratov, V.M.Olevsky, A.A.Pushkov, I.I.Ponikarov, L.S.Raginsky, A.I.Solodov, L.I.Sklokin.

Personel and education. There are important research schools on solvent extraction in the country, a number of known scientists have grown. About 80 specialists have Doctor of Science' degree (much higher level than Ph.D). Among them there are several members of the USSR Academy of Sciences and academies of sciences of the Soviet Republics: Academicians I.P.Alimarin, V.V.Kafarov, V.N.Laskorin, A.S.Nikiforov, V.A.Purin, Yu.A.Zolotov, corresponding members

V.A.Malyusov, V.M.Sedov, G.A.Yagodin, full member of Latvian AS Yu.A.Bankovsky, corresponding member of Belorussian AS G.L.Starobinetz. In the past, great was the contribution to the solvent extraction made by Academician A.V.Nikolaev, corresponding members V.V.Fomin, V.M.Vdovenko, A.A.Yakovkin, Doctors of Sci. A.I.Busev, A.A.Lipovsky, V.B.Shevchenko, V.S.Shmidt.

During last years Dr.Sci.' degrees were obtained mainly in MICT, Vernadsky Institute and ICI. Dissertations defended belong to different scientific disciplines - inorganic, analytical or physical chemistry, radiochemistry, chemistry and technology of rare elements. This situation seems to be prolonged in future because of interdisciplinary character of liquid-liquid extraction.

Commission on the solvent extraction of the Scientific Council on Inorganic Chemistry of the USSR Academy of Sciences developed the typical program for Ph.D. examination on solvent extraction; the program is used in most institutions dealing with extraction methods.

Lectures on solvent extraction are given in a number of universities and technological institutes (either special courses or significant sections in other courses).MSU, MICT, MIFCT, Leningrad University and Technological Institute should be mentioned. For instance, a special course "Solvent extraction methods of radioisotopes preparation" is given in the chair for radiochemistry and chemical technology in MSU. It should be desirable to accumulate and analyse the information on education in solvent extraction. Unfortunetely, having so many monographs on solvent extraction, we did not compact text books for students. The preparation of such books is now an important task.

Publications. At least 20 soviet scientific journals publish papers on solvent extraction. Some journals are worth mentioning: Zhurnal Neorg.Khim., Radiokhimija, Zhurnal Analyt. Khim., Zhurnal Prikladn.Khim., Izvestiya Sibir.Otd.AS USSR.,Ser. Khim. Bibliographical Guide on Solvent Extraction of Inorganic Substances in three volumes comprises publications till 1972 [5,6].

As for the books on solvent extraction in Russian, there are a lot of them. Three volumes of the Handbook edited by A.M.Rozen should be noted [7]. It is worth to mention the books of last decade [8-25] and some large reviews [26,27].

Organization and coordination of the research. Investigations in the field of extraction and its applications are sponsored by several scientific councils of the USSR Academy of Sciences. The above mentioned Commission on Solvent Extraction is the main coordinating body, but it deals mainly with chemical aspects of the method. The members of the Commition: Yu.A.Zolotov (Chairman), G.V.Korpusov, B.F.Myasoedov (Vice Chairman), V.M.Shkinev (Scientific Secretary),

Yu.A.Bankovsky, A.M.Chekmarev, G.P.Giganov, L.M.Gindin, B.S.Iofa,
A.A.Kopyrin, V.A.Michailov, A.I.Michailichenko, A.I.Nikolaev, A.M.
Orlov, G.L.Pashkov, O.M.Petrukhin, M.Ph.Pushlenkov, A.M.Rozen, V.V.
Sergievsky, I.A.Shevchuk, O.A.Sinegribova, L.I.Sklokin, B.Ya.Spiva-
kov, V.V.Tarasov, G.A.Yagodin, V.V.Yakshin, A.N.Zelikman.

The Commission organizes All-Union conferences, considers in-
vestigations in different regions of the Soviet Union. The Commis-
sion sponsores seminars on solvent extraction in Moscow, Novosi-
birsk and Leningrad. For young scientists and industry specialists
so called "schools" are set up, where well-known scientists give
lectures for the participants on the theoretical fundamentals and
practical applications of solvent extraction.

The scientific Council on Chemical Engineering deals mainly with
engineering processes and technological aspects (processes and appa-
ratus). Applications of solvent extraction are partially sponsored
by the Council on Analytical Chemistry, Radiochemistry, Physico-
Chemical Fundamentals of Metallurgical Processes and others.

There are two series of regular national conferences: on che-
mistry of solvent extraction (there were 7 conferences beginning
from 1959) and on liquid-liquid and liquid-solid extraction. There
were 4 such conferences. The first series conferences are organized
by the Commission on Solvent Extraction, the second series - by the
Council on Chemical Engineering. On preparing the ISEC'88, we orga-
nized the first joint conference in September 1987 combining both
series. Besides, works on solvent extraction are widly presented
at conferences on radiochemistry, analytical chemistry, chemistry
of non-aqueous solutions, hydrometallurgy and others.

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In solvent extraction systems of metal ions, various types of
complexes are formed in the both phases. Since the extraction is
enhanced and/or impaired by such complex formations, the over-all
extraction equilibrium is dependent on them. For this reason, sys-
tematic studies of complex formation is very important in order to
know how the metal ions are extracted and also why they are extracted
to such an extent under the given conditions in that solvent ex-
traction system.

Complex formation Equilibria in Solvent Extraction Systems

Kinetic studies of solvent extraction of metal ions often indicate
that complex formation of metal ions with an extractant occurs on the
interface. Consideration of reaction mechanism should naturally be
done strictly on the basis of such kinetic observations. However,
when the chemical equilibrium is discussed, several different expres-
sions are possible and still, each of which interprets the experi-
mental results reasonably. Metal chelate extraction offers a good
example for this. When a metal ion, M^{m+}, in an aqueous phase is
extracted with a chelating extractant which is an organophilic weak
acid, HA, the extraction equilibrium and, consequently, the
extraction constant, Kex, is often written for the interfacial reac-
tion;

$$M^{m+} + m\ HA(org) \rightleftarrows MA_m(org) + m\ H^+$$

$$Kex = [MA_m]_{org}[H^+]^m[M^{m+}]^{-1}[HA]_{org}^{-m} . \qquad (1)$$

The distribution ratio can easily be calculated from the concen-
tration of the extractant in the organic phase and of the hydrogen
ions in the aqueous phase, if the value of Kex is known;

$$D = [MA_m]_{org}/[M^{m+}] = Kex[HA]_{org}^m[H^+]^{-m} . \qquad (2)$$

In order to estimate the amount extracted under certain given condi-
tions, these equations are very useful. However, it is not easy to
connect this type of extraction equilibrium with our knowledge of
complex formation in aqueous solutions. This is because the chemical
reactions which take place in such an area as the interface have not
been studied very much from the standpoint of coordination chemistry

and since the above equilibrium constant, Kex, represents the over-all effect of several unit equilibria involved in the extraction process, the physical meaning is not quite clear.

Another approach to interpret the extraction equilibrium is that (i) a part of the extractant which is initially present in the organic phase is transferred into the aqueous phase, (ii) the metal ion in the aqueous phase forms an extractable complex with the ligand thus transferred, (iii) the complex formed in the aqueous phase is extracted into the organic phase across the interface, and, in some cases, (iv) the extracted complex undergoes solvation or adduct formation in the organic phase with an organophilic ligand in it. The equilibrium represented by Eq.1 can be written from this standpoint as follows.

$$HA \rightleftarrows HA(org) \qquad Kd=[HA]_{org}/[HA], \qquad (3)$$

$$HA \rightleftarrows H^+ + A^- \qquad Ka=[H^+][A^-]/[HA], \qquad (4)$$

$$M^{m+} + m\ A^- \rightleftarrows MA_m \qquad \beta_m=[MA_m]/[M^{m+}][A^-]^m, \qquad (5)$$

$$MA_m \rightleftarrows MA_m(org) \qquad Kdm=[MA_m]_{org}/[MA_m]. \qquad (6)$$

The distribution ratio when only M^{m+} is the metal species in the aqueous phase can be given by the following equation although several complexes may be formed in the aqueous phase and the equation should usually be much more complicated;

$$D = [MA_m]_{org}/[M^{m+}] = Kdm\beta_m[A^-]^m. \qquad (7)$$

This type of consideration is very favorable because the constants for the unit equilibria treated are already known or can be determined by various methods and thus the physical meaning of each equilibrium constant is clear.

Complex Formation Equilibrium in Aqueous Phase

Complex formation equilibrium in the aqueous phase can be determined by analyzing the extraction data which are measured as a function of the ligand concentration. From these values, a reasonable understanding can be made about the relation between the solvent extraction behavior of the metal ion and the experimental conditions of the aqueous phase. However, the concentration of coexisting electrolytes in the aqueous phase of a solvent extraction system is often extremely high and the electrolytes may be co-extracted into the organic phase. Thus reasonable control or estimation of the

16

activity of solutes which is necessary for an accurate evaluation of the equilibrium is sometimes difficult. Furthermore, the extraction of coexisting materials may change the free extractant concentration and also the nature of the organic phase and the correction for these is, in some cases, indispensable.

Liquid-Liquid Distribution Equilibrium of Complex Species

Some metal ions in a solvent extraction system are very well extracted as a complex with a certain ligand but some other metal ions are not under the same conditions. Such a difference in the extractability of metal ions is very often explained in terms of the difference in the stability of the extractable complexes.

However, the two-phase distribution equilibrium of them which can be given by Eq.6 is also important. This is because, as seen from Eq.7, the constant for the extraction is the product of the stability constant and the two-phase distribution constant of the extractable complex. The two phase distribution equilibrium of the extractable complex explains the reason why some less stable complexes are more extractable than more stable complexes in the same aqueous phase.

In order to elucidate the difference in the extractability of solutes in aqueous solutions, hydrophobic tendency which has a close relation with the volume of molecule and hydrophilic tendency which is caused by the interactions of the solute and water molecules are considered. However, estimation of the latter, especially that of metal complexes, is difficult. This has not been considered very much from the standpoint of coordination chemistry but it is important for the discussion of solvent extraction of metal ions. The regular solution theory has successfully been applied for the explanation of the difference in the solvent extraction of a material from a certain aqueous phase into several different organic solvents. However, the interactions of water molecules with those complexes in which the ligand is the same but the metal ion is different have not been studied very much.

Complex Formation Equilibrium in Organic Phase

When the extracted complex is solvated in the organic phase, the extraction is very effective. This kind of solvation equilibrium is very often given as a reaction on the interface. However, when it is considered as a reaction of the metal complex with the solvating extractant in the organic phase, the solvent extraction of the metal ion can be understood more clearly.

Such a solvation is indispensable for the extraction of several metal complexes in which the ligand is monodentate and is not bulky. The number of solvation of the complex can usually be determined

rather easily but, unfortunately, the estimation of solvation or adduct formation equilibrium of a metal complex in the organic phase is often difficult.

Complex formation in the organic phase, especially when it is non-polar, is quite different from that in the aqueous phase. Some of the reasons for that may be given as follows. (i) The solutes are, in many cases, non-charged and thus the complexes are formed among non-charged molecular species. Even when the solvent is polar and/or highly dielectric, still the dissociation of ionic species and thus the complex formation is quite different from that in aqueous solutions. (ii) In the aqueous phase, water molecules are a donor and at the same time, they are an acceptor. In non-polar solvents, however, the molecules are inert and the solutes are rather independent from the medium. This difference in the solvation makes a great effect in some cases.

Synergistic effect of the metal extraction with a chelating extractant and an organophilic neutral ligand can be elucidated by solvation or adduct formation of the extracted metal chelate with the ligand in the organic phase. However, it is not always possible to make a systematic explanation why a certain metal chelate forms stable adducts with a certain neutral ligand in the organic phase but another does not. The reason for this seems to be similar to that for the difference in the extractability of noncharged metal complexes in the aqueous phase with a certain solvating type organophilic extractant.

Oxidation of some metal ions such as manganese(II) and cobalt(II) in chelate complexes in the organic phase by atmospheric oxygen has been found but the oxidation is not found in the aqueous phase in an equilibrium with the organic phase. The rate of such oxidation of the metal ion is quite different when the ligand and/or the solvent is different.

There are examples which indicate that the stability of a certain metal complex is quite different in the aqueous and organic phase. For example, the extraction of the anionic complex of a metal ion as ion-pairs with a large cation, in other words, the extraction of ternary metal complex, is quite different when the chelating ligand is different. A general tendency that less stable anionic complexes are more extractable as ion-pairs than more stable anionic complexes of the same metal ion is found among β-diketonate complexes of di-valent transition metal ions. It could be possible to describe such observations as that when the anionic complexes are more stable in the aqueous phase they are less stable in the organic phase and thus they can not be extracted into the organic phase across the inter-face.

RECOVERY OF POLAR-ORGANIC SUBSTANCES BY SOLVENT EXTRACTION PROCESSES UTILIZING REVERSIBLE COMPLEXATION

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There are a number of important processing situations where polar organic substances must be removed or recovered from relatively dilute and complex aqueous solutions. Examples include plant-effluent and waste streams, and the recovery of chemical products made from alternative raw materials, such as biomass and coal.
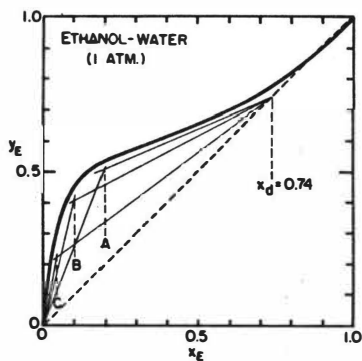
Many of these situations are well suited for separations based upon reversible formation of complexes, or adducts. With a suitable chemical extractant, the Law of Mass Action provides a high equilibrium distribution ratio into a receiving phase, and chemical specificity provides selectivity with respect to competing solutes. The utility of this approach is borne out by the recent commercial success of a process for purifying and concentrating citric acid by extraction with a tertiary amine, followed by back extraction into water at a higher temperature [1].

The Role of Reversible Complexation for Separations of Polar Organics from Water. Solute characteristics which tend to favor the use of reversible chemical complexation for separation of polar organics from water, in comparison with alternate methods, are [2]:
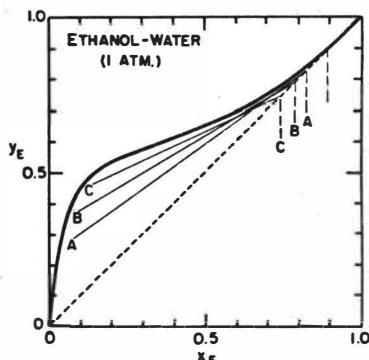
1. The presence of functional groups capable of complexation.

2. Low solute concentration [Law of Mass Action].

3. Low activity coefficient of solute in water. [Because complexation can overcome this handicap, it gains a relative advantage.]

4. Low solute volatility, in comparison with water.

Reversible chemical complexation has been compared with other alternatives for recovery of acetic acid, phenol, and ethanol from aqueous solution [2].

Ethanol. The situation for ethanol is worthy of further analysis. Fig. 1a shows McCabe-Thiele diagrams for binary feeds with different concentrations of ethanol in water, producing a given distillate. The energy requirement, expressed through the ratio of vapor flow to distillate flow, increases markedly as the feed becomes more dilute, reflecting the strong curvature of the equilibrium relationship. Fig. 1b shows a similar analysis for different enrichments of ethanol in the distillate. The downward convexity of the equilibrium relationship near the azeotrope causes the energy consumption, expressed as the molar ratio of the vapor flow to ethanol flow in the product, to increase sharply for higher distillate enrichments. The energy penalties for low feed concentrations and high distillate concentrations lead to distillation being most effective for

ETHANOL-WATER
(1 ATM.)

y_E
0.5

$x_d = 0.74$

A
B
C

0.5
x_E
1.0

CASE	x_F mol	wt.	L/d	v/d
A	0.20	0.39	0.75	1.75
B	0.10	0.22	1.1	2.1
C	0.04	0.096	2.9	3.9

ETHANOL-WATER
(1 ATM.)

y_E
0.5

B
A
C

0.5
x_E
1.0

CASE	x_d mol	wt.	L/d	v/dx_d
A	0.825	0.923	2.47	4.21
B	0.785	0.903	1.40	3.06
C	0.74	0.879	0.83	2.47

Fig. 1. McCabe-Thiele Diagram for Distillation of Ethanol-Water Mixtures (a) with Varying Feed Composition, (b) with Varying Distillate Purity

concentrating ethanol over the range of feed and product compositions shown in Fig. 2.

As is also depicted in Fig. 2, the range of feed and product compositions over which solvent extraction is most appropriate coincides almost exactly with the range where distillation is most effective. Extraction is limited at high and low concentrations by phase-miscibility considerations and by competition with adsorption, respectively. Thus, even if better complexing agents for ethanol are identified, use of solvent extraction with reversible complexation for recovery of ethanol will still be held back by the fact that extraction competes with distillation in the range of feed and product compositions where distillation is most attractive economically.

Products of Most Interest. The most attractive industrial opportunities for recovery of polar organics by reversible chemical complexation exist for those substances which fit the four criteria above, have substantial markets, and have unit values of about $2.00 (U.S.) per kg, or greater. Examples include several dicarboxylic acids (succinic, fumaric, etc.), hydroxycarboxylic acids (citric, lactic, malic, etc.), and pharmaceutical products and intermediates containing multiple functional groups. If effective and economical complexants are found for the -OH group, then recovery of diols (propylene glycol, butanediols, etc.) is also likely to be an attractive application.

Selection of Extractants. The interaction energy should be high enough to provide the desired capacity and selectivity, but low enough
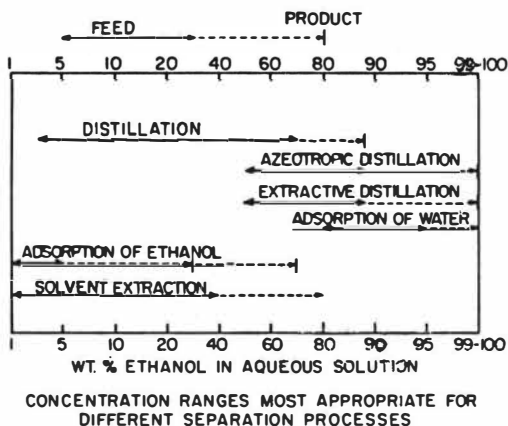
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Fig. 2. Ranges of Optimal Applicability of Different Separation Processes for Concentrating Aqueous Solutions of Ethanol. Solid Line = Range of Feed Concentrations. Solid Line plus Dashed Line = Range of Ethanol Product Concentrations

so that regeneration is not unduly expensive. The complexation reaction should have sufficiently fast kinetics so that equilibrium is approached within a reasonable residence time (i.e., small enough equipment volumes). The complexing agent should be stable, and should give no irreversible side reactions.

Because unit values of high-volume polar organics tend to be lower than those of metals, losses of extractant (by solubility in water, entrainment, emulsification, incorporation into micelles, or simply start-up and handling) have even greater economic importance for extraction of polar organics. Such losses can also lead to contamination of effluent or recycle water streams, especially in bioprocessing and in streams to be released to the environment. The economic factor leads to a preference for lower-cost extractants. Both factors lead to use of extractants with very low aqueous solubility.

Another approach to the contamination problem is to utilize the appropriate extractive functional groups in modes that preclude losses and contamination. Examples are the use of functionalized polymeric sorbents and membranes impregnated with an extractant.

Most extractants or sorbents imbibe water to significant extents. Co-extraction of water limits the degree to which a solute is concentrated. This factor leads to a preference for extractants which minimize co-extraction of water, or which facilitate subsequent dewatering of the extract.

21

On the basis of present knowledge, tertiary alkylamines appear to be the most satisfactory liquid extractants for carboxylic acids [3-5]. The amine group proves difficult to regenerate when it is incorporated into polymeric sorbents and used for recovery of carboxylic acids. Polybenzimidazoles and polyvinylpyridines give high capacities and much easier regenerability [6-8], although both sorbents in present commercial forms give very large water uptakes [6]. Phosphine oxides are effective, regenerable extractants for carboxylic acids [9, 10] and phenols [11]. However, they are expensive, and therefore even relatively low levels of extractant loss are costly.

Of the solvents and extractants that have been tested [12], substituted phenols appear to give the highest equilibrium distribution ratios (D) for the lower alcohols and diols [13].

Criteria for Selection of Diluents. Diluents are often used with extractants to dissolve a solid extractant, reduce viscosity, control density or interfacial tension, reduce co-extraction of water, and/or determine the reboiler temperature when regeneration is accomplished by distillation of a volatile solute. The choice of diluent can also have a major effect upon D, and can lead to a strong maximum in D at an intermediate concentration of the extractant, in cases where solvation of the complex by the diluent is important [2,5,10,14-16]. The diluent can therefore also be chosen to enhance extraction, to facilitate subsequent removal of the solute from the extractant, and/or to enhance selectivity among solutes.

Methods of Regeneration. If the extracted solute is sufficiently volatile, it can removed from the extractant by distillation [3]. In the design, allowance must be made for the suppression of solute volatility by residual complexation of the solute with the extractant.

In cases where the solute has low volatility, it is unlikely that a suitable complexing extractant can be found which can be distilled overhead from the solute; therefore avenues other than distillation are needed. For carboxylic acid solutes, back-extraction into NaOH or other aqueous bases can be used, but this results in degradation of the acid to the carboxylate salt. The free acid can be recovered by adding another, stronger acid to the solution of the carboxylate salt, but this entails costly consumption of chemicals, can lead to a difficult crystallization of the free acid, and also leads to a waste-disposal problem.

Back-extraction into water will be enhanced by a change in any condition which causes the distribution ratio to change substantially. A desirable goal, then, is to find "swing" variables which cause large changes in D. The successful process for citric acid already mentioned [1] utilizes an increase in temperature to reduce D for citric acid between water and an amine/hydrocarbon solvent by a factor of five or more.

Another approach is to change the composition of the diluent so as to change the distribution ratio [17]. In such a situation the diluent would consist of varying proportions of an active (solvating) substance and an inactive (non-solvating) substance. The diluent components can be picked so that their volatilities will permit use of distillation or another inexpensive separation method to subtract one or more of the components from the mixture, and thereby alter the composition. The active component would be present in a greater proportion in the diluent mixture during the forward extraction than in the back-extraction. Diluent change and temperature swing can be used in combination to give greater changes in D than are achievable with either means alone.

In the case of sparingly soluble polar organics, a change in temperature or diluent composition may also create a separate solute-rich solid or liquid phase, thereby facilitating regeneration.

Another method which has been suggested [18] for regeneration of tertiary amines laden with a carboxylic acid is to contact the extract with an aqueous solution of a displacing acid, thereby facilitating back-extraction of the carboxylic acid into the aqueous phase. This method leads to problems of chemicals consumption and disposal of a waste stream, unless some other method can be used to free the amine from the anion of the displacing acid.

Yet another approach is to back-extract a carboxylic acid from the extract into aqueous ammonia, forming the ammonium carboxylate. The aqueous ammonium carboxylate solution would be concentrated, if necessary, and decomposed thermally, liberating the free carboxylic acid and ammonia for recycle. It has, however, been found that amides are formed irreversibly upon heating of at least some ammonium carboxylates.

A way to overcome the amide-formation problem is to use an aqueous solution of a volatile tertiary amine, e.g., trimethylamine, to form the trimethylammonium carboxylate, which can then be decomposed thermally. The liberated tertiary amine would be distilled overhead for recycle.

When functionalized sorbents are used instead of extractants, other regeneration possibilities occur. These include leaching the solute from the sorbent into a solvent, which does not need to be immiscible with water. Feeding vaporized solvent to a sorbent bed can enhance fractionation between solute and co-sorbed water through an entrainer-distillation process [19]. Another approach is to convert the carboxylic acid _in situ_ to an ester [19], which may be more volatile than the acid, and which will certainly be more readily recovered by solvent leaching.

Development of reliable and inexpensive means of regeneration is one of the most essential needs for increasing industrial use of reversible

23

chemical complexation for recovery of polar organic solutes from aqueous solution.

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MULTIFUNCTIONAL ORGANOPHOSPHORUS EXTRACTANTS: A STATUS REPORT ON
DEVELOPMENT AND APPLICATIONS

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INTRODUCTION

As solvent extraction chemists and technologists, most of us usually live
and work in a one-dimensional world of monofunctional extractants. Thus, we
are familiar and comfortable with such monofunctional reagents as tri-n-
butylphosphate, the workhorse in the nuclear industry, and bis-2-ethylhexyl-
phosphoric acid used extensively in the hydrometallurgical industry. And
the list of monofunctional extractants, both old and new, of interest to
researchers in academic institutions is boundless.

But -- the solvent extraction world is not, of course, only one-
dimensional. Our solvent extraction larder contains many useful and
interesting bi- and tri- as well as monofunctional extractants. The
multifunctional organophosphorus reagents to be discussed in this plenary
lecture are a particularly noteworthy example. Researchers in many lands,
but especially in the United States and in the Soviet Union, have spent
considerable energy over the last four decades in synthesizing and studying
the liquid-liquid extraction properties of some 200+ multifunctional
organophosphorus reagents. This effort has been motivated and sustained by
both natural intellectual curiosity and by the actual or potential use of
some of the bifunctional organophosphorus compounds in important nuclear
separations processes.

This plenary lecture is structured and organized to provide an overview
of the current state of development of the science and technology of
multifunctional organophosphorus extractants. It is concerned with
definitions and classifications of such extractants, with a discussion of
the different types of functional groups which occur in these
multifunctional reagents, and with a brief description of some important
extraction systems involving multifunctional organophosphorus compounds.
Mention is also made in the latter part of the lecture of some important
uses of selected multifunctional extractants in analytical chemistry and in
plant-scale nuclear separations.

CLASSIFICATION OF MULTIFUNCTIONAL ORGANOPHOSPHORUS EXTRACTANTS

Definition. For application in liquid-liquid extraction systems, a
multifunctional organophosphorus extractant is an organic compound which
contains two, or more donor groups, at least one of which is bound to a
phosphorus atom, potentially capable of reacting with selected metal ions to

form stable organic-phase soluble species. This definition is broad enough to allow inclusion of compounds such as alkylaminophosphine oxides [(G)$_2$-P-N-G] and thioalkylphosphine oxides [(G)$_2$-P-(CH)$_2$ -S-G] where it is not completely clear that the N or S atoms can act as potential donor groups. For purposes of this lecture, HO-P=O (POOH) and (HO)$_2$-P=O [PO(OH)$_2$] moieties are considered to contain only a single donor group; this restriction is desirable to avoid considering compounds such as (GO)$_2$POOH as multifunctional organophosphorus extractants.

Currently known bifunctional organophosphorus extractants (Table 1) typically contain combinations of P=O, C=O, -N-C=O, P=S, HO-P=O, and (HO)$_2$-P=O groups.

Table 1

Combinations of Functional Groups in Multifunctional
Organophosphorus Extractants

Number of Groups	Combinations of Functional Groups	
2	P=O, P=O	P=O, S=O
	P=O, C=O	P=S, P=S
	P=O, -C(O)-N-[a]	POOH, POOH
	P=O, -N(H)-	POOH, P=O
	P=O, N--->O	POOH, C=O
	P=O, -S-	PO(OH)$_2$, PO(OH)$_2$
(a) Carbamoyl group.		

Major Types of Extractants. All multifunctional organophosphorus extractants can conveniently be divided into two broad groups: Neutral Compounds and Acidic Compounds.

Acidic extractants are those that contain at least one POOH or PO(OH)$_2$ group in the molecule regardless of what other functional groups may be present. (Certain cyclotriphosphazenes containing hydroxy substituents on the ring phosphorus atoms are an exception to this definition.) All other multifunctional organophosphorus extractants are classified as neutral extractants even though groups such as COOH and SO(OH)$_2$ may be present in the molecule.

Neutral multifunctional organophosphorus extractants can be conveniently further subdivided into homofunctional and heterofunctional compounds. In the former class of extractants, as its name implies, all the functional groups present are identical (e.g., all P=O, all P=S, etc.) Heterofunctional neutral extractants contain different functional groups in the same molecule.

26

Paralleling the case with their monofunctional counterparts, many of the currently-known neutral multifunctional organophosphorus extractants can be assigned to one of three broad types (Table 2), namely, phosphonates, phosphinates, and phosphine oxides. Other types of neutral multifunctional organophosphorus extractants are known also (Table 2), but, in most cases, only a few representative compounds of each of these miscellaneous classes of neutral extractants have been synthesized and studied.

Table 2

General Classification of Neutral Multifunctional
Organophosphorus Extractants

General Classification	Class Functional Group
PHOSPHONATES	$(GO)_2P(O)-$
PHOSPHINATES	$(GO)GP(O)-$
PHOSPHINE OXIDES	$(G)_2P(O)-$
PHOSPHINE SULFIDES	$(G)_2P(S)-$
MISCELLANEOUS TYPES[a]	
Aminoalkylenephosphine oxides	$(G)_2P(O)CH_2N(G)_2$
Amine oxide-phosphine oxides	$(G)_2P(O)N(O)(G)_2$
Ketophosphonates	$(G)_2P(O)CH_2C(O)G$
Phosphoramidates	$(G)_2P(O)N(H)C(O)G$
Sulfinylmethylphosphine oxides	$(G)_2P(O)CH_2S(O)G$
Thioalkylenephosphine oxides	$(G)_2P(O)(CH_2)SG$

(a) Also includes cyclotriphosphazenes, $[(G)_2-P-N=]_3$

The currently-known acidic multifunctional organophosphorus extractants include (Table 3) only phosphonic, phosphinic, and pyrophosphoric acids.

Table 3

Classification of Acidic Multifunctional
Organophosphorus Extractants

General Classification	Class Functional Group
PHOSPHONIC ACIDS	$GOP(O)OH-$
PHOSPHINIC ACIDS	$GP(O)(OH)-$
PYROPHOSPHORIC ACIDS	$(GO)(HO)P(O)OP(O)(OH)(OG)$

Sub-Classes of Phosphonate and Phosphine Oxide Extractants. Neutral multifunctional phosphonate and phosphine oxide extractants can be

conveniently further classified to reflect particular combinations of
functional groups, e.g., diphosphonates, carbamoylphosphonates,
carbamoylalkylphosphonates, hypophosphonates, and pyrophosphonates
(phosphonates); bis(tris, etc.)phosphine oxides, carbamoylalkylphosphine
oxides (phosphine oxides).

EXTRACTION SYSTEMS

At present (September 1987) the solvent extraction properties of
approximately 160 and 40, respectively, different neutral and acidic
multifunctional organophosphorus extractants have been reported. By far,
the preponderance of the known neutral compounds are bifunctional
phosphonates (15); phosphine oxides (65); carbamoylphosphonates and
carbamoylphosphine oxides (36). Similarly, pyrophosphoric acids account for
about one-third of the acidic multifunctional organophosphorus reagents.
The remaining neutral and acidic extractants have typically been synthesized
and studied, on a limited scale, by a single investigator or single group of
scientists.

Typically, two general systems have been employed to investigate the
solvent extraction properties of neutral and acidic multifunctional
reagents.

Type 1. Neutral Extractants

   Aqueous Phase: 0.01 to ~10M Mineral Acid (HNO_3, HCl, $HClO_4$ or H_2SO_4)
                  ~10^{-5} to 0.1M Actinide (Am, U(IV,VI), Np(IV,VI),
                  Pu(IV,VI)] or Lanthanide

   Organic Phase: ~10^{-3} to 0.1M Extractant-Diluent

Type 2. Acidic Extractants

   Aqueous Phase: Actual/Synthetic Wet Process Phosphoric Acid
                  5-6M PO_4^{3-}; 0.2 g/L U(IV) or U(VI); Fe(III)

   Organic Phase: 3-30 vol% Extractant-Diluent

Diluents in both systems include pure aliphatic and aromatic compounds,
mixtures of such compounds, and halogenated aliphatic compounds.

Interest in these two extraction systems is driven by: (1) the great
affinity of certain neutral bi-functional phosphonates, phosphine oxides,
and, especially, carbamoylalkylphosphonates and phosphine oxides for
trivalent Am as well as +4 and +6 actinides and +3 lanthanides from strong
mineral acids, and (2) the ability of certain alkylpyrophosphoric acids to
extract U(IV) very efficiently from strong phosphoric acid solutions.

Although most investigations of the extraction properties of multi-
functional organophosphorus compounds have focussed on their reactions with
actinide and lanthanide metals, the propensity of certain classes of these
compounds to extract other metals from aqueous media have been at least
partially studied. For example, data have been reported for the extraction
of Ag(I) and Hg(II) from HNO_3, HCl, and $HClO_4$ media by bifunctional

28

phosphine sulfides and thioalkylenephosphine oxides. Also, the ability of
certain ketophosphonates to extract such metals as Fe(III), Ga(III),
In(III), V(IV), Zn(II), Cd(II), and Al(III) from aqueous KSCN and $NaClO_4$
media has also been examined with a view to establishing extraction
mechanisms exhibited by this class of multifunctional organophosphorus
compounds.

APPLICATIONS

Considering the rather large number of fundamental studies of
multifunctional organophosphorus solvent extraction reagents reported in the
literature, applications of these reagents in either analytical- or
industrial-scale separations processes have been remarkably sparse. This
circumstance reflects, to a large extent, the limited availability of many
of the multifunctional compounds in sufficient quantity and purity for
direct use. And, of course, in analytical applications the multifunctional
organophosphorus reagents must compete with well-established alternative
reagents and procedures.

Three important generalizations can be made concerning applications of
multifunctional organophosphorus extractants:

1. All actual and proposed industrial-scale uses have been in the
   nuclear field.

2. Only carbamoylmethylphosphonates (CMP) carbamoylmethylphosphine
   oxides (CMPO), and pyrophosphoric acids have actually been used or
   proposed for use in industrial-scale extraction processes.

3. Analytical applications of multifunctional organophosphorus
   extractants have generally employed only certain pyrophosphoric
   acids, diphosphine oxides, or carbamoylmethyl type (i.e., CMP or
   CMPO) compounds.

Kletenik, Levin and their Russian associates[1,2] published an extensive
series of papers in the early 1960's concerning the analytical applications
of diisoamylpyrophosphoric acid and bis-2ethylhexylpyrophosphoric acid.
Selective extraction-stripping procedures were developed for determination
of Bi(III), Fe(III), Ga(III), In(III), Sb(III), Sn(IV), and Ti(IV) in
mineral acid matrices. In the same time frame, O'Laughlin[3] and his
colleagues in the U.S. utilized various neutral bifunctional phosphine
oxides (e.g., methylenebis(di-n-hexylphosphine oxide) in extraction
chromatographic procedures for separation and determination of various metal
ions including rare earths, yttrium, actinides, and alkaline earths.
Currently, Horwitz et al.[4] have developed an extraction chromatographic
procedure (ABEX procedure) for routine determination of very low
concentrations of actinide elements in acidified urine solutions; the active
reagent in the ABEX procedure is octyl(phenyl)-N,N-diisobutylmethyl-
carbamoylmethylphosphine oxide. Other analytical applications of this

29

latter reagent for determination of Am(III) in acidic nuclear waste solutions have been reported.

Industrial-scale applications of CMP- and, more recently, CMPO-type reagents for solvent extraction removal of ^{241}Am and other transuranium (TRU) elements from certain acidic nuclear waste solutions have received much attention in the U.S. in the last decade. Large economic incentives exist for partitioning TRU-type (i.e. $\geq$ 100 nCi TRU elements/g) wastes into a large volume of low-level waste which can be disposed of in relatively inexpensive near-surface facilities and a small volume of TRU waste requiring expensive deep geologic disposal. Research efforts in the U.S. have lately culminated in the development of the TRUEX process by Horwitz et al.[5] Technology for potential plant-scale deployment of the TRUEX process is currently being developed at several U.S. DOE sites including Hanford, Los Alamos, and Idaho.

Experimental investigations of the applicability of various pyrophosphoric acids to recover uranium (as U(IV)) from wet-process phosphoric acid solutions have been conducted in various countries for nearly four decades. Uranium recovery processes employing as the extractant octylpyrophosphoric acid or caprylpyrophosphoric acid or a mixture of mono and dioctylphenylpyrophosphoric acids were operated on a commercial-scale in the U.S. in the 1960's and 1970's.[6] The DEPA-TOPO process, which employs a mixture of bis-2ethylhexylphosphoric acid and trioctylphosphine oxide to extract U(VI), has largely supplanted extraction schemes based on pyrophosphoric acid reagents.

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TRI N-BUTYL PHOSPHATE - THE UNIVERSAL SOLVENT FOR THE NUCLEAR FUEL CYCLE

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GENERAL

The potential of TBP as a metal extractant was first observed in the early 1940s by workers engaged on the war-time Manhattan Project in the US. Since that date, or to be more historically correct 1949 when the first journal reference appeared, a substantial number of reports, papers and books have been published describing the science and technology of this chemical, possibly more than any other extractant. However, it should be remembered that only a relatively small proportion of the total quantity of TBP manufactured each year is destined for hydrometallurgical processes. Its commercial availability relies heavily on its other applications, namely as a plasticiser, antioxidant or catalyst and in antifoaming agents, hydraulic fluids and fire retardants. These varied applications require a commercially available source and currently TBP is manufactured in several countries at a UK equivalent cost of ~£1.8/Kg.

Tri-n-butyl phosphate is now employed in all of the actinide hydrometallurgical processes associated with the nuclear fuel cycle. It is exclusively used in the refining of uranium ore concentrates or "yellow cakes" to produce reactor grade uranium. Similarly, it is the chosen solvent for all commercial nuclear reprocessing operations for the separation of plutonium and uranium from fission products and other nuclides and for the purification of plutonium and uranium. In recent years the use of TBP has been extended to the mining/milling operations for the recovery and concentration of uranium from various ore bodies and its potential for the treatment of nuclear waste liquors arising from reprocessing operations has also been evaluated.

CURRENT APPLICATIONS IN THE NUCLEAR INDUSTRY

Although TBP is now being employed by at least two mining/milling operations producing a few hundred t U pa, it is the nature of the ore body and its geographic location which dictates the selection of the leaching and uranium recovery processes. Where ore bodies are more amenable to leaching of uranium with nitric acid, TBP is the chosen solvent. The decontamination factors required for metals such as Th, Fe, Zr are readily achieved by this solvent whilst the other principal requirement in the mining/milling operation, namely the concentration of uranium prior to the precipitation stage, can easily be achieved by the judicious selection of both the solvent concentration and back-washing reagent.

In the early 1950's the recovery and purification of uranium from UOCs was achieved using either diethyl ether or methyl isobutyl ether with obvious disadvantages for use on an industrial scale. However with the proliferation of civil nuclear reactors, a high volume, low cost and more environmentally acceptable separative route was necessary. Currently, in the western world, four commercial refineries have the capacity to process approximately 60,000 t UOC pa employing a TBP-diluent purification circuit.

This multistage process achieves decontamination factors of between 10 and 1000 for Zr, Ti, V, Cr, Mo, Fe etc and finally generates a pure uranyl nitrate liquor easily converted to a variety of reactor fuels.

Tri-n-butyl phosphate is now and has been for the last thirty years the chosen solvent for the nine or so commercial and demonstration reprocessing facilities situated in about seven countries. More recently other solvents, namely amides have

been considered by Italian workers, although they have only been evaluated in pilot-plant facilities. In the separation of uranium and plutonium from other actinides and fission products, recovery efficiencies of 99.9% are required whilst decontamination factors of 10^4 to 10^6 are necessary. These criteria in addition to solvent compatibility and low aqueous phase solubility are achieved by TBP.

The potential of TBP for the treatment of nuclear waste liquors arising from reprocessing operations for the separation of long lived α emitters such as Np, Pu, U from relatively short lived β / γ emitters eg fission products has been examined, but more highly selective reagents are now considered to be more efficient and afford the best practical and economic approach.

In all the above applications the solvent is employed to extract and separate heavy metals from nitrate liquors. However, other anions such as chloride, bromide, iodide, thiocyanate and perchlorate will also permit metal extraction, whereas metal fluorides, sulphates, phosphates and carbonates are generally almost insoluble in TBP.

The success of TBP as a metal extractant is due to both its excellent chemical stability and to its physical properties. In the following sections some of the key physical and chemical properties of this solvent are reviewed.

PHYSICAL PROPERTIES

Many physical properties of TBP such as its molecular weight of 266, high boiling and freezing points, a density of ~0.97 g/cm^3 and viscosity of ~3 cP are consistent with the majority of commercially available metal extractants. Its solubility in water or 1M-nitric acid of approximately 400 ppm is lower than for long chain aliphatic ketones and/or ethers but higher than for metal-complex forming solvents such as di-2-ethyl hexyl phosphoric acid.

Although the use of TBP is limited by its relatively high viscosity and density, desirable physical properties are attained by blending the solvent with an inert hydrocarbon of low specific gravity and viscosity, to permit greater dispersal and more rapid phase disengagement. For separation processes associated with the nuclear fuel cycle diluents of low aromaticity are employed but the concentration of TBP in the solvent phase varies according to the particular flowsheet conditions and the type of contactor employed.

In the refining of UOCs for instance TBP concentrations range from 20 o/v (BNFL, UK) to 40 o/v (Comurhex, France) whilst reprocessors appear to favour either 20 or 30 o/v. With the higher solvent concentration the organic phase is capable, under plant conditions, of attaining a uranium loading of 120 g/l thereby minimising the volume of solvent required at the cost of some increase in the risk of third phase formation. Even at this high metal loading the difference in density between the organic and aqueous phases is adequate for good phase disengagement and the viscosity is still comparatively low (of the order 5 cP).

Although the physical properties of TBP are not dissimilar to other commercially available extraction solvents its capacity for high metal loading without significant increase in density and viscosity and a tolerable solubility in the aqueous phase, contributes to its universal application in the nuclear fuel cycle. One of the most cogent reasons for its predominance may be the massive investment represented by the accumulated store of data on this solvent.

CHEMICAL PROPERTIES AND REACTIONS

The extraction of metals and acids by TBP (particularly nitric acid), are of paramount interest in the process technologies developed for the nuclear fuel cycle. In reprocessing operations the extraction and separation of uranium and plutonium is more complicated in comparison with mining/milling and UOC refining due to the

presence of other extractable species. Effective separations of some of the actinides can be enhanced by utilising the difference in the extractabilities of the different valency states. For example, the reduction of plutonium in the TBP-solvent phase to its trivalent state achieves an efficient separation from uranium. These process considerations, in conjunction with the fundamentals of metal extraction by TBP are briefly examined.
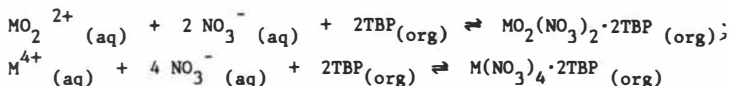
i.   Extraction of Metals

In comparison with other metal extractants, TBP is moderately powerful. Its affinity for metals derives mainly from its phosphoryl group, the oxygen forming coordinate links with cations, viz;

$$(C_4H_9O)_3P = O \rightarrow M$$

It forms adducts with the extracted species, a classical example of which is the extraction of uranium as $UO_2(NO_3)_2 \cdot 2TBP$.

The nitrates are extracted as neutral molecular species with a definite number of attached TBP molecules. The complexes for the different actinides have been established as: trivalent, $M(NO_3)_3 \cdot 3TBP$; tetravalent $M(NO_3)_4 \cdot 2TBP$; hexavalent, $MO_2(NO_3)_2 \cdot 2TBP$.

The mechanism of uranium and that of other actinides is one of simple complex formation, the reactions being formally -

$$MO_2^{2+}{}_{(aq)} + 2 NO_3^{-}{}_{(aq)} + 2TBP_{(org)} \rightleftharpoons MO_2(NO_3)_2 \cdot 2TBP{}_{(org)};$$
$$M^{4+}{}_{(aq)} + 4 NO_3^{-}{}_{(aq)} + 2TBP_{(org)} \rightleftharpoons M(NO_3)_4 \cdot 2TBP{}_{(org)}$$

although in practice the nitrato complexes may already have a substantial degree of formation in the aqueous phase from which they are extracted. For that reason the dependence of distribution ratio on nitrate ion concentration is less than might be expected. Because of non-idealities, the dependence on TBP concentration in the solvent is also less than the simple square law predicted by elementary theory.

Thermodynamic and kinetic data for uranium show that the extraction is exothermic. The rates in the forward direction increase with increasing TBP concentration, but those in the reverse direction (back washing) decrease. The effect of temperature on the extraction of actinides is small, although back washing from the loaded solvent is encouraged by higher temperature.

With TBP, the nitric acid concentration of the aqueous phase is judiciously controlled to ensure that the nitrate content is sufficiently high to effect an efficient separation of the actinides from other solutes in the forward extraction. With extractants such as Hexone, salting agents such as aluminium nitrate were necessary to ensure a sufficiently high nitrate concentration. The use of salting agents is intolerable in both the refining of UOCs and reprocessing operations due to added costs and enhanced problems in the evaporation of high active fission product waste respectively.

Additionally, in reprocessing operations use is made of the difference in extractability due to different valency states. In the first and second solvent extraction cycles, for example, the influence of acidity and presence of reducing agents such as U(iv) affect the distribution of Np. Approximately half of the total quantity is discarded in the high active waste liquor as Np(v) ions , these being the least extractable by TBP, whilst the remainder has to be finally separated in the purification cycle.

The distribution ratios for some actinides and various fission products with TBP are presented in Table 1.

TABLE 1

APPROXIMATE DISTRIBUTION RATIOS FOR SOME ACTINIDES AND
FISSION PRODUCTS FROM NITRIC ACID
SOLUTIONS WITH 20 o/v TBP/OK

Element	1 M Nitric Acid	6 M Nitric Acid
Th(iv)	0.2	3
U(vi)	7	30
Pu(vi)	0.8	3
Pu(iv)	2	20
Pu(iii)	<0.01	0.01
Np(iv)	0.8	7
Np(v)	0.01	0.02
Np(vi)	5	22
Ru	⁻0.001 to ⁻2	⁻0.001 to ⁻2
Zr	<0.01	1
Nb	<0.001	0.01

The extraction mechanism for the fission products, zirconium, niobium,
ruthenium, is similar to that of actinides with TBP in nitric acid solutions.
Two solvates of zirconium having the composition $Zr(NO_3)_4 \cdot TBP$ and
$Zr(NO_3)_4 \cdot 2TBP$ are formed with varying TBP concentrations from nitric acid
solutions.

Of the different series of nitrato and nitro complexes of ruthenium, only the
nonionic trinitrato and the tetranitrato acid complexes of nitrosyl ruthenium
are fairly extractable by TBP. The species formed in the organic phase have
been confirmed to be $RuNO(NO_3)_3 \cdot 2TBP$ and $H[RuNO(NO_3)_4] \cdot 3TBP$.

More recently attention has been paid to the extraction of Tc from 3M nitric
acid liquors. It was observed that the extractability of the pertechnetate ion
TcO_4^-, was low ($D_{Tc} \sim 0.2$) but was enhanced by the presence of uranium, thorium
and zirconium. In the presence of the latter the D_{Tc} value increased to ~0.5.
The technetium also enhanced the distribution ratio of zirconium in the
extraction stages, but did not prevent back-extraction on scrubbing.

The recovery of uranium from a loaded TBP diluent system is achieved by
contacting the organic phase with dilute nitric acid at 60°C. A small quantity
of acid is employed to prevent hydrolysis of the uranium in the aqeous phase.
This approach is common to both UOC refiners and spent fuel reprocessors.

The wealth of TBP extraction data affords many exploitable differences for the
separation of two or more given elements. Distribution coefficients may be
enhanced by the selection of acid strength, temperature and salting agents, all
of these parameters being utilised in the extraction and purification of
actinides.

ii. Extraction of Nitric Acid

Although nitric acid has little or no effect on the kinetics of actinide
transfer into the TBP phase, at high concentrations (>6M) its extraction
competes with the transfer of metal ions. This observation has been attributed
to the formation of a complex with TBP of the type $HNO_3 \cdot TBP$. As a result,
particularly where high solvent to aqueous ratios are used, extracted acid may
dominate the acidity of backwash stages.

The extraction of nitric acid in the uranium purification cycle of either a UOC
processing or a reprocessing operation is minimised by maintaining the uranium
loading of the TBP phase near to its operating saturation value. This control
is necessary to minimise carryover of the acid into the uranium product stream
and thereby ensuring that the corrosion of downstream equipment such as
evaporators is limited.

HYDROLYTIC AND RADIOLYTIC DEGRADATION OF TBP

TBP, being an ester, is susceptible to hydrolysis catalysed by either acids or alkalies. Acid-catalysed hydrolysis is probably the most important reaction from the standpoint of UOC refining although less important for nuclear fuel reprocessing. It occurs in both the organic and aqueous phases and proceeds stepwise, yielding in turn dibutyl phosphate (DBP), monobutyl phosphate (MBP) and finally phosphoric acid; however, under extraction conditions the first step is by far the most important.

Ionizing radiation like mineral acids cause decomposition of TBP; the degradation products from radiolysis include DBP, MBP, H_3PO_4, various gases eg H_2, CH_4, C_2H_4, alcohols and other hydrocarbons. The proportion of the products generated is largely dependent on the radiation dose which the parent TBP molecules adsorb and the selected diluent. The acid butyl phosphates produced either by hydrolysis or radiolysis of TBP cause retention of small amounts of uranium, plutonium and certain fission products (zirconium, niobium) in the solvent and therefore lead to -

i.   uranium and plutonium losses;

ii.   reduced decontamination of the uranium, and plutonium from fission products, and

iii. a stripped solvent containing plutonium and fission products.

In extreme cases, precipitates may be formed which may result in "crud" formation at liquid-liquid interfaces which may influence phase separation and thus the control of the extraction equipment.

In a system where there are a number of metal ions, eg U, Pu, Zr with varying concentrations and different stability constants related to the formation of metal DBP and MBP complexes, then the overall effect on process performance can be somewhat difficult to predict. It also assists in explaining the differences sometimes observed between the laboratory and plant trials on TBP degradation effects.

Although the decomposition of TBP produces degradation products which would seriously influence the efficiency of spent fuel reprocessing, UOC refining and possibly mining/milling operations, fortunately a simple aqueous wash with an alkaline solution (generally sodium carbonate) will remove DBP and MBP and the majority of the fission products such as Ru, Zr and Nb from the solvent phase. Hence by a comparative simple treatment the selectivity, affinity and efficiency of TBP can be maintained.

The choice of contacting equipment can influence the rate of degradation product formation. With mixer-settlers the majority of radiolytic damage occurs in the settling area, whilst with shorter residence contactors, such as pulse columns, this problem is greatly minimised. Contactors with an even shorter residence time, eg centrifugal, have been successfully employed for the high active cycle in reprocessing operations where there is a very strong radiation field and hence potentially considerable degradation. The main consideration limiting the extension of this practice is the difficulty of mechanical maintenance under highly active conditions. This alternative and complementary means of minimising TBP degradation is made possible by the rapid kinetics of plutonium and uranium extraction in conjunction with the physical properties of the TBP diluent system.

ANTAGONISTIC SYSTEMS

The art of solvent extraction is ultimately to produce an aqueous product liquor containing the appropriate purified metal(s) and amenable to downstream process conditions. With some extractants, notably di-2-ethyl hexyl phosphoric acid, the affinity for certain metals is very high (distribution values >1000) and therefore the recovery of the metal(s) from the loaded solvent can be extremely difficult or

require reagents which are incompatible with subsequent processes. The addition of a second solvent such as TBP to the organic phase reduces this affinity and in doing so improves the back-washing of the appropriate metal(s).

PREVENTION OF THIRD PHASE FORMATION

A second organic phase can form in some extraction systems when the concentration of the extracted species exceeds the solubility of the solvate in the organic system. This condition can be overcome by the addition of a third reagent (modifier) to the organic phase. The modifier, unlike a synergist, does not participate in the extraction process, but solely improves the solvation of the extracted species. In the TRUEX process, for the recovery of transuranic elements, TBP is employed to ensure that the extracted metal-carbamoyl methyl phosphine-oxide complex remains soluble.

TBP/diluent systems are themselves subject to third-phase formation under certain conditions. The tendency depends very strongly on the choice of diluent and even within a given type of diluent, such as the n-paraffins, increases sharply with carbon chain length. This consideration has raised doubts about the advisability of using n-dodecane as diluent in reprocessing systems.

SUMMARY

It is in solvent-extraction processes, particularly those employing aqueous nitrate media in the nuclear fuel cycle that TBP finds one of its major applications. The potential problems associated with the separation and purification of actinides previously described can be readily overcome by the careful choice of diluent, solvent concentration, solvent clean-up, aqueous phase acidity and temperature.

Confidence in TBP is demonstrated by its selection for both the French and British new commercial reprocessing plants and possibly the proposed German and Japanese facilities. UOC refiners are well satisfied with this reagent and current indications are that future plants will remain with TBP. Its use in mining/milling operations is being extended as alternative leaching circuits to sulphuric acid are being developed.

ENGINEERING PROBLEMS IN LIQUID-LIQUID EXTRACTION - THE DIMENSIONING OF EXTRACTORS

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1. Introduction. engineering tasks

Various special disciplines cooperate in the field of liquid-liquid extraction (SX). This paper wants to illustrate to other disciplines task and procedure of engineers by using the dimensioning of extractors as an example and thus demonstrate the state of art.

Systematic procedure is fundamental principle of the work of engineers. Thus, the problem solving cycle of systems engineering presents itself. It consists of the procedural steps of the situations analysis and the formulation of objectives, of the synthesis and analysis and of evaluation and decision. The essential engineering tasks applied to the extractor dimensioning turn out to be:

- the systematic preselection of suitable constructions of extractors based on a carefully defined problem and with the aid of an information system for available constructions. The paper deals with the main points of situation analysis and of pre-selection of extractors;
- the systematic experimental analysis, evaluation and choice of an apparatus best for the respective task. The paper deals with the main steps of experimental measures;
- theoretical and experimental analysis of the complex processes in extractors, in order to complete the information system for the preselection on one hand, and, on the other, to be able to dimension the chosen type of extractor correctly. In the following this part of the paper is demonstrated in detail.

2. Problems of engineering analysis

The paper deals with the drop size, the counter-current flow of phases and the axial mixing as central dimensioning problems in order to introduce theoretical and experimental tools of engineering and at the same time demonstrate the state of art.

2.1. Drop sizes

In modern counter-current extractors one of the two phases, usually the solvent, can be pur-posefully disintegrated into drops by power input with agitation or pulsation. The smaller the drops, the greater is the interfacial area per unit volume and is the mass transfer coefficient and the higher the coalescence time t_c (Fig.1,2 and 3). The setting of the drop size in the extractor must consider this fact.

As measuring methods the photography (Fig.4) and a probe technique (Fig.5) are compared and a new laser scattered light technique for very small drops is introduced. The measuring results must be correlated with the influencing parameters with the aid of physical mathematical methods. In doing so three steps of engineering penetrating depth are gone through: the simple empiric correlation , the similarity theoretical description by way of relations between dimen-sionless characteristic numbers and, finally, the physical-mathematical modelling of the physi-cal processes. For an example the paper deals with an empiric correlation for the calculation of drop sizes during mass transfer into the drops, a relation of characteristic numbers for the calculation of drop sizes on sieve plates without pulsation and a new modelling of drop sizes on liquid-pulsed sieve plates (Fig.6).
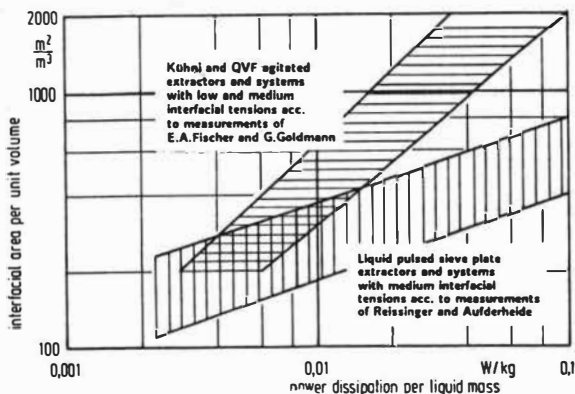
Fig. 1. Interfacial area per unit volume in dependence
on power dissipation per unit mass(E.A.Fischer, Ph.D.
thesis ETH Zürich 1973; G.Goldmann, Ph.D.thesis TU
München 1986; K.H.Reissinger, Ph.D.thesis TU Graz;
E.Aufderheide, Ph.D.thesis TU Clausthal 1985).
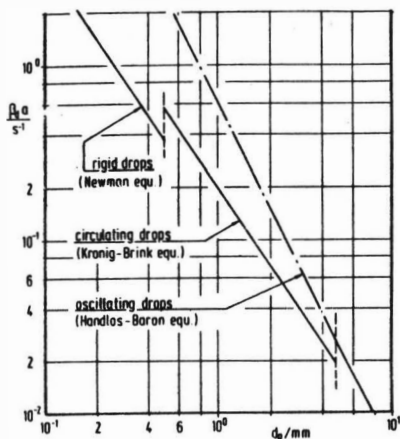
Fig. 2. Volumetric mass transfer coefficients
$\beta_d \cdot a$ of Shellsol drops in water of 20 °C in
dependence on drop diameter d_p (drop holdup 10 %)
———— gravity field
—·—— centrifugal field

$$Ar^{1/3} = 11.7 \left[(Re \cdot Fr)^{1/3} \right]^{0.305}$$
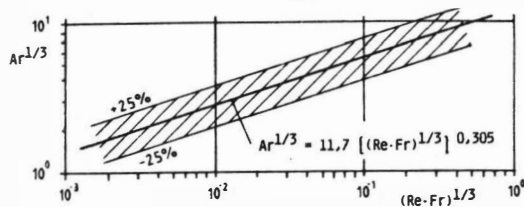
$Ar = d_{32}^3 \, \dfrac{\rho_c^2 \, g}{\eta_c^2} \, \dfrac{\Delta \rho}{\rho_c}$ Archimedes number

$Re \cdot Fr = \left(\dfrac{H_0 \epsilon_d}{t_c} \right)^3 \cdot \dfrac{\rho_c^2}{g \cdot \eta_c \cdot \Delta \rho}$ Reynolds-and
Froude numbe

$d_{32} = 11.7 \, t_c^{-0.305} \, F(H_0; \, \epsilon_d; \, \rho_c; \, \Delta \rho; \, \eta_c)$

Fig. 3. Coalescence time t_c dependent on mean sauter diameter d_{32},
on height of dispersion H_0, on holdup ϵ_d, on mass density ρ_c and
viscosity η_c of disperse phase (d), on density difference of both
phases. The given function fits batch settling experiments of dif-
ferent authors within ± 25 %.

38
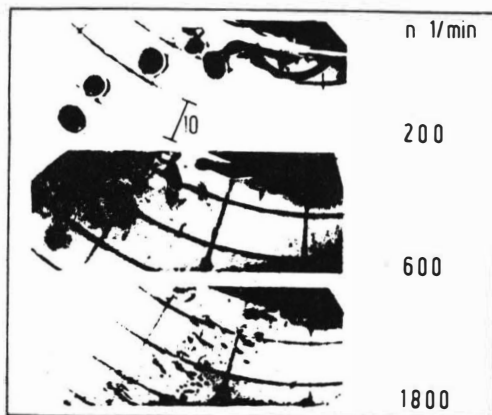
Fig. 4. Drops in a centrifugal field
n number of revolutions
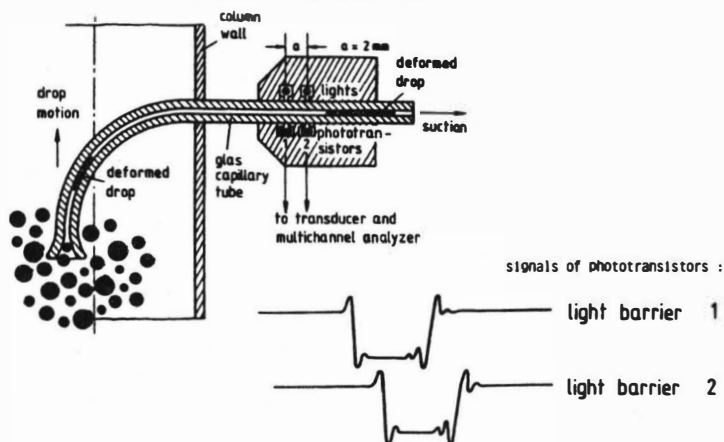
Fig.5. Probe measuring technique with photoelectric detection
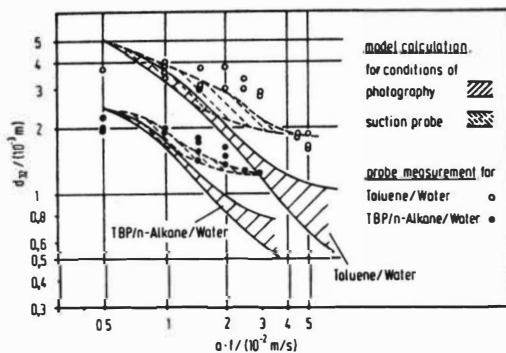
Fig. 6. Measured and calculated drop sizes in pulsed sieve-plate columns

39

2.2. Counter-current flow of phases

The counter-current flow of phases is necessary when a separator performance of more than one theoretical stage is needed. Counter-current flow is the most important principle of operation of modern extraction columns (Fig.7). Two main problems concerning this fact must be solved: the transport of phases in the gravity or centrifugal field and the reducing of the axial mixing of each phase. The phase transport dies out at a critical throughput, the flooding throughput. Task of the engineer is the dimensioning of the column diameter thus, that the flooding point cannot be reached in practical operation conditions (Fig.8). The axial mixing reduces the differences of concentration between the phases and thus the separation power to be reached. It is demonstrated that counter-current apparati of a mixer-settler character subdue the axial mixing just like unpulsed sieve plates or Podbielniak centrifugal extractors do when they are operated correctly. However, ordinary counter-current extractors require a careful analysis of the axial mixing.

RDC   ARD

KÜHNI   OVF-RZE
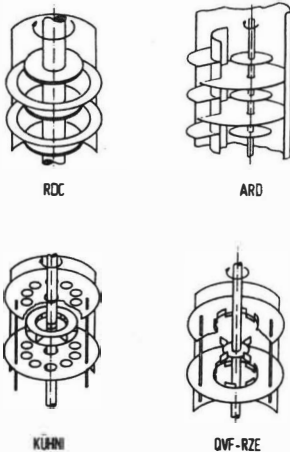
Fig. 7. Agitators and stators of different agitated extractors
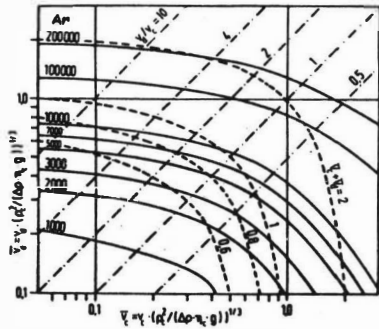
Fig. 8. Phase throughputs at flooding point of unpulsed and pulsed plate columns and of agitated columns (Pilhofer, Chem.-Ing.-Tech. 51(1979) 231)
v superficial velocity; other symbols see Fig.3

2.3 Axial mixing

The analysis of axial mixing is an excellent example for the extraordinary experimental, mathematical and numerical problems which an engineer is confronted with during the analysis of apparati. For the description of the complex flow of phases in extractors similar to reactor engineering the concept of residence time is used and there are three problems to be coped with: the measurement of the residence time, the evaluation and the interpretation of the measuring results:

a) tracer are used for measurement (Tab.1) and suitable sensors are needed in order to gain cross-sectional averaged signals;

b) the information provided by the residence time curves must be decoded by means of suitable mathematical-physical models. For an example the paper presents the dispersion model which is frequently used. It describes the flow of each phase as plug flow, which is superimposed by a merely stochastic liquid motion and in its function as a model parameter introduces an axial dispersion coefficient D_{ax} whose value is the dimension figure for the axial mixing of the respective phase:

$$\frac{\delta c}{\delta t} = D_{ax} \frac{\delta^2 c}{\delta_z^2} - w \frac{\delta c}{\delta t}$$

c tracer concentration; t time; z coordinate; w fluid velocity

Table 1. Common tracers and probes for residence time measurement (Blass et al., Ger.Chem.Engng. 9,1986,222-238)

phase	tracer material	variable/probe	remarks
aqueous	NaCl or KCl solution	electrical conductivity/Pt conductivity probes stainless steel rods	verify linearity of salt concentration and conductivity; relatively low experimental effort, most frequent application in pilot-scale columns
	Na-fluorescein ($\lambda = 515$ nm)	fluorescence/UV-light source photomultiplier	verify linearity of multiplier signal and tracer concentration; if partially soluble in organic phase, material balance errors occur, high exp. effort; column must be transparent
	radionuclide ^{87} = Sr ^{113} = In ^{128} J	radiation intensity/scintillation counter	it is possible to apply several measurement points, external mounting in industrial plants also possible, very expensive; handling of radioactive substances mostly subject to official regulations
organic	9,10 diphenyl ethinyl anthracene ($\lambda = 470$ nm)	fluorescence/UV-light source photomultiplier	see above
	Calco Oil Blue ($\lambda = 500$ nm) Sudan Red ($\lambda = 650$ nm)	light absorption/photometer, continuous sampling	effect on surface tension (attention when measuring with simultaneous mass transfer) identical suction probes necessary
	temporary change of the fraction (for example TBP/n-alkane)	concentration or density; continuous sampling	specific case of application; identical suction probes are necessary
	radionuclide ^{18}F, ^{61}Cu	radiation intensity/scintillation counter	see above

Table 2. Comparison between short cut methods of parameter identification
(Krizan : PhD Thesis, Techn. University Munich 1987)

		momentum method	Oestergaard method	Vergnes method	Maximum method	Covariance method	Asymtote method
suppositions	one measurement point	X	X	X	X		
	two measurement points	X	X			X	X
	solution of Feller	X	X		X	X	X
	solution of Levenspiel	X		X	X	X	X
result	mean residence time	X	X			X	
	Bodenstein number	X	X	X	X	X	X
computing expense	small			X	X		X
	medium	X				X	
	large		X				
measurement expense	small	X	X	X	X		
	large					X	X
sensitivity	to noise		X	X	X		X
	to failing	X	X				
	to zero time	X	X	X			
	to DC	X	X	X	X	X	X
error	with respect to						
	mean residence time (%)	± 10	± 10			± 30	
	Bodenstein number (%)	± 50	± 100	± 150	± 100	± 100	± 200

42

Since the fifties solutions for the model differential equation have been known, but only recently the solutions could be definitely related to the underlying boundary conditions by means of the random walk theory;

c) a sufficiently exact evaluation implies powerful computers. It is obtained by fitting the theoretical solution function of the dispersion model to the measured residence time curves by varying the dispersion coefficient as fitting parameter. Thus it is
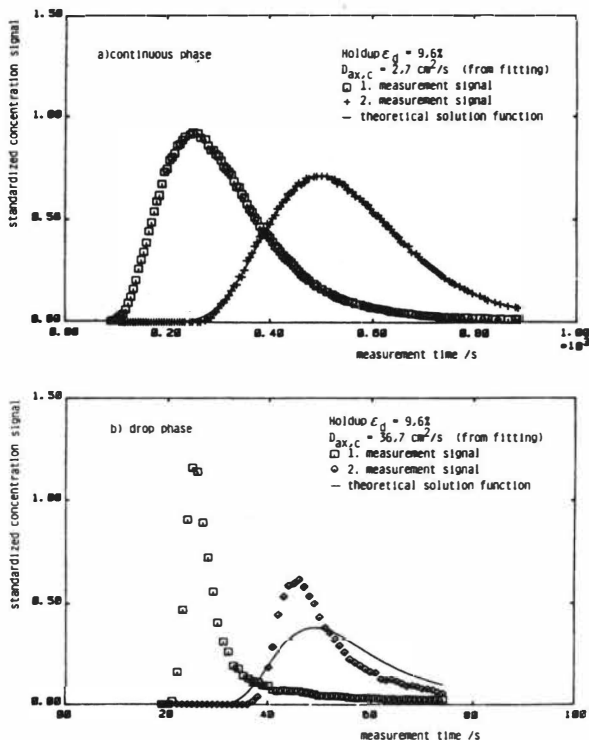
Fig. 9. Evaluation of residence time measurements
(E. Auderheide, Ph.D.thesis TU Clausthal 1985)

gained out of the measured curves. Only the exact modern evaluation methods make the estimation of the quality of formerly used methods of approximation possible (Tab.2);

d) the dispersion model describes well the course of the measured signals and thus the hydrodynamic behaviour of the continuous liquid in all counter-current columns, as long as no radial differences in velocity and no large-scale circulations appear (Fig.9). However, it does not meet the hydrodynamic behaviour of the polydisperse drop phase and thus can at best only be regarded as a formal model.

3. Scale up of extraction columns

One of the main engineering tasks is the dimensioning of technical extractors whose main dimensions are substantially larger than those of laboratory columns. Out of a balance of the particle flows at a differential element dh of the counter-current extractor a system of

43

equation is won by a suitable kinetic formulation for the mass transfer from the continuous to the drop phase which provides the numerical calculation of the concentration profile of the transfer component along the height of the apparatus:

$$-(1-\varepsilon_d) \cdot D_{ax,c} \; d^2c_c/dh^2 + v_c \cdot dc_c/dh - \beta_{od} \cdot a \cdot (c_d - c_c \cdot m) = 0$$

$$-\varepsilon_d \cdot D_{ax,d} \; d^2c_d/dh^2 - v_d \cdot dc_d/dh + \beta_{od} \cdot a \cdot (c_d - c_c \cdot m) = 0$$

c_c, c_d molar density of continuous and disperse phase; v_c, v_d superficial velocity of both phases; β_{od} overall mass transfer coefficient; m slope of equilibrium line; a drop swarm surface per unit volume; ε_d holdup of disperse phase; $D_{ax,c}$, $D_{ax,d}$ dispersion coefficients of both phases; h coordinate of extractor height

If the dimensioning parameters drop size and hold-up (drop swarm surface a resp.), flooding velocity, mass transfer coefficient and dispersion coefficients determined by laboratory columns and by mathematical models can be transferred to technical columns as well, a column of technical dimension can be designed based on the equations mentioned above. Experience shows that the column diameter based on the laboratory investigations can be determined exactly enough, but not the column height which would be calculated too small. The paper discusses the main differences between the processes in laboratory columns and in technical columns and mentions the special boundary conditions of engineering investigations. Quintessence of the chapter is that a safe scale up depends on the experience and the skill of the engineer, which goes far beyond knowledge.

Literature

Since the fifties more than 1000 relevant engineering publications on extractors were published besides textbooks and handbooks. This number is still growing immensely, which is proved by the international solvent extraction conferences.

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The processes of concentration and metal separation find wide and increasing application in hydrometallurgy of nonferrous, rare and radioactive elements. Improvement of the existing and development of principally new processes of concentration and metal separation have allowed two main trends of investigation to be singled out. The first one includes the purposeful change of aqueous phase properties due to acid-salt content, the latter is based on the use of new effective extractants. For a long time the first trend of the study has been prevailing due to the accumulated experimental data $/$ 1, 2 $/$. The second trend has been clearly formed only in the past decade, when the use of new selective extractants became the obligatory condition of the further development of extraction technology in hydrometallurgy $/$ 3, 4 $/$. One of the most important problems of chemistry is the determination of the reactivity dependence on the structure and the composition of chemical compounds. One of the sections of this problem is the selection of synthesis and the study of physico-chemical properties of selective extractants. Empirical search for new extractants is unproductive, therefore the development of the theory of electron donor-acceptor interactions (EDA) $/$ 5, 7 $/$, conceptions of chelate reagents mechanisms $/$ 8, 9 $/$ and the appearance of new types of stereoselective reagents $/$ 10, 11 $/$ made it possible to obtain the extractants with the predetermined useful properties.

For solution of this problem a new trend of investigation to reveal, obtain and study physico-chemical properties and the extractants reactivity has been formed in the USSR. Some thousands of different elementoorganic derivatives have been synthesized and analyzed. More than two dozens extractants have been recommended for application .

At the present step of the development of science the purposeful selection of "strong" and "superstrong" extractants makes it possible to use the general theory of compounds reactivity $/$ 12 $/$, the theory of electron donor-acceptor interactions $/$ 5-7 $/$ and the relations between physico-chemical properties of extractants and their reactivity, which allow to predict successfully the extractive ability of reagents of neutral, cation-, anion-exchange ampholyte types.

In accordance with these conceptions, the most "strong" extractants are elementoorganic compounds as $R_n E=O$, where $E=N$, P, As, Sb, C, Se, Te, R- aliphatic or aromatic radicals. The calculation of bond overlap integrals $E=O(S_{E=O})$ indicates, that the increase in the

value of $S_{E=0}$ with rising the grade of its double-bonding results in a sharp decrease of electronodonor properties of oxidic oxygen being the active center of these types of reagents $\angle$ 15, 16 $\angle$. Therefore, one can draw the conclusion, that the most strong reagents will be such compounds, where the conjugation of the central heteroatom is minimum and heteroatom itself has a very low electrononegativity. Using these parameters, one can arrange the following row: $C \angle S \approx$ $\approx P \angle As \approx Se \angle Te \approx Sb \angle N$, which coincides with the row of these compounds basicity and the row of their extractive ability under optimal conditions.

At the initial steps of the development of extraction technology ethers (dialkyi ethers ROR), chlorex $(ClCH_2CH_2)_2O$, poly (ethylene glycol) ethers $RO(CH_2CH_2O)_nR$ and ethers of carboxylic acids RCOOR have been used as extractants. The use of such extractants has required the introduction of salting-out agents, prohibiting the wide application of these processes. The extraction processes with linear and cyclic ketones $R_2C=C$, the wellknown of which being methylisobutylketon and cyclohexanon have proved to be free of such a defect. However, the most perspective carbonylated extractants appeared to be amides of carboxylic acids $RC(O)NP_2$ and alkylated ureas $R_2C(O)NR_2$, recovering by metals from the concentrated solutions of mineral acids (more than 5 M).

The transition to sulfur-and organophosphorus compounds $R_2S=0$ and $R_3P=0$ results in increasing oxidic oxygen reactivity and maximum extraction moves towards the region of medium acid concentrations (1-5 M). Finally, for the derivatives $R_nE=0$ (E=N, Sb,Te,As,Sc), where the grade of group double-bonding E-0 is close or equal to 1, the oxidic oxygen reactivity is maximum and these compounds are "superextractants" in the region of acidities close to the neutral one.

There is an additional possibility of controlling the extractive ability of elementoorganic extractants due to a change of spatial and electronic structure of substituents R with a central heteroatom. This allows to obtain a broad spectrum of extractants, recovering any metals from the different acid-salt solutions.

The transition from monodentant to bi-and polydentant extractants, as a rule, causes increasing of distribution coefficients of metals and one can observe the selectivity of individual elements. This may be confirmed by the example of phosphororganic compounds $(RO)_2\overset{\|}{\underset{O}{P}}(CH_2)_n$

$\underset{O}{\overset{\|}{P}}(OR)_2$ and $R_2\underset{O}{\overset{\|}{P}}(CH_2)_n\underset{O}{\overset{\|}{P}}R_2$ of carbonylated $R_2N\underset{O}{\overset{\|}{C}}(CH_2)_n\underset{O}{\overset{\|}{C}}NR_2$ and mixed

derivatives $(RO)_2\underset{O}{\overset{\|}{P}}(CH_2)_n\underset{O}{\overset{\|}{C}}NR_2$, $(RO)_2\underset{O}{\overset{\|}{P}}(CH_2)_n\underset{O}{\overset{\|}{C}}OR$, $(RO)_2\underset{O}{\overset{\|}{P}}(CH_2)_nSO_2R$

$(R=C_4H_9,\ C_8H_{17},\ n=0 \div 4)$. More complicated oligomeric cyclic and linear extractants
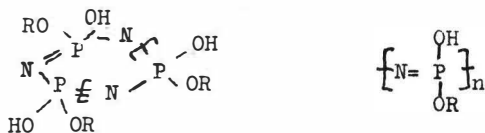
$(R=C_6H_{13} \div C_{12}H_{25},$ aryl, $n=1 \div 12)$ allow to solve the problems of hydrometallurgy in those cases, when the maximum concentration of elements from complex solutions is needed.

At present, the problem of forming "strong" and "superstrong" mono- and polidentant extractants and technological processes on their basis has been solved, but a search for the selective extractants is at its peak. The point is that when constructing strong collective extractants of general action one can use the theoretical conceptions of complexation mechanisms, while the prediction of the extractants selective properties succeeds very seldom. In this connection, empirical search for selective extractants is of great importance in broadening their nomenclature although one can generalize these studies.

One of the perspective classes of selective extractants are amides of phosphoric acids in which nitrogen of amide group contains as one of the radicals carbonyl, carboxyl, carbomide, sulfo-, phosphoryl groups or is included into heterocyclic system. Among the studied compounds there are extractants, which behave as if they have two or more structures. The conception of tautomerism, which have been worked out for keto-enol and amide-imidol rearrangements was suggested to be used for explaining the observed phenomena.

Phosphorus and sulfur-containing compounds belong to the group of potentially selective extractants, where oxygen of phosphoryl group is substituted for sulfur or alctiol radicals being introduced into the extractant molecule. The comparison of these compounds with oxygen analogs shows, that when oxygen is substituted for sulfur, the distribution coefficients of hard metals fall sharply (by 3-4 orders) but the extraction of malleable hard metals sharply rises, that may be used in practice.

At present, the main trend in manufacturing selective extractants remains the introduction of stereospecific chelate groupings into the structure, where the stable intermolecular chelate cycle with the specific protone properties are realized due to the formation of strong intermolecular hydrogen bond. The derivatives of 2-oxyphens, 2-oxyphenonoxymes and 8-oxyhynolines, widely used in hydrometallurgy of nonferrous and rare metals may be used as such extractants. Among the new selective extractants one should note the macrocyclic compounds, belonging to bioinorganic systems and reacting with metal ions according to the little-known conceptions in coordination chemi-

stry. It is a matter of forming the inclusion compounds arranged in a "guest-host" type fashion, when the interaction between ligand and ion metal reaches maximum in entering the ion into inner cavity of macrocycle. According to this principle many vitamines, antibiotics, ferments and other biopolymers have been formed. The simplest models of such systems are crown-ethers and cryptands, which have high selectivity characteristic of macrocyclic biological systems.

The study of the extractive ability of crown-ethers and criptands has shown that they were stereosphecific reagents and were capable of separating chemical analogs, differing in ion radii. With the derivatives of 18-crown-6 processes of recovery and purification of alkaline and alkali-earth elements, lead, mercury, gold, silver, plutonium and neptunium have been developed.

Wide perspectives open due to the use of the extractant mixtures in hydrometallurgy, possessing the synergetic effects or polydentant extractants with intermolecular synergetic properties. Double, triple and more complicated extraction mixtures are used one way or another in an overwhelming majority of extraction processes in uranium hydrometallurgy.

The manufacturing of a wide variety of effective and selective extractants for recovery and separation of nonferrous, rare and radioactive elements has allowed the extraction production of the most important metals to be realized. The extraction technology of recovering uranium from nitric, sulfuric and phosphoric and solutions, concentration and purification of plutonium and neptunium from nitric acid systems, the technology of rare-earth and transplutonium elements separation, the recovery processes of lithium, rubidium and cesium from alkaline solutions, rhenium and indium from sulfuric acid solutions, the extraction processes of separation of circonium and hafnium, niobium and tantalum, uranium and molebdenum, platinum metals, copper, nickel and cobalt, gold, silver and tungsten and some other processes have been developed in the USSR.

The main direction in the further improvement of the extraction processes in hydrometallurgy up to 2000 year in our opinion will be the development of processes such as: extraction dissolving and leaching, extraction desorption, membrane extraction, condensed gases extraction, extraction from gas-air phase, the development of fully closed and unwasted technological processes. This will require the manufacturing of new apparatuses and essentially expand the field of application of extraction technology.

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EXTRACTION KINETICS: RESULTS AND PROBLEMS

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Extraction kinetics - an intensively developing field - lies at the junction of extraction chemistry, physical chemistry of heterogeneous systems, hydrodynamics and mass transfer in two-phase flows. It is this fact that determines the complexity of the subject and the difficulties of discussing it.

In order to understand the content of extraction kinetics, we list the key questions:

1. What phenomena determine the extraction rate?

2. What pecularities give the existence of two phases and the interfacial region when chemical reactions proceed?

3. What new can yield the studies of extraction kinetics for the aforementioned branches?

4. Is it possible to control the extraction rate not by adding energy but by using nontraditional techniques?

The first three questions have scientific significance and the last one has practical importance.

The aim of this topic is to generalize recent advances of kinetic studies and to present our views on the prospects of works that will be done in this field.

Factors determining the extraction rate. Extraction rate is determined by the interfacial area, the motive force of the process, and also the resistance on the way of the system to the equilibrium state. Incorrect consideration of any of these components may lead to improper explanation of the results. In further discussion we shall assume that the interface area is known and the kinetics is characterized by the mass flux across the unit surface area. We call it the extraction rate (R). Dividing R by the motive force we obtain the mass transfer coefficient or a reciprocal to it value - resistance, which can be used to compare different systems.

It has been proved that the latter is concentrated in the interfacial region and all those factors which affect the composition, properties, concentration gradients and velocity field in this region, also influence the mass transfer coefficient. Among these factors are: (a) chemical reactions; (b) blocking of interface due to the accumulation of difficultly soluble reaction products, microdrops, and solid particles on it, i.e. due to the formation of microheterogeneity zones and condensed interface films (CIF); (c) adsorption and desorption barriers as well as the energy barrier of electric nature; (d) spontaneous interfacial conveotion (SIC), i.e. movement of fluids along the interface caused by interfacial tension gradients during mass transfer. Thus, information on the enumerated phenomena is contained

in the mass transfer coefficients. To get this information, we must know what properties these coefficients have.

"Simple" mass transfer. As motive force we take the difference between global-equilibrium and local concentrations in one of the phases. And, instead of two mass-transfer coefficients, K_1 and K_2, appearing in the additivity rule, we obtain

$$K = K_1 + K_2 = (1 + \alpha) \, \beta_1 \beta_2 / (\beta_1 + \alpha \beta_2). \tag{1}$$

This composite coefficient has the following properties:

- it is computed from the results of kinetic experiments using the following formula:

$$K = -(at)^{-1} \ln(1 - E) \tag{2}$$

i.e. without the knowledge of partial mass-transfer coefficients β_i as well as of the distribution coefficient. It is sufficient to know the specific surface a, time t, and the extent to which the system deviates from equilibrium -E;

- it weakly depends on α , i.e. on the nature of the substance being distributed and the extraction system; according to (1), the values of K are bounded by the inequality

$$\beta_{min} < K < \beta_{max} \tag{3}$$

and its magnitudes, under usual hydrodynamic conditions, amount to 10^{-4}-10^{-3} cm/s;

- it exhibits almost the same dependence on the mixing intensity ω as β_i:

$$\lg \beta_i = \text{const} + p \lg \omega, \tag{4}$$

where $p \approx 0.5 \div 1$;

- it in almost the same manner as β_i depends on temperature ($E_{activation} < 20$ kJ/mole).

Mass transfer with chemical reactions. Numerous attempts to use the kinetic method for the study of chemical reaction mechanism in extraction have lead only to very modest successes. The methodology used as a

Table 1. Types of reactions and their regimes

Reaction	Instantaneous	Fast	Slow
Regime	Diffusion	Transient	Kinetic
Zone width	0	Depends on the reaction rate	∞

51

guide was mainly oriented to the study of either purely surface or purely homogeneous reactions.

The Astarita-Danckwerts theory provides explanation to the pecularities of reactions occuring in two-phase systems and to the evolution of topological schemes of a diffusion chemical process. On reducing the reaction rate the regimes gradually change and the reaction zone widens.

On supplimenting this picture with surface reactions involving the participation of adsorbed substances, it becomes evident that the reactions are multiway reactions, and, therefore, cannot be characterized by the only rate constant. Thus, for their study is needed a more flexible methodology. Such a methodology is under development.

It is based on

- the study of processes under such conditions when the contribution of only one of the topological schemes becomes dominant or on the use of methods that enable the contribution of each of the schemes to the extraction rate to be computed;

- the study of processes under such conditions when the role of interfacial phenomena is reduced to a minimum or when the contribution of these phenomena can be measured;

- the calibration of devices against standard systems or on the use of comparative components;

- the use of independent methods such as measurement of interfacial tension and of rheological, electrical and optical properties of interfacial region. If the role of interfacial phenomena is reduced to a minimum, then the topological schemes and the regimes can be identified using the data of Table 2.

Table 2. Identification of topological schemes and regimes

Method	Parameters	Results	Conclusions
Reactor with a controlled surface of emission (RE)	S, ω, t	$S \to \infty; RS \to const$ $S \to \infty; RS \to \infty$	Kinetic regime There are no slow homogeneous reactions
Diffusion cells with stirring (DC)	ω, t	$\omega \to \omega_{cr}$ $R \to const$ $lgR \sim lg\omega;$ $0.5 < p < 1$	Kinetic regime of surface reaction or transient regime of bulk reaction Diffusion regime
Short-time contacting method (STCM)	t	$t \to 0; R \to const$ $t \to 0; R \to 0$	Surface reaction Bulk reaction

The interfacial processes play different roles under the conditions of each of the enumerated methods. Continuous "purification" of the interfacial surface takes place in the ER, and therefore the formation of CIF does not play a significant role, while this formation may become dominant in DC. Spontaneous interfacial convection strongly affects the results obtained by the short-time contacting method. These methodological pecularities may be used as basis for studying interfacial processes.

Diffusion regime. This is a very important practical case, because most of the known extractants react almost instantaneously with the extractable substances. If use is made of microconcentrations and the ionic force is maintained constant, then all the aforementioned properties of K will hold. This has been confirmed by a computer analysis of mass transfer with reactions of various complexity. From this follows an important conclusion: the described properties of K can be used to identify a diffusion regime and the deviations from these properties point to phenomena like barriers, CIF, and SIC. The new for the extraction chemistry is that the stoichiometric coefficients and the extraction reaction equilibrium constants can be found by analyzing the dependence of initial velocities (R^O) as well as of K_1 and K_2 on concentration. In certain cases it is possible to determine the equilibrium constant not of the entire reaction but of its fastest stages. For instance, in extraction of acids with amines one can determine the equilibrium constant of the protonation stage, and, in stripping, of the ion-dissociation stage. Making use of the properties of K and of the STCM it has been ascertained that the extraction process occurring due to hydrogen-bond formation, ionic pairs formation, and ion exchange can be regarded as processes of mass transfer with instantaneous reactions. The deviations of experimental data from the theory of mass transfer with instantaneous reactions are due to the formation of CIF and SIC.

Transient regime. In this case a bulk reaction is localized in the near-surface layers. The reaction kinetics can be described by the models developed by Sharma, Hanson, Hughes, and Rod using the Astarita-Danckwerts theory. These models predict a situation when the extraction rate will be independent of the stirring intensity. This regime is often erroneously taken by many scientists as kinetic regime of a surface reaction. In this regime the extraction rate is a complex function of diffusion coefficients D and rate constants k and concentration C:

$$R = \left[2D \int_{C_1}^{C_2} r(k, C)dC \right]^{0.5} \tag{5}$$

53

It is believed that this regime occurs in the extraction of certain metals with alkylphosphoric acid as well as of copper with hydroxy-oximes.

Kinetic regime. Attention to this regime is being given since the appearance of the pioneer works of Irving, Freiser, and Zolotov. This regime is typical for very slow processes of extraction of chelates and also for the processes of formation of organic substances in liquid-liquid systems. It is the most simple case when it is possible to obtain information on reaction mechanisms. A correct methodology should incorporate the measurement of interfacial surface area (see Table 2).

Surface reactions. The pecularities of surface reaction kinetics, formulated by Langmuir-Hinshelwood and Ely-Rideal, provide bases for the identification of surface reactions. "Pure" surface reactions take place only for practically insoluble-in-water extractants having pronounced surface active properties. If the solubility of extractants is appreciable, then surface reactions play a significant role only at low concentrations. A successful example is the extraction of Fe(III) with tri-n-butylacetohydroxamic acid, studied by Danesi. We obtained similar results in extracting Cu with different hydroxyoximes. In nonstationary processes a surface reaction dominates at small phase exposures, but its significance decreases with time. On this is based one of the methods of calculating the contribution of surface reactions to the extraction rate using the short-time contacting method.

Acceleration of chemical reactions. The task of accelerating chemical reactions in extraction and, particularly, in two-phase synthesis of organic substances is of great practical importance. For example, using the salts of quarternary ammonium bases permits the synthesis rate of certain organic compounds to be increased by many orders. In, extraction, the rate of a surface reaction and of bulk reaction strongly depends also on the presence of traces of some substances, say of surface active substances. The acceleration is attributed to electrostatic causes, the presence of micelles, and microhomogeneity in the interfacial region and also to the transfer of substances into the reaction zone, which are important for the occurrence of a reaction. The ionic surface active substances have more effect on the surface reaction rate than on the rate of fast bulk reaction. For example, the presence of 10^{-3}M sodium lauryl sulphate causes the rate of extraction of copper with 2-hydroxy-5-octylbenzophenoxime to increase by about an order. In the case of slow homogeneous reactions, as shown by Freiser, the effects may be even much more significant.

The study of acceleration mechanisms seems to have considerable promise.

54

Microheterogeneity zone (MZ) and condensed interfacial films. These phenomena strongly affect the results of kinetic measurements. They can be the source of erroneous conclusions, say, about the occurrence of a slow surface reaction in the systems where there are no such reactions but only instantaneous or fast reactions occur. The formation of CIF in commercial equipment lowers the productivity because of the decrease in the rate of mass transfer and the emulsion separation rate. The above said determines the scientific and practical significance of studying the formation of ZM and CIF.

Microheterogeneity zones appear due to local supersaturations which sometimes occur near the surface. The interfacial region attains a complex ("sandwich") structure. The diffusion resistance increases abruptly and the reaction conditions change. The formation of CIF has been found to be genetically associated with ZM. At definite concentrations the ZM changes into CIF. In these cases the process is often accompanied by an abrupt change in rheological properties of the interfacial region. The mechanisms of formation of CIF have been studied in detail in extraction of metals with acidic extractants. However, the phenomenon of formation of CIF is characteristic of the process of extraction of inorganic substances with any extractants.

Spontaneous interfacial convection. This phenomenon offers possibilities of developing cheap extraction-intensification methods and of reducing the dimensions of industrial equipment. Increase in the mass transfer rate due to spontaneous interfacial convection permits the use of more "mild" mixing conditions under which more large drops exist. Thus, the equipment productivity can be raised by making use of much higher phase separation rates. Losses of extractants also decrease due to better separation into phases in settlers. This is the reason why the SIC phenomenon has received the attention of a large number of researchers. SIC is closely related to concentration fluctuations in the interfacial region and, hence, to the formation of ZM and CIF. If the time of formation of CIF is comparable with the mass transfer period, then extraction is almost always accompanied by the appearance of SIC and therefore proceeds faster than when condensed interfacial films are not formed.

New prospects of creating highly efficient equipment are associated with the recently found phenomenon that very intense regimes of SIC appear when the thickness ratio of contacting phase layers attains a critical value.

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Liquid pertraction or liquid membrane separational processes appeared
in chemical engineering relatively recently, attracting the attention of
many scientists and engineers.There are more than hundred research teams
at present, exploring this new separation operation.

The principal idea inherent in liquid pertraction is explained by
Fig.1. Two aqueous solutions, a feed solution F and a stripping liquor R
are separated by a third organic liquid, which is immiscible with   both
aqueous solutions. This intermediate organic solution is the membrane S.
A specified component A is extracted from the feed F into the membrane S
due to the existing favourable thermodynamic conditions, set around the
first interface F/S and simultaneously stripped by the receiving liquid
R, responding to the new equilibrium at the second interface S/R.

Obviously, the liquid pertraction is a combination in time and space
of two well known separation operations - extraction and solvent   strip-
ping [1] which offers some attractive features unattainable in the clas-
sical solvent extarction. First, the liquid pertraction provides maximum
driving force for transportation of extracted species and therefore   in
many cases there is no need of multistage or counter-current operations.
Second, the organic phase S is a short time selective mediator and hence
its capacity is not very important characteristic. The low carrier con-
centration makes it possible to avoid the use of modifiers and to decre-
ase the rafinate polution. In this way, harmless and innert liquids con-
taining small amount of very selective carriers, for example chelating
agents, can be used. Even solid, slightly soluble in the membrane, but
selective additives are prospective carriers. This reveals new horisons
for syntheses of very selective solid "extractants".

There are various transport mechanisms controling removal and concen-
tration of the solute A in liquid pertraction. Three of them are shown
in Fig.1. In the first case, known as "up-hill" transport solute A is
pumped against its apparent concentrational gradient because of the irre-
versible chemical reaction A+B=AB that takes place in the stripping solu-
tion R. The product AB or its dissociated ions are insoluble in the mem-
brane S.

The second mechanism is known as a facilitated transport.The membrane
contains a chelating carrier X, soluble in the membrane only and playing
a role of shuttle between the two interfaces, transporting the specie A
into the stripping liquor R, where an irreversible reaction of the pre-
vious type takes place, too.

The third diagram in Fig.1 represents an ionexchange process or a cou-
pled transport mechanism. The transfer of the solute A from F to R is

accompanied by equivalent counter trans-
port of another specie from R to F.

These and some other transfer and reac-
tion mechanisms are ussually incorporated
in the proposed mathematical process des-
criptions. They include system thermodyna-
mics and geometry, too. Some of them take
into account the existing hydrodynamic con-
ditions also, as well as the additional
side phenomena which may occur.

There are in principle two approaches
to model the liquid pertraction processes.
The differential approach follows the way
in which the polymer membrane separational
processes are described assuming that the
membrane controls only the transport inten-
sity and separational efficiency. The inte-
gral approach [2,3,4] takes into consideration the concentration and volu-
me changes in both aqueous phases, their diffusional and rate resistance.
On this base, several sophisticated models were proposed recently [5,6,7,
8,9,10].

Fig.1

Obviously, the idea to create a separational method based on a three-
liquid-phase combination is not recent. But the lack of suitable techni-
que, which provides a stable system of three liquids, with two large in-
terfacial areas and an intensive mass transport, was a serious obstacle
on its way to industry. However, in the last 15 years several prospecti-
ve techniques were proposed and some of them, an object of intensive stu-
dies today, are undergoing pilot-plant or even industrial tests.

In the begining of 70-ties N.N.Li proposed the so-called Double Emul-
sion Method (DEM) [11,12]. The stabilization of the triple liquid system
in this method is achieved by means of emulsifiers [1,5,11-17].The strip-
ping solution R is finely dispersed and emulsified into the membrane pha-
se S. After the encapsulation of R in the membrane liquid, the emulsion
obtained is dispersed on its turn in the feed solution as shown in Fig.
2a. Due to the large interfacial area F/S and extremely large relative
interface S/R, the solute A is transfered into the encapsulated stripping
liquor generally in few minutes. This attractive, three steep method, has
several serious drawbacks: first of all, the emulsion prepared is far to
be ideal, its stability depends on the type and the amount of emulsifier
used. During the second, extraction step, it partially breaks-up, deteri-
orating the process efficiency and selectivity. The emulsifiers added,so-
me times up to 10% or more, pollute the outgoing rafinate solutions.Very
often, side phenomena like feed occlusion, water transfer from the feed
into the strip solution, etc. reduce the process efficiency to unaccepta-
ble levels. In spite of these shortcomings, DE-method is suitable to be

a

b

c

Fig.2

applied in a number of cases and was the first to reach an industrial recognition in R.P.China [18] and Austria [19].

Supported Liquid Membranes (SLM) made real success in the last years due to the continuing progress of the polymer technology.In this technique, the open pores of very thin porous polymer sheets or hollow fibers are filled with the membrane liquid S as shown in Fig.2b. The oleophylic properties of the polymer keep the organic liquid in the pores and prevent the feed and the stripping aqueous solutions to get into direct contact. The SLM-method,as confirmed by numerous studies [20,33], avoids practically all drawbacks of the previous technique. However,the mass flux across the membrane is quite low. Further attempts to reduce the membrane thickness increase the risks of water in the pores due to the unavoidable pressure differences. This phenomenon occurs easily when the solutions contain surfactants.Furthermore, organic liquid filling the pores,dissolves in both aqueous flows. This means that the membrane must undergo some kind of regenerative treatment to prolong its life.Nevertheless, a large number of research laboratories and even commercial companies in US A, Japan, USSR and other countries, are on the way to introduce SLM separational processes in full industrial scale.

An essential weakness of both described methods is that at least one of the participating liquid is stagnant. According to the mass transfer theory, postulating that the slowest transfer step in any multistep process controls the over all transfer rate, the molecular diffusion in a stagnant liquid phase will slowdown considerably the mass flux intensity.

In contrast to SLM and DE methods, all three liquids in the Liquid Film Pertraction (LFP) method [34-36],are in motion as shown by the principal diagram in Fig.2c. The feed and the stripping solutions, flow down along the vertical solid porous supports, arranged in an alternative sequence and spaced at small distances. The narrow interspaces between the alternating supports as well as the whole pertractor volume are filled by

the intermediate organic phase S,which circulates continuously in co-current, forced by an external pump. At these conditions the eddy diffusion is responsible for specie transfer in all consecutive steps.Although the thickness of the vertical liquid membranes is in the range of several milimeters, these flowing "membranes" are equivalent to stagnant liquid films few microns thick only.

Fig.3 shows the effects of two process parameters of the LFP-process: the mean residence time of the feed solution in the active apparatus part and the linear upward velocity of membrane liquid on zinc removal from zinc-containing waste water. The initial zinc concentration in the feed was 0,22 g/l. Normal paraffines (C_{11}-H_{13}) with 2% carrier - di-2-ethyl-hexyl-phosphoric acid are used as membrane phase S, while a 10% solution of sulfuric acid was the stripping liquor R.The flowrate ratio Q_F/Q_R=120:1, provided up to 25 g/l zinc in the final R product.As it can be seen pertraction efficiency reaches 99.8% when the membrane liquid is pumped and 92% when the circulating pump is stopped.
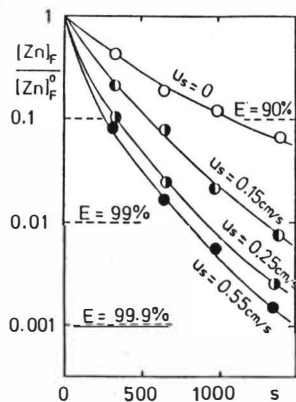
Fig.3

Comparing the three described pertraction techniques it can be concluded that all of them have their specific advantages and drawbacks.The DE-method provides higher transfer rates and mass fluxes than the other two, but its efficiency is limited by the mentioned negative phenomena.By SLM and DE methods one can treat solutions containing reasonable amount of fine solids, while the LFP demands a careful prefiltration of both aqueous solutions.

An atttractive feature of LFP technique is its continuous, round o-clock operation, with no maintenance for very long time periods.Up to several hundred times the concentration of the transfered specie in the product R can be obtained simply by adjusting the flowrate ratio Q_F/Q_R.Higher concentration degrees can be obtained by recirculation of the stripping liquid R. A special feature of the LFP is that it is the only technique among the three considered allowing some kind of scrubbing of the membrane liquid. The introduction of scrubbing operations, commonly used in solvent extraction, often improves the separation selectivity and the product quality.

Economic estimations show that the liquid film pertraction is among the cheapest separation processes due to the simple inventory and low running cost. Potential application areas of liquid pertraction are large and diverse, starting with hydrometallurgy and ending in the medicine,for blood detoxification, as an example. Biotechnology is another area of inte-

rest, where pertraction can be applied in down-stream processing or as reactors with fixed in one phase enzymes. Redox chemical reactions with simultaneous specie separation, applying or not electrical field, is another point of interest. The list of potential interesting applications is long enough to stimulate further research efforts in this field.

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This paper generalizes investigations $[1-20]$; prediction methods,
regularities determining extraction ability (EA) of mono- and biden-
tate neutral compounds, amines, organic acids, crown-ethers are dis-
cussed.

Extraction is based on a metal-extractant complex formation (at
the Gibbs' energy ΔG_c) required to overcome hydration forces while
the extraction equilibrium is a result of competion between organic
and aqueous phases for a substance distributed:

$$\Delta G_{ex} = \Delta G_{solv} - \Delta G_{hydr} \; ; \; \Delta H_{ex} = \Delta H_{solv} - \Delta H_{hydr}. \tag{1}$$

Extraction is appreciable when $\Delta G_{solv} \approx \Delta G_{hydr}$, ΔG_{hydr} and ΔH_h
(kcal/mole) real values of some typical compounds first found in $[21]$
(the standard state - pure substance) are given below:

Comoound	HNO_3	HCl	$NaCl$	$MgCl_2$	$CaCl_2$	$LaCl_3$	UO_2Cl_2	$UO_2(NO_3)_2$	$ThCl_4$
$-\Delta G_h$	7.3	10.7	2.1	30.3	15.5	21	-	16.1	-
$-\Delta H_h$	7.95	14.8	0.9	37.2	19.8	33	25.7	20	56.7

It can be seen that ΔG_h and ΔH_h values increasing with a cation
charge and its radius decrease range from several unities to several
tens kcal/mole. Therefore energy $\Delta G_c \approx \Delta G_{hydr}$ is characteristic of
an electron-donor-acceptor (EDA) interaction based complex formation.
Due to its relative weakness one cannot expect any significant donor
(extractant) and acceptor molecule reconstruction on complex forma-
tion $[22]$. This permits prediction of the formed complex strength and
EA control based on the properties of an extractant molecule, viz.,
chemical (electronegativity (EN) of substituents X, constants σ', ba-
sicity pK) and quantum-chemical ones (oxygen core level energy E_{1S} (O),
ionization potential IP, proton affinity PA).

Quantum Chemistry for EA Prediction. In previous work, e.g.$[10]$ it
was concluded that the extraction -substituent electronegativity X
correlation (see eq.2) is equivalent to those with the electron den-
sity on a donor atom (oxygen) q_o as $|q_o| = a - b\Sigma X$, $lgK_{ex} = A' + B'|q_o|$,
the higher is the charge the higher is EA. However the quantum-chemi-
cal calculations (see the paper by the author, N.M.Klimenko and B.V.
Krupnov) for the classical series I $R_3PO(1) - R_2ROPO(2) - (RO)_2RPO(3) -$
$(RO)_3PO$ (4) did not confirm this correlation, although there exists
an EA - core level energy $E_{1S}(O)$ correlation (the latter is usually
considered a charge measure). However at a relatively large q_o varia-
tion ($\Delta q_o = -0.07$) the charge "operates". This is seen from a very
instructive example of carboxylic acid amides series II $R_2CO-RCONR_2' -$
$(NR_2')_2CO$. The investigations $[23,24]$ showed that the introduction of
the first amide group greatly increases EA; the second one practical-

Data on ketone-amyde-urea

	R_2CO	$NR'_2C(O)R$	$(NR'_2)_2CO$
Distribution coefficient, $\alpha_c \cdot 10^5$	37	88500	61900
ν_{CO}, cm^{-1}	1730	1640	1642
Donor number (ΔH with SbCl$_5$)	17,0	27,8	29,6
$\Delta\nu$(OH)/phenol/cm^{-1}	224	343	340
q_o	-0.29	-0.36	-0.37
PA,kcal/mole	-189,0	-205,2	-210,3
$E_{1s}(O)$, eV	538,0	536,78	536,70

ly gives nothing. The Table shows that the quantum-chemical calculation fully confirms the uneven property changes in series II, charges on oxygen included. The weak effect of the second group is explained by its leaving the plane, the impossibility of the conjugation with the CO π-system. The calculated ionization potential IP proved [17] a useful parameter correlating with EA: the higher is IP the stronger is the functional atom bond and the lower is EA. However, with two reaction centres (e.g., O and N in amides) the IP method is not serviceable. To predict EA it seems most reliable to use the energy of test reactions - H-bond formation (E_H) and protonation (PA) (see fig. 1d). PA determines correctly the reaction centre if they are several and is rather easy to compute.

Monodentate neutral organophosphorus compounds (NOPC). As EA characteristics it is advisable to use the extraction equilibrium constant, e.g., for series I - reactions $UO_2^{2+}+2NO_3+2L=UO_2(NO_3)_2L_2$. Fig. 1a shows that in series I the lg K value correlates with a change in the substituent EN sum [1]:

$$\lg K = A - B\Sigma X - p\Sigma 1, \qquad (2)$$

where 1 is the effective length of a substituent hydrocarbon chain (for normal radicals $1=n_c$), A,B,p are constants dependent on the element nature and the X values are determined from the spectral scale [1] ($R=C_nH_{2n+1}$ with $n > 3$):

Group	F	Cl	CCl$_3$	ClCH$_2$	Cl(CH$_2$)$_2$	C$_6$H$_5$	CH$_3$	R	RO	H
X	4.0	3.0	2.95	2.60	2.32	2.34	2.07	2.0	2.9	2.25
σ^*	-	-	2.65	1.05	0.6	0.6	0	0.13	1.4	0.49

When counting from the standard compound relation (2) gives Hammet-Taft equation:

$$\lg K/K_o = -B\Sigma(X-X_o)-p\Sigma(1-1_o) = \rho^*\Sigma\sigma^* + \delta\Sigma E_s \qquad (3)$$

and, indeed, it was found that $\sigma^* = 2(X-2.07)$ [2], i.e., Taft constants are relative EN. The conclusion on a decrease of NOPC EA with an electronegative substituent introduction is rather general. However, when considering a wider class of NOPC comprising groups C_6H_5 (5),
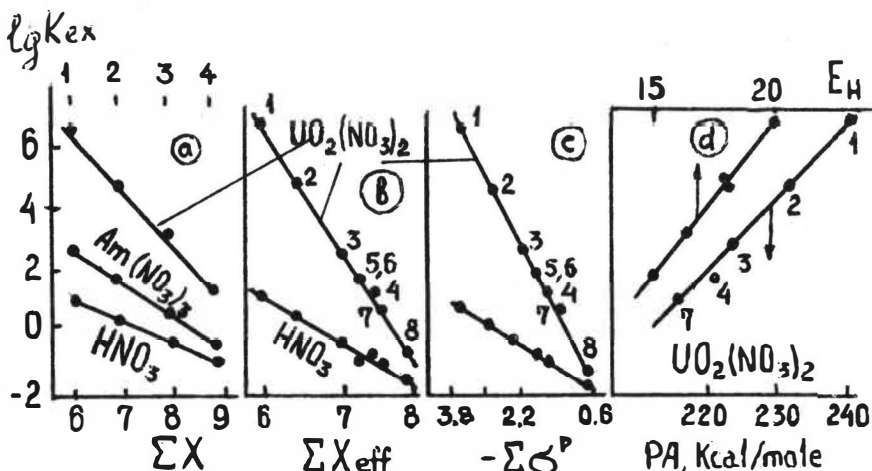
Fig.1. Effect of the structure on K_{ex}

$Cl(CH_2)_2$ (6), $ClCH_2$ (7), CCl_3 (8) to obtain a common correlation
equation (2) had to be refined /2/ by introducing effective (lower)
EN for alkoxy groups, $X_{eff}=2.5$ and $\sigma^*_{eff}=0.75$ (Fig.1b). The cause is
in that X and σ^* describe only the induction effect while for RO a
resonance one is also observed. Instead of (2) one can write down

$$lg\ K = A-B\sum X_{eff}- p\sum l = A-B\sum X + B'\sum \sigma_z\ -p\sum l,$$
$$lg\ K/K_0 = B\sum(X-X_0)+B'\sum(\sigma_r-\sigma_{ro})-p\sum(1-l_0) = \rho^P\sum \sigma^P, \qquad (4)$$

where σ_z is a resonance interaction constant, $X_{eff}=X-\sigma_z \cdot B'/B$; ratio
(4) is equivalent to the use of Kabachnik constants σ^P, taking acco-
unt of the resonance and (actually) steric effects. Therefore, the
correlation with σ^P does not require effective quantities introduct-
ion (Fig. 1c). Although as compared to (2) equation (4) is more gener-
al its applicability is still limited; remember the series: Ketone-
amideurea (Table) where the first and second amide groups act dif-
ferently; inadditivity is not a rare exception. Therefore, at present
the best correlation seems to be based on the quantum chemical calcu-
lations (Fig.1d):

$$lgK = a + bPA = a' + b'E_H. \qquad (5)$$

Fig.1 also shows that through the choice of substituents the NOPC
extraction constant can be varied by 3-8 orders. In contrast, the
hydrocarbon chain length n_c weakly affects EA (Fig.2).

Amines. Inorganic acids are extractable with amines (addition re-
action) with the extraction constants 10^5-10^7 characteristic of a com-
plex formation with a proton transfer amine salts $(R_3NH)^+A^-$. EA vari-
ations on extraction with amine salts are described with equations
(1,2). As the EN of hydrogen (2,3) is less than that of alkyl (2.0)
the EA grows in the series: salts of primary amines (1) - salts of
quaternary aminonium bases (4) (Fig.3 /3-6/).
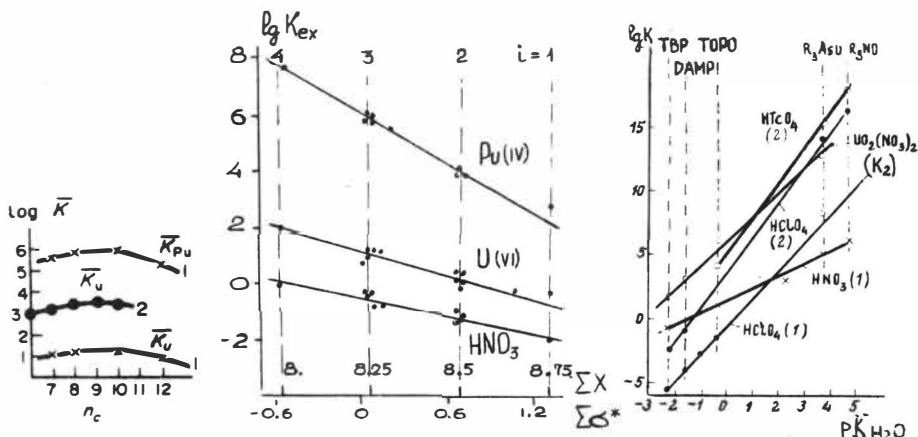
Fig.2. Effect of $n_c \cdot 1$-amines, 2-phosphonates
Fig.3. Amine salt EA vs EX of cation $R_1H_{4-1}N+$
Fig.4. EA vs basicity

With the basicity growth in the series $R_2O-R_2CO-(RO)_3PO$ (pK= -2.3)-
-R_2SO-R_3PO (pK=0.5)-R_3AsO (pK=4.0)-R_3NO (pK=4.6) there occurs not only
a very strong improvement of extraction (Fig.4)

$$lg\ K = a''+b''pK, \qquad (6)$$

but also a qualitative change in the coordination character [6-9].
At first this is a transition from a hydrate-solvate mechanism to a
direct extractant oxygen-metal coordination. At adequate basicity
(for HNO_3 - at pK=4) a second transition is observed - from H-bond
complexes to the ones with a partial or full proton transfer
($R_3AsOH\ ^+NO_3^-$, $R_2NOH\ ^+NO_3^-$). Then the extraction constant grows from
0.2 (TBP) and 20(TOPO) to 10^6 characteristic of amine neutralization.
(For strong acids the transition occurs at lower pK, e.g., for $HTcO_4$ -
at pK= -1.1). Along with monocomplexes LH^+A^- more strongly extractable
dicomplexes $(LHL)^+A^-$ are also formed ($\overline{K}_2$ up to 10^{18}, Fig.4). Extrac-
tant complexes with a proton transferred $(LH)^+A^-$ similar to amine
salts; a corresponding (ion exchange) metal extraction mechanism re-
sults [7], e.g., $LH^+[UO_2(NO_3)_3]^-$ complex forms, where $L=R_3AsO,R_3NO$.
This fact explains [7-9] the formely incomprehensible proximity of α
for U and Pu on amine and amine oxide extraction (Fig.5). Thus, orga-
nic oxides become similar to amines; the conventional extractant sub-
division into neutral and basic ones becomes senseless.

Finally at low acidity a third change of the extraction mechanism
is observed that is especially distinct in arsine oxides. Fig.5 shows
that α_V grows with $[H^+]$ decrease, ie., R_3AsO extracts like an organic
acid, $lg\alpha =a''' + b'''$ pH [12]. Possibly the oxide reconstructs to
$R_3As(NO_3)OH$. One more peculiarity of R_3AsO and R_3NO extraction should
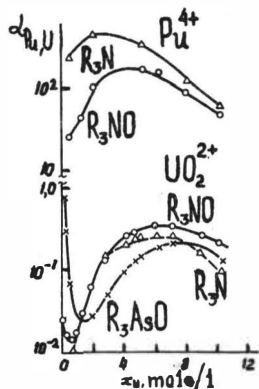
Fig.5. R₃NO and R₃AsO extraction
Fig.6. EA vs EN (AASI)
Fig.7. EA of OPA
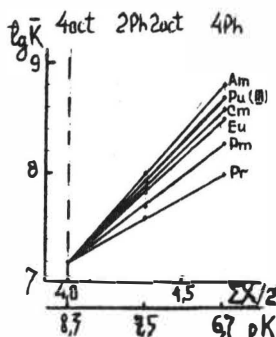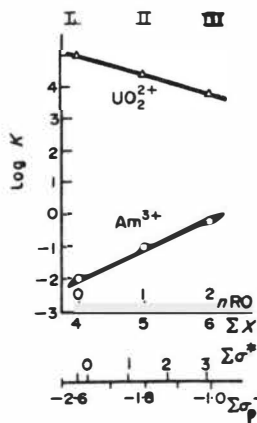
be pointed out: acids extracted (constants of 10^6-10^{10}) start compet-
ing with metals. In conclusion it should be noted that by varying sub-
stituents and reaction centre (SO,PO,AsO,NO) EA can be changed by 10
orders in any needed direction.

Bidentate extractants with functional groups of the same or close
nature are diphosphine dioxides $R_2P(O)(CH_2)_n(O)PR_2'$ (abbreviated
$2R2R'(CH_2)_n$, at n=1 the bridge length is not given) and carbamoylphos-
phine oxides $R_2P(O)CH_2(O)CNR_2'$ (abbreviated R_2/R_2'). On monodentate co-
ordination (HNO_3, $HClO_4$ extraction) equation (1) is fulfilled; in par-
ticular, the introduction of phenyl groups (X=2.3) instead of alkyl
ones (X=2.0) impairs extraction ∠13,14J. On bidentate coordination
(actinide extraction) the substitution of alkyl groups by more electro-
negative ones such as RO(X=2.5) or $Cl(CH_2)_2$ (X=2.3) also lowers EA.
Dependences (1)-(6) were disturbed ∠13J when aryl substituents (phenyl,
tolyl, X=2.3) were introduced into a dioxide molecule in place of al-
kyl ones. Despite ΣX growth and a decrease of dioxide basicity and
its oxygen donor ability (evidenced not only by decreased HNO_3 extrac-
tion, but also by IR and X-ray PES) the distribution coefficient and
actinide and lanthanide (III) extraction constants increase by two
orders (see review ∠4J and the paper by the author, Nikolotova Z.I.
and Kartasheva N.A.). This effect called the anomalous aryl stabili-
ty increase (AASJ) is observed in different media (HNO_3, $HClO_4$, HCl,
H_2SO_4) and also depends on the element nature (Fig.6). For actinides
(IV) and (VI) in 4Oct-2Ph2Oct-4Ph series the distribution coeffici-
ents α grow and the extraction constants slightly decrease ("visib-
le" stability increase); increased α is explained by an increased

66

free extractant concentration due to HNO_3 extraction suppression by electronegative aryl substituents. According to the estimate [14] the addition to ΔG_{ex} through AASI is ~3 kcal/mole per two aryl groups. AASI and disturbed regularities (1)-(7) indicate a substantial extractant molecule reconstruction on complex formation due to this the EA prediction based on extractant molecule properties becomes incorrect (so far the only instance knows). What is the nature of AASI? Calorimetric measurements (unfortunately, only one paper) indicate the bond nature of the effect. The AASI disappearance with the Ar separation from P with CH_2-group (tetrabenzyl dioxide) points to Ph conjugation with π-system of PO resulting from complex formation (6 member cycle), to electron density delocalization from Ph to cycle (this is also confirmed by X-ray PES and quantum chemical calculations). A three order decrease of the effect with the replacement of a methylene bridge by an ethylene one, its full disappearance with the introduction of a propylene one and AASI recovery with the introduction of vinylene one CH=CH (despite the cycle elongation to a 7 member one) as well as a very high methylene bridge proton mobility permits suggestion of a cycle aromatization.

The isotherm character $\alpha_{Am}=f[HNO_3]$ is explained as in case of lanthanides, see the paper by the author, V.S.Vlasov and L.G.Andrutsky at this conference.

Bidentate compounds with reaction centres of different nature. This class comprises organophosphorous acids (OPA) R_1R_2POOH with the functional groups PO and OH. The OPA salient feature is that substituents R have an opposite effect on the reaction ability of these groups: the EN growth increases the acid strength and the OH group EA but weakens the donor ability and phosphoryl oxygen EA. As a result, the character of the structure effect depends not only on the extractant properties as for neutral compounds but also on the extracted element nature, on how this element reacts with each of the centres:

$$lg\ K = A' + (B_{OH} - B_{PO})\Sigma X_R. \tag{8}$$

Thus, in series III R_2POOH (1)-RORPOOH (2)-$(RO)_2POOH$ (3), i.e., with the ΣX growth extraction of actinides and lanthanides (III) weakly coordinated with phosphoryl oxygen improves [2,4,5] and, on the contrary, extraction of actinides (VI,IV) strongly coordinated with the PO group weakens (Fig.7). This fact was explained in [4,5] and later was repeatedly "reopened".

Extraction with acid salts, e.g., zirconium salt of D2EHPA proved very efficient. This can be explained considering a salt, e.g., $ZrA_4(HA)_2$ to be a strong metalloacid, e.g., H_2ZrA_6. Of great interest as extractants are organic acid salt HA with organic bases, e.g., R_4NA (binary extraction [26]). The binary process can be shown to be a thermodynamic analogue of extraction with a neutral extractant (e.

g., alcohol) with the compound dissociation in the organic phase [27]:
in both cases the number of particles (ions) does not vary on extrac-
tion and therefore at $C \rightarrow 0$ the distribution coefficient α=const. Howe-
ver, the possibilities of a binary process control are far greater.
In particular, it is important that the binary extractant EA can be
improved using a weaker acid HA; ($K_{ex} \sim K_{dis}^{-m}$, where K_{dis} is HA acid
dissociation constant [26]). This conclusion can be generalized to
metalloacid extraction.

Extraction with polydentate phosphonitrile acid P2EHPNA [18]. The
EA of OPA is much lowered due to dimerization binding PO and OH reac-
tion centres. Hence, a new way of controlling EA is possible, to in-
hibit dimerization, e.g., multi-link polyphosphonitrile acids. Am(III)
and Eu(III) extraction constants were found to be 7 orders higher as
compared to D2EHPA. However, for actinides (IV) and (VI) EA increa-
se was not so high, possibly due to imide rearrangement.

Polydentate extractants - crown ethers are known for their stereo-
specific extraction. However, it shows up essentially (although not
always due to cycle flecibility) on alkaline and alkaline earth metal
extraction, when the interaction is chiefly electrostatic. On extract-
ion of acids and metal salts-strong electron acceptors the important
part is played by electron factors, EDA interactions. From the data
of Fig.8 [15] it is concluded that the regularities are fulfilled,
characteristic of the hydrato-solvate mechanism, e.g., curves with
a maximum (Pu) are observed which as it was explained in 1957 [25]
are due to the combination of acid salting out and displacing effects.
Equations (1)-(6) are fulfilled, therefore the crown-ether EA can be
controlled by replacing substituents.
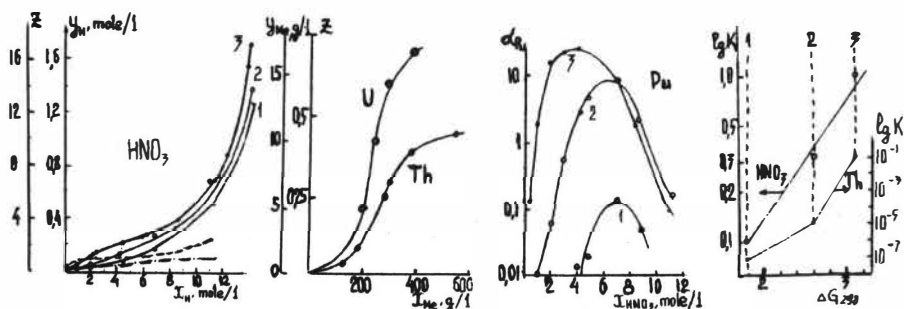
Fig.8. Crown ether R_2-18-C_6 extraction (0.1 mole/l in DCE). R: 1-Ph,
2 - without, 3 - cyclohexyl; Z=y/[L]

Control of some physico-chemical properties of extractants. Such
properties as their compatibility with diluents, water solubility can
be controlled. The second organic phase formation in non-polar dilu-
ents is due to high positive deviations from Raoult's law; the latter

68

are significantly related to the association. By elongating the hydrocarbon chain and using the isostructure the association can be inhibited and correspondingly the compatibility improved. Simultaneously the water solubility of an extractant - lg $S=a+bn_c$ decreases (b= 0.3-0.5) $\angle$19, 20$\overline{/}$.

The practicability of the theoretical results grounds for TBP replacement by optimized hydrocarbon chain phosphates (that excludes the second organic phase formation with actinide (IV) solvates in hydrocarbons) and use of bidentate organophosphorus compounds to extract TPE from effluents see $\angle$19-21$\overline{/}$ and the paper by Nikiforov A.S. et al. at this conference.

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Promising extractants choice with theoretical methods is now an important problem. The purpose of this paper is to discuss the possibility of electronic structure MO calculations in predicting extraction ability (EA) for neutral compounds $R_nXO(X=C,S,N,P)$. The most reliable EA predictions based on direct complex (extractant+ metal salt) calculations is a matter of future. So far as the metal extraction with neutral compounds is related to electron-donor-acceptor (EDA) interaction with relatively small electronic density redistribution in extractant molecules, the Klopman perturbation treatment [1] may be applied and the EDA interaction energy (E) can be estimated from MO calculations of isolated donor (D=extractant) and acceptor (A=metal) molecules. An alternative approach is to use complex formation energy of D with the simplest A=proton in protonization (PA) or hydrogen bond formation (E_H) reactions. In the Klopman approximation E consists of electrostatic (E_{el}) and covalent (E_{cov}) components. For a given metal E_{el} is proportional to donor atom charge (in our case q_o); E_{cov} in frontier orbital approximation is proportional to contribution of donor atom AO to the high occupied MO(HOMO) of D (c_o^2) and inversely proportional to the energy difference between HOMO of D and the lowest unoccupied MO (LUMO) of A, i.e., E_D-E_A. The E_D value is close to D ionization potential(IP). The direct calculations by the Klopman method are complicated, so we have analyzed the EA dependence on all D parameters [1]: q_o, c_o^2 and IP. It should be mentioned that in previous qualitative theories EA was related to the only q_o dependent on the electronegativity of X and group substituents at X [2,3].

In our calculations we have applied standard MNDO method and its modification for the evaluation of E_H [4] (E_H is too high, but the trends in H-bond energy variation in the series of compounds are just the same). Ab initio calculations were performed for some model compounds using the 4-31 G basis set with optimized at MNDO geometry.

1. $\underline{E_{el}: \text{ donor atom charge } q_o}$. Our calculations have shown, that estimated (both MNDO an ab initio) q_o values canot always be used to predict EA. This can be demonstrated for series I: $(RO)_{3-k}R_kPO$ (k=0-3,R=Alk) where correlation of q_o with EA (extraction constant K_{ex}) is only for high dipole conformation (the dotted line in fig.1) but not for structures corresponding to a global minimum at a potential surface (their dipole moments are close to experimental ones).

In series II: R_2SO-R_3PO-R_3NO with a large change of oxygen basicity the q_0 values are close (Table) while EA varies by 8 orders of magnitude. More over, the weakening of the electronegative substituent inductive effect cannot be described correctly in series III: $CH_3P(O)H_2$ - $Cl(CH_2)_nP(O)H_2$. The q_0 values of methyl- and Cl-derivatives are close, if n=1, while experimental EA are close only for n=3. At the same time there is series IV (ketone-amide-urea) having relatively high change of q_0, its value reflects the peculiarities of the series, viz, a non-monotonic change of nucleophility: a marked increase of electron density on O (q_0= -0.07) and FA (by 3 orders for uranium) when the first amino group is introduced, and lacking of changes with introduction of the second one (fig.2, points N^0 are compounds N^0 in Table). An increase of the electron density on O corresponding to a growth of amide and urea donor ability, as compared with ketones is the result of lone pair (LP) - N atom conjugation with π-electron of the C-O bond. The weak influence of the second amino group is mainly related to its deviation from molecule plane which prevents from the conjugation.

It should be noted that when estimating E_{el} for a compound with ionic bonds one should, probably, also take into consideration charges on other atoms in extractant molecules by introducting, e.g., a molecular electrostatic potential [5] (although it isn't always adequate, e.g., it doesn't reproduce the site of proton attack [6]. In series I and II (Table) the electron density on X significantly increases, that should pro-

$lg K_{ex}^U$

Fig.1. Correlation K_{ex}^u vs q

Calculated Date for Molecules (MNDO/4-31)

№	compound	q_0	q_x	$-E_{1s}^{(0)}$, eV	IP, eV	PA, kcal/mole	E_H, kcal/mole H2O	kcal/mole HNO3
1	H_2CO	-0,29	0,29	559,2	11,04	177,2	4,3	10,4
2	$MeCOH$	-0,29	0,24	558,9	10,84	183,2		
3	Me_2CO	-0,29	0,18		10,74	189,0	4,7	10,8
4	$FCOH$	-0,30	0,41	560,1	12,45	168,4		
5	FCH_2COH	-0,25	0,22	559,5	11,14	174,7		
6	FC_2H_4COH	-0,27	0,27	559,3	11,18	178,6		
7	FC_3H_6COH	-0,28	0,25		11,00	181,2		
8	NH_2COH	-0,35	0,34		11,50	198,4		
9	$(NH_2)_2CO$	-0,36	0,39		11,81	203,8		
10	$(NMe_2)COMe$	-0,36	0,33		10,84	205,2		
11	$(NMe_2)_2CO$	-0,37	0,48		11,27	210,2		
12	H_2SO	-0,63	0,81	558,3	10,53	213,1		
13	Me_2SO	-0,64	0,68		9,83	227,4	7,8	17,0
14	H_3PO	-0,60	0,77	556,5	10,34	222,9		
15	$FPOH_2$	-0,60	1,08	557,7	11,03	208,6		
16	$HOPOH_2$	-0,64	0,96	557,2	10,64	215,7		
17	NH_2POH_2	-0,63	0,85	556,5	10,39	223,1		
18	$MePOH_2$	-0,61	0,73	556,1	10,07	229,2		
19	$ClPOH_2$	-0,52	0,84		11,36	207,2		
20	$ClCH_2POH_2$	-0,60	0,74		10,45	224,1		
21	$ClC_2H_4POH_2$	-0,60	0,75		10,26	226,1		
22	$(NH_2)_3PO$	-0,70	0,84		10,65	229,9		
23	Me_3PO	-0,64	0,61		9,55	241,4	9,1	20,0
24	$MeOPOMe_2$	-0,66	0,88		10,00	233,1	8,5	18,9
25	$(MeO)_2POMe$	-0,67	1,14		10,67	223,0	8,0	16,8
26	$(MeO)_3PO$	-0,64	1,41		11,29	220,3	6,8	14,6
27	$(NMe_2)_3PO$	-0,66	1,30		10,71	233,1		
28	H_3NO	-0,63	0,35	555,2	9,67	214,5		
29	Me_3NO	-0,65	0,20		9,05	231,5	7,9	17,9

mote the metal complex strengthening (there is a correlation with the EA, fig.1).

The energies of 1 s core levels (E_{1s}) are an important characteristics of molecular electron density distribution. They are often used to estimate the effective atomic charges. The experimentally found (method of X-ray PES) $E_{1s}(O)$ correlate with K_{ex} of different
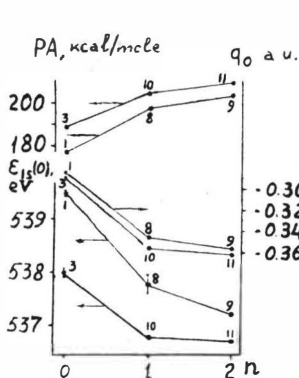
Fig.2. Variation PA, q_O and $E_{1s}(O)$ in series IV
Fig.3. Dependence of E_H and $E_{1s}(O)$ on PA
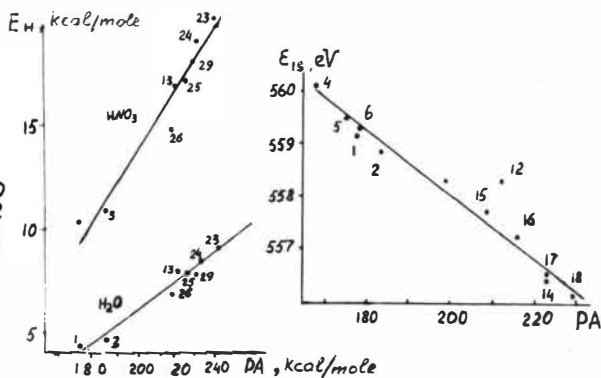
metals in series I and in the series $R_3PO-R_3NO-R_3AsO$ [7-8]. Ab initio calculated $E_{1s}(O)$ values decrease in series H_nXO with a variation of $X=N,P,S,C$ and by substitution of H with electronegative groups. This is obviously corresponds to a decrease of electron density on O and of its donor ability (e.g. PA, fig.3). In series V: $F(CH_2)_nC(O)H$ with $n=0,1,2$ $E_{1s}(O)$ increases, which correlates with oxygen nucleophility growth. The violation of correlation PA vs $E_{1s}(O)$ (fig.3) for H_3NO and H_2SO is probably related to large MNDO errors in their geometry and PA. Thus, despite the absence of the direct correlation between EA and q_O, which is likely due to the defects of Mulliken population analysis, it may be concluded that donor and extraction ability of compounds studied depends on donor atom O electron density.

2. $\underline{E_{cov}: C_O^2}$ and Ionization Potential. In studied molecules except for amides the HOMO responsible for the first IP is LP orbital n_O of O atom (50-80% $2p_\sigma$ -AO). In amides of carboxylic and phosphoric acids HOMO is mainly formed from nitrogen AO (n_N), while the orbital n_O lies below. The contribution of X atom AO to n_O-orbital is small (1-7%) [9] and the n_O electron density is delocalized mainly to substituents R, which explains the effect of the latter on IP. In general the C_O^2 values don't correlate with EA, although, e.g. in series $Me_2CO-Me_2SO-Me_3PO-Me_3NO$ c_O^2 increases (62,73,80,85% $2p_\sigma$ -AO) symbatically with the EA growth.

Correlation of EA with IP for series I and II is given in fig.4. According to the theory $\angle 1 \rfloor$ the correlation should be generally non-linear and a decrease of IP should lead to an increase of EA, which is the case. In contrast to q_0, the IP describe correctly the weakening of inductive effect of Cl-atom in series III with n growth (this is not fulfilled in series V because of insignificant variations of IP themselves). The IP values are also more sensitive to the substitution of H with CH_3-groups at X $\angle 9 \rfloor$. We have established $\angle 9 \rfloor$ an adequate correlation of IP with Taft constant and electronegativity of substituent at X for amine- and phosphinoxide series. However, in case of two reaction centers (e.g. O and N in series IV) there is no correlation with EA. Nevertheless, if there is only one donor atom the IP along with $E_{1s}(O)$ (instead of q_0) are valuable parameters for EA prediction.
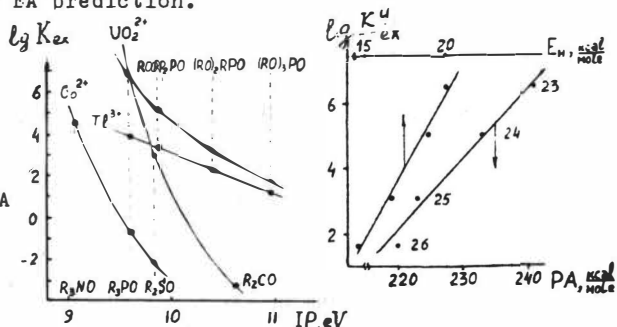
Fig.4. Correlation of K_{ex} with IR and PA

3. <u>Proton Ability and H-bond Energy.</u> As can be seen from fig.4, PA and E_H correlate well with EA (K_{ex} of uranium). There is also an intercorrelation between PA and E_H as well as correlation of PA with $E_{1s}(O)$ (fig.3). It should be noted, that only PA calculations make it possible to establish, that O is a donor atom in amides not N, as it would follow from the Klopman treatment $(|q_N| > |q_O|)$. Besides, PA estimation is relatively simple. Thus, the energy of test reactions E_H and PA are the best parameters to be used for EA prediction.

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ELECTRON STRUCTURE AND ELECTROSTATIC POTENTIAL OF SOME NEUTRAL
ORGANOPHOSPHORUS EXTRACTANTS AND THEIR COMPLEXES

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The distribution of molecular electrostatic potential(MEP) received
from the data of quantum chemical calculations is widely used for teo-
retical analysis of ion-molecule interaction (1). This work is an at-
tempt to use MEP as a criterion of extraction ability for neutral or-
ganophosphorus compounds (NOPC). The series "phosphate-phosphonate-
phosphinate-phosphine oxide" was chosen as an object of this investi-
gation. Some compounds from this series (e.g. tributylphosphate, di-
iso-amylmethylphosphonate, trioctylphosphine oxide) are used as ext-
ractants on a large scale and their extraction ability is thoroughly
studied in the experiments. It was interesting also to use MEP for
analysis of alcylphosphate acidic hydrolysis mechanism. The solvates
of some metals with tributylphosphate(TBP) were investigated by NMR
spectroscopy method to explain the catalytic effect of metals on TBP
hydrolysis.

The charge distribution and NOPC electrostatic potential. The quan-
tum chemical calculations for series "phosphate-phosphine oxide" were
accomplished by CNDO/2(sp- and spd-basis) and MNDO methods. The calcu-
lation was realized for the simplest series: trimethylphosphate-tri-
methylphosphonate-trimethylphosphinate-trimethylphosphine oxide be-
cause it was ascertained earlier that lengthening of alcyl chain did
not result in the considerable change of charge values on carbon,
oxygen and phosphorus atoms (2). The values of valent and torsion ang-
les were varied. Two stable conformations with torsion angles OPOC (γ)
equal $0°$ and $180°$ were determined for trimethylphosphate(TMP) (Fig.1).
Their dipole moments found out CNDO/2 (spd) data are 0.73D and 7.5D
correspondingly. The low dipole TMP conformation (γ=0) occured to be
more stable because the lowest value of complete energy corresponds
to it. The data of charge distribution in P=O fragment of NOPC molecu-
les received from the calculations are presented in the Table.

Charge distribution on P=O fragment in NOPC (low dipole conformat.)

Calc.method	MNDO		CNDO/2(spd)		CNDO/2(sp)	
NOPC	O_{Ph}	P	O_{Ph}	P	O_{Ph}	P
$(CH_3O)_3PO$	-0.695	1.467	-0.342	0.566	-0.490	1.361
$(CH_3O)_2CH_3PO$	-0.689	1.193	-0.328	0.450	-0.489	1.355
$CH_3O(CH_3)_2PO$	-0.668	0.893	-0.311	0.351	-0.480	0.904
$(CH_3)_3PO$	-0.639	0.579	-0.297	0.276	-0.467	0.676
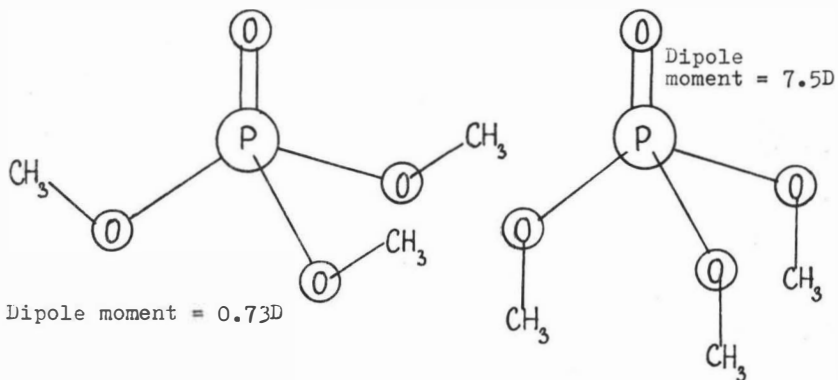
Fig.1. The conformations of TMP

Fig.2(a)

Fig.2(b)

Fig.2. MEP distribution
(kcal/mole) in neutral (a)
and protonated (b) TMP.
————— - positive MEP values
– – – – - negative MEP values
——·—— - zero MEP values
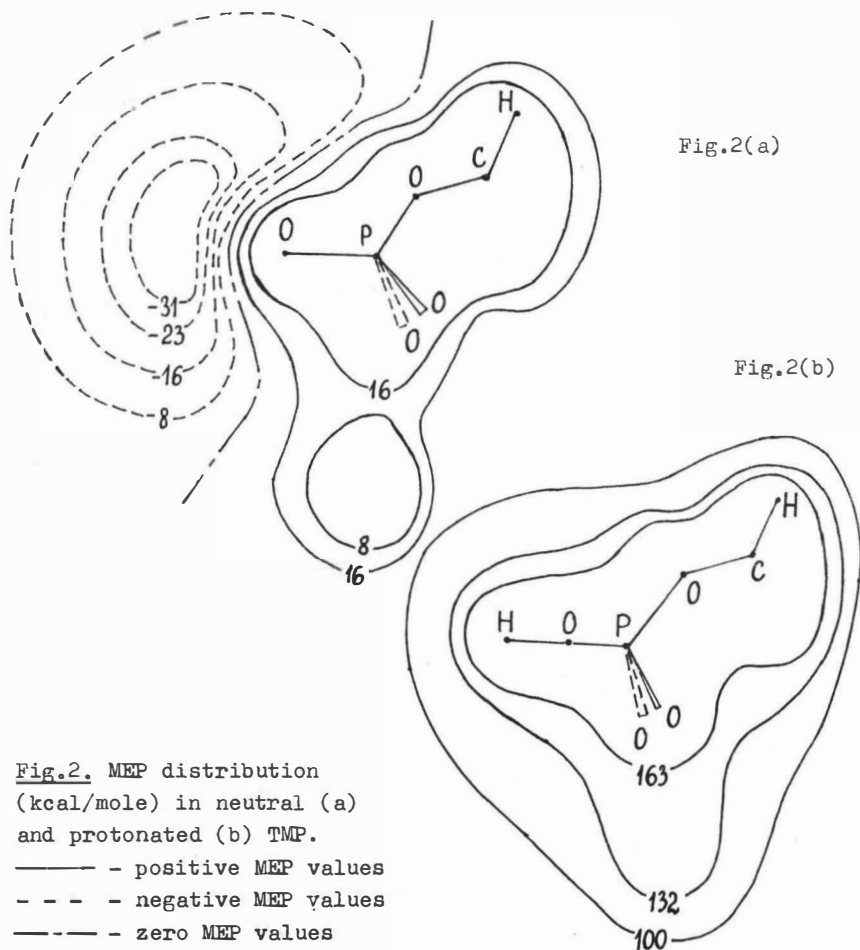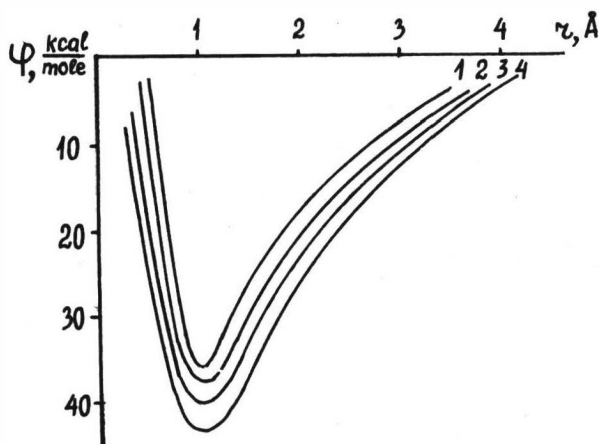
Fig.3. MEP distribution along the line of P=O bond
1 – TMP;
2 – DMMP;
3 – MDMP;
4 – TMPO

The presented data indicate that negative charge on oxygen of phosphoril group (O_{ph}) decreases from TMP to TMPO while the extraction ability in such series increases.But calculation results don't contradict the traditional view on the influence of electronegativity of substitutial group at phosphorus atom on the extraction ability.In reality the substitution of alcoxyl by less electronegative alcyl leads to transference of electron density on the phosphoryl group and therefore to enhancement of negative charge at the P=O group as a whole. These values calculated by CNDO/2(spd) method for series TMP-TMPO are 0.22, 0.12 0.04 and -0.02e correspondingly.We suppose more correct to consider as a criterion of extraction ability instead of O_{ph} charge the distribution of MEP representing for a molecule in whole the charge distribution and the peculiarities of its conformation. The electrostatic potential φ ($\imath$) is calculated from

$$\varphi(\imath) = \int \frac{\varrho(\imath')}{|\imath' - \imath|}\, d\imath \simeq \sum_i \frac{q_i}{|\imath - R_i|} \; ,$$

where ϱ ($\imath$) – the charge density distribution of ligand,
q_i, R_i – a charge and a coordinate of ligand i-atom.

MEP distribution for low dipole conformation of TMP constructed from approximation of point charges, calculated by CNDO/2(spd) method is presented at Fig.2.The region of negative MEP values near O_{ph} atom indicates the high coordinating ability of O_{ph} in ion-molecular interaction. MEP distribution along the line of P=O bond for the series TMP-TMPO is presented at Fig.3.The comparison of the curves convinces of the shift of corresponding curve to more negative MEP values when changing of alcoxyl substitutional group for alcyl group that correlates with known experimental data concerning extraction ability.

The investigation of NOPC compounds with acid and metals. The quantum chemical calculations of protonated TMP by CNDO/2(spd) method were carried out to elucidate a cause of catalytic effect of acids on hydro-

Fig.4. NMR ^{31}P spectra of TBP and its complexes. Dotted line — new signals after long (2 weeks) duration
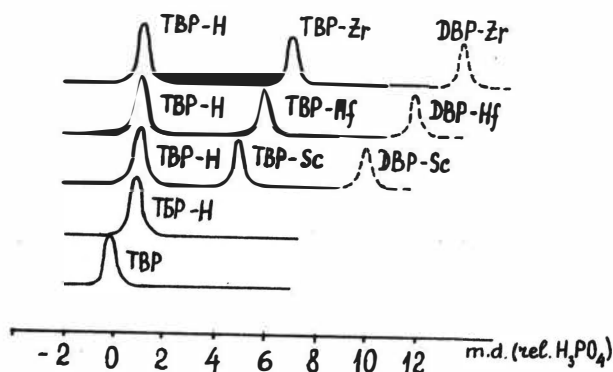
lysis of alcylphosphate.It occured that the protonation of alcoxyl or phosphoryl oxygen atom as well leads to some decrease of positive charge at C_α atom.Therefore the traditional idea about the enhancement of charge at C_α atom and promotation of water attack and subsequent hydrolysis is inadequate.It is advisible to use the data of MEP distribution for the explanation of effects stipulated by the protonation. The comparison of MEP distribution for neutral orbit and the orbit protonated at phosphoryl oxygen (Fig.2) indicates the considerable increase of positive MEP values close atom C_α , that convinces of electrostatic effect enhancement in the reaction between water and TMP protonated. The calculations show the decrease of valent molecular orbitals (MO) energy when protonating and the increase of portion atomic orbitals C_α into these MO as well. So the donor-acceptor constituent in the reaction $TMP \cdot H^+ - H_2O$ becomes stronger.

NMR spectroscopy of TBP in complexes with HNO_3 and nitrate of Zr, Hf and Sc was made (Fig.4).In spectrum NMR ^{31}P a shift of signal to stronger field relative to a signal for free TBP was observed. The solvate shifts for metal-complexes are more than for acid-complexes. Therefore the changes in TBP electron structures in the complexes with nitrate of Zr,Hf or Sc have analogous nature as in complex with HNO_3 but are more considerable.It is possible to expect their greater influence on TBP hydrolysis.It was observed in practice for Zr and Hf (2).The metals not increasing hydrolysis (3) probably influence on TBP electron structure in another way.In NMR ^{13}C and ^1H spectra of $HNO_3 \cdot TBP$ the shift of signal for $\alpha-CH_2$-group to faint fiels takes place.

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THE APPLICATION OF EDA INTERACTIONS FOR EXPLAINING AND FORECASTING THE EXTRACTIVE ABILITY OF ELEMENTOORGANIC REAGENTS

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The application of linearity principle of free energies is an effective method for explaining and forecasting reaction ability of elementoorganic compounds in the solutions. It may be represented as an equation :

$$lgK_i = lgK_0 + \rho_i \Sigma\sigma_i, \tag{1}$$

where lgK_i and lgK_0 - logarithms of rate constants or equilibria for the standard reaction serieses and being in study ones, ρ_i and σ_i - constants of the reaction serieses and the substituents.

Presently, there are hundreds of the reactions of acid extraction and metal salts, in which lgK_i linearly depends on $\Sigma\sigma_i$. More than 20 such equations have been obtained for explaining the extraction of nitric acid and nitrates of actinides by the neutral phosphororganic compounds of the type XYZP=O, where $lgK_{extr.}$ linearly depends on the sum of the reaction constants σ^ϕ of vicinal substituents X,Y,Z (Table 1).

This means, that the linearity principle of free energies in a number of cases may be successfully used for forecasting the extractive ability in the processes of EDA type. Wide perspectives open due to the formation of the intermolecular hydrogen bond between the extragents and the protonodonors in the organic solvents as a standard one.

According to Iogansen's study for the formation of intermolecular hydrogen bond of electronodonors (ED) with phenol, one can represent:

$$\Delta H_{EDA} = - 5,3 \quad P_i \quad E_j ,$$

where P_i and E_i - protonodonor and electronodonor factors (for phenol $P_i = 1$).

The comparison of E_j for series XYZP = O with the extraction constants of nitric acid and nitrates of actinides has allowed to obtain 21 equations:

$$lgK_{extr} = aE_j + b, \tag{2}$$

where a and b -coefficients of linear equation(Table1).

These equations have enough high correlation coefficients (r) and may be used for estimating the extractive ability of elementoorganic reagents.

Table 1. The relations between the electronodonor properties of neutral phosphororganic compounds and the extractive ability

Y	$lgK_Y = a\Sigma\sigma + b$			$lgK_Y = aE_j + b$			n	Solvent
	a	b	r	a	b	r		
HNO_3	0.41	-1.49	0.983	4.22	-5.93	0.999	3	$C_{12}H_{26}$
HNO_3	- 0.73	-1.69	0.973	3.97	-5.34	0.978	5	CCl_4
HNO_3	- 0.505	-1.905	0.990	2.64	-4.24	0.993	10	$CHCl_3$
HNO_3	- 0.685	-1.60	0.930	3.95	-5.27	0.946	10	C_6H_6
HNO_3	- 0.50	-1.21	0.999	0.85	-0.79	0.979	3	kerosin
$UO_2(NO_3)_2$	-1.57	-0.19	0.968	8.25	-7.62	0.965	7	C_6H_{14}
$UO_2(NO_3)_2$	-1.55	-0.31	0.969	14.26	-15.12	0.988	3	$C_{12}H_{26}$
$UO_2(NO_3)_2$	-2.18	-1.21	0.997	11.44	-11.52	0.967	5	CCl_4
$UO_2(NO_3)_2$	-1.17	-1.56	0.973	7.92	-7.98	0.954	8	$CHCl_3$
$UO_2(NO_3)_2$	-1.35	0.87	0.980	7.74	-6.45	0.959	10	C_6H_6
$UO_2(NO_3)_2$	-1.88	-0.59	0.996	8.19	-7.46	0.980	3	kerosin
$Am(NO_3)_3$	-1.37	-1.81	0.969	5.91	-6.94	0.954	4	-
$Pu(NO_3)_3$	-1.28	-2.26	0.981	7.44	-9.09	0.995	4	C_6H_6
$Pu(NO_3)_4$	-1.77	0.97	0.999	8.89	-6.93	0.997	4.	CCl_4
$Pu(NO_3)_4$	-2.13	-1.41	0.950	11.83	-12.12	0.933	9	C_6H_6
$Np(NO_3)_4$	-2.20	-1.83	0.848	11.85	-12.45	0.835	8	C_6H_6
$NpO(NO_3)_3$	-0.97	-1.64	0.961	5.67	-6.87	0.988	3	C_6H_6
$NpO_2(NO_3)_2$	-1.23	0.04	0.966	7.00	-6.41	0.967	9	C_6H_6
$PuO_2(NO_3)_2$	-1.54	-1.10	0.886	8.84	-9.30	0.905	9	C_6H_6
$ZrO(NO_3)_2$	-2.71	-2.99	0.998	11.74	-12.80	0.979	3	CCl_4
$HTlCl_4$	1.17	-0.18	0.993	5.98	-5.53	0.987	4	CCl_4

n- number of studied compounds, r-correlation coefficient.

On the basis of the obtained experimental data, one can attribute the extraction processes of nitric acid and nitrates of actinides of neutral phosphororganic compounds to isoentropy reaction series [1]. It confirms an attempt of using multiparameter equations for equilibrium constant counts of extraction processes [2]

$$lgK_{extr} = C_A^k \quad C_B + E_A^k \quad E_B + lgK_o,$$ (3)

79

Table 2. The relations between the sum of overlap integrals (S_i) of substituents with phosphorus atom in molecules of neutral phosphororganic compounds and their extractive ability

Y	$lgK_Y = a \sum S_i + b$			n	Solvent
	a	b	r		
HNO_3	3.74	− 5.69	C.972	5	CCl_4
HNO_3	2.52	− 4.65	0.988	5	$CHCl_3$
HNO_3	2.83	− 4.32	0.847	8	C_6H_6
HNO_3	2.58	− 3.97	0.972	3	kerosin
$UO_2(NO_3)_2$	5.80	− 5.64	0.925	6	C_6H_{14}
$UO_2(NO_3)_2$	11.17	− 13.15	0.996	5	CCl_4
$UO_2(NO_3)_2$	9.17	− 11.66	0.994	3	$CHCl_3$
$UO_2(NO_3)_2$	5.99	−5.34	0.968	8	C_6H_6
$UO_2(NO_3)_2$	9.70	−10.98	0.989	3	kerosin
$Am(NO_3)_3$	7.39	−9.97	0.999	3	−
$Pu(NO_3)_3$	5.67	−8.31	0.991	3	C_6H_6
$Pu(NO_3)_4$	8.99	−8.62	0.992	4	CCl_4
$Pu(NO_3)_4$	8.44	−9.65	0.897	6	C_6H_6
$Np(NO_3)_4$	10.85	−13.64	0.923	5	C_6H_6
$NpO_2(NO_3)_2$	5.50	−5.65	0.955	5	C_6H_6
$PuO_2(NO_3)_2$	4.07	−3.38	0.940	5	C_6H_6
$ZrO(NO_3)_2$	13,96	−17,94	0.993	3	CCl_4
$HTlCl_4$	5.94	−6,50	0.984	4	CCl_4

where C_B and E_B - are covalent and electrostatic contributions of extragent, C_A^k and E_A^k - covalent and electrostatic contributions of compound extract, lgK_o - absolute term of the equation, representing the specific features of interaction between all the components of reaction system and the solvent.

One can observe enough good coincidence of design and experimental values, when the equations (3) are to be used for explaining all

80

the data on extraction processes, using neutral phosphororganic compounds with the wide variation of extragent properties, compound extracts and solvents, when lgK_{extr} varies between 1,3 and 8,23.

In 75 cases, the divergence is lower than 20% and lower than 10% in a half of 112 extraction processes, that corresponds to the accuracy of determining lgK_{extr} The obtained results have shown, that the elements of the theory of EDA interactions in the solutions could be successfully used for explaining heterophase extraction systems and forecasting the extraction properties of neutral type reagents.

According to the current ideas on quantum chemistry, the ability of elementoorganic compounds to EDA interactions rises with increasing electron density on the active center of the molecule. The value of electron density on phosphoryl fragment is determined by the sum of overlap integrals of the substituents X,Y,Z with the phosphorus atom $(\sum S_i)$. The counted values S_i for 18 types of the neutral phosphororganic compounds have been compared with the values lgK_{extr} in 84 reactions of extraction of acids and metal salts [3] (Table 2).

Linear equations with enough high correlation coefficients (r) , estimating the extractive ability of neutral phosphororganic compounds have been obtained for the majority of investigated processes. These relations are one of the first semiempirical equations,connecting the electron structure of neutral phosphororganic compounds with their extractive ability.

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X-ray emission and EXAFS spectroscopy have been used to study the
electronic structure and spatial structure of extractants and complex-
es formed in the extraction systems and also the interaction of the
molecules of the extractants and complexes with the solvent. A proce-
dure has been developed for measuring X-ray emission spectra of
liquids which allows the electronic structure of ligands and complexes
to be studied directly in the solutions.

The studies were performed on dialkylsulfides (R_2S),which are widely
used as extractants for some noble metals, and their complexes with
$PdCl_2$. SK_{α}-spectra were obtained for dihexylsulfide, the complexes
$PdCl_2 \cdot 2(C_6H_{13})_2S$, $[PdCl_2(C_6H_{13})_2S]_2$, $PdCl_2 \cdot 2(C_3H_7)_2S$, and their
solutions in $n-C_7H_{16}$, C_6H_6, $CHCl_3$. Also SK_{β} -, PdL_{β_2} - , ClK_{β}-spectra
were obtained for the complexes and their solutions in C_6H_6 .

X-ray emission spectra were measured on a "Stearat" spectrometer
with a quartz crystal-analizer which was focussed according to the
Johann scheme with a curvature radius of 500 mm. The spectral resolu-
tion of the instrument was 0.5 eV. The EXAFS spectra were measured
using synchrotron radiation of the VEPP-4 storage ring of the Institu-
te of Nuclear Physics of the Siberian Division of the USSR Academy of
Sciences. The spectra were processed using the standard procedure and
the radial structural functions were obtained for mono- and binuclear
complexes and their solutions in C_6H_6 and $1,2-C_2H_4Cl_2$.
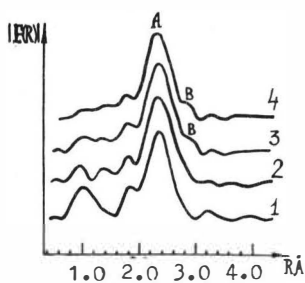
Fig. 1. Radial structu-
ral functions F(r) for
(1) - $PdCl_2 \cdot 2(C_6H_{13})_2S$
and (2) its 0.5 M solu-
tion in $1,2-C_2H_4Cl_2$,
(3) - 0.5 M in C_6H_6, (4)-
0.3 M in C_6H_6

EXAFS-spectra. The position of the main ma-
ximum A of the radial structural function
(Fig. 1) corresponds to equal distances of
the sulfur and chlorine atoms in the first
coordination sphere from the palladium atom.
According to the X-ray structural data
such distances for the known planar-square
palladium complexes with sulfur and chlorine
atoms in the first sphere coincide to within
0.01 Å and are equal to 2.30 Å . As can be
seen from Fig. 1 dissolution of $PdCl_2$
$2(C_6H_{13})_2S$ in benzene and in 1,2-dichloro-
ethane does not cause any change in the po-
sition of the main maximum but in C_6H_6 , in
contrast to 1,2-dichloroethane , there appe

ars a weak maximum corresponding to a scattering distance of 2.85 Å .
On dissolution of the binuclear complex in C_6H_6 , $1,2-C_2H_4Cl_2$, and
$CHCl_3$ the main maximum (2.26 Å) becomes somewhat shifted, with
the radial structural function retaining in general its shape. The
appearance of a weak shoulder B (2.85 Å) in the spectrum of a ben-
zene solution of the mononuclear complex (Fig. 1) may be a result
of scattering from a solvent molecule which has approached the cent-
ral palladium atom, probably in the direction perpendicular to the
plane of the complex molecule. A small (0.04 Å) increase of the dis-
tance to the main maximum A and a decrease of the maximum B for the
radial structural function of the binuclear complex upon dissolution
is probably associated with a decrease in the intermolecular inter-
action on passing from crystal to solution.

SKα - and ClKα -spectra In Ref. [1] a quantitative relationship
was obtained between the shifts in the SKα - and ClKα -spectra
and the effective charges on the chlorine and sulfur atoms in com -
pounds. The results of the present work for the values of the shifts
in the SKα and ClKα spectra suggest that the effective charge on
the sulfur and chlorine atoms does not change upon complexation and
dissolution of the sulphides and their complexes with $PdCl_2$ with an
accuracy to within $\pm$ 0.02 of an atomic unit.

PdL$_{\beta_2}$ - spectra. X-ray emission spectra PdL_{β_2} arise from the
Pd(4d-2p) transitions and are known to be only slightly sensitive to
the chemical state of the palladium atoms. For the complexes studied
by us these spectra were practically the same and showed no changes
upon dissolution of the complexes in benzene.

SK$_\beta$ -spectra . SK$_\beta$ emission spectra result from transitions from
molecular orbitals (MO) having contributions of the 3d orbitals of
sulfur to the 1s atomic orbitals (AO) and give direct information
about these MO 's. According to [1,2] the main maximum C in the SK$_\beta$ -
spectra of dialkylsulfides is determined by the levels of the non-
bonding electrons and the maxima A and B are determined by the cor-
responding levels of the σ -bond. The spectra of $(C_6H_{13})_2S$ in
solutions and in the pure form are practically the same. X-ray SK$_\beta$ -
spectra of sulfur in complex compounds of palladium and rhodium with
sulfur-containing ligands were studied in [3]. It was shown that
the interaction of the non-bonding sulfur electrons with the metal
atom gives rise to a system of levels of the complex which have an
admixture of the non-bonding electrons of the sulfide molecule.
Due to this, instead of a certain level, the complex contains a
group of levels which may show themselves in the spectrum by a dec-
reased intensity of the peak C and be interpreted as the transfer
of a part of the "unshared" pair to the metal atom [3]. From Fig. 2
it can be seen that there occur substantial changes in the SK$_\beta$ -

spectrum on passing from the pure sulfide to the one coordinated in complexes. Complexation leads to a broadening of the SK_β -spectrum and the spectra become more diffused for all of the complexes, in accord with /3/. But a substantial decrease in the relative intensity of the maximum C is observed only for the $PdCl_2 \cdot 2(C_3H_7)_2S$.
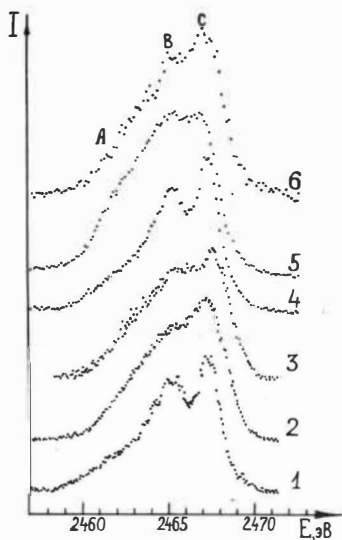
Fig. 2. X-ray SK_β -spectra (1) - $(C_6H_{13})_2S$ (liquid); (2) - $PdCl_2 \cdot 2(C_6H_{13})_2S$ and (3) its 0.5M solution in C_6H_6 ; (4) - $(C_3H_7)_2S$ (liquid); (5) - $PdCl_2 \cdot 2(C_3H_7)_2S$ and (6) - its 0.5 M solution in C_6H_6

Small differences in the full widths at half maximum between the SK_β -spectra (d SK_β) of the studied complexes may be associated with the differences in the intermolecular interactions determined by differences in the molecular packing. The value of d SK_β is the lowest for $PdCl_2 \cdot 2(C_6H_{13})_2S$ (5.2 eV) suggesting weaker molecular interactions for this complex. For the complexes dissolved in C_6H_6 the values of d SK_β are practically equal to each other (5.3-5.6 eV) which is somewhat higher than for the pure $PdCl_2 \cdot 2(C_6H_{13})_2S$ (5.2 eV) but smaller than for solid $PdCl_2 \cdot 2(C_3H_7)_2S$ (6.0 eV) and $[PdCl_2(C_6H_{13})_2S]_2$ (5.8 eV). A small broadening of the SK_β -spectrum on passing from $PdCl_2 \cdot 2(C_6H_{13})_2S$(5.2 eV) to its solution in benzene (5.6 eV) appears to be due to an interaction with the solvent.

ClK$_\beta$ -spectra . The ClK$_\beta$ -spectra are due to electron transitions from the MO's having chlorine 3p-contributions to the 1s AO of the chlorine. In Fig. 3 are shown ClK$_\beta$ -spectra of the $PdCl_2 \cdot 2(C_6H_{13})_2S$ and $[PdCl_2 \cdot (C_6H_{13})_2 S]_2$ complexes and their 0.5 M solutions in benzene. According to /4/ the long-wave shoulder A corresponds to transitions from the б -bonding levels, consisting of s, d - AO of palladium and p-AO of chlorine, and is partially associated with an interaction of the ligands via the central atom. Maximum B arises from transitions from the $\overline{\pi}$ -levels of the complex which are mainly constructed from the p$\overline{\pi}$ -AO of chlorine. It splitting is largely due to the direct interligand interaction of the chlorine atoms. The shoulder C is associated with transitions from the б -nonbonding levels consisting mainly of the p$\overline{\pi}$ -AO of chlorine. As can be seen from Fig. 3 there is a considerable increase in the full width at half maximum of the ClK$_\beta$ -spectrum on passing

84

from mono- to binuclear complexes , i.e. there is a splitting of the 6 - and π- levels with the decreasing symmetry of the complex.

Dissolution of $PdCl_2 \cdot 2(C_6H_{13})_2S$ in benzene leads to an appreciable increase in the intensity of the shoulder A, which corresponds to the interaction of the chlorine with the palladium and the ligands with the palladium atom (see above). According to the EXAFS spectra acting as one of the ligand may be a benzene molecule which has approached the Pd atom. Dissolution of the binuclear complex in benzene leads to a noticeable splitting of the main maximum B in the ClK_β - spectrum which may be explained by the chlorine atoms directly interacting with a benzene molecule. From the analysis of the obtained data it follows that the interaction of the mononuclear complex with benzene occurs by a different mechanism than with 1,2-dichloroethane and also differs from that of the binuclear complex with C_6H_6. It appears that the dissolution of $PdCl_2 \cdot 2(C_6H_{13})_2S$ in benzene makes possible realization of a π-inter-

Fig. 3. X-ray ClK_β -spectra of (1) - $PdCl_2 \cdot 2(C_6H_{13})_2S$ and (2) - its 0.5 M solution in C_6H_6; (3)-$[PdCl_2 \cdot (C_6H_{13})_2S]_2$ and (4) - its 0.5 M solution i in C_6H_6

action of palladium with an aromatic solvent. Thus, it is shown that a combined use of X-ray and EXAFS spectroscopy makes it possible to obtain additional information about the state and the interaction of complexes in solutions and to substantiate the effect of the solvent on the extraction. The developed method can also be applied to the studies of other systems.

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On the basis of the individual partition coefficient values the new way of extraction constant determination has been proposed. The extraction constant is proposed to be calculated from the following equation:

$$K'_{ex} = \frac{[H^+]n}{[HL^+]n} \sum_{n=0}^{N} \left\{ \frac{\beta_n [L]^n}{1 + \sum_{n=1}^{N} \beta_n [L]^n} P_n \right\},$$

where $[H^+]$ = free ligand concentration;

$[HL^+]$ = concentration of protonated form of the ligand;

β_n = stability constant of the n-th successive complex;

P_n = individual partition coefficient for the n-th successive complex.

K'_{ex} values were correlated with the softiness and hardiness of the extraction solvents measured by the $\log \beta^*$ constant. This constant was defined as an equilibrium constant of the following substitution reaction:

$$\left[M (H_2O)_6 \right]^{+2} + \left[HL^+ \right] \rightleftharpoons \left[ML (H_2O)_5 \right]^{+2} + \left[H_3O^+ \right],$$

$$\log \beta^* = \log \frac{\left[ML (H_2O)_5 \right]^{+2} \left[H_3O^+ \right]}{\left[HL^+ \right] \left[M (H_2O)_6 \right]^{+2}} = \log \beta_1 - pK_a.$$
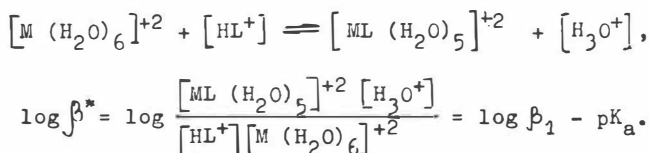
It has been found that the highest values of the extraction constants are achieved for the extraction of those metal complexes of pyridine derivatives that are characterized by the highest $\log \beta^*$ values (i.e. the softest complexes extracted with the softest extraction solvents, see Table)

K'_{ex} and $\log \beta^*$ values for the selected metal complexes

COMPLEX EXTRACTED	EXTRACTION SOLVENT	$\log \beta^*$	K'_{ex}
Cu(II)- 3-methylpyridine	acetylacetone	-3.78	6.191 ± 0.160
Ni(II)- 3-methylpyridine	acetylacetone	-3.87	0.214 ± 0.012
Co(II)- 3-methylpyridine	acetylacetone	-4.45	$4.402 \cdot 10^{-3} \pm 2.390 \cdot 10^{-4}$
Zn(II)- 3-methylpyridine	acetylacetone	-4.85	$7.265 \cdot 10^{-3} \pm 9.900 \cdot 10^{-4}$

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Simultaneous extraction of metals is of interest, especially in
cases when one metal is present in micro quantities and the other in
macroscopic amount. The extraction of the microelement is affected
by the macroelement - it may be decrease (extraction suppression) or,
conversely, increase (co-extraction). It is clear that the study of
the mechanism and the quantitative description of metals extraction
suppression in such difficult systems as the salts of tertiary high
molecular weight amines and quaternary ammonium bases (QAB) requires
the knowledge of the aggregation and dissociation processes of the
organic phase components. One of the most effective approaches, ma-
king it possible to solve this problem, can lie in measuring the con-
ductivity, the IR and NMR spectra of extracts.

^{1}H and ^{13}C NMR was used to investigate the structure of ion pairs
formed by alkylammonium cation and metal-containing anions in organic
solvents. It has been shown that the cation-anion distance in the in-
vestigated compounds increases with growth of the n-alkyl chain of the
alkylammonium cations. Some experimental results with trioctylmethyl
(TOMA), trioctylethyl (TOEA), trioctylpropyl (TOPA), trioctylbutyl
(TOBA) and tetraoctylammonium (TeOA) salts are summed in Table 1. The
NMR investigations have shown that, for a given geometry of ionic as-
sociates, not more that two trioctylalkylammonium cations can be easi-
ly positioned in the vicinity of the metal-containing anion. The in-
sertion of a third and subsequent cations is geometrically impossible.

The occurence and conditions of formation of various extractable
complexes in the systems with tri-n-octylammonium chloride (TOAHCl)
were also investigated by means of loading experiments, IR spectrosco-
pic investigations and measurements of the conductivity of the metal
bearing extracts of various compositions, including the N-deuterated
compounds. Besides the well-known 1:1 and 2:1 complexes, complexes
with a stoichiometric ratio TOA:M=3 were found. Their cations con-
tain the groups (TOAH ... Cl ... HTOA)$^+$ and TOAH$^+$. The specific con-
ductivity data $æ$ and the wave numbers of the $\vee$NH and $\vee$ND absorpti-
ons of the metal-containing extracts are given in Table 2.

Table 1. Cation-anion distances (nm) in ion pairs formed by tri-octylalkylammonium cations with lanthanide pentanitrates and pentachlorides in benzene and nitrobenzene

QAB cation	Benzene		Nitrobenzene	
	Chloride system	Nitrate system	Chloride system	Nitrate system
TOMA	–	–	73	78
TOEA	84	91	77	81
TOPA	88	106	78	81
TOBA	–	108	78	82
TeOA	–	–	78	82

Table 2. Specific conductivity data $\varkappa$ and wave numbers (cm^{-1}) of the νNH and νND absorptions (Metal concentration: 0.1 M; diluent: benzene)

Complexes		νNH	$\nu NH/\nu ND$	$\varkappa \cdot 10^{-5} \, \Omega^{-1} cm^{-1}$
$TOAHFeCl_4$	1:1	3122	1.34	2.75
$TOAHGaCl_4$	1:1	3122	–	2.71
$TOAHSbCl_6$	1:1	3155	1.34	2.34
$TOAHInCl_4$	1:1	3107	–	2.26
$TOAHSnCl_3$	1:1	3030	1.33	2.18
$TOAHSnCl_5$	1:1	3120	1.34	1.23
$TOAHCuCl_3$	1:1	3015	1.33	1.84
$TOAHZnCl_3$	1:1	2790	1.28	0.034
$TOAHSbCl_4$	1:1	2735,2785	1.28	0.0082
$(TOAH \cdot Cl \cdot HTOA)SnCl_3$	2:1	2613	1.28	7.18
$(TOAH \cdot Cl \cdot HTOA)InCl_4$	2:1	2606	1.28	6.06
$(TOAH \cdot Cl \cdot HTOA)FeCl_4$	2:1	2611	1.28	6.02
$(TOAH \cdot Cl \cdot HTOA)GaCl_4$	2:1	2611	–	5.89
$(TOAH \cdot Cl \cdot HTOA)SbCl_6$	2:1	2610	1.28	5.72
$(TOAH \cdot Cl \cdot HTOA)SbCl_4$	2:1	2610	1.27	2.08
$(TOAH)_2SnCl_6$	2:1	3069	1.34	0.128
$(TOAH)_2CuCl_4$	2:1	2800	1.28	1.54
$(TOAH)_2ZnCl_4$	2:1	2790	1.28	0.089
$(TOAH)_2CoCl_4$	2:1	2790	1.28	0.062
$(TOAH \cdot Cl \cdot HTOA)TOAHCuCl_4$	3:1	2615,2790	1.28	2.14
$(TOAH \cdot Cl \cdot HTOA)TOAHZnCl_4$	3:1	2615,2790	1.28	1.85
$(TOAH \cdot Cl \, HTOA)TOAHCoCl_4$	3:1	2615,2790	1.28	1.72
$(TOAH \cdot Cl \cdot HTOA)TOAHSnCl_6$	3:1	2615,2790		1.36

With the help of the aggregation and dissociation common model [1] and the Fuoss-Onsager theory [2] we have calculated the dissociation constants for various trioctylalkyl and trioctylammonium species in benzene and nitrobenzene. The data obtained are listed in Table 3. It has been found that dissociation constants of simple and metal-containing alkylammonium compounds differ between one another in chloride systems to a much higher extent than in a nitrate systems.

Table 3. Dissociation constants for QAB compounds in benzene and nitrobenzene

Complexes	Benzene	Nitrobenzene
TOMANO$_3$	$(5.9\pm1.3)\cdot10^{-5}$	$(3.2\pm0.5)\cdot10^{-2}$
(TOMA)$_2$Er(NO$_3$)$_5$	$(7.0\pm1.9)\cdot10^{-4}$	$(8.4\pm2.7)\cdot10^{-2}$
(TOMA)$_2$Th(NO$_3$)$_6$	$(9.9\pm1.9)\cdot10^{-6}$	$(6.3\pm3.1)\cdot10^{-3}$
TOMACl	$(4.9\pm1.5)\cdot10^{-7}$	$(3\pm1)\cdot10^{-4}$
TOMAFeCl$_4$	$(22.6\pm4.7)\cdot10^{-3}$	$(1.22\pm0.33)\cdot10^{-1}$
(TOMA)$_2$ErCl$_5$	$(10.4\pm4.3)\cdot10^{-3}$	$(9.9\pm2.7)\cdot10^{-2}$
(TOMA)$_2$ThCl$_6$	$(8.1\pm1.2)\cdot10^{-3}$	$(4.4\pm0.3)\cdot10^{-2}$
TOPABr	–	$(1.5\pm0.5)\cdot10^{-3}$
TOPAFeCl$_4$	–	$(3.8\pm0.2)\cdot10^{-1}$
(TOPA)$_2$ZnCl$_4$	–	$(3.0\pm0.3)\cdot10^{-3}$
TeOABr	–	$(9.92\pm0.12)\cdot10^{-3}$
TeOAFeCl$_4$	–	$(8\pm5)\cdot10^{-3}$
TeOAInCl$_4$	–	$(9\pm2)\cdot10^{-3}$
(TeOA)$_2$ZnCl$_4$	–	$(4\pm3)\cdot10^{-3}$

Generally, the character of the influence of all factors on the behaviour of the microelement in the presence of the macroelement during the extraction by amine and QAB salts can be analysed by application of the following equation:

$$S = \frac{[R_4NB]_1^{n}1(1-\beta C_{A1,2})\left[1+K_M[R_4N^+]_1^{-1}+K_A(1-\beta C_{A1,1})^{-1}([R_4N^+]_1^{-1}+[B^-]_1)\right]^{-1}}{[R_4NB]_2^{n}1(1-\beta C_{A1,1})\left[1+K_M[R_4N^+]_2^{-1}+K_A(1-\beta C_{A1,2})^{-1}([R_4N^+]_2^{-1}+[B^-]_2)\right]^{-1}}, (1)$$

where β is the stepwise solvation constant, K_A is the dissociation constant of the extractant, K_M and $K_{M'}$ are the dissociation constants of the metal-containing compound of micro and macroelements in the organic phase, S is the extent of extraction suppression, n_1 and n_2 are the stoichiometry coefficients for micro and macroelement extraction, C_{A1} is the concentration of the monomeric alkylammonium species present in the solution, C_A is the analytical concentration of the al-

kylammonium salt, $[R_4NB]$ is the concentration of the free extractant in the organic phase, $[R_4N^+]$ is the concentration of the "common" alkylammonium cations, C_M and $C_{M'}$ are the concentrations of the micro and macroelement in the organic phase. In equation (1) the values $[R_4N^+]+[B^-]=(K_A[R_4NB]+[R_4N^+]^2)/(K_A[R_4NB][R_4N^+])$, and $[R_4N^+]$ can be calculated from equation

$$[R_4N^+]=(K_{M'}C_{M'}+K_AC_A- h_2K_AC_{M'})^{1/2} \tag{2}$$

The value of C_{A1} in equation (1) was determined from the following relationship:

$$c_{A1}^2\beta^2(C_A-C_{M'})-C_{A1}(1+2\beta C_A-3\beta C_{M'})+C_A-2C_{M'}=0 \tag{3}$$

Analysis of equation (1) has shown that, in accordance with the previously studied regularities of the extraction suppression of microelements, the degree of this suppression increases with increasing alkylammonium "common ion" concentration and with increasing macroelement concentration and its dissociation contant in the organic phase.

Equation (2) allows us to draw a very important conclusion on the possibility of the "common ion" mechanism existence itself in a concrete extraction system. If expression $K_{M'}-K_Ah_2$ in equation (2) is less than or equal to zero, an increase in the macroelement concentration in the organic phase will not lead to the growth of the concentration of alkylammonium cations. Therefore, neither will there exist any precondition for the "common ion" mechanism to be actualised.

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The principle of linearity of the free energy changes when applied
to extraction processes implies the same sequence of the relative ex-
tractive power of the extractants with the change of both the compound
being extracted and the diluent [1]. However, in the extraction of
acids with trialkylphosphine oxide and heterocyclic N-oxides the sys-
tems studied by us showed deviations from this principle [2,3].

The extraction of the following acids (HA): CH_3COOH- a weak acid,
HNO_3- a medium-strength acid, and $HClO_4$- a strong acid, with two ext-
ractants (L)- triisoamylphosphine oxide (TAPO) and 2-nonylpyridine N-
oxide (2-NPO), in a series of diluents of different solvating power
($n-C_7H_{16}$, CCl_4, C_6H_6, $CHCl_3$, $1,2-C_2H_4Cl_2$) was studied. The choice of
these two extractants was determined by the inversion in their relati-
ve basicities in the case of H-bonding ($\Delta V_{OH}(H_2O)$ - 240 and 224 cm^{-1}
for TAPO and 2-NPO, respectively) and in protonation (pK_a = -0.5 and
+ 1.2 for TAPO and 2-NPO, respectively).

Stoichiometry and the extraction constants. Using extract dilution
and saturation methods and IR spectroscopy of the extracts the compo-
sition of the extracted complexes HA:L was established. It was 1:1
for HNO_3, 1:1 and 2:1 for CH_3COOH, 1:2 and 1:1 in the case of $HClO_4$.
The extraction constants were calculated taking into account $\Gamma^{\pm}$ and Γ_L
(Tables 1,2). The deviations of the obtained data from the values cal-
culated on a computor for the systems with $HClO_4$ (σ) did not exceed
the experimental error.

Table 1. Extraction constants of 1:1 complexes for CH_3COOH and HNO_3

Solvent	lg $\overline{K}_{1,1}$			
	$L \cdot CH_3COOH$		$L \cdot HNO_3$	
	2-NPO	TAPO	2-NPO	TAPO
$n-C_7H_{16}$		1.15±0.06	−0.31±0.03	1.02±0.02
CCl_4	0.20±0.04	0.89±0.02	−0.22±0.01	0.62±0.02
C_6H_6			0.76±0.03	1.12±0.02
$CHCl_3$	0.30±0.04	0.43±0.05	0.60±0.10	−0.07±0.02
$1,2-C_2H_4Cl_2$	0.45±0.02	0.79±0.03	1.40±0.06	1.12±0.04

The dependence of the extraction constants on the solvating pro-
perties of the diluent is not an unambiguous one since it reflects the
interaction characteristics of the diluent with the extractant and
the complex. The sequence of the efficiencies of the diluents in

extraction of acids differs from one studied acid to another and for a particular acid differs for 2-NPO and TAPO. In the extraction of CH_3COOH, TAPO is a better extractant than 2-NPO in all of the diluents according to their basicity in H-bonding. On the contrary, in the case

Table 2 . The extraction constants of 1:2 and 1:1 complexes for $HClO_4$

Solvent	TAPO			2-NPO		
	$lg \overline{K}_{1,2}$	$lg\overline{K}_{1,1}$	σ	$lg \overline{K}_{1,2}$	$lg\overline{K}_{1,1}$	σ
CCl_4	2.58 ± 0.04		0.105			
C_6H_6	2.98 ± 0.02	-0.60 ± 0.04	0.032	3.38 ± 0.02	0.98 ± 0.02	0.038
$CHCl_3$	0.64 ± 0.03	-1.97 ± 0.10	0.086	2.17 ± 0.03	-0.23 ± 0.05	0.045
$1,2-C_2H_4Cl_2$	3.68 ± 0.06	-0.57 ± 0.06	0.11	4.11 ± 0.05	0.75 ± 0.08	0.13

of $HClO_4$, 2-NPO has higher $\overline{K}_{1,1}$ and $\overline{K}_{1,2}$ values than TAPO (Table 1,2) according to their basicities in protonation. For HNO_3 there is inversion of the relative extractive powers of 2-NPO and TAPO with the change of the solvent: TAPO > 2-NPO in weakly solvating ($n-C_7H_{16}, CCl_4$, C_6H_6) and 2-NPO > TAPO in strongly solvating ($CHCl_3$ and $1,2-C_2H_4Cl_2$) diluents.

The state of the extracted complexes in the diluents. The state of the extracted complexes in different systems was established by analizing UV and IR spectra of the extracts (Table 3). The absorption

Table 3. Characteristics of the IR spectra of extracts with L·HA

$L \cdot CH_3COOH$

L	Solvent	$\nu(C=O)$	$\nu(X=O)$	$\nu(OH)$ bonded
TAPO	$CCl_4, CHCl_3, 1,2-C_2H_4Cl_2$	1710-1715	1140	1900,2500,2600,2750
2-NPO	$CCl_4, CHCl_3, 1,2-C_2H_4Cl_2$	1710-1715	1220	1900,2500,2600,2750

$L \cdot HNO_3$

L	Solvent	$\nu^{NO_2}_{sym}$	$\nu^{NO_2}_{asym}$	$\nu_3(NO_3^-)$	$\nu(OH^+)$	$\nu(OH)$ bonded
TAPO	$CCl_4, CHCl_3$	1300	1650			1800,2250,2430
2-NPO	CCl_4	1300	1670			
2-NPO	$C_6H_6, CHCl_3$			1250,1470	2300,2500	

$L \cdot HClO_4$

L	Solvent	$\nu(X=O)$	$\nu(ClO_4^-)$	$\nu(OH^+)$
TAPO	$C_6H_6, CHCl_3, 1,2-C_2H_4Cl_2$	1140	1140,630	2300,2750
2-NPO	$C_6H_6, CHCl_3, 1,2-C_2H_4Cl_2$	1125-1135	1125-1135,630	2600-2670

bands present in the IR spectra of the extracts of CH_3COOH with TAPO and 2-NPO in all of the studied diluents in the region from 1100 to 3000 cm^{-1} indicate the formation of a molecular complex with H-bonding [4] there are the absorption bands of the carbonyl group at

1710-1715 cm^{-1} and the bands of the bound OH group of the acid near 1900, 2500, 2600, and 2750 cm^{-1} . The shape and the intensity of the UV-spectra of the extracts with 2-NPO confirms that the complex of 2-NPO with CH_3COOH exist as a molecular complex with H-bonding (λ_{max} = 262-269 nm, ε = $1 \cdot 10^4$) The IR spectra of the extracts with HNO_3 fall into two groups. The extracts with TAPO in all of the solvents and with 2-NPO in CCl_4 show absorption bands of symmetrical and asymmetrical vibrations of the NO_2 group at 1300 and 1650-1670 cm^{-1} and of the bound OH-group of the acid at 1900 and in the region 2500-2700cm^{-1} which indicates the presence in these systems of molecular H -complexes [5]. To the second group belong the spectra of the extracts with 2-NPO in C_6H_6 and $CHCl_3$ which have the absorption bands of NO_3^- group at 1250 and 1490cm^{-1} and of a protonated OH^+ group at 2300, 2500 cm^{-1} characteristic of a hydrogen-bonded ionic pair [6]. The UV-spectra of the two groups of extracts with 2-NPO also differ substantially from each other confirming the existence of different forms of the complexes (λ_{max} = 262 nm, ε = $1 \cdot 10^4$ for the extracts in n-C_7H_{16} and CCl_4, and, respectively, 270 nm, $4 \cdot 10^3$ for the extracts in $CHCl_3$ and 1,2-$C_2H_4Cl_2$). The systems with $HClO_4$ form ion pairs in all of the solvents - there are absorption bands of the ClO_4^- ion at 630 and 1130 cm^{-1} and of the OH^+ group near 2600 cm^{-1}. The UV spectra of the extracts with 2-NPO show absorption bands characteristic of protonated complexes (λ_{max} = 278 nm, ε = $7.5 \cdot 10^3$).

The state of the complexes and the extractive power. Comparison of the extraction constants of the complexes in which the states of the complexes in the organic phase is taken into account gives the following regularities for the relative extractive power of 2-NPO and TAPO: TAPO > 2-NPO when extraction occurs in the form of molecular H-complexes which corresponds to the basicity of the extracts in H-bonding (the extraction of CH_3COOH in all of the solvents, HNO_3 in C $_7H_{16}$ and CCl_4) . 2-NPO > TAPO when protonated complexes are extracted , according to the basicity of L in protonation (HNO_3 in $CHCl_3$ and 1,2-$C_2H_4Cl_2$, $HClO_4$ in all of the solvents). Thus the inversion takes place both with the change of the proton donor and with the change in the solvating properties of the solvent occuring as a result of different solvation of the starting and end products of the reaction.

Estimation of the solvation effects. Isolation of the solvation effects was based on calculating the free energies of transfer of various forms (i) from a standard diluent to a particular one (ΔG_{tran}^i = 2.3 RT lg Γ_i /(Γ_i)$_{stan}$ [7], in our case L and L·HA were transfered from CCl_4 (Table 4). For all of the extractants and complexes the highest transfer energies are those to $CHCl_3$ which appears to be due to the ability of this solvent to a specific in-

93

teraction - hydrogen bonding although in solvating properties $1,2-C_2H_4Cl_2$ is superior to $CHCl_3$ (E_T = 175.4 kJ/mol and 163.7kJ/mol for $1,2-C_2H_4Cl_2$ and $CHCl_3$, respectively). The value of ΔG_{tran} for TAPO in $CHCl_3$ is noticeably higher than for 2-NPO according to the greater basicity of TAPO in H-bonding. The transfer energies of com-

Table 4. The energies of transfer for L and L· HA

Solvent	2-NPO	TAPO	L·CH$_3$COOH		L·HNO$_3$	
			2-NPO	TAPO	2-NPO	TAPO
n-C$_7$H$_{16}$	6.7	7.1		5.1	7.2	4.8
C$_6$H$_6$	-1.4	-0.5			-7.0	-3.3
CHCl$_3$	-8.8	-11.9	-9.6	-9.5	-13.8	-7.9
1,2-C$_2$H$_4$Cl$_2$	-3.5	-5.4	-4.9	-4.8	-13.2	-8.1

plexes with CH_3COOH are close to each other for 2-NPO and TAPO which is consistent with the similarity of their forms. In the case of HNO_3 the values of ΔG_{tran} are considerably higher for complexes with 2-NPO than with TAPO which is due to the increased contribution from the solvation of the protonated species compared with the molecular form in the case of TAPO.

Thus on the basis of all of the data it can be concluded that the most important factor when comparing the extraction of acids with TAPO and 2-NPO is the form in which the extracted complex exist (a molecular H-complex or an ion pair). For strong and weak acids the state of the complex is determined by the nature of the acid ($HClO_4$ and CH_3COOH) and is independent of the solvent. For medium strength acids (HNO_3) the form of the complexes is determined by solvating properties of the solvent and the inversion of the relative extractive power occurs with the change of the diluent. The fact that the molecular H-complex may change to an ion pair with the strengthening solvating properties of the solvent for the complex with 2-NPO (and the absence of the latter form in complexes with TAPO) is probably associated with the features of the electronic structure of the heterocyclic aromatic N-oxide. In contrast to alkylphosphine oxides the unshared electron pair of the oxygen atom in 2-NPO is involved in the mobile $\mathfrak{K}$ - system belonging to the whole molecule and the interaction of HNO_3 with 2-NPO changes, therefore, the charge state not only of the donor atom but also of the atoms of the heterocycle.

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Determining the stoichiometry of an extraction reaction is necessary for studying the process chemistry. This is mostly done using techniques based on the law of mass action, chemical analysis data on extracts, ets. Physico-chemical and physical techniques including ESR are very important means of determining the composition and properties of extracted species. The principal limitation of ESR is the possibility to study compounds with paramagnetic central atoms only. The introduction of a spin label into molecules of extractants extends the range of elements can be learned by this method. The use of paramagnetic reagents enables employing ESR in studies of extraction and complexation of diamagnetic ions.

An ESR spectrum of a paramagnetic compound contains information on the structure and properties of the central atom, the organic part of the complex, and the complex as a whole. Analyzing ESR spectra enables one to determine the number of coordinated ligands, the type of coordination, the inner coordination sphere structure, and relative mobilities of molecular fragments. In this work the ESR technique have been used to study two extraction systems.

1. In the extraction of palladium by 2,2,5,5-tetramethyl-4-thioxo-3-imidazolidine-1-oxyl (HA), the reagent acts as both a monodentate sulphur-containing ligand and a bidentate chelating S,N-type agent. Extracts contain $Pd(HA)_2Cl_2$, $Pd(HA)_2Cl_3$, PdA_2, and Pd_2A_4. Relative complex concentrations are determined by the extraction conditions. Extracts for ESR studying prepared under specially chosen conditions when one of the complexes predominated in the organic phase. $Pd(HA)_2Cl_2$ was found to be the major species extracted from hydrochloric acid solutions with Pd:HA=1:2 ratio. With Pd:HA 1:2 ratios, $Pd(HA)_3Cl_2$ was also extracted. From neutral and alkaline solutions, Pd_2A_4 was extracted into the organic phase. This species also extracts from acidic solutions. The concentration region of extracting Pd_2A_4 ie limited by the value of $1 \cdot 10^{-5}$ M. At lower concentrations, ESR spectra of freshly prepared extracts were indicative of the biradical PdA_2 formation. In the course of time PdA_2 produces more stable thermodynamically Pd_2A_4 dimer.
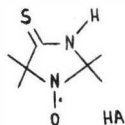
The ESR spectrum of $Pd(HA)_2Cl_2$ represents a multiplet characteristic of biradicals (Fig. 1b). This is indicative of two reagent molecules being coordinated to the central atom. The temperature dependence of the exchange integral, $|J/a|$, shows $Pd(HA)_2Cl_2$ to exist in at

least two exchange conformations with fast interconversions between them. The energy of $Pd(HA)_2Cl_2$ conformational transitions calculated from the temperature dependence corresponds to vibrations or hindered rotations of molecular fragments with respect to each other. It is equal to 3.0 ± 0.5 and 2.8 ± 0.9 kJ/mol for solutions of $Pd(HA)_2Cl_2$ in chloroform and toluene, respectively. The data obtained well fit the suggestion that the complex is a coordination-solvation compound where rotation of ligand radicals is hindered by intramolecular H-bonds formation. A monodentate sulphur-coordination of HA to palladium and the presence of NH...Cl bonds also follow from electronic and IR spectroscopy data. The distance between the biradical O-N fragments was determined from the second ESR spectrum central moment value obtained for a polycrystalline toluene solution of the complex at 77 K. This value of $(10.6\pm0.4)\cdot 10^{-8}$ m is a direct proof of a monomeric structure of $Pd(HA)_2Cl_2$
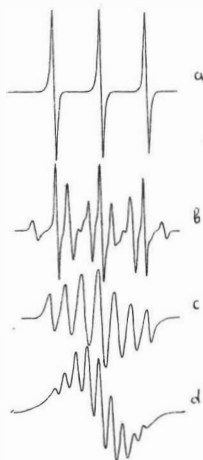
Fig.1. The ESR spectra of HA(a), $Pd(HA)_2Cl_2$(b), $Pd(HA)_3Cl_2$(c), Pd_2A_4(d) in chloroform
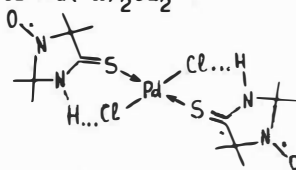
The ESR spectrum of $Pd(HA)_3Cl_2$ is a septet (Fig. 1c) with a component intensity ratio close to 1:3:6:7:6:3:1 which is an unambiguous evidence of the formation of a triradical complex with equivalent O-N fragments. The independence of the spectrum shape on temperature in the range of 287 to 314 K, the positions and intensities of all the spectrum components enables a suggestion to be drawn that the spectrum corresponds to an individual conformation with a strong exchange, $|J/a|\gg 1$. The calculated distance between the O-N fragments of $(10.1\pm0.4)\cdot 10^{-8}$m, the equivalence of the nitrogen atoms, and also the presence of a broad ν_{NH} band in the IR spectrum of the compound make it possible to conclude that the coordination polyhedron of $Pd(HA)_3Cl_2$ is a trigonal bipyramid with chlorine atoms in the axial positions.

The ESR spectrum of Pd_2A_4 (Fig. 1d) consists of nine lines with a 1:3:7:14:20:14:7:3:1 intensity ratio close to the theoretical one for a tetraradical with equivalent nitrogen atoms and a strong spin-exchange interaction in the absence of alternate broadening of exchange components. An exchange-narrowed nature of the spectrum of a poly-

crystalline toluene solution of Pd_2A_4 at 77 K substantiates that $|J/a|>300$. The independence of the ESR spectrum of both solvent and temperature in the range of 287 to 333 K is indicative of the presence of Pd_2A_4 as a single conformer, that is of geometrical rigidity of the complex molecular structure. This observation suggests a bidentate S,N-coordination of HA to palladium with the chelate formation. The structure of the inner coordination sphere in Pd_2A_4 deduced from ESR evidence is in a complete agreement with electronic and IR spectroscopy data, vapour phase osmometry measurements, the results of X-ray structure studies and elemental analyses data.

The results obtained have been used to suggest a scheme of reactions occurring in the extraction system under investigation:

$$\left[PdCl_4\right]^{2-} + 2\ HA_{(o)} \rightleftharpoons Pd(HA)_2Cl_2{}_{(o)} + 2\ Cl^-,$$
$$\left[PdCl_4\right]^{2-} + 3\ HA_{(o)} \rightleftharpoons Pd(HA)_3Cl_2{}_{(o)} + 2\ Cl^-,$$
$$\left[PdCl_4\right]^{2-} + 2\ HA_{(o)} \rightleftharpoons PdA_2{}_{(o)} + 2\ H^+ + 4\ Cl^-,$$
$$2\left[PdCl_4\right]^{2-} + 4\ HA_{(o)} \rightleftharpoons Pd_2A_4{}_{(o)} + 4\ H^+ + 8\ Cl^-,$$
$$2\ PdA_2{}_{(o)} \rightleftharpoons Pd_2A_4{}_{(o)}.$$
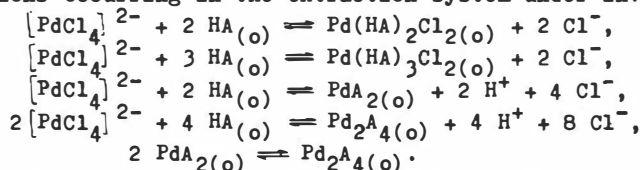
2. Synergetic extraction by mixtures of chelating agents and neutral basic reagents is widely used to isolate metals. The efficiency of extraction is then determined by the formation, stability constant, and other properties of mixed- ligand complexes. The possibility of using ESR to study such systems has been demonstrated for the extraction of nickel(II) by 2,2,5-trimethyl-5-phenyl-3,4-dioximepyrrolidine -1-oxyl (HB) in the presence of pyridine. The ESR spectra of NiB_2, NiB_2Py, and NiB_2Py_2 are shown in Fig.2. The spectroscopic differences of these species has enabled us to establish the fact of the adductformation, determine the predominant form of metal occurrence in extracts, and study the kinetics of process.
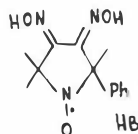
The ESR spectrum of a polycrystalline toluene NiB_2 solution was used to determine information about its structure and spin-exchange interactions. The dipole-dipole interaction, $D=1600$ A/m, and exchange integral, $J=+6400$ A/m, were determined. Also, the mutual orientation of the O-N fragments and the distance between the radical centres, $r=(11.2\pm0.2)\cdot10^{-8}$ m, were found from the spectrum. The data obtained are indicative of a planar structure of the NiN_4 coordination polyhedron of NiB_2 in solutions and an effective spin density conductivity of low-spin Ni ions. The formation of adducts causes a decrease in $|J|$ and promotes Ni to the high-spin state. The coordination polyhedron changes in line with from a NiN_4 square in NiB_2 to a tetragonal pyramid NiN_5 in NiB_2Py and a tetragonal bipyramid NiN_6 in NiB_2Py_2. A comparison of anisotropic spectra of NiB_2 and the monoadduct shows mutual spatial orientations of radical fragments to be similar in these two compounds. The distance between paramagnetic centres calcu-
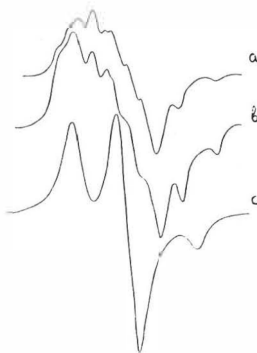
Fig.2. The ESR spectra of NiB_2(a),NiB_2Py(b), NiB_2Py_2(c) in toluene at 77 K

lated from these spectra corresponds to an increase in equatorial Ni-N bond lengths caused by the adduct formation, that is gives an indirect evidence of a decrease in bond covalency.

Solvent nature effects on the energy and kinetics of the adductformation are quite substantial. A step-wise formation of NiB_2 adducts with Py is observed in toluene. With chloroform as solvent, the bisadduct is formed immediately:

$$
\begin{array}{ccc}
 & NiB_2Py & \\
+Py & \diagup \quad \diagdown & +Py \\
\text{toluene} & \diagup \qquad \diagdown & \text{toluene} \\
NiB_2 & \xrightleftharpoons{\qquad\qquad} & NiB_2Py_2 \\
 & +2Py,\ \text{chloroform} &
\end{array}
$$
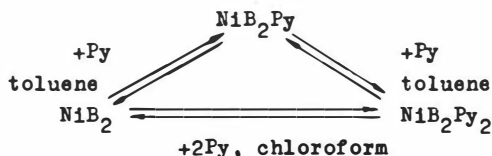
This can be the result of coordination of solvent molecules to NiB_2 with the formation of outer-sphere complexes which has an antibonding effect on equatorial Ni-N bonds and favours the formation of axial adducts /1/. A step-wise adductformation is also observed in the interaction of NiB_2 solutions in toluene with DMSO, 4-aminopyridine, triethylamine, and piperidine. Like pyridine these agents noticeably weaken spin-exchange interactions between radical centres to a degree increasing with their basicity. This correlation between the exchange integral value and the pK_a value of a base implies a change in covalency of in-plane σ-bonds.

Thus the ESR method can be as a tool for studying the complexation of both diamagnetic and paramagnetic metal ions with spin-labeled reagents in extraction and other systems provided there are exchange interactions between paramagnetic centres.

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BASICITY DETERMINATION FOR NEUTRAL PHOSPHORUS ORGANIC EXTRAGENTS BY NMR^{31}P-METHOD IN TWO-PHASE SYSTEMS, AND QUANTITATIVE INTERRELATIONS OF ACIDO-BASIC EXTRACTIVE PROPERTIES

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There are numerous correlations known that associate acidobasic properties of extragents with reactivity in the processes of acids and metal salts recovery, which can be used for the most effective extragent structure selection. Still, all known methods for extragent basicity determination concern aqueous solutions or organic media with a high molarity. At the same time, for aliphatic and aromatic hydrocarbons, which are mostly used as diluents in extraction processes, the basicity of extragents is not known.

In order to determine basicity of the neutral phosphorus organic extragents of the type $XYZP=O(XYZ=C_4H_9, C_8H_{17}, C_6H_5)$ a method has been suggested. The method is based on the chemical shift alterations of phosphorus nuclei in a two-phase extraction system depending on acidity function H_O, H_A, H_{PO}.

It has been found that phosphine oxides and sulfuric acid form monosolvates and disolvates, too, in two-phase extraction systems, while phosphates, phosphinates and aromatic phosphine oxides form monosolvates only. After the analysis of the dependence $\Delta\delta^{31}$P on H_O function, the dissociation constants pK_{BH+}, pK_{BH}^{2+} of the studied extragent series in dodecane, benzene, toluene, acetylene tetrachloride have been calculated.

Comparing values pK_{BH+} with the basicity in nitromethane (pK_{BH+}^{HM}), with enthalpies of complex-formation with a charge transfer with a standard acid - iodine in heptane ($\Delta H_{J_2}^\bullet$); as well as with enthalpies of hydrogen complexes formation; with phenol ($\Delta H_{C_6H_5OH}^O$), water ($\Delta H_{H_2O}^O$), Kabachnik's constants ($\Sigma\sigma^+$) and with $lg\tilde{k}_{H_2SO_4}$ and $lg\tilde{k}_{UO_2SO_4}$ one can find not only qualitative but quantitative interrelations between these values as well. And that can be used for evaluation and prediction of extractability of the type $XYZP=O$ compounds in recovery processes of UO_2SO_4 from aqueous sulfuric acid solutions.

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Solvent extraction of (metal) ions from aqueous solutions frequently involves at least quaternary systems, i.e., systems involving at least four components: water, the salt an ionic constituent of which is to be extracted, the extractant, and the organic diluent. In such systems the extractant reacts with the salt to form, e.g., a chelate of the metal ion to be removed from the aqueous solution, or separated from other metal ions. Often, however, a simpler ternary system can be employed, where the organic extractant and its diluent are one and the same compound. In such cases, a classic example being the ether extraction of uranyl nitrate from aqueous solutions [1], the extraction proceeds due to two effects. One is the occurrence of changes in the solvation of the ions on transfer from the aqueous environment to the organic environment. The other is the association of ions in the organic phase of low relative permittivity.

If the organic phase is predominantly non-aqueous, i.e., has a very low water content, and involves an organic solvent of appreciable ion solvating power, then an important (conceptual, but not necessarily kinetic) step in the overall scheme of the extraction reaction is the dehydration of the ions extracted. The considerable investment in Gibbs free energy that must be made by the system for the dehydration is returned, with a small margin of profit, by the ion association and resolvation of the ions (and the ion pairs) by the organic solvent [2]. The theory of ion association is sufficiently well established, e.g., according to Bjerrum's original ideas as later substantiated and developed [3], but until recently there was no firm basis, on which to predict the solvating abilities of a given solvent for a given ion.

The hydration enthalpy and Gibbs free energy of ions were found to depend practically only on their charges and ionic radii in a well understood manner [4]. Hence instead of the quantities pertaining to the solvation of the ions, the Gibbs free energy and enthalpy of the transfer of the ions from water to nonaqueous solvents can give the desired information. Advances have been made in the understanding of the transfer energetics of ions into organic solvents, and the properties of the solvents and of the ions that are relevant to this process have been established [5,6,7]. A detailed analysis of this problem, involving the Gibbs free energy of the transfer of ions from water to organic solvents and the enthalpy changes involved has now been made [7]. According to this analysis it is possible to point out those features in a solvent that should enhance its abilities to extract an ion of given properties, or to separate ions of differing properties. It was found necessary in this respect to deal separately with small cations, small anions, and large, hydrophobic ions.

For small cations the most important solvent property is its ability to donate a pair of electrons for solvation, as measured by its Gutmann donor number [8] or its Taft-Kamlet solvatochromic parameter β [7]. Subsidiary solvent properties are its polarity and polarizability, measured by the solvatochromic π*, and its self association (requiring more work to create a cavity for the ion), measured by its hydrogen bond donating ability, the solvatochromic α. Multivariable regressions on transfer energetics data established
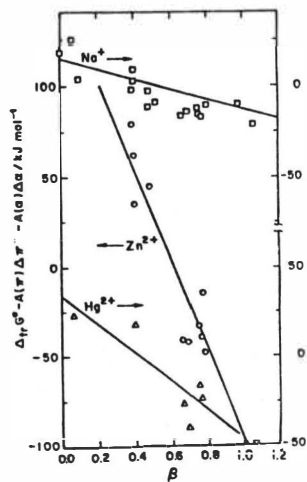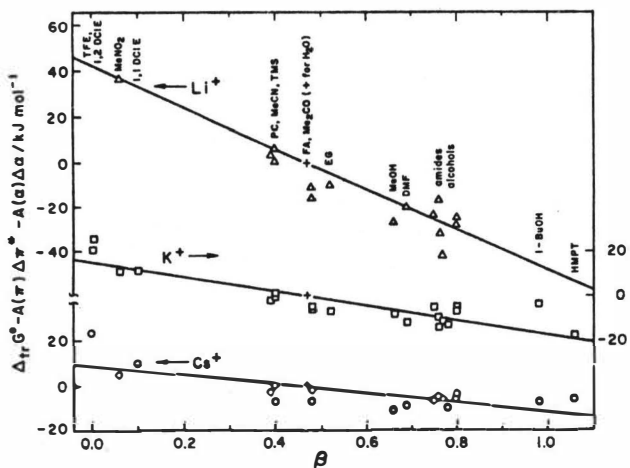
Figs. 1 and 2. Dependence of the transfer Gibbs free energies of Li^+, K^+, Cs^+, Na^+, Zn^{2+}, and Hg^{2+} on the β-parameter of various solvents

101

these solvent dependencies. Subtraction of the less important π^* and α effects brings out the main effect of the β parameter, as shown in Figs. 1 and 2.

The relevant ion properties, for small cations, are mainly their electric field strength, z/r, and to a less important extent their volume, r^3, and their softness, σ. The latter parameter, however, plays a very important role when the solvent itself is soft, i.e., when it has a softness parameter $\mu > 0.2$ [9]. Such a solvent favors strongly soft ions, such as Ag^+, Cu^+, Hg^{2+}, etc.

For small anions the most important solvent property is its acidity, measured by its Gutmann acceptor number or by its hydrogen bond donating ability solvatochromic paraameter α. Subsidiary solvent properties are its polarity/polarizability, measured by π^*, and its molar volume, V, that indicates how many solvent molecules can pack around the anion. The important ion properties are, again, its electric field strength, z/r, where z is taken algebraically, i.e., in the opposite sense to that for the cations, and to a lesser extent its softness σ, volume, r^3, and molar refraction, R_D.

For large, hydrophobic ions, such as the tetra-n-alkylammonium and tetraphenylarsonium cations and picrate and tetraphenylborate anions, the above dependencies do not hold, because of the hydrophobic interactions in the aqueous phase. For such ions the polarity/polarizability parameter π^* and the cohesive energy, δ^2 (δ is the Hildebrand solubility parameter) are the pertinent solvent properties, and the volume of the ion (or its molar refraction) becomes its predominant property, besides the reciprocal of its radius, $1/r$, irrespective of the sign oof the charge.

These dependencies of the standard Gibbs free energy and enthalpy of transfer of ions from water into nonaqueous solvents are readily rationalized in terms of the interactions that take place in the two environments. Cavity formation, dispersive interactions, ion-dipole interactions, hydrogen bond formation (with anions) and donation of electron pairs (for cations) are the main interactions that account fully for these dependencies. Once the coefficients A_{ij} in the expression

$$\Delta_{tr}G(\text{or } H)^o(\text{ion, } W{\rightarrow}S) = \Sigma_j \; \Sigma_i \; A_{ij} \; P_i \; [P_j(S) - P_j(W)]$$

where W is water, S is the organic solvent, P_i is tne i-th property of the ion, and P_j is the j-th property of the solvent (or water) have been established, they can be used to predict transfers energetics. In particular, the infinite dilution Gibbs free enrgy of the transfer of an ion with known properties P_i (as described above) from water into a

solvent S with known properties P_j (as described above) can be estimated to a good approximation.

The distribution ratio of a salt, at infinite dilution, is then given by the exponent of $1/RT$ times the sum of the $\Delta_{tr}G^o$ of its ions, weighted by the appropriate stoeichiometric coefficients.

Some examples of such predictions and their comparison with experimental results can be given. For example, the distribution ratio of CsI_3 between nitrobenzene and water is about 7 and the predicted value is the same number, 7.4. For NaI_3 the predicted value is 0.03, the experimental value is even lower. The predicted distribution ratio of tetrabutylammonium perchlorate between 1,2-dichloroethane and water is 16, that of the iodide is 0.45 and of the chloride it is 10^{-5}, and this is, in fact the order of the extractabilities of these salts into this solvent. It must be borne in mind that in practical extraction systems at finite salt concentrtations ion association plays at least as important a role as ion solvation [2], and that organic phases are seldom completely nonaqueous. Nevertheless, the above considerations permit some better-based selection of solvents for given ion extraction problems.

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The role of hydration phenomena in solvent extraction of metal com-
plexes, especially in the partition step of the process, was discussed
by numerous authors [1-8]. For further elucidation of the problem let
us distinguish two different parts of a molecule of a metal complex
with simple organic ligands: 1) hydrophilic centre composed of a cen-
tral metal ion and electron donor atoms of coordinated ligands, and
2) hydrophobic residue composed of hydrocarbon groups of the ligands.
It was shown that the hydrophilic centre of coordinatively unsaturated
complexes (i.e. those in which the coordination number of the central
metal ion is greater than the total number of donor atoms in all n li-
gands; CN >2n for metal acetylacetonates)undergoes inner-sphere hy-
dration in aqueous solutions [1,2]. The hydrocarbon residue of chelate
solute causes water-structuring effects in its aqueous environment [4],
called sometimes "hydrophobic hydration" [8]. The character of hydra-
tion of the hydrophilic centre in coordinatively saturated chelates
(CN=2n for acetylacetonates) remained unexplained [3,7]. The author of
this work,basing on a comparative analysis of thermodynamic functions
of partition, presented a hypothesis that hydrogen bonds are formed
between a chelate solute and water molecules from its aqueous environ-
ment, donor oxygen atoms of coordinated ligands being the centres of
this "outer-sphere hydration" [6]. The original evidence for the hypo-
thesis was rather scarce:
- large difference of about 30 kJ mol^{-1} [6] between the experimental
  standard free energy of partition of bis(acetylacetonato)beryllium(II)
  and the value calculated by using a semi-empirical model of solvent
  extraction [4], based on the theory of regular solutions and a rela-
  tionship between aqueous solubility of hydrocarbons and their molar
  volume;
- similarity of thermodynamic characteristics of two processes: chelate
  transfer from organic to aqueous phase and solution in water of
  nonelectrolytes consisting of a functional group and a hydrocarbon
  residue, hydration of the functional group in aqueous solution being
  already evidenced;
- thermodynamic and spectral evidence for hydrogen bond formation bet-
  ween protic solvents (e.g. chloroform) and metal acetylacetonates in
  organic solutions.

Recently, new experimental results have been obtained in support of
this hypothesis. These are: indirect spectral (NMR and IR) data and
thermodynamic effects of replacing donor oxygen atoms for sulphur in

acetylacetonate ligands, detected in the functions of partition of the respective chelates.

Because of low aqueous solubility of metal chelates having large hydrophobic ligands, only a small fraction of water molecules in the solution forms hydrogen bonds to the solute molecules. The resulting spectral signals are thus very weak and overlapped by much stronger signals from bulk water molecules. Therefore, outer-sphere hydration can hardly be detected in such systems by the use of spectroscopic methods. In order to obtain spectral evidence for this kind of interactions, we had to use an indirect way, by studying benzene solutions of coordinatively saturated metal acetylacetonates, containing small amounts of water [9]. The 1:1 water adduct have been found on beryllium and cobalt(III) chelates, by means of the proton chemical shift method (Fourier-transform NMR). The values of stability constants of the adducts as well as standard enthalpy and entropy of hydration are typical for weak H-bonded complexes: $K=1$ to 4 dm^3mol^{-1}, $\Delta H^o=-5$ to -9 kJ mol^{-1}, and $\Delta S^o=-15$ to -30 J $K^{-1}mol^{-1}$ at $25°C$. A comparison of these values, referring to one water molecule, with the total effect of hydrating the chelate molecule [6], indicates that a number of water molecules is engaged in the outer-sphere hydration of one chelate molecule in the aqueous phase.

Detection of new broad bands of H-bonded water at about 3530 cm^{-1}in the IR spectra of the same solutions [9], brings a further support for the hypothesis presented.

Replacing of donor oxygen atoms in acetylacetonate ligands by atoms of lower electronegativity, e.g. sulphur, should result in weakening outer-sphere hydration of the chelate. In fact, both standard enthalpy and entropy of partition of tris(monothioacetylacetonato)cobalt(III) are distinctly smaller than those for tris(acetylacetonato)cobalt(III), the differences being 27 kJ mol^{-1} and 30 J K^{-1} mol^{-1}, respectively. This results in much higher extractability of the former chelate [10], and more or less corresponds to the expected quantities.

An additional argument in favour of outer-sphere hydration results from Yamamoto's comparison of experimental standard entropy of solution in water of tris(acetylacetonato)chromium(III) with the value calculated by the scaled particle theory. The difference found was interpreted as due to a specific solute-solvent interaction weakening hydrophobicity of the chelate [11].

The phenomenon discussed can be useful in explaining small experimental differences [3,12] in the thermodynamics of liquid-liquid partition of coordinatively saturated chelates of various metals, having the same number of the same ligands in their molecules. The extent of outer-sphere hydration should depend on the electron density on the

hydrophilic centre of the molecule, which in turn ought to be affected
by electron configuration of the central metal ion and by the energy
of metal-to-ligand bond, both different for various metal ions. Table 1
presents the experimental thermodynamic values of partition of some co-
ordinatively saturated acetylacetonates and coordinatively unsaturated
bis(acetylacetonato)zinc(II). The values for chromium(III) and neptu-
nium chelates are representative for groups of coordinatively saturated
acetylacetonates of tervalent [3] and tetravalent [12] metals.

Table 1. Standard thermodynamic functions of partition of metal ace-
tylacetonates (MeL_n) in the system inert organic solvent (hexane or
heptane)/water, and salting-out coefficients (in $NaClO_4$ solutions),
k_s, of the chelates, at 25°C. Standard states expressed in the mola-
rity terms

Chelate	CN	sol-vent	ΔG_p^0 kJmol^{-1}	ΔH_p^0	ΔS_p^0 J K^{-1}mol^{-1}	$\Delta S_p^0/n$ dm^{3}mol^{-1}	k_s	Reference
BeL_2	=2n	hx	-2.7	25	92	46	0.192	[7]
CrL_3	=2n	hp	2.7	50	157	52	0.285	this work
NpL_4	=2n	hx	(-0.8)	(78)	(265)	(66)	-	extrapolated from [12]
ZnL_2	>2n	hp	10.6	63	174	87	0.293	this work

It is of interest to see how the entropy of partition, referred to
one ligand molecule, $\Delta S_p^0/n$, changes in the range of coordinatively sa-
turated acetylacetonates of di-, ter-, and tetravalent metal ions. Di-
lute solutions of coordinatively saturated metal acetylacetonates in
inert organic solvents obey the theory of regular solutions, thus dif-
ferences in their $\Delta S_p^0/n$ values are the measure of differences in their
interactions in the aqueous phase. Assuming hydrophobic hydration of
the same ligands in various chelates to be the same, the former dif-
ferences may be attributed to various strength of outer-sphere hydra-
tion of the chelates. The resulting conclusion on the increase of the
degree of this hydration with increasing valency of central metal ion
in the chelate, is in agreement with the NMR data [9] indicating for
stronger hydrogen bonding between water and tris(acetyloacetonato)co-
balt(III) that for bis(acetylacetonato)beryllium(II).
    This conclusion can be useful to explain why partition coefficients
of many coordinatively saturated metal acetylacetonates differing in
the number of ligands, are close to each other in the same extraction
systems, though their hydrophobic interactions are evidently different.
The increase of the activity coefficient of metal acetylacetonate in
the aqueous phase, caused by a greater number of ligands and a resul-
ting enhancement of hydrophobic hydration of the chelate, becomes lar-

gely compensated by an accompanying effect of enhanced outer-sphere hydration, decreasing the activity coefficient. Such a compensation is not very probable for other chelating extractants.

Salting effects in metal chelate partition, exerted by inert electrolytes, are also connected with hydration phenomena in the aqueous phase. Because hydropholic hydration of the chelates is more strongly influenced by increased electrolyte concentration than their outer-sphere hydration, salting-out coefficients of coordinatively saturated metal acetylacetonates increase with increasing number of ligands in the molecule (Table 1).

A more complex picture is observed in the case of coordinatively unsaturated metal chelates, their hydrophobic and outer-sphere hydration being accompanied by inner-sphere hydration of the central metal ions. This brings about a significant increase of thermodynamic values of partition of such species (Table 1).

On the basis of the presented examples, one may conclude that the phenomenon called outer-sphere hydration plays an important role in liquid-liquid partition of metal complexes, complementing the other kinds of interactions of the complexes in the aqueous phase. The outer--sphere hydration ought to be accounted for in further developing models of solvent extraction of metal ions, as well as models concerning solubility of metal chelates in water.

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THE STATE OF WATER IN EXTRACTS AND ITS INTERACTION WITH MICROWAVE FIELD

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Behaviour of water plays an important role in processes of ext-
raction and separation of valuable components.Both the activity of
water in aqueous phase and the state of water in organic phase have
an influence on extraction process.

Water can pass into organic phase due to hydration of extractant
and its complexes with the metal.In a few cases when the extractants
possess the surface-active nature, water can pass into organic phase
with micelles and even microemulsions formation.Their formation can
both improve the process of metal extraction (for example, in crea-
tion of the concentrated organic solution of light rare elements),
and hamper it.

It appears the difference in extraction behaviour of primary and
tertiary amines towards the zirconium sulphate [1] can be linked to
difference state of water in organic phases. There is difference in
influence on extraction by these amines of sulfuric acid concentra-
tion in aqueous phase and octanol additions into organic phase. Be-
sides that, in the process of sulphate zirconium extraction by ter-
tiary amines relation of amine:H_2O = 1:1 is practically constant,
at the same time in extraction of sulfuric acid by primary amines
(Primene IMT) relation of amine:H_2O = 1:3, but after zirconium ex-
traction water is almost completely forced out of the organic phase.
It can be supposed that the sulphate salt of primary amine exists
in organic phase in the form of associates in which water molecules
are included inside aggregates and hold by hydrogen bonds with ami-
ne salt molecules, which form the cover (reverce micelles). Being
extracted zirconium forces water out of aggregates, inside which it
is also hold by bonds formed between metal ion (or neutral sulfate)
and anions of amine salt. The sign of reverce micelles formation
can be sharp change of physical-chemical properties of the system.
The dependence of dielectric constant of amines salts solutions
from their concentration is given in fig.1. The dielectric constant
of primary and tertiary amines solutions increase equally with con-
centration growth, then the growth speed of dielectric constant of
primary amine salt decreases in comparison with it for tertiary
amine. This phenomenon doesn't contradict the supposition about the
aggregates formation.

The most important property of reverce micelles in organic phase

is their ability to solubilize significant ammounts of water, which is confirmed by increased relation H_2O:amine for primary amines. Water in form of reverce micelles differs in its properties from ordinary (bulk) water. The scale of differences is determined by the degree of hydration of reverce micelles. On small relation of water:SA (surfactant) the properties of micelles and
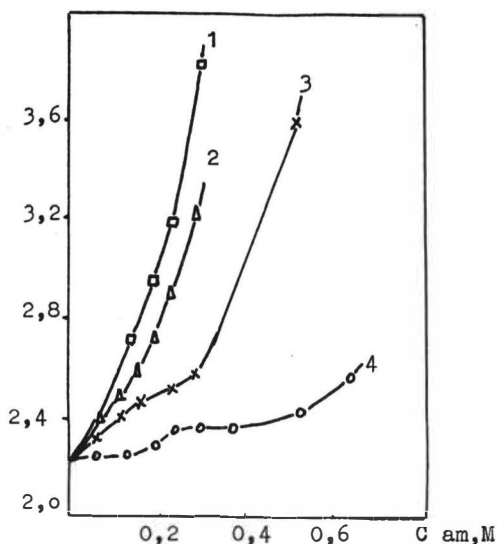
Fig.1. The dependence of dielectric penetrability versus amine concentration
1 - the extraction 1 M H_2SO_4 by TOA;
2 - the extraction 0.25 M $Zr(SO_4)_2$ by TOA;
3 - the extraction 1 M H_2SO_4 by IMT;
4 - the extraction 0.25 M $Zr(SO_4)_2$ by IMT

bulk water differ especially much. So for small relations H_2O:SA viscosity of water which is solubilized by reverce micelles of aerosol OT exceeds that for bulk water as much as 200 times and its polarity equal to the polarity of $CHCl_3$. On growth of the relation the difference in properties decreases monotonously [2].

In connection with it the evidence for reverce micelles formation in organic phase can be registration of specific interaction with solubilized water. Micro-wave radiation can heat dielectrics specifically. Amount of produced heat on account for micro-wave radiation absorption depends on the electric field strength, fre-

quency and dielectric properties of the substance - viz. tangent of dielectric loss and dielectric constant. In general on interaction of micro-wave radiation with the substance the greatest absorption of radiation energy is in the case of water. Therefore in this process the water concentration and chemical composition of substance have important significance as well as the state of water in the substance because the dielectric properties of water differ widely in connection with bonds formation. In organic solutions water will be heated faster than other components and any changes in its properties must influence the speed of heating of material.

For experiments we used solutions of extractants and SA (aerosol OT for organic solutions of which it was demonstrated the existance of reverce micelles and the field of their existance were determined [3]) in toluene (saturated with water) is less and in general can be explained by convectional heating.

The speed of heating of tertiary amine salt increases sharply in comparison with the speed for free amine. The reason is the increase of dielectric constant due to formation of amine salt with increase of water content in organic phase.

Under the same conditions the speed of heating of primary amine salts and SA with water content equal or a few times higher than for the solution of tertiary amine salts is small. The experimental sets with octanol adding and with different relation alcohol: SA confirm the supposition about connection of intensity of heating with different state of water in organic phase.

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Substituted phenols are highly efficient for extracting alkali
elements from aqueous alkali solutions [I]. However, there is a de-
arth of information for extracting alkali elements from strongly al-
kaline media (pH > I3). The process itself varies, depending on the
nature of the phenolic extractant. In some cases water is very solub-
le in the organic phase, or the extractant is highly soluble in the
aqueous phase; in others, these phenomena is completely absent. The
causes of such behavior of phenolic reagents in the extraction of al-
kali elements from strongly alkaline solutions are not clear.

It has been reported [2,3] that substituted alkali metal phenola-
tes are surface-active colloidal substances capable of forming in
aqueous and nonaqueous solutions lyotropic liquid crystals and micel-
les. In this work it is shown that the extraction of potassium, rubi-
dium, and cesium with phenolic reagents in hydrocarbon solvents under
strongly alkaline conditions is determined by the tendency of alkali
metal phenolates produced during the extraction to form micelles in
the aqueous and organic phases. And the tendency of the phenolate to
form micelles is determined mainly by the size and position of the
hydrocarbon substituent group in the molecule.

Micelle formation in the aqueous phase of the extraction system
was detected with the aid of additions of a color indicator. As the
latter we used a pinacyanol chloride or sudan III. Besides, the de-
tection of the micelle formation in the aqueous phase was based on
the inflection of the curve obtained by plotting the surface tension
of the aqueous phase as the function of the concentration of alkali
metal hydroxide in the aqueous phase. Micelle formation in the orga-
nic phase was indicated by a sharp rise in the extractability of wa-
ter. This was determined on the basis of the magnitude of the relati-
ve volume of organic phase, V_o, at equilibrium (relative to the total
volume of aqueous and organic phases). In addition, micelle formati-
on in the organic phase was determined by the extraction by the phe-
nolic reagent of the inorganic salt, alkali metal carbonate or alkali
metal sulfate. The anion of the salt was detected in aqueous phase
after stripping of extract by hydrochloric acid followed by chemical
analysis. Also, the analysis of the anion was carried out directly
in the extract with the aid of infrared spectroscopy.

It was found that alkali metal phenolates of p-alkylphenols with
small hydrocarbon substituents form micelles more readily in aqueous
than in hydrocarbon solutions. Similar behavior was observed for

o-substituted phenols with different molecular mass. When the extraction was carried out with p-alkyl- or p-arylphenols having a small substituent groups (e.g., 4-$\underline{t}$-butylphenol) and with o-substituted phenols (e.g. 2-benzylphenol, 4-methyl-2-$\underline{t}$-butylphenol), micelles form only in the aqueous phase, L_w, and not in the organic phase, L_o (Fig. I). Micelles form only when the concentration of alkali metal hydroxide in the extraction system is sufficiently high. Upon a further increase in alkali metal hydroxide concentration, the solid precipitate of alkali metal phenolate (S) which has formed becomes fully dissolved. And practically all of the extraction reagent passes into the aqueous phase (the extraction efficiency of 2-benzylphenol into the aqueous phase, R_{BP}, approaches I00%). At the same time extraction of alkali metal stops (the distribution coefficient for cesium, D_{Cs}, approaches zero).

Fig. I. Extraction of cesium by IN toluene solution of 2-benzylphenol from water solutions of CsOH + Cs_2SO_4. (Concentration of Cs_2SO_4 in the starting aqueous phase - 0.25 mole/l). I - R_{BP}; 2 - V_o; 3 - D_{Cs}; 4 - boundary for micelle formation in the aqueous phase

In the case of alkali metal phenolates of p-alkylphenols and p-arylphenols with a large hydrocarbon group (e.g., I,I,3,3-tetramethylbutyl-phenol, p-alkylphenol with C_4-C_8-alkyl groups), micelles form only in the organic phase, and not in the aqueous phase of the extraction system (Fig. 2). Owing to the solubilization in reverse micelles, the extraction of water sharply increases. This is shown in Fig. 2 by hydration number y_{H_2O}/y_{Cs_Σ} and leads to an increase in the volume of the organic phase at the expence of the aqueous phase until the aqueous phase completely passes into the organic phase. Our results show that when micelles form in the organic phase the alkali elements can be extracted not only via the cation-exchange mechanism but also via the micellar mechanism. The latter process is descovered when the alkali elements pass into the organic phase together with their inorganic anion (Fig. 2, curve 5) owing to the secondary solubilization in reverse micelles [4]. The micellar mechanism makes it possible to extract alkali elements above the stoichiometric level (Fig. 2, cur-

ve 3). The formation of micelles in the organic phase begins only when the concentration of the alkali metal phenolate is sufficiently high; this concentration is characterized by a molar ratio, alkali metal:phenolic reagent, N, in the organic phase. A further increase in the concentration of the alkali component results in the formation of the lyotropic liquid crystal phase followed by the precipitation of solid alkali metal alkylphenolate.

As a rule, micelles form only in one of the phases

Fig. 2. Extraction of cesium by 2N n-octane solution of p-alkyl(C_4-C_8)phenol from water solutions of CsOH + Cs_2SO_4. (Concentration of Cs_2SO_4 in the starting aqueous phase - 0.4 mole/l). I - D_{Cs_Σ}; 2 - V_0; 3 - N; 4 - y_{H_2O}/y_{Cs_Σ}; 5 - $D_{Cs_2SO_4}$

of the extraction system. However, when the extraction of alkali elements is carried out with a toluene solution of 4-(α,α-dimethylbenzyl)phenol micelles form in both the organic and aqueous phase practically at the same concentration of the alkali. At the beginning the process of aggregation predominates in the organic phase. A further increase in the concentration of the alkali metal hydroxide in the original aqueous phase results in micelle formation predominantly in the aqueous phase.

Alkali metal disubstituted phenolates with a large hydrocarbon groups in the o- and p-positions (e.g., 2-(α-methylbenzyl)-4-(I,I,3, 3-tetramethyl)phenolate), do not, owing to the steric effect, form micelles either in aqueous or organic solutions. And consequently no micelle formation takes place when extraction is carried out with such phenolic reagents.

The formation of micelles in the organic phase also occurs when the alkali elements are extracted by phenolic oligomers (e.g., p-al-

113

kyl- and arylphenol disulfides and polysulfides), the phenolates of which are capable of forming micelles in an organic medium but not in aqueous solutions. In the oligomer systems the alkali elements can pass into the organic phase via the micellar mechanism and through super-stoichiometric extraction (Fig. 3). Under conditions of micelle formation in the organic phase in a region of relatively low alkali concentration, the extraction of alkali elements by phenolic oligomers proceeds in a similar way as the extraction by monomeric p-alkylphenols containing large alkyl groups (Fig. 2). However, when extracting alkali elements by phenolic oligomers, an increase in the
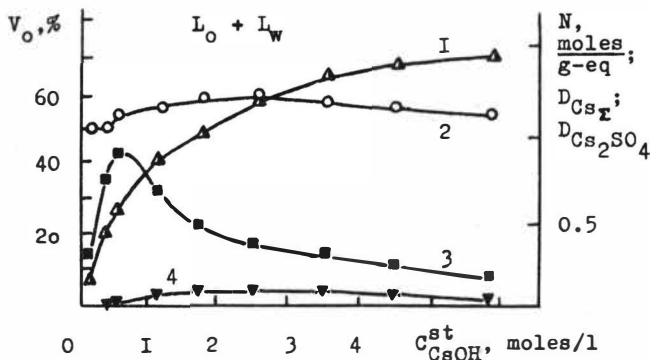
Fig. 3. Extraction of cesium by 1N toluene solution of p-alkylphenol disulfide from water solutions of $CsOH + Cs_2SO_4$. (Concentration of Cs_2SO_4 in the starting aqueous phase - 0.25 mole/l). I - N; 2 - V_o; 3 - $D_{Cs_{\Sigma}}$; 4 - $D_{Cs_2SO_4}$

concentration of the alkali metal hydroxides in the starting aqueous phase leads not to the formation of solid phenolate but to an increase in the volume of the aqueous phase. The extractability of water in the region of high alkali concentrations of aqueous phase decreases when there is an increase in the concentration of alkali (Fig. 3, curve 2) or when there is an increase in inorganic salt (alkali metal sulfate or alkali metal carbonate). These processes result from the competition for water between the aqueous and organic phases: at higher concentrations of alkali metal derivatives water is held more strongly in the aqueous phase owing to hydration. Our experiments show that the tendency of oligomer phenolates to form reversible micelles decreases with an increase in molecular weight of the oligomer.

The considerable losses of the phenolic reagent, which is soluble in the aqueous phase, are caused by the formation of micelles from the corresponding phenolate in the aqueous phase. Also the diluent can transit into the aqueous phase owing to the solubilization effect of the direct micelles of the phenolate. At the same time there is a decrease in the ex traction of alkali elements. Therefore, the extraction of alkali elements from strongly alkaline media requires a correct choice of the extracting agent: the phenolate of the alkali me-

tal being extracted should be free of the tendency to form micelles in aqueous solutions. Consequently, o- and p-substituted phenols with small hydrocarbon substituents are unfit for extracting alkali elements from strongly alkali aqueous solutions. Our experiments with 4-(α, α -dimethylbenzyl)phenol and 4-$\underline{t}$-butylphenol have shown that the increase in the size of the hydrocarbon substituent in the molecule of the phenolic reagent does not resulting to the decrease in its solubility in strongly alkaline aqueous solutions, if the resulting, in the extraction system, phenolates tend to form micelles mainly in the aqueous phase. On the contrary, the increase in the hydrophobic part of the extracting agent leads to the increase of the ability of the alkali phenolate to the micelle formation and apparition of micelles at lower concentration of alkali in the aqueous phase. However, the growth of the size of the hydrocarbon substituent in case of p-alkyl- or p-arylphenols can lead to fact, that micelles will start in the organic phase and not in the aqueous phase. It decreases considerably the solubility of the phenolic reagent in the aqueous phase.

The employment of phenols with hydrocarbon substituents in p-position for extracting alkali elements from strongly alkaline mediums is not the best variant. The micelle formation in the organic phase increases noticeable the alkali metal capacity of the organic phase due to the micellar mechanism of extraction. However, the aggregation in the organic phase, going rather deeply, makes more difficult and even impossible the extraction process. If the formation of micelles in the organic phase is limited, then the aggregation does not breach the extraction process and the characteristic advantages of the micelle formation are preserved. Therefore, the phenolic oligomers are more preferable for extracting alkali metals from strongly alkaline mediums if chosen among the above reviewed compounds.

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EXTRACTION OF METAL $\mathcal{\widetilde{U}}$-COMPLEXES AND ORGANOMETALLIC COMPOUNDS WITH AROMATIC AND UNSATURATED COMPOUNDS

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The aliphatic and aromatic hydrocarbons and their halogen derivatives represent the most effective extractants for molecular halogenides of IVA-VIA subgroup elements. Due to a wide acceptance of the concepts of a "physical" distribution of simple molecules the effect of the nature of these extractants was considered to be unimportant and therefore earlier it was not taken into consideration. An approach to the extraction of molecular species which takes into account solvating (E_T, kJ/mol) and $\mathcal{\widetilde{U}}$- donor properties (I, eV) of hydrocarbons [1] made possible to establish some general regularities.

Classification of the extraction processes. According to the nature of the extracted species the extraction processes can be classified into three groups. First, the extraction of simple molecules which is independent of the above mentioned properties of the extractants. It is characteristic of neutral coordinatively saturated molecules with a tetrahedral structure (Ge and Sn halogenides and OsO_4). In this case the extraction is satisfactorily described within the theory of regular solutions as it was demonstrated in [2] for Ge halogenides and in [3] for OsO_4 (12 extractants). The second group of processes involves the extraction of solvated molecular VA-VIA halogenides with saturated hydrocarbons. The charge asymmetry of the pyramidal As, Sb, Bi, Se, and Te halogenide molecules determines their interaction with the media which results in a linear correlation of the distribution constant logarithms ($\widetilde{K}_{1,0}$) with E_T (Table 1). The correlations for other extraction systems are given in [1] . This type of

Table 1. Constants correlations with E_T

Extracted form *	$lg\,\widetilde{K}_{1,0}(\widetilde{K}_{1,1})=aE_T-b$		$lg\,\bar{\beta}_{1,1}=-aE_T+b$	
	a	b	a	b
$SbBr_3$	0.027	4.7	-	-
$SbCl_3$	0.028	6.2	-	-
$BiBr_3$	0.078	15.3	-	-
BiJ_3	0.056	11.3	-	-
$SbLBr_3$	-	-	0.024	5.6
$SbLCl_3$	-	-	0.010	3.9
$BiLBr_3$	0.027	3.5	0.048	11.4
$BiLJ_3$	0.022	3.4	0.035	8.5

*L - hexamethylbenzene (HMB)

correlation is not followed by the aromatic hydrocarbons which form a separate group showing a reversed dependence of $\widetilde{K}_{1,0}$ on E_T . To the third group of extraction processes belongs the extraction with aromatic hydrocarbons of the $\mathcal{\widetilde{U}}$-complexes of the metals from the second

group having vacant orbitals. Based on the coordination concepts it was proposed to use as extractants alkylbenzenes having 3 to 6 substituents, phenyl derivatives of methane, linear and condensed (naphtaline, diphenyl and other) polycyclic compounds which have never been used as extractants before.

The extraction of metal π-complexes. In the extracts and nonaqueous media the arsenic subgroup metal halogenides give rise to mononuclear complexes of the composition 1:1 irrespective of the nature of the emetal, the extractant (L), and the diluent. The extraction method in which the stability constants of the complexes ($\bar{\beta}_{1,1}$) are determined as the ratio of the extraction constants ($\widetilde{K}_{1,1}$) to the distribution constants of the molecular species , $\widetilde{K}_{1,0} = D/n$, (n is the number of moles in 1l of water saturated organic phase), the spectrophotometric method, and NMR gave close stability constants which coincide with those reported in [4] for the complexes $SbLHal_3$ with the early members of the series of methyl benzenes.

Table 2. Correlations of the stability constants with I of extractants

Complex (diluent)	$lg\,\bar{\beta}_{1,1} = -aI+b$		Complex (diluent)	$lg\,\bar{\beta}_{1,1} = -aI+b$	
	a	b		a	b
$SbLBr_3$ (CCl_4) L-methylbenzenes	0.87	9.03	$BiLBr_3$($CHCl_3$) L-methylbenzenes	1.45	14.8
L-phenylderivatives of methane	0.91	10.2	L-phenylderivatives of methane	1.80	17.7
L-polycyclic compounds	0.27	3.62	L-polycyclic compounds	0.30	4.5
$SbLCl_3$(CCl_4) L-methylbenzenes	1.11	11.1	$BiLJ_3$($CHCl_3$) L-methylbenzenes	1.46	14.0
($CHCl_3$)	1.09	10.6			
($1,2-C_2H_4Cl_2$)	1.2	11.3			

The donor-acceptor nature of the formed complexes is indicated by the observation of a linear correlation between $lg\bar{\beta}_{1,1}$ and I in genetically related series of compounds (Table 2), the increase in the stability constants with increasing acceptor properties of the metal in $MeHal_3$ with the change of the halogen ($MeLCl_3 > MeLBr_3 > MeLJ_3$) and the metal ($BiLHal_3 > SbLHal_3 > AsLHal_3$) [1,4], the appearance in the electronic absorption spectra of the extracts of bands characteristic of complexes with a charge transfer (bathochromic shift of the maxima of these bands increases with decreasing value of I of the extractant).

The characteristics of the extraction of OsO_4 with methylbenzenes (increased values of $\widetilde{K}_{1,0}$ as compared with those calculated in the absence of chemical interaction, the trend of $\widetilde{K}_{1,0}$ to increase with

with decreasing I of the extractant, some regularities of the changes in the electronic spectra 3 indicate the occurence of an interaction of OsO_4 with the π-system of the aromatic compounds (Table 3). Calculations show that in a hexane medium the stability constants for OsO_4 are 2 to 4 orders of magnitude lower than for Sb and Bi halogenides (Table 3) and somewhat higher than for complexes of J with methylbenzenes.

On the example of the most effective aromatic extractant, hexamethylbenzene (HMB) it was found that with the increase in the solvating properties of the solvent there is an increase in $\tilde{K}_{1,1}$ and a decrease in $\bar{\beta}_{1,1}$ at a linear correlation of these quantities with E_T (Table 1) which is due to different solvation of the starting and end products of the extraction. Using the known values of $\tilde{K}_{1,0}$, $\tilde{K}_{1,1}$ and specially

Table 3 . Extraction of OsO_4 with methylbenzenes and complexation in hexane medium (* and ** - extraction and spectrophotometric data)

Extractant (I, eV)	$\tilde{K}_{1,0}$	$\tilde{K}^{cal}_{1,0}$	$\bar{\beta}^*_{1,1}$	$\bar{\beta}^{**}_{1,1}$	λ_{max}, nm
Benzene (9.25)	$1.67^{\pm}0.07$	1.99	2.9	1.1	329
Toluene (8.82)	$1.93^{\pm}0.04$	1.74	3.4	1.8	339
p-Xylene (8.42)	$2.4^{\pm}0.4$	1.62	4.0	1.6	345
Pseudocumene (8.27)	$2.78^{\pm}0.08$	1.60	5.0	1.9	364
Durene (8.03)	-	-	-	-	417
Hexamethylbenzene(7.85)	-	-	-	-	478

Table 4. Resolvation energies (kJ/mol) for different species

Diluent (E_T)	ΔG^L_{tran}	SbCl$_3$		BiBr$_3$		BiJ$_3$	
		$\Delta G^{1,0}_{tran}$	$\Delta G^{1,1}_{tran}$	$\Delta G^{1,0}_{tr}$	$\Delta G^{1,1}_{tr}$	$\Delta G^{1,0}_{tr}$	$\Delta G^{1,1}_{tr}$
Heptane (129.3)	1.5	0.31	2.20	2.8	4.4	5.3	7.7
Chloroform (163.7)	-1.4	-4.70	-3.70	-7.9	-3.7	-3.3	-1.9
Dichloroethane(175.4)	1.6	-8.80	-2.8	-18.9	-4.5	-11.3	-1.6

determined distribution constants of of the extractants the free transfer energies (resolvation energies) were calculated for different species (L, MeHal$_3$, MeLHal$_3$) for the transfer from the standard diluent (CCl_4) to a particular diluent (ΔG^i_{tran}). The changes in the resolvation energies for HMB for the studied diluents are insignificant which is characteristic of weakly basic ligands and justifies the use of the electronic characteristics of the extractant (I) as a correlation parameter in a comparison of different extractants. The greater change in the resolvation energy for MeLHal$_3$ as compared with L and for MeHal$_3$ as compared with MeLHal$_3$ at an insignificant change in the resolvation energy of L with increasing E_T of the solvent (Table 4) are the reasons for the increase in the extrac-

tion constants with E_{π} and the inversed order of the stability constants in the same series of diluents.

Increased extraction in the series benzene-hexamethylbenzene is also observed for Se and Te bromides. Thus for Te the correlation is $lgD = 8.71-1.17I$ but the distribution coefficients are small. A substantial improvement of the extraction of these metals and OsO_4 was achieved when using unsaturated hydrocarbons as extractants, in particular α-olefins.

Extraction with α-olefins. α-Olefins have a high ionization potential (9.46 eV for hexene-1) and with respect to As,Sb, and Bi their behaviour is that of organic solvents, in accord with their solvating power (E_{π}). Formation of π-complexes was established for the extraction of Pd with mixtures trioctylammonium chloride(TOAHCl)-hexene-1. Addition of hexene-1 to TOAHCl solutions was shown to give rise to mixed species $(TOAH)PdCl_3$ and $(TOAH)Pd_2LCl_5$ which results in increased extraction of Pd, especially in the region of complete saturation of TOAHCl. A quantitative description of these processes is presented.

The irreversible extraction of Se, Te bromides and OsO_4 with α-olefins is determined by their addition at the double bon bond which proceeds in time. Methods are presented to accelerate formation (and extraction) of organometallic compounds by changing from chloride media to bromides ones and by using aromatic sol-

Table 5. Extraction rate constants of $OsO_4(s^{-1}mol^{-1})$ with octene-1 solutions

Diluent	D	$K \cdot 10^2$
Hexane	$3.6^{\pm}0.3$	$0.9^{\pm}0.3$
Isoamyl alcohol	$10.4^{\pm}0.3$	$1.1^{\pm}0.2$
Tetrachloromethane	$11.6^{\pm}0.3$	$1.6^{\pm}0.3$
Benzene	$14.5^{\pm}0.8$	$3.2^{\pm}0.5$
Chloroform	$16.1^{\pm}1.3$	$3.9^{\pm}0.5$
Nitrobenzene	$20.9^{\pm}0.7$	$7.8^{\pm}1.3$

vents for α-olefins. All this ensures a rapid transfer of the π-complexes to the organic phase and their subsequent transformation to organometallic compounds. The addition of the metal bromides to olefines occurs according to (Se) and against (Te) the Markovnikov rule to form (in the case of hexene-1) bis-2-brominehexyl-1-selenium dibromide and bis-1-brominehexyl-2-tellurium dibromide,respectively. In the case of Os the constants of the rate-determining osmium diester formation reaction change in a symbate manner with the extraction constants of OsO_4 with pure diluents (Table 5) and for a given solvent - with the increasing length of the hydrocarbon radical in alkene-1.

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The ability of binding solvent particles to dissolved substance
was called solvation by Jones [1]. In agreement with Mishchenko's
proposition [2] it contains the sum of all energy changes caused
by the appearance of solute in a solution. This value is generally
determined as a solvation energy. In the case of water it is called
hydration energy. In the extraction process this energy is known as
free solvation energy and determines the ability of passing of sol-
vate across the interface from one phase to another. The value of
electrical distribution potential that appeares on the interface is
the measure of this phenomenon. From values of this potential chan-
ges thermodynamic partition coefficient and solvation energy of salt
in organic solvent can be calculated [3].

The changes of electric distribution potential were measured
with the aid of a special vessel (fig.1) and ionization sonde
with a ^{239}Pu or ^{241}Am source as an α-emitter. After the extrac-
tion and separation of phases, the vessel was simultaneously fil-
led with aqueous and organic phases in order to obtain the inves-
tigated interface. Thus the measuring cell was obtained (1) which
EMF was measured electrometrically. All the measurements were per-
formed at room temperature.

Hg/Hg$_2$Cl$_2$/KCl sol./aq. phase//org. phase/air/Ag   (1)
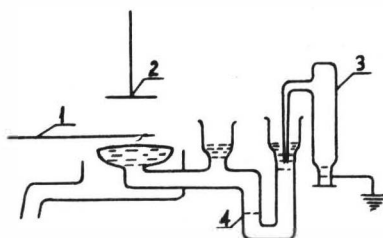
Fig. 1. Measuring vessel
1 – Measuring Ag electrode;
2 – Radioactive source;
3 – Reference calomel electrode;
4 – Interface o/w

Subsequently the examined extraction system with the investigated
salt in the form of chloride was replaced by the extraction system
with HCl only, without varying other parameters, and the EMF of
such cell was again measured. The difference $\Delta\Psi$ of measured EMF
of cells is equal to:

$$\Delta\Psi = \frac{RT}{F} \ln \frac{S^o_{MeCl}}{S^o_{HCl}} ,$$

where S^o is thermodynamic partition coefficient of salt and of HCl
respectively. The solvation energy E_s of the salt is:

$$E_s = 2RT \ln S^o_{MeCl} + E_{H_2O},$$

where E_{H_2O} is the energy of hydration and is equal to the algebraic
sum of the energy of cristal lattice of salt calculated from the Ka-
pustinski's equation [4] and of the dissolution energy of this salt
in water.

In result of those measurements extraction systems with tributyl
phosphate (TBP) or acetylacetone (AA) the hydration energy, solva-
tion energy, thermodynamic distribution coefficient and analytical
distribution coefficient were determined.

In the Table the results of investigations of extraction systems

Physico-chemical values obtained for the extraction system with
TBP an AA as extractants

System TBP as extractant	$\Delta\Psi$, mV	Δs, J/m	analyt. part.coef.	thermod. part.coef.
TBP-1mHCl	–	–	–	$3 \cdot 6 \times 10^{-2}$
TBP-1mNaCl-1mHCl	-5	$23906 \cdot 6$	$0 \cdot 195$	$1 \cdot 1 \times 10^{-3}$
TBP-1mUO$_2$Cl$_2$-1mHCl	0	$16328 \cdot 5$	–	$3 \cdot 6 \times 10^{-2}$
TBP-1mZnCl$_2$-1mHCl	-90	$33578 \cdot 1$	$1 \cdot 04$	$4 \cdot 11$
TBP-1mCuCl$_2$-1mHCl	-60	$28721 \cdot 4$	$0 \cdot 15$	–
TBP-1mFeCl$_3$-1mHCl	-170	$48985 \cdot 6$	$3 \cdot 00$	$30 \cdot 00$
TBP-1mThCl$_4$-1mHCl	-60	$27507 \cdot 3$	$0 \cdot 0009$	–
AA as extractant				
AA-1mHCl				$0 \cdot 1$
AA-0$\cdot$01mCuCl$_2$-0$\cdot$01mHCl	0	$10048 \cdot 3$	–	$0 \cdot 13$
AA-0$\cdot$1mFeCl$_3$-0$\cdot$1mHCl	0	$12141 \cdot 7$	$0 \cdot 75$	$8 \cdot 4 \times 10^{-2}$
AA-1mInCl$_3$-0$\cdot$1mHCl	0	$12141 \cdot 7$	$0 \cdot 015$	$8 \cdot 4 \times 10^{-2}$
AA-0$\cdot$5mTiCl$_4$-1mHCl	–	–	$0 \cdot 29$	–

containing TBP or AA as extractant are presented. $\Delta\Psi$ is the difference between the measured potentials ($\Psi_{MeCl}-\Psi_{HCl}$), and ΔE is the difference between the solvation and hydration energies.

Conclusions

1. There is the correlation between the values of ΔE (difference of solvation and hydration energies of separate extraction systems) and the distribution coefficient of these systems. The higher the value of the difference of energy, the higher the partition coefficient.
2. In the case of AA as an extractant the value of ΔE for separate systems becomes practically constant, which means that the distribution coefficient is independent of valency of metal ions.
3. For the Fe^{+++} ions and Cu^{++} ions the solvation energy with TBP molecules is considerably higher than that of AA molecules. This also causes a considerable difference in partition coefficients.
4. The thermodynamic distribution coefficient of HCl in the TBP system is lower than that in the AA system. This means that HCl is solvated with AA molecules more strongly than with TBP molecules.

Notice: In the case of chelate systems otherwise than in TBP systems it is impossible to perform investigations in wide range of concentrations both of the salt and the acid, because of the poor dissolution of chelates formed.

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THERMODYNAMICS OF SOLVENT EXTRACTION
ON $(C_8H_{17})_3N-C_6H_5CH_3-UO_2Cl_2-HCl$ SYSTEM

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In the process of solvent extraction the static and dynamic mathe-
matical models are necessary. In order to establish such models the
activity coefficients of all components involved in both phases are
always required. We have worked on extraction thermodynamics for years
and have developed a procedure to measure or calculate the activity co-
efficients of all components [1-4]. In this paper the thermodynamics
of n-trioctyl amine (TOA)-toluene-UO_2Cl_2-HCl system is described.
The mechanism of HCl and UO_2Cl_2 extraction by TOA is [5,6].

$$R_3N+H^++Cl^- \xrightleftharpoons{K_A} R_3NHCl, \qquad (1)$$

$$2R_3NHCl+UO_2^{2+}+2Cl^- \xrightleftharpoons{K_2^u} (R_3NH)_2UO_2Cl_4, \qquad (2)$$

from Eqs. (1) and (2) we get

$$2R_3N+UO_2^{2+}+2H^++4Cl^- \xrightleftharpoons{K_2} (R_3NH)_2UO_2Cl_4, \qquad (3)$$
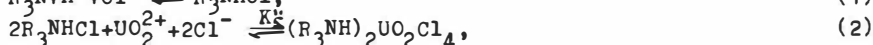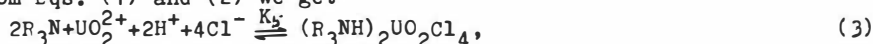
where R_3N is TOA $((C_8H_{17})_3N)$.

Experiment

7ml TOA-toluene organic solution and 7ml UO_2Cl_2-HCl aqueous solu-
tion were added into a centrifugal tube fitted with ground stopper,
and shaked for 60 minutes at $25^{\circ}C$. The original concentration of TOA
was 0.69M, 0.92M and 1.12M respectively. The UO_2^{2+} concentration was
analyzed by $K_2Cr_2O_7$ titration. The acidity was analyzed by titration.
The activity of toluene was analyzed by gas chromatographic headspace
analysis. The concentration of water in organic phase was analyzed by
Karl-Fischer method. Pretest showed that 50 minutes shaking is enough
for reaching equilibrium.

Calculation and Result

1. Activity coefficients of electrolytes in aqueous phase

The aqueous phase in this system is HCl-UO_2Cl_2 mixed electrolyte
solution. The Frank-Thompson model improved by the authors [2] was ap-
plied to calculate the activity coefficients of electrolytes. The de-
duced equations are

$$\ln\gamma_{\pm UO_2Cl_2}=\ln\gamma_{\pm UO_2Cl_2}(0)+ \frac{2}{3}\frac{m_{H^+}}{m_{H^+}+m_{UO_2^+}}(\ln\gamma_{\pm HCl}(0)-\frac{1}{2}\ln\gamma_{\pm UO_2Cl_2}(0)),$$

$$\ln\gamma_{\pm HCl}=\ln\gamma_{\pm HCl}(0)+\frac{1}{2}\frac{m_{UO_2^+}}{m_{H^+}+m_{UO_2^+}}(\frac{1}{2}\ln\gamma_{\pm UO_2Cl_2}(0)-\ln\gamma_{\pm HCl}(0)),$$

where $\gamma_{\pm}$ is the mean activity coefficient, m is the molal concentration,
$\gamma_{\pm}(0)$ is the mean activity coefficient in single electrolyte solution
with the ionic strengh being equal to that in mixed electrolyte solu-
tion, it was calculated by Pitzer equation [7].

2. Activity coefficients of constituents in organic phase.

There are 5 components in equilibrated organic phase, i.e. water, toluene, TOA, R_3NHCl and $(R_3NH)2UO_2Cl_4$. We express them by the subscripts 1, 2, 3, 4 and 5 respectively in this paper.

A. f_1. The activity of water can be calculated by the equation (1)

$$\ln a_1 = -0.018 \sum_i (\vartheta_i m_i \varphi_i),$$

where ϑ is the number of ions dissociated by an electrolyte in water, φ is the practical osmotic coefficient which is calculated by Pitzer equation, subscript i is various electrolytes in aqueous solution. From a_1 and X_1 the f_1 is obtained, where X_1 is the mole fraction of water in organic phase.

B. f_2. At room temperature the vapour pressure of toluene is so low that it can be considered as an ideal gas. The activity coefficient of toluene is given by

$$f_2 = P_2 / X_2 P_2^0$$

where P_2 is the partial pressure of toluene in the equilibrated gas phase and is measured by gas chromatographic analysis, P_2^0 is the saturated vapour pressure of pure toluene.

C. f_3. From Eqs. (1) and (3) the thermodynamic equilibrium constants K_4 and K_5 are given by

$$K_4 = \frac{X_4 f_4}{m_H + m_{Cl} - \gamma_{\pm HCl}^2 X_3 f_3} = K_4' \frac{f_4}{f_3}, \tag{4}$$

$$K_5 = \frac{X_5 f_5}{m_{UO_2} + m_{H^+}^2 m_{Cl}^4 \gamma_{\pm UO_2Cl_4}^3 \gamma_{\pm HCl}^4 X_3^2 f_3^2} = K_5' \frac{f_5}{f_3^2}, \tag{5}$$

where $K_4' = \frac{X_4}{m_H + m_{Cl} - \gamma_{HCl}^2 X_3}$; $K_5' = \frac{X_5}{m_{UO^+} m_H^2 m_{Cl}^4 \gamma_{\pm UO_2Cl_4}^3 \gamma_{\pm HCl}^4 X_3^2}$.

Differentiating Eqs. (4) and (5), we obtain

Substituting these two equations into Gibbs-Duhem equation of the quinary system $\sum_1^5 X_i d \ln f_1 = 0$ and integrating it, we obtain

$$\ln f_3 = \ln f_{3(X_5=0)}^* + \int_{X_5=0} \frac{X_4}{X_3 + X_4 + 2X_5} d \ln K_4' + \int_{X_5=0} \frac{X_5}{X_3 + X_4 + 2X_5} d \ln K_5' -$$

$$- \int_{X_5=0} \frac{X_1}{X_3 + X_4 + 2X_5} d \ln f_1 - \int_{X_5=0} \frac{X_2}{X_3 + X_4 + 2X_5} d \ln f_2, \tag{6}$$

where $\ln f_{3(X_5=0)}^*$ can be got from a set of experiments of HCl extraction by TOA-toluene.

$$\ln f_{3(X_5=0)}^* = \ln f_{3(X_4=0)}^* + \int_{X_4=0} \frac{X_4^*}{X_3^* + X_4^*} d \ln K_4 - \int_{X_4=0} \frac{X_1^*}{X_3^* + X_4^*} d \ln f_1^* - \int_{X_4=0} \frac{X_2^*}{X_3^* + X_4^*} d \ln f_2^*,$$

where $\ln f_{3(X_4^*=0)}^*$ can be got from a set of gas chromatographic analysis of TOA-toluene binary organic system.

$$\ln f_{3(X_4=0)}^* = - \int_{X_2^{**}=0}^{X_2^{**}} \frac{X_2^{**}}{X_3^{**}} d \ln f_2^{**}.$$

D. f_4. Being similar to f_3, f_4 is given by

$$\ln f_4 = -\int_{X_4=1} \frac{X_3^*}{X_3^{**}+X_4^{**}} d\ln K_4' - \int_{X_4=1} \frac{X_1}{X_3^{**}+X_4^{**}} d\ln f_1^* - \int_{X_2=0} \frac{X_3^*}{X_3^*+X_4^*} d\ln K_4'$$

$$- \int_{X_2=0} \frac{X_1}{X_3^*+X_4^*} d\ln f_1^* - \int_{X_2=0} \frac{X_2}{X_3^*+X_4^*} d\ln f_2 - \int_{X_5=0} \frac{X_3+2X_5}{X_3+X_4+2X_5} d\ln K_4'$$

$$+ \int_{X_5=0} \frac{X_5}{X_3+X_4+2X_5} d\ln K_5' - \int_{X_5=0} \frac{X_5}{X_3+X_4+2X_5} d\ln f_1 - \int_{X_5=0} \frac{X_2}{X_3+X_4+2X_5} d\ln f_2 ,$$

where the first two terms are obtained from a set of experiments of H_2O-TOA-HCl ternary organic system, the next three terms are obtained from a set of experiments of H_2O-TOA-toluene-HCl quaternary organic system and the last five terms are obtained from a set of experiments of H_2O-TOA-toluene-UO_2Cl_2-HCl quinary organic system.

E. f_5. Being simular to Eq. (6), f_5 is given by

$$\ln f_5 = \ln f_{5(X_5=0)} - \int_{X_5=0} \frac{2X_1}{X_3+X_4+2X_5} d\ln f_1 - \int_{X_5=0} \frac{2X_2}{X_3+X_4+2X_5} d\ln f_2 +$$

$$+ \int_{X_5=0} \frac{2X_4}{X_3+X_4+2X_5} d\ln K_4' - \int_{X_5=0} \frac{X_3+X_4}{X_3+X_4+2X_5} d\ln K_5' , \tag{7}$$

where the last four terms are obtained by graphical integration method. If we use the infinite dilution as reference state and use f_5 to express this activity coefficient of $(R_3N)_2UO_2Cl_4$, $\ln f_5^*$ is the sum of the last four terms. From thermodynamics we know that the difference between $\ln f_5$ and $\ln f_5^*$ is a constant, i.e. the first term in Eq. (7). Combining with the modified Scatchard-Hildebrand model, we obtain this value by least-squares method.

3. Thermodynamic equilibrium constant.

Since all terms in the right side of Eqs. (4) and (5) have been obtained, the K_4, K_5 and $K_5''=K_5/K_4^2$ can be calculated. The result is shown in Table.

Thermodynamic equilibrium constants of TOA-toluene-UO_2Cl_2-HCl system (25°C)

C_{TOA}^*	K_4	K_5	K_5''
0.69	$1.46\cdot10^3$	$3.79\cdot10^5$	0.177
0.92	$1.46\cdot10^3$	$3.00\cdot10^5$	0.141
1.15	$1.46\cdot10^3$	$2.48\cdot10^5$	0.116

* Original molar concentration of TOA in toluene.

From Table 1 it can be seen that the K_4 keeps as a real constant despite of different TOA concentration but there is some difference between the K_5 values. Perhaps the complex mechanism of extraction of UO_2Cl_2 is responsible for such a difference.

4. Improved Scatchard-Hildebrand model.

The Scatchard-Hildebrand model which is improved by the authors is used to correlate the activity coefficients of the components in organic phase [3]. According to this model the activity coefficients in quinary system are given by

$$\ln f_1 = \frac{V_1}{RT}\left[A_{12}\phi_2^2 + A_{13}\phi_3^2 + A_{14}\phi_4^2 + A_{15}\phi_5^2 + (A_{12} + A_{13} - A_{23})\phi_2\phi_3 + (A_{12} + A_{14} - A_{24})\phi_2\phi_4\right.$$
$$+ (A_{12} + A_{15} - A_{25})\phi_2\phi_5 + (A_{13} + A_{14} - A_{34})\phi_3\phi_4 + (A_{13} + A_{15} - A_{35})\phi_3\phi_5$$
$$\left. + (A_{14} + A_{15} - A_{45})\phi_4\phi_5 \right.$$

where V is the molar volume, ϕ is the molar volume fraction $\phi_i = (V_i X_i)/(\Sigma V_i X_i)$, A_{ij} is terminal constant of the S-H equation. The equations of f_2 to f_5 are similar to f_1.

The calculated data from improved S-H model coincide quite well with the experimental ones in the whole range of concentration ratio of R_3NHCl to $(R_3NH)_2UO_2Cl_4$ in organic phase. It shows the reliability of our thermodynamic model.

The thermodynamics of UP_2Cl_2-HCl extraction by TOA-toluene is studied. It includes:

1. The Pitzer equation and improved Frank-Thompson equation are used to calculate the activity coefficients of electrolytes in aqueous phase;

2. The activity coefficients of all components in organic phase are measured or calculated;

3. The thermodynamic equilibrium constants for this system are obtained;

4. The improved Scatchard-Hildebrand model is applied to correlate the activity coefficients of all components in organic phase.

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Recently the significant progress has been reached in the extraction thermodynamics.At first we would like to mark the success of the thermodynamics of multicomponent aqueous solutions where the methods of computation of component activities have been elaborated. Thus the main problem is to receive accurate experimental data which are necessary for calculation.

The situation is less satisfactory in the thermodynamics of multicomponent non-aqueous solutions which form the organic phase of extraction systems.Here the problems are more complicated because the number of components and the interval of variation of their activity coefficients are more than in aqueous solutions.Moreover in real systems with non-volatile solvents it is practically impossible to determine directly activity coefficients of any component except water.Therefore the elaboration of methods to compute activities in these solutions is very important.

Non-ideality of the organic phase in extraction systems is known to be described often by means of the conception of ideal associated solutions (IAS) in which deviations from ideality are explained with the formation of associates, solvates etc.the equilibrium between them being ruled by the mass action law and their solution being ideal at all the concentrations.Thus for two solutes A and B there are

$$p A + r B \rightleftharpoons A_p B_r ,$$ (1)

$$\beta_{pr} = \frac{[A_p B_r]}{[A]^p \cdot [B]^r} .$$ (2)

If we do not consider the physical meaning of constants β_{pr} the conception IAS can be treated as a method of description of deviation from ideality in which the monomer concentration is equal the component activity a:

$$[A] = a_A \quad \text{and} \quad [B] = a_B .$$ (3)

The application of IAS shows that there are some difficulties:

1. As a rule it is neccessary to use more than one constant for the description of the simple binary solutions with self-association of solutes.

2. The number of constants increases rapidly when the number of components rises.Therefore there is no example of the application of IAS in a strict way to describe the solution with three or more solutes.

3. It is possible to find some sets of constants to describe the solution.

4. The procedure of the determination of constants from indirect experimental data in multicomponent solutions (cryoscopy, ebullio-metry etc.) has not elaborated yet. We mean especially the procedure which guarantees the fulfillment of the conditions (3). As a matter of fact we meet here the same difficulties as at the determination of activity coefficients.

Instead of IAS the method of activity coefficients can be used to describe non-ideality of the organic phase. The main problem is the elaboration of an universal method to calculate a variation of activities of solutes from the activities of the other component when a new solute has been introduced to the solution. The universality of a method should permit to calculate activity coefficients of extractant or extracted complex in multicomponent solutions by means the same procedure adding solutes into binary solution one by one. For this purpose McKay [1] offered to use the relations

$$\left(\frac{\partial \ln a_i}{\partial r_{jk}}\right)_{r_{ik}} = \left(\frac{\partial \ln a_j}{\partial r_{ik}}\right)_{r_{jk}} \tag{4}$$

and

$$\left(\frac{\partial \ln f_i}{\partial r_{jk}}\right)_{r_{ik}} = \left(\frac{\partial \ln f_j}{\partial r_{ik}}\right)_{r_{jk}}, \tag{5}$$

where $r_{ik} = x_i/x_k$ is the relative concentration; x_i, a_i and f_i are the mole fraction, the activity and the mole activity coefficient of the component i. The molality m_i is another form of r_{i1}:

$$m_i = \frac{10^3}{M_1}, \tag{6}$$

where the subscript "1" refers to solvent, M_1 is the molecular mass of solvent.

This method permits us to describe the effect of hydration on extraction equilibrium [2]. Details of the procedure of the description are considered for alkylammonium salts. The water concentration m_w in their solutions is often the linear function of salt concentration m_s:

$$m_w = m_w^o + h m_s = m_w^o (1 + k_h m_s), \tag{7}$$

where m_w^o is the water concentration in pure solvent and is proportioned to the water activity a_w, h is the hydration number, k_h is the hydration parameter which does not depend on a_w. Because m_s does not effect on h the water activity coefficient f_w decreases when m_s rises. It is proved also that the solvent activity a_1 is not effected with hydration water:

$$\ln a_1 = \ln a_1^* - \frac{M_1}{10^3} m_w^o , \tag{8}$$

where the asterisk means that the activity is determined in the dry solution ($m_w \equiv 0$). Introduction (7) into (4) or (5) and integration leads to

$$\ln a_s/a_s^* = - \frac{\kappa_h \, m_w}{1 + \kappa_h \, m_s} = - h . \tag{9}$$

It means the hydration results in the decrease of a_s in the extent determined with the value of h. Because h does not depend on m_s the decrease of a_s is the same size for different m_s and the effect of hydration on the extraction equilibrium can be only marked when a_w is changed. Introduction (9) in Gibbs–Duhem's equation for tertiary solution leads to the equation (8).

The equations (7) – (9) include the only constant k_h. They can be extended for the solutions with several solutes with different k_h and h. Then instead of (9) we get

$$\ln \frac{a_s'}{(a_s')^*} = - \frac{\kappa_h' \, m_w}{1 + \kappa_h' \, m_s' + \kappa_h'' \, m_s'' + \dots} = - h' . \tag{10}$$

The application of IAS to describe the hydration is connected with difficulties. It is shown 2 the indefinite number of the constants β_{pr} should be used instead of the equations (7) – (9).

The above-mentioned method of the description of the hydration is not universal because the binary solution water-ammonium salt is not a good base to calculate activities. Apparently one should choose the binary solution solvent-ammonium salt as this base and carry out the calculation through solvent activities. The procedure of the calculation has been shown [3] for the introduction of another solute in the binary solution. Then the integration of (5) along the line r_{23} = const gives

$$\ln f_2/f_2' = \int_{r_{13}'}^{r_{13}} \left(\frac{\partial \ln f_1}{\partial r_{23}} \right)_{r_{13}} dr_{13} . \tag{11}$$

As r_{13} and $r_{23} \longrightarrow \infty$ at $x_3 \longrightarrow 0$ it is necessary to alter the variables, then

$$\ln f_2 = - \frac{10^3}{M_1} \int_0^{m_3} \left(\frac{\partial \ln f_1}{\partial m_2} \right)_{m_3} \frac{dm_3}{m_3} . \tag{12}$$

When non-ideality of a solution is big enough the dependance of $\ln f_1$ on m_2 is not linear whereas the dependance of $\ln f_1/f_1^*$ (the asterisk means that the activity coefficient is determined in binary solution at $m_3 = 0$) on m_2 is linear. Then instead of (12) we find

$$\ln f_2/f_2^* = - \frac{10^3}{M_1} \int_0^{m_3} \left(\frac{\partial \ln \frac{f_1}{f_1^*}}{\partial m_2} \right)_{m_3} \frac{dm_3}{m_3} , \tag{13}$$

where f_1^* is the solvent activity coefficient in binary solution at $m_2 = 0$. The equation (13) can be used to describe the effect of the hydration on the extraction equilibrium. We find from (7) and (8)

$$\ln f_i = \ln f_i^* - \ln\left(1 + \frac{M_i}{10^3}m_s\right) - \frac{M_i}{10^3}m_w^o + \ln\left[1+\frac{M_i}{10^3}(m_s + m_w)\right] . \qquad (14)$$

After the expansion of logarithms in Taylor's series and the neglect of all the terms except the first one we find

$$\ln f_i/f_i^* = 0.001 \cdot M_i \cdot m_w^o \cdot \kappa_h \cdot m_s . \qquad (15)$$

Usually $f_1^o = 1$ and the introduction of (15) into (13) and the integration gives

$$\ln f_s/f_s^* = - \frac{\kappa_h \cdot m_w}{1 + \kappa_h \cdot m_s} = - h . \qquad (16)$$

As $f_s/f_s \approx a_s/a_s$ the equation (16) is equivalent to (9).

The equation (13) permits to calculate activity coefficient of a component in a multi-component solution from solvent activities.The first step is the computation in the binary solutions from Gibbs-Duhem's equation and then the alteration of activity coefficients is calculated when new solutes are added one by one.In another report the equation (13) is used to describe the effect of extractant concentration on activities of extracted complex.

One of the advantages of the method under consideration is the application of the rather small number of empiric parameters to describe non-ideality in multicomponent solutions.However it is necessary to take into account that the accuracy of calculation rapidly decreases when $|\lg f_i| > 2$.Therefore it is worth describing the largest or significant part of non-ideality through the reaction like (1).This combined description has been used for the systems tetrachloromethane-tridodecylammonium (TDA) nitrate-Eu extracted with TDA nitrate [4].Although the extracted complex is known to contain 2 molecules of TDA nitrate the formation of the complex with 3 molecules of TDA nitrate has been assumed.As a result of this the values of activity coefficients have become smaller and the accuracy of the calculation has increased.

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The metal extraction with substituted ammonium salts is usually
described with the equation

$$M^{+n} + n\, A^- + q\, \overline{R_4\, NA} \rightleftharpoons \overline{(R_4\, N)_q\, M A_{n+q}} \tag{1}$$
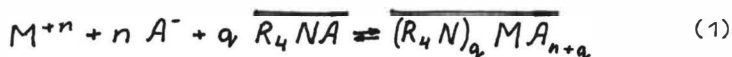
with the equillibrium constant

$$K_T = \frac{c_c \cdot \gamma_c}{[M^{+n}] \cdot [A^-]_{\cdot}^n\, \gamma_{\pm}^{n+1} \cdot c_s^{q} \cdot \gamma_s^{q}}, \tag{2}$$

where the line over the symbols shows the substance is in the organic
phase, c and γ are the concentration and the activity coefficient,
the subscripts "c" and "s" correspond to the extracted complex and
the ammonium salt.

Now there is a significant progress in the determination of acti-
vity coefficients $\gamma_{\pm}$ in multicomponent aqueous solutions. The prob-
lem is considered to be principally resolved although sometimes there
is a lack of experimental data neccessary for calculation. Therefore
the main difficulty is connected with the determination of the acti-
vity coefficients γ_c and γ_s in organic phase.

When calculating γ_c and γ_s one should take into account the
next phenomena in organic phase:
1. The association of ammonium salt and extracted metal complex.
2. The hydration of ammonium salt and metal complex.
3. The solvation of ammonium salt and metal complex with modificator.
4. The decrease of γ_c in presence of ammonium salt and similarly the
   decrease of γ_s in presence of metal complex.

The direct determination of γ_c and γ_s is known to be impossible
and it is neccessary to calculate them from the activities of sol-
vent or other components. This report is concerned with the progress
in this field for the last five years.

The solvation of ammonium salts with alcohols.It was shown [1]
that the effect of solvation on activities of ammonium salt a_s and
solvent a_1 could be described as

$$\ell n\, a_s/a_s^o = -\frac{K_s \cdot m_{\rho\ell}}{1 + K_s \cdot m_s}, \tag{3}$$

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^o \cdot a_1^*} = \frac{K_s \, m_s \, m_{a\ell}}{1 + K_s \, m_s} , \tag{4}$$

where m_s and m_{al} are the molalities of salt and alcohol; a_s^o and a_1^o are the activities of ammonium salt and solvent in the binary solution at $m_{al} = 0$; a_1^* is the activity of solvent in the binary solution at $m_s = 0$; M_1 is the molecular mass of solvent; k_s is the solvation parameter of a salt.The values k_s have been determined for a number of systems and they are shown to increase when anion radius decreases in consequence: iodide, bromide, chloride[2.3].

Extracted metal complexes are proved to be solvated with alcohols [3].Then the equation (3) is transformed into

$$\ln \frac{a_s}{a_s^o} = - \frac{K_s \, m_{a\ell}}{1 + K_s \, m_s + K_c m_c} , \tag{5}$$

$$\ln \frac{a_c}{a_c^o} = - \frac{K_c \, m_{a\ell}}{1 + K_s \, m_s + K_c m_c} , \tag{6}$$

where k_c is the solvation parameter of metal complex after the introduction of (5) and (6) into (2) it is possible to find the effect of alcohol on the distribution coefficient D [3] of metal for microconcentrations ($m_c \rightarrow 0$)

$$\lg D = \lg D_o - \frac{K_s q - K_c}{2,3(1 + K_s m_s)} . \tag{7}$$

The equation (7) allows to calculate slopes of the dependance of lg D on m_{al} from values of k_s and k_c determined in independent experiments.The calculated values of sloped were near experimental ones [3].

The equation (7) is suitable for systems where the dependence of water concentration in the organic phase m_w on water activity a_w and m_s is linear.If there are deviations from the linearity (so called "nonlinear hydration") it is neccessary to take into account the effect of alcohol on the hydration of ammonium salt.The equilibrium description of these systems was considered for the extraction of uranyl sulphate with benzene solutions of tri-n-octylammonium sulphate contained n-octanol [4].The distribution coefficient of uranyl D_u is shown to pass through a maximum when an alcohol concentration increases [5].It is known as well the activity of tri-n-octylammonium sulphate decreases rapidly when the water activity rises.The experimental data are given in the table [4].

Effect of n-octanol on the extraction of uranyl sulphate $(7.3 \cdot 10^{-4}$ mole/l) with 0.025 mole/l tri-n-octylammonium sulphate in benzene. $25.0 \pm 0.1^{\circ}C$ [4]

C_{al} mole/l	D_u	C_w mole/l	h	C_{al} mole/l	D_u	C_w mole/l	h
/0	840	0.142	4.38	0.10	1005	0.088	2.20
0.01	1248	0.132	3.98	0.15	431	0.089	2.24
0.02	1598	0.123	3.59	0.20	292	–	–
0.03	2051	0.103	2.81	0.25	173	0.091	2.33
0.04	1850	0.088	2.20				

The distribution coefficient Du passes through the maximum at C_{al} = 0,03 mole/l. The decrease of D_u at C_{al} > 0,03 is connected with extractant solvation with alcohol and can be described the equation like (7) with the parameters lg D_o = 3.459 $\pm$ 0.055, k_s = = 6.69 $\pm$ 0.11 l/mole (in the molar scale), q = 2 and k_c = 0. The difference lg D_o - lg 840 = 0.535 is due to the decrease of hydration ratio of extractant from 4.38 to 2,20. Effect of the decrease of h is calculated as it offered in (6):

$$ ln \frac{\gamma_s}{\gamma_s^o} = h_\infty - h_{int} , \qquad (8) $$

where γ_s and γ_s^o are the activity coefficients of ammonium salt in the solution under consideration and in the diluted solution in which the hydration ratio h_∞ does not depend on salt concentration and are proportional to water activity; h_{int} is the integral hydration ratio which are equal 2.88 for 0.025 mole/l tri-n-octylammonium sulphate in benzene [6]. For h_∞ = 2.20 ln $\left(\gamma_6/\gamma_s^{-c} \right)$ = -0.68 that results in the increase of lg D_u on 0.59.

Decrease of f_c in presence of ammonium salt. This effect observed for extraction of $FeCl_3$, lanthanide nitrates etc. with ammonium salts. Then the decrease of the mole activity coefficient f_c can be calculated only from solvent activities. At first the next equation has been derived at $m_c \longrightarrow 0$ [7]:

$$ ln f_c = - \frac{10^3}{M_1} \int_0^{m_s} \frac{1}{m_s} \left[\frac{M_1}{10^3} + \left(\frac{\partial ln a_1}{\partial m_c} \right)_{m_s, m_c = 0} \right] dm_s , \qquad (9) $$

where f_c = 1 at m_s = 0 and m_c = 0.
Afterwards [8] the equation (9) has been transformed into

$$ ln f_c = - \frac{10^3}{M_1} \int_0^{m_s} \frac{1}{m_s} \left(\frac{\partial ln \frac{a_4}{a_1 \cdot a_1}}{\partial m_c} \right)_{m_s, m_c = 0} dm_s , \qquad (10) $$

133

where a_1^o and a_1^* are the solvent activities in binary solutions at $m_c = 0$ and $m_s = 0$ correspondingly. The values f_c of complexes of cerium and europium nitrates with tridodecylammonium nitrate which were calculated from the equation (10) have been used to find out the extraction constants [8].

When $m_c \neq 0$ the next equation has been derived instead of (10):

$$\ln f_c/_{f_c^*} = -\frac{10^3}{M_1} \int_0^{m_s} \frac{1}{m_s} \left(\frac{\partial \ln \frac{f_1}{f_1^* \cdot f_1^*}}{\partial m_c} \right)_{m_s} dm_s , \qquad (11)$$

where f_c^* is the mole activity coefficient of complex at $m_s = 0$. It is possible to show that the equation (11) transforms into (10) at $m_s \longrightarrow 0$. Moreover for above-mentioned systems with cerium and europium nitrates the calculation from (10) and (11) results in approximately equal values that is the alteration of $\ln f_c$ does not depend on complex concentration.

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THE DETERMINATION OF THERMODYNAMIC CHARACTERISTICS OF
EXTRACTION EQUILIBRIA IN THE SYSTEMS CONTAINING AMMONIUM
SALTS AND ORGANIC PHOSPHORUS COMPOUNDS

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A vast diversity of the intermolecular interactions in the organic
and water phases of extraction systems used in practice requires a
special search for both experimental methods and suitable liquid mix-
tures models which should be theoretically strict, based on the mini-
mal number of empirical parameters and relatively simple mathematical
apparatus.

Our investigation of the extraction systems containing alkylammoni-
um salts and organic phosphorous compounds has shown that the organic
phase imperfection was caused by the extractant association and the
formation of a set of extracting complexes, the extraction being taken
from the concentrated solution of electrolytes.

Pitzer's [1] and Mikulin's [2] methods were found to be the most
convenient for the calculation of the water phase components activity,
as they make it possible to calculate the multicomponent solutions
properties using the data obtained for binary systems.

Having analyzed the literature data for 29 binary solutions of 1-3
group metal nitrates as well as uranyl and thorium nitrates we found
that Pitzer's equation range of use could be widened up to saturation
regions by taking into consideration $\beta^{(2)}$ coefficient recommended by
Pitzer only for the sulfates of bivalent metals. The statistical sig-
nificance of the coefficients was estimated according to Fisher's cri-
terion.

The experimental water isoactivates in 7 ternary systems (nitrate
solutions uranyl-thorium; uranyl-praseodymium; uranyl-lithium; ura-
nyl-magnium; lithium-ammonium; magnium-ammonium; sodium-aluminium)
could be described well by means of equations containing $\beta^{(2)}$, with-
out using Pitzer triple coefficients. Ammonium nitrate systems are an
exception because of the ion association in the concentrated solutions
with ammonium ions.

Zdanovski-Mikulin's equations determine water isoactivates in ter-
nary systems with approximately the same accuracy as that of Pitzer's
equations. However their application is limited because one has to use
additional data on water activity in supersaturated binary solutions
to make the calculations.

While choosing a suitable theoretical model for the organic phase
we have focused mainly on different versions of the theory of associa-
tion equilibria which enables to take into account (by means of asso-

ciation constants) the main interactions of the hydrogenbonds type or dipole-dipole interactions.

We have considered 5 versions of associative equilibria theory differing in the accuracy of the estimation of the associates mixture imperfection. Besides we have investigated two semiempirical equations for the solvent activity coefficients (f_S). The equation

$$m_A^2 / \ell n f_S = \mathcal{B}_0 + \mathcal{B}_1 m_A \tag{1}$$

was proposed in [4] and equation

$$m_A^2 / \ell n f_S = \mathcal{B}_0 \sqrt{m_A} + \mathcal{B}_1 m_A \tag{2}$$

has been used for the first time. It may be considered as analogous to Deby-Hückel equation for organic solutions.

All the models and both equations have been examined for more than so organic solutions, the solvent activity data being obtained in our crioscopic and vapour pressure osmometric (VPO) experiments or taken from literature [4-6]. Both in dilute and concentrated solutions the best results have been achieved by means of an ideal associative solution model without making an assumption that all association constants are the same. The values of tributiphosphate (TBP) dimerisation constants in the various solvents are in good agreement with the equation

$$\ell n \beta_{2,TBP} = 0,63 - 1,24\, SE, \tag{3}$$

where SE is the parameter of solvent effect. For several alkylammonium salts (AS) in benzene the association constant depends on the molecular structure in the following manner:

$$\ell n \beta_{AS} = \ell n \beta^0 + 2,32 \Sigma 6^* + 2,17 \Sigma E_S, \tag{4}$$

where $6^*, E_S$ are Shmidt's parameters of inductive and steric effects.

The temperature dependence of β for trioctylammonium (TOA) nitrate in benzen is calculated according to the equation

$$\ell n \beta_{TOA} = -5,77 + 2600/T. \tag{5}$$

Examining the organic solutions of alkylammonium salts and organic phosphorus compounds containing metal nitrates we have completed and specified the literature data by our UR-, NMR- and VPO results.

It has been demonstrated that metalcontaining complexes could be solvated by free extractant molecules:

$$\overline{Me(NO_3)_m \ (n-1)S} + \overline{S} \overset{k_n}{\rightleftharpoons} \overline{Me(NO_3)_m \ nS} \cdot$$
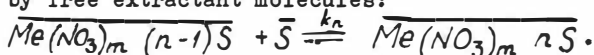
The values of the additional solvation were found to be:
in the system " $Ce(NO_3)_3$- TBP - benzene"
$$k_4 = (3,4\pm0,4)\cdot 10^2 \qquad k_5 = 8,1\pm0,4$$
" $Pr(NO_3)_3$- TBP - benzene"
$$k_4 = 1,2\pm0,1$$

$$" UO_2(NO_3)_2 - \text{TBP} - \text{benzene}"$$
$$k_3 = 1,6\pm0,1,$$
$$"Th(NO_3)_4 - \text{TBP} - \text{benzene}"$$
$$k_3 = 52\pm3 \qquad k_4 = (1,2\pm0,1)\cdot10^{-1},$$
$$"Ce(NO_3)_3 - \text{trilaurylammonium nitrate } (\text{TLA}\cdot HNO_3)-CC\ell_4 \quad [4]$$
$$k_4 = (3,4\pm0,4)\cdot10^2, \qquad k_5 = 8,1\pm0,4,$$
$$"Eu(NO_3)_3 - TLA\,HNO_3 - CC\ell_4"[4]$$
$$k_4 = (2,9\pm0,6)\cdot10^3, \qquad k_5 = (2,2\pm0,6)\cdot10^3.$$

The calculated constants of the association and the additional sol-vation have been used in the extraction mathematical model based on a more thorough consideration of all the interactions by means of the mass action law.

Another way of description of the extraction equilibriums is the method based on the partition law in a general form, thermodynamic par-tition constant (K) being the only main parameter. This constant is equal to the relation of the extracting component activity in the or-ganic phase to that in water phase. We have introduced the method of calculating the component activity in metalcontaining organic solu-tions from VPO data. It is based on integrated Gibbs-Dugem equation in the ternary organic systems analogous to the calculation method for water solutions. We have calculated the activity of europium nitrate in water and organic phases using literature data [4]. The partition constant in the system "$(7,23m\ LiNO_3 + 1,96m\ Ca(NO_3)_2 + Eu(NO_3)_3)-$ $- TLA\cdot HNO_3 - CC\ell_4$" was found to be

$$K_{Eu(NO_3)_3} = \bar{a}_{Eu(NO_3)_3} / a_{Eu(NO_3)_3} = (3,4\pm1,4)\cdot10^{-7}.$$

Though the partition law has been rarely used in its general form up till now we find it to be very attractive because of its simplici-ty and strictness. Future research will make it possible to determine some regularities for its further simplification and to apply it to a wide range of extraction systems.

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SOLVATION OF INORGANIC IONS AND EXTRACTION EQUILIBRIA

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The Gibbs energy change of the ion exchange reactions

$$(RA)_s + X_h^- = (RX)_s + A_h^- \qquad (1)$$

is determined by the sum of the resolvation energy contributions of
the exchanging ions $[\Delta G_{tr}^0(X^-) - \Delta G_{tr}^0(A^-)]$ which depends on the
composition and properties of the nonaqueous solvent. The present
work investigates the exchange reactions and water solubility in the
extraction of inorganic anions with the tetraoctylammonium salts
R_4NX and of alkali metal cations Me^+ with the tetraphenylboron salts
$MeBPh_4$ depending on the composition and properties of the mixed sol-
vent.

Solvation of an anion X^- in a nonaqueous solution S can be regarded
as formation of solvates of the composition $X^-(S)_s$ in a continuous
medium S. In the presence of water or other solvents L the solvent S
may be partially or completely displaced from the first sphere of the
anion with the formation of a hydrate-solvate. The change in the
standard chemical potential of the ion on changing from the "dry" to
the water-saturated solvent can be expressed as a function of comp-
lexation

$$\Delta \int u^0 = \int u_s^0 - \int u_{sh}^0 = -RT \ln \Phi_x . \qquad (2)$$

The addition to the solution of protic compounds L (alcohols,
phenols, $CHCl_3$) may give rise to a mixed hydrate-solvate

$$X^-(S)_s \xrightarrow{+hH_2O} X^-(H_2O)_h S_{s'} \xrightarrow{+\ell L} X^-(H_2O)_{h_i} L_\ell S_{s_i} \qquad (3)$$
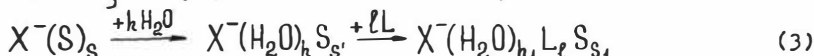
with the displacement of a portion of water or solvent molecules from
the coordination sphere of the ion.

The collective effect of small concentrations of solvating additi-
ves and water on the anion solvation process can be estimated on the
basis of complexation equations. Let us assume that an alcohol mole-
cule displaces, on its dehydration, one water molecule in the hydrat-
ion shell of the anion according to the reaction

$$[X^-(H_2O)_h]_0 + \ell[L(H_2O)_k']_0 = [X^-(L)_\ell(H_2O)_{(h-\ell)}]_0 + (\ell h' + 1)H_2O , \qquad (4)$$
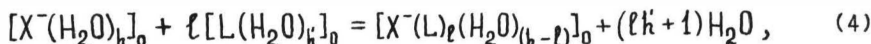
where ℓ is the total number of water molecules displaced from the
hydration shell of the ion. Let us now form three balance equations
for the nonaqueous phase: with respect to water, the R_4NX salt, and
octyl alcohol. By simultaneously solving these equations we obtain
the expression :

$$C_{H_2O}^{tot} = C_{H_2O}^{in} + hC_{QAB} + (h'+1)[L(H_2O)_k'] - C_L , \qquad (5)$$

138

where $c_{H_2O}^{tot}$ is the total content of water in the nonaqueous solution, $c_{H_2O}^{in}$ is the concentration of water in the pure solvent which is independent of the salt concentration within the 0-0.2 M interval.

Fig.1 shows the results for the water extraction with solution of quaternary ammonium bases (QAB) in the presence of different solvatinf additives. Addition of octanol to nonaqueous solutions of tetraoctylammonium salts results in a decrease in the amount of the dissolved water due to displacement of a portion of water molecules in the hydration shell of the anion by alcohol. The extent of water displacement by octanol increases with the increasing proton affinity of the anion. However, no complete displacement of water from the hydration shell occurs in this case. In contrast to octanol, 4-tert. butylphenol has stronger protogenic properties and more actively solvates the anion. It can be seen from Fig.1 that the presence of alkylphenol may result in complete displacement of water from the hydration shell of the anion. In contrast to this, electron-donating additives, such as tributylphosphate (TBPh) do not affect appreciably the hydration shell of the anion which indicates the absence of solvation of the QAB salts by these compounds.
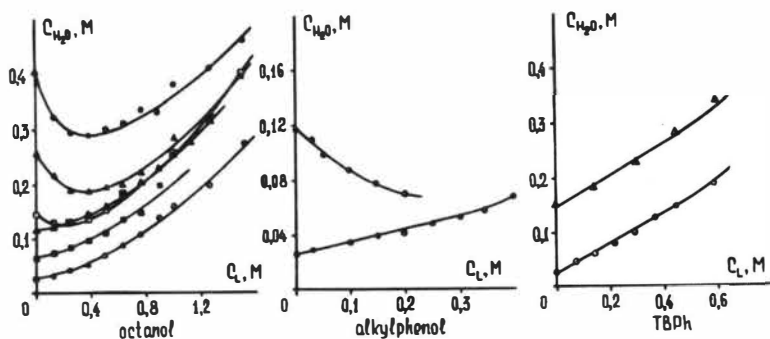
Fig.1. Water solubility in the organic phase as a function of concentration of the solvating additives at a constant concentration of tetraoctylammonium salt in benzene
c_{salt}: C - no salt; ■ 0.107 M R_4NJ; $\triangle$, ◑, ▲ 0.113 M R_4NNO_3; ⊡ 0.1 M R_4NBr; ▲ 0.089 M R_4NCl; ● 0.027 M $(R_4N)_2SO_4$

In the case of mixed and water-saturated solvents there is often no additivity of the properties which indicates that solvation is by predominantly one of the solvent components. The formation of mixed solvates results in a change in the water solubility in the nonaqueous phase and the exchange constants. The changes in the exchange cons-

tant with the change in the solvent composition can be estimated on the basis of complexation considerations.

According to equ. (3) the overall concentration of the ions C_x in the solution is formed by the set of all species the stability of which can be expressed through the formation constants.

$$C_x = [X^-](1 + \beta_1 a_w + \beta_2 a_w^2 + \ldots + \delta_1 C_L a_w + \delta_2 C_L^2 a_w^2 + \ldots) = [X^-](\Phi_x + F_x), \quad (6)$$

where C_L is the equilibrium ligand concentration in the solution, a_w is the activity of water in the system, X is the activity of the ion in the solution, $\Phi_x = 1 + \sum_{i=1}^{k} \beta_i$, $F_x = \sum_{i=1}^{l} \delta_i C_L^i$ at a_w = const. In a dry solvent $\Phi_x = 1$ and $F_x = 0$, then $\Delta \mu^0 = 0$. When the solution S is saturated with water $\Delta \mu^0 = -RT \ln \Phi_x$. In the presence of water and the additives L $\Delta \mu^0 = -RT \ln(\Phi_x + F_x)$.

For the exchange reaction (1) of the ions X^- and A^- the change in the exchange constant K_{ex} upon addition of a solvating additive L to a water-saturated solution is determined by the equation

$$\Delta \lg K_{ex} = \lg(\Phi_A + F_A)/\Phi_A - \lg(\Phi_x + F_x)/\Phi_x . \quad (7)$$

Let us consider some typical systems.

At F_x and $F_A = 0$ and in the absence of solvation $\Delta \lg K_{ex} = 0$. An example are the anion exchange reactions in the presence of tributylphosphate (Fig. 2).
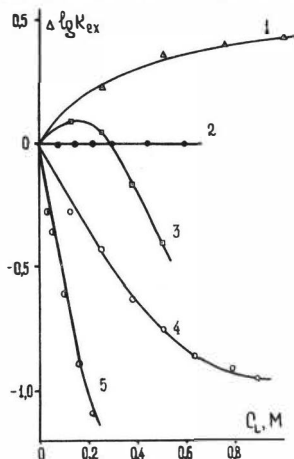
Fig. 2. The values of $\Delta \lg K_{ex}$ of the anions in the systems with the tetraoctylammonium salts in different solvents as a function of the solvating additive concentrations

Systems :
1. WO_4^{2-} - CO_3^{2-} - tetrachloroethylene-2-ethylhexanol ;
2. NO_3^- - Cl^- - benzene - tributylphosphate
3. Cl^- - F^- - toluene - octanol ;
4. NO_3^- - Cl^- - benzene - octanol ;
5. NO_3^- - Cl^- - benzene - 4-tert. butylphenol

At $F_x > F_A$ $\Delta \lg K_{ex} < 0$. This is a typical instance of the effect of alcohols on the extraction of metals in the form of complex compounds and on the exchange of stable anions with a small degree of hydration in the solution.

At $\Phi_x \gg \Phi_A$, it is possible that for ions with strongly

differing degrees of their hydration in the nonaqueous solution and at small concentrations of L when $\Phi_x \gg F_x$ $\Delta\lg K_{ex}$ will be zero. This is a rare case of the increase in the exchange constants upon addition of aliphatic alcohols to solutions (with the exchanges $Cl^- - F^-$, $WO_4^{2-} - CO_3^{2-}$).
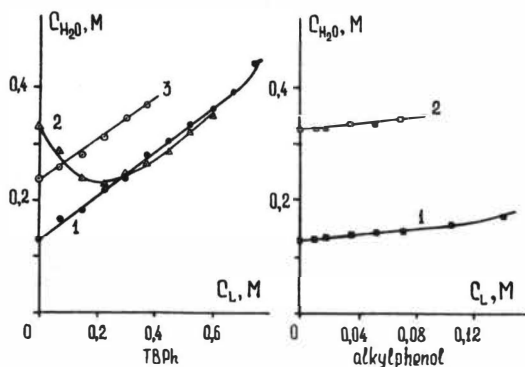
Fig. 3. Water solubility in the organic phase against concentrations of tributylphosphate and 4-tert. butylphenol in nitrobenzene at constant concentrations of R_4NCl and $NaBPh_4$ salts.
C_{salt} : 1 - no salt;
       2 - 0.065 M $NaBPh_4$;
       3 - 0.026 M R_4NCl

In contrast to the anions, the Na^+ cation in the solutions of tetraphenylboron is solvated only by electron-donating compounds. Protic solvents, such as alkylphenols, displace water from the hydration shell of the Cl^- anion while being indifferent with respect to the Na^+ cation. On the contrary, the electron-donating solvents, such as TBPh , dehydrate Na^+ and are indifferent with respect to the anion (Fig. 3). The differences in action between the same solvating additives with respect to the QAB salts and $NaBPh_4$ are explained by the different mode of coordination of the water and solvent molecules to the Na^+ cation and the anions of the QAB salts.

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Quantitative data on self-association of higher quaternary ammoni-
um salts (QAS), used as extractants, were obtained by indirect methods
[1] and they are not always agree with their behaviour in extraction
systems. The application of a direct method to study QAS extractants
self-association is difficult because of high values of extraction
constants in water-organic solvent systems. Neither it is possible to
use data on lower QAS self-association, obtained by means of the in-
terphase distribution method [2-3] to describe extraction equilibria
with participation of their higher homologues, which is evidently due
to dependence of association processes on a radical length. The values
of concentration limits of the beginning of QAS self-association, ob-
tained by means of different methods differ by 2-3 orders of magnitu-
de. The ion self-association contribution into deviation of QAS beha-
viour from the ideal one remains unclear.

The present paper investigates both molecular and ion self-asso-
ciation of different QAS in inert solvents by means of methods of
electrical conductivity and interphase distribution in the toluene –
ethyleneglycol extraction system.

The application of the toluene – ethyleneglycol extraction system
allows to study the distribution of higher QAS, used as extractants.
Close values of QAS, at which the self-association for toluene-water
and toluene – ethyleneglycol systems begins (Table 1) certificates
the absence of a noticeable aeffect of hydration and solvation by
ethyleneglycol on this process.

Table 1 shows, that the association boundary slightly decreases
with the growth of anion and QAS cation radical, which agrees well
with the literature data. Addition of octane to toluene leads to the
self-association strengthening and addition of alcohol leads to its
weakening (Fig.1).

High conductivity of higher QAS solution in toluene in concent-
rated solutions shows, that they provide for a formation of charged
current-conducting particles (three-ion associates and more complica-
ted formations). The QAS dissociation process can be written in the
following way:

$$(m+n+1) \, R_4N^+A^- \rightleftharpoons (R_4N^+A^-)_m R_4N^+ + (R_4N^+A^-)_n A^-. \quad (1)$$
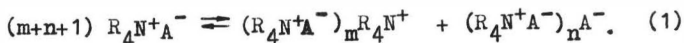
Table 1. Concentrations of self-association beginning of different QAS in toluene

QAS cation	Anion		
	Cl^-	I^-	Pic^-
1. $(C7H_{15})_2NCH_2CH_2N^+(C_7H_{15})_3$	–	$1.2 \cdot 10^{-3}$	–
2. $(C_{12}H_{25})_2(CH_3)_2N^+$	–	$1.0 \cdot 10^{-3}$	–
3. $(C_{10}H_{21})_3CH_3N^+$	–	$1.6 \cdot 10^{-3}$	–
4. $(C_{10}H_{21})_3C_2H_5N^+$	$1.9 \cdot 10^{-3}$	$6.4 \cdot 10^{-4}$	–
5. $(C_6H_{13})_3C_2H_5N^+$	–	$4.5 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
6.* $(C_6H_{13})_3C_2H_5N^+$	–	$4.0 \cdot 10^{-4}$	–
(*) toluene – water extraction system			
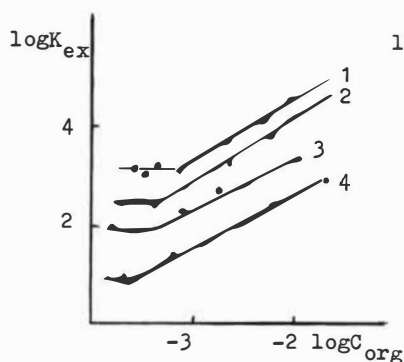
Fig.1. Dependence of extraction constant of iodide tridecyl-ethylammonium on its concentration in toluene (1) and with addition of octane -20% (2),40%(3), 60% (4)
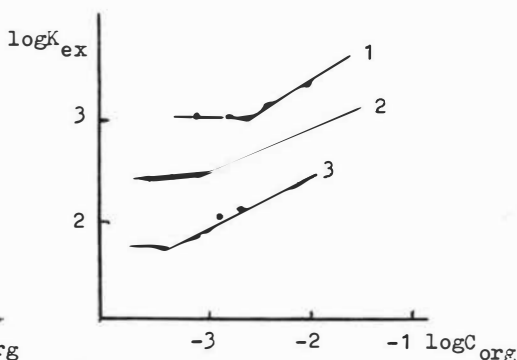
Fig.2. Dependence of extraction constant of iodide dilaurylmethyl ammonium on its concentration in toluene with addition of dodecanol: 0,06 M (1); 0,2 M (2); 0,5 M (3)

The dissociation constant will be equal to:

$$K = \frac{\left[(R_4N^+A^-)_m R_4N^+\right]\left[(R_4N^+A^-)_n A^-\right]}{\left[R_4N^+A^-\right]^{m+n+1}} , \qquad (2)$$

where m+n+1 – is the number of QAS molecules,participating in the formation of ions pair;m,n – is the number of QAS molecules,solvating the cation and anion respectively.

Taking into account the electroneutrality condition,the dissociation degree can be written in the form:

143

$$\mathcal{d}=\frac{\sqrt{K[R_4N^+A^-]^{m+n+1}}}{\sqrt{K[R_4N^+A^-]^{m+n+1}}+\dfrac{[R_4N^+A^-]}{m+n+1}}=\frac{\lambda_i}{\lambda_\infty}, \qquad (3)$$

where λ_∞ is the equivalent conductivity of the i-th QAS concentration and λ_i is the equivalent conductivity ofQAS solution,corresponding to total salt dissociation in the process (1).

If the QAS portion, subjected to dissociation is small,expression (3) acquiree the form :

$$\lambda_i = \lambda_\infty (m+n+1) \sqrt{K[R_4N^+A^-]^{m+n-1}} \qquad (4)$$

or in the bilogarithmic form :

$$\log \lambda_i = \log\left\{\lambda_\infty (m+n+1)\sqrt{K}\right\} + \frac{m+n-1}{2} \log[R_4N^+A^-]. \quad (5)$$

The term $\log\left\{\lambda_\infty (m+n+1)\sqrt{K}\right\}$ of expression (5) changes with the change of QAS concentration at the expence of the conducting particle structure change. As it follows from Stocks equation[4],it slightly increases with the QAS concentration decrease and ion radius reduction. But as it is seen from Fig.3 and 4,the QAS concentration reduction from 0,08 to 0,06 leads to abrupt reduction of $\log \lambda_i$ .Hence, the determining factor of $\log \lambda_i$ change is the change of concentration of ions,but not their mobility. Then in the first approximation one can write:

$$\log \left\{\lambda_\infty (m+n+1)\sqrt{K}\right\}\approx\text{const}$$

and the slope of the bilogarithmic dependence (5) will be equal to m+n-1.

As it is seen from Fig.3,the values of slope are negative at concentrations of all studied QAS more than 3.10^{-3}M and they are positive in more concentrated solutions. The negative (close to -0,5) slopes certificate a small quantity of three-ion associates at QAS are predominantly in a nonassociated state.In the minimum point m+n-1/2 = 0,hence,m+n=1,i.e، an average molecules number of QAS , solvating the ions pair in the minimum point is equal to 1.

The obtained data on conductivity of higher QAS solutions in toluene show,that when describing the process of their self-association one should take into account not only neutral associates,but also the charged ones. Exactly their presence in the solution may distort the results of the association study in the solution by the solvent activity.

The obtained data well agree with those on anion exchange extra-

ction.Fig.4 shows,that the constants values of exchange of a number
of anions do not depend on QAS concentration in toluene.

The obtained data show,that noticeable deviations of the higher
QAS behaviour begin from concentration 10^{-3}M and higher.
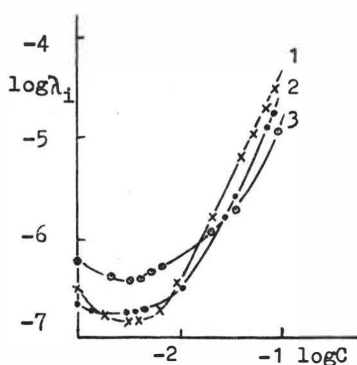
Fig.3. Bilogarithmic depen-
dence for toluene solutions
of tributyloctadecylammonium:
1 - $R_4N^+I^-$; 2 - $R_4N^+SCN^-$;
3 -$(R_4N^+)_2Zn(SCN)_4^{-2}$ and
$(R_4N^+)_2Co(SCN)_4^{-2}$
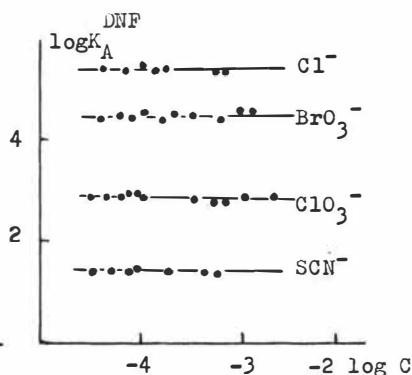
Fig.4. Bilogarithmic depen -
dence of exchange constant
log $K_{A_i}^{DNF}$ on log $C_{R_4N^+DNF^-}$.
DNF^- - $C_6H_3(NO_2)_2O^-$.
Solvent - toluene

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CORRELATION OF HYDROPHOBICITY AND POLARIZABILITY OF THE MOLECULE FRAGMENTS WITH THE EXTRACTION CHARACTERISTICS OF THE ORGANIC COMPOUNDS AND THEIR METAL COMPLEXES

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Recently, several correlations have been proposed between the properties of the system and its components to reveal the regularities of the extraction processes. It was shown [1,2] that for the homologue series of organic compounds the extractibility may depend on the number of carbon atoms in alkyl substituent, while for halogen derivatives with the various halogenide atoms - on the compound molecular mass or molar volume. Since these empirical regularities do not characterise the molecule nature, it is desirable to use more fundamental properties, such as, for example, the mean polarizability of the molecule.

The mean polarizability α characterizes the ability of the atom or the molecule to adopt the dipole moment in the electric field and is determined by the expression $\alpha = (3/4 \pi N) R_M = 0.3964 \cdot 10^{-24} R_M$ cm^3 = $0.3964 R_M$ Å^3, where N - Avogadro number, R_M - molecular refraction. The latter may be determined by the different experimental or calculation methods. In the present work the value of the molecular refraction was calculated according to Eisenlohr additive scheme [3] on the base of the atomic and group refractions of the radicals, as well as the multiple bond increments.

The analysis of the literatural and experimental data on the interphase distribution of a number of hydroxyl- and carboxylcontaining organic compounds and their complexes with the metals was carried out. The correlation was found between the partition coefficients (P) values of the individual compounds and the mean polarizability of their molecules or the complexes stability constants and the mean polarizability of the ligand molecules. Below are the graphical and mathematic expressions of the obtained dependences.

Carboxylic acids.
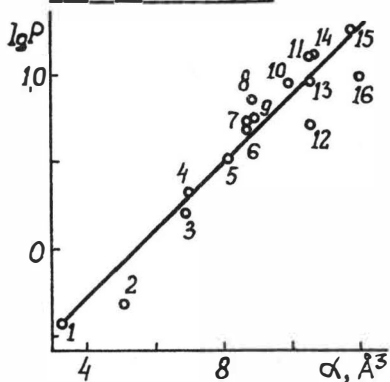
Fig.1. Plot of lg P [1, p.151] vs. α for the formic (1), acetic (2), propionic (3) chloroacetic (4), bromoacetic (5), butyric (6) isobutyric (7), 2-chloropropionic (8), dichloroacetic (9), 2-bromopropionic (10), trimethylacetic (11), valeric (12), isovaleric (13), 2-chlorobutyric (14), 2-bromobutyric (15), 2-iodopropionic (16) acids in the system water - diethyl ether. lg P_x = lg $P_{HCOOH} + \gamma \Delta \alpha$, γ = 0.20, $\Delta \alpha = \alpha_x - \alpha_{HCOOH}$

146

<u>Phenols.</u> P values were taken from [2].

<u>Fig.2.</u> Plots of lg P vs. α for phenol (ph, 1), p-cresol (2), 4-ethyl-(3), 4-n-propyl- (4) and 4-n-butylphenol (5) in the systems water - cycloxecane (I), tetrachloromethane (II), benzene (III), dichloroethane (IV), nitrobenzene (V), n-amyl acetate (VI). lg P_x = lg P_{ph} + $\gamma_\Delta\alpha$, $\Delta\alpha = \alpha_x - \alpha_{ph}$, γ = 0.306 (I), 0.312 (II), 0.294 (III, IV), 0.284 (V), 0.207 (VI)
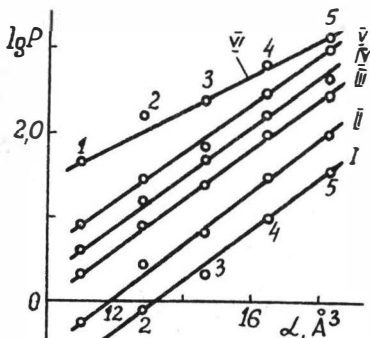
<u>Fig.3.</u> Plot of lg P vs. α for phenol (1), 2-fluoro- (2), 2-methyl- (3), 3-methyl- (4), 4-methyl- (5), 2-chloro- (7), 2-bromo-(9), 2,4-dimethyl-(10), 2,5-dimethyl-(11), 2,6-dimethyl-(12), 3,4-dimethyl-(13), 3,5-dimethyl-(14), 2-ethyl-(15), 4-ethyl-(16), 2-iodo-(18), 4-propyl-(19), 2-isopropyl-5-methyl phenol (21), salicylic aldehyde (6), salicylic acid (8), methyl salicylate (17), 2-naphthol (20) in the system water - n-butyl acetate. lg P_x = 0.168 α_x+0.09
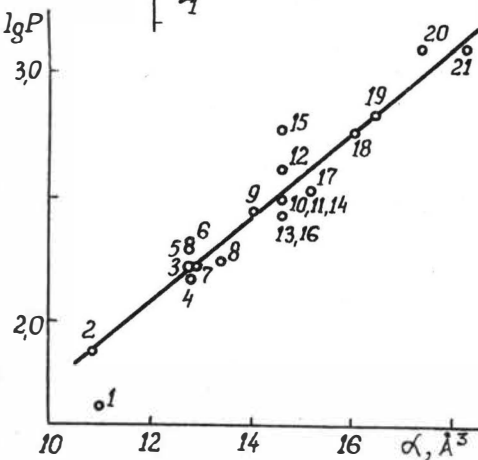
The similar dependences were obtained for some other series of compounds (Fig. 4). The found regularities are also kept for some complex compounds (Fig.5).

We have earlier studied the extractable ionic associates of the rare earth elements acidocomplexes with salicylic acid and 8-hydroxyquinoline derivatives (L) and rhodamine B (RB) of the composition LnL_4RB and their stability was determined [5]. For the ionic associates with hydroxyquinoline derivatives the one-phase stability constant was found in the organic phase - chloroform, K = $[LnL_4RB]/[LnL_3]\cdot[RB^0][HL]$, and for the ionic associates with the salicylic acid derivatives - the value of the β formation degree calculated from the change of the extracts light absorption at stoichiometric and optimum reagent concentrations, β = $A^{stoich}\cdot c_{Ln}^{opt}\cdot100/$ $A^{opt}\cdot c_{Ln}^{stoich}$, %.

The correlation of the ionic associates stability with the ligand molecule polarizability is observed (Fig. 6, 7, a) as well as with empirical hydrophobic fragmental constants (f) according to Rekker[6] (Fig. 6, 7, b).
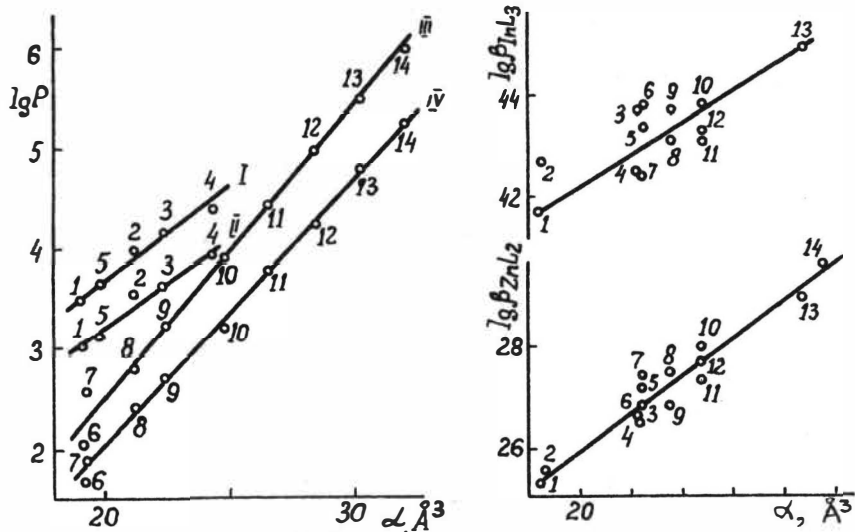
Fig. 4. Plots of lg P [4] - α for mercaptohydroxyquinoline (7) and its derivatives: 5-fluoro-(1), 5-chloro-(2), 5-bromo-(3), 5-iodo-(4), 1,2,3,4-tetrahydro-(5), 7-fluoro-(6), 7-chloro-(8), 7-bromo-(9), 5-S-methyl-(10), 5-S-ethyl-(11), 5-S-propyl-(12), 5-S-butyl-(13), 5-S-amyl mercaptohydroxyquinoline (14) in the systems water - chloroform (I,III) or tetrachloromethane (II, IV)

Fig.5. Plot of the logarithms of the biphase stability constants of zinc and indium complexes with mercaptohydroxyquinoline derivatives vs. α of the ligand molecules. Ligands: mercaptohydroxyquinoline (2), 5-fluoro-(1), 4-methyl-(3), 6-methyl-(4), 5-chloro-(5), 6-chloro-(6), 7-chloro-(7), 4-methoxy-(8), 5-methoxy-(9), 5-bromo-(10), 6-bromo-(11), 7-bromo-(12), 5-iodo-(13), 2-isopropyl mercaptohydroxyquinoline (14). Extractant - chloroform
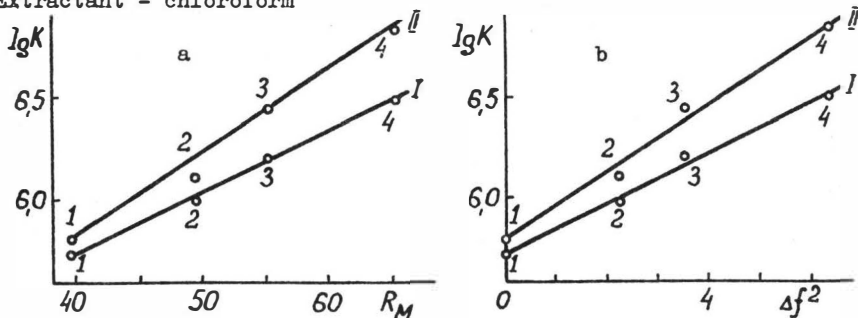
Fig.6. Plots of lg K of the ionic associates of Nd (I) and Er (II) with 8-hydroxyquinoline (1), 5,7-dichloro-(2), 5,7-dibromo(3), 5,7-diiodo-8-hydroxyquinoline (4) and rhodamine B vs. R_M value (a) and hydrophobicity (b) of the ligand; a: $\lg K_{der} = \lg K_{Hq} + \gamma \Delta R_M$, $\gamma = 0.030(I)$, $0.041(II)$; b: $\lg K_{der} = \lg K_{Hq} + \gamma \Delta f^2$, $\gamma = 0.123(I)$, 0.167 (II)

148
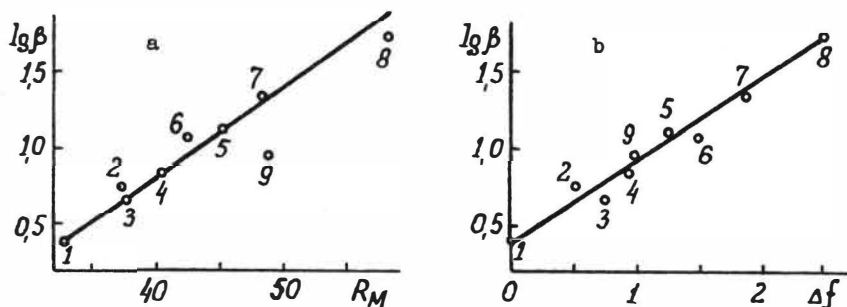
Fig.7. Plots of lg β of the lanthanum ionic associates with salicylic (1), 3-methyl-(2), 5-chloro-(3), 5-bromo-(4), 5-iodo-(5), 3,5-dicloro-(6), 3,5-dibromo-(7), 3,5-diiodosalicylic (8), 2,3-hydroxynaphthoic (9) acids and rhodamine B vs. R_M value (a) and hydrophobicity (b) of the ligand; a: lg β_{der} = lg β_{SA} + $\gamma \Delta R_M$, γ = 0.062; b: lgβ_{der}= lg β_{SA} + $\gamma \Delta f$, γ = 0.528

Fig.8. Plots of f vs. R_M for some molecule fragments: -H (1), -CH$_3$ (2), -C$_2$H$_5$ (3), -C$_3$H$_7$ (4), -F (5), -Cl(6), -Br (7), -I (8), -OH (9),-NH$_2$ (10)

As it was suggested the hydrophobic fragmental constants correlated with the polarizability of the corresponding radicals since they are calculated from the partition coefficients of a great number of the various compounds. It was shown that the mean polarizability of the molecule is an important parameter determining the compounds extractibility. It may be used for the prediction of the extraction characteristics of the organic compounds and their complexes with metals.
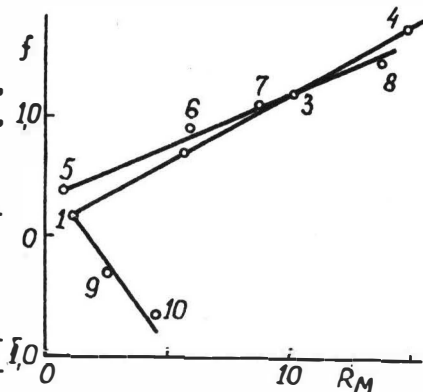
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In the systems with neutral extractants the process of electrolytes
distribution is usually accompanied by the extraction of considerable
quantities of water $[1-3]$. The methods of determination of the solvate
composition have been proposed and reported in $[2-5]$. They take into
account the contribution of the nonstoichiometric hydration effect to
the nonideality of the extract. This study expands upon the establish-
ment of useful correlation between distribution of the electrolytes
and their the nonstoichiometric or stoichiometric hydration.

The activity coefficients of the solute in the wet organic solvents
(γ), saturated at the water activity a_w, can be obtained using the
known values of the activity coefficient of the same solute in a dry
solvent (γ_0) $[2, 3]$.

$$\gamma = \gamma_0 \exp\left[h_1(1-a_w)\right], \tag{1}$$

where h_1 is the degree of solute hydration in the solvent, saturated
by water at $a_w=1$.

By introducing (1) into equations for the distribution constant of
the electrolytes dissociated in the organic phase into $\bar{\nu}$ ions we
obtain $[5]$:

$$K_{a_w,\bar{\nu}} = \frac{\bar{Q}\cdot\bar{m}\cdot\bar{\gamma}_{\bar{\nu}}^{\bar{\nu}}}{Q\cdot m^{\nu}\cdot\gamma_{\pm}^{\nu}} = K_{\bar{\nu}}\cdot\bar{Q}\cdot\bar{\gamma}_{0,\bar{\nu}}^{\bar{\nu}}\cdot\exp\left[\bar{\nu}\cdot h_{1,\bar{\nu}}\cdot(1-a_w)\right], \tag{2}$$

where $\bar{m}$ and m are the molal concentration of the electrolyte in orga-
nic and aqueous phases, $\nu = \nu_+ + \nu_-$ is the mole number of ions in one
mole of electrolyte, $K_{a_w,\bar{\nu}}$ and $K_{\bar{\nu}}$ are the thermodynamic and effective
distribution constants, $\gamma_{\pm}$ is the mean activity coefficient of the
electrolytes, $h_{1,\bar{\nu}}$ is the hydration degree at $a_w=1$ of electrolytes dis-
sociated into $\bar{\nu}$ ions or ion associates ($h_{1,1}$ at $\bar{\nu}=1$), $Q = \nu_+^{\nu_+}\cdot\nu_-^{\nu_-}$.
The values of the electrolytes activity coefficient in dry organic sol-
vents ($\bar{\gamma}_{0,\bar{\nu}}$) have been obtained experimentally only for a few systems.

For the systems with a partially dissociated electrolytes in ext-
racts and $\bar{\gamma}_{0,\bar{\nu}}=1$ the following equation has been derived:

$$\bar{m} = \sum \bar{m}_{\bar{\nu}} = \sum \left\{Q\cdot\bar{Q}^{-1}\cdot K_{a_w,\bar{\nu}}\cdot m^{\nu}\cdot\gamma_{\pm}^{\nu}\cdot\exp\left[\bar{\nu}\cdot h_{1,\bar{\nu}}\cdot(a_w-1)\right]\right\}^{\nu/\bar{\nu}}, \tag{3}$$

where $\bar{m}_{\bar{\nu}}$ is the concentration of the electrolyte dissociated into $\bar{\nu}$
ions.

It follows from the equations (2) and (3) that the analysis of
$LnK_{\bar{\nu}}$ as a function of a_w makes it possible to determine the state of

the electrolyte in the extract: in the general case when the dissociation is not complete the functions are non-linear, in the particular cases of the total dissociation into $\bar{v}$ ions or in the absence of dissociation ($\bar{v}=1$) the functions are linear.

We used the equation (3) to describe equilibrium in a wide variety of systems. We have found that in many cases the determination of parameters is often a poorly stipulated task. Moreover, there is a strong correlation between the thermodynamic distribution constants and the degree of hydration: within given experimental error it is possible to describe the extraction equilibrium using different sets of parameters for the model. Nevertheless, for the systems where the organic phase nonideality is mainly due to hydration and dissociation of electrolytes the equation (3) provides wide possibilities for the interpolation of the experimental data. Moreover this equation describes different types of the extraction isotherms. An adequate description of the equilibrium is obtained for a wide range of the component concentrations. For example Pendin at al [6] have reported the data on the perchloric acid extraction by alyphatic alcohols for 4 and 5 order changes of the acid concentration in the aqueous and organic phases.

In this case mean relative deviations between the results of the equation (3) and the experimental data, as we have found, are 8-10%, mean absolute deviations are about 0.006-0.06 mol/kg of alcohol. The results are given in the Table for the system with nonyl alcohol. The values $\gamma_\pm$ and a_w for aqueous solution of the acid were obtained by the interpolation of data tabulated in [7]. The values of

The isoterm extraction of the perchloric acid by nonyl alcohol

m	a_w	$\gamma_\pm$	$\overline{m}$	$\overline{m}_1$	$\overline{m}_2$
0.0006	0.99997	0.972	$1.0 \cdot 10^{-5}$	$8.4 \cdot 10^{-6}$	$9.0 \cdot 10^{-8}$
0.0011	0.99996	0.963	$1.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$3.0 \cdot 10^{-7}$
0.0017	0.99993	0.955	$2.1 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$7.1 \cdot 10^{-7}$
0.0056	0.99980	0.925	$1.2 \cdot 10^{-4}$	$7.2 \cdot 10^{-5}$	$7.2 \cdot 10^{-6}$
0.0073	0.99974	0.917	$9.2 \cdot 10^{-5}$	$9.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
0.0076	0.99973	0.915	$1.8 \cdot 10^{-4}$	$9.7 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$
0.076	0.9974	0.814	0.0020	0.0009	0.0010
0.141	0.9952	0.786	0.0048	0.0015	0.0031
0.183	0.9938	0.776	0.0070	0.0020	0.0050
0.628	0.9715	0.777	0.0474	0.0068	0.043
1.02	0.9601	0.828	0.129	0.012	0.11
1.06	0.9588	0.835	0.130	0.012	0.12
1.97	0.9213	1.045	0.392	0.028	0.37
3.06	0.8586	1.478	0.732	0.061	0.72
4.32	0.7691	2.353	1.08	0.13	0.99
5.22	0.6922	3.398	1.30	0.23	1.06
5.47	0.6768	3.775	1.41	0.26	1.07
6.98	0.5503	7.379	1.80	0.63	1.07
7.92	0.4737	11.404	2.15	1.08	1.09

$\gamma_\pm$ for diluted solutions were determined using the Debay - Hukkel equation.

The results of the equilibrium description enable one to analyse the concentration dependences of the dissociation degree ($\alpha = \bar{m}_{\bar{\nu}}/\bar{m}$) of a electrolytes in the mixtures of water-organic solvents. For example, the complete dissociation of the percloric acid is observed at $\bar{m} < 0.0001$ (Table).

For the extractants with high extraction power the contribution of solvation into the nonideality of the organic phase should be taken into account. If we neglect the activity coefficients of the complex and extractant (S), then for the extraction constant of the electrolyte dissociated into $\bar{\nu}$ ions we can obtain:

$$K_{\bar{\nu},\bar{q},a_w} = \frac{\bar{Q}\,\bar{m}^{\bar{\nu}}\,\bar{\gamma}_{\bar{\nu}}^{\bar{\nu}}}{Q\,m^\nu\,\gamma_\pm^\nu\,\bar{m}_s^{\bar{q}}\,\bar{\gamma}_s^{\bar{q}}} = K_{\bar{\nu},\bar{q}}\cdot\bar{Q}\cdot\exp\left[\Delta h(1-a_w)\right], \qquad (4)$$

where $\Delta h = \bar{\nu}\,h_{\bar{\nu},\bar{q}} - \bar{q}\,h_s$, h_s is the degree of extractant hydration.

The breaks on the curves $LnK_{\bar{\nu},\bar{q}}$ as a function of a_w enable one to determine the solvation numbers $\bar{q}$, as well as can show the presence of electrolytical dissociation in the extracts. The composition of complexes thus obtained agrees with the acoustic investigations /8/.

Nowadays there are different methods of the activity coefficients calculations for components of multicomponent aqueous electrolyte solutions. They make it possible to describe the effect of the extracted and nonextracted salting-out on the distribution of micro- and macrocomponents. For the systems with the nonstoichiometric hydrato-solvates we have found that curves $LnK_{\bar{\nu},\bar{q}}$ as a function of a_w for binary and multicomponent solutions fit one curve, whereas for the systems with stoichiometric solvates a spread of data is observed.

In literature an approach based on the idea of stoichiometric hydration is widely spread. We have compared the hydration numbers, determined for a number of systems within the framework of this approach using the slope analyses (h), with the values $h_{1,\bar{\nu}}$ and $h_{1,\bar{\nu},\bar{q}}$. It has been found that in several cases a simple dependence is observed:

$$h = (h_{1,\bar{\nu},\bar{q}}\,a_{w,1} + h_{1,\bar{\nu},\bar{q}}\,a_{w,2}) / 2 , \qquad (5)$$

where $a_{w,1}$ and $a_{w,2}$ are the maximum and minimum water activities in the electrolyte aqueous solutions, used in the experiments for h determination.

In aqueous-organic solutions of several electrolytes it is necessary to take into account not only nonstoichiometric, but also coordinational hydration. It can be shown that in this case the contribution of hydration into the activity coefficient of the solute is given by the formula

$$\Upsilon = \Upsilon_0 \exp\left[h_c + h_1 \, (1 - a_w)\right], \tag{6}$$

where h_c is the stoichiometric hydration number. The value of h_c depends on the electrolyte nature.

Extractants hydration, as it had been shown previously by numerous investigation [2], has in general a nonstoichiometric character. That is why, taking (6) into account the expression for the extraction constant can be written as follows:

$$K_{a_w, \bar{\nu}, \bar{q}} = K_{\bar{\nu}_{>}} \, \bar{q} \, \bar{Q} \, \exp\left[\bar{\nu} \, h_c + \Delta h \, (1 - a_w)\right]. \tag{7}$$

As it follows from (7), the effect of the stoichiometric hydration on the extraction equilibrium, does not depend on the water activity. The contribution of this factor can be taken into account by the value of the thermodynamic constant.

Thus, the approach which takes into account the hydration of organic phase components, provides the possibility of a simple determination of the distributed substance state in the extracts and description of the extraction equilibrium.

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The solubility of extractant in aqueous phase is valuable, because
it will cause a loss of extractant and will influence the economics
of the extraction process. In this paper the solubility of di(2-ethyl-
hexyl) phosphate acid(D2EHPA) in chloride solutions is measured and
some solution theories are applied to this study.

Experiment and Result

An improved pH titration method was used to determine the solubili-
ty of D2EHPA in pure water, S_0, and the dissociation constant, K_a. The
result is $S_0 = 87.0$ mg/l and $K_a = 10^{-3.60}$ (25°C).

The P-32 tagged D2EHPA was prepared by isotope exchange and it was
equilibrated with chloride solutions. The chlorides include LiCl,
NaCl, KCl, RbCl, CsCl, NH_4Cl and HCl. The highest concentration of the
salts was 3-5 M. The radioactivity in aqueous phase was measured by a
liquid scintillometer to determine the solubility of D2EHPA. The aci-
dity of aqueous solution was kept at about pH 2 in order to prevent
the extraction of metals. The increase of radioactivity because of the
presence of salts in water was corrected. The effect of 0.01 M HCl on
the solubility of D2EHPA subduced also.

The data show that the addition of these salts to the aqueous solu-
tion causes a decrease of solubility of D2EHPA. It can be expressed by
the Setschenow equation

$$k_s = \frac{1}{C} \lg \frac{S_0}{S}, \tag{1}$$

where C is the concentration of salt, S_0 and S are the solubility of
D2EHPA in water and in salt solution, k_s is the salting effect con-
stant. The experiments show that k_s are 0.267, 0.322, 0.283, 0.277,
0.260 and 0.177 for LiCl, NaCl, KCl, RbCl, CsCl and NH_4Cl respectively.
For HCl the k_s increases with the acidity until 1M, after that it is
0.0699.

Calculation

The electrostatic theory, the internal pressure theory and the
scaled particle theory are the representative theories for salting
effect. These three theories and the Pitzer equation are applied to
this study.

1. Electrostatic Theory. The equation deduced by Debye and McAulay
is [1]

$$k_s = \frac{\beta e^2 N_0}{2 \cdot 2.303 \cdot 10^2 kT D_0} \sum_j \frac{\nu_j z_j^2}{\ell_j}, \tag{2}$$

where $\beta = \frac{D_0 - D_n}{D_0} V_n$ [2], D_0 and D_n are the dielectric constants of water
and organic solvent respectively, V_n is the molar volumn of organic
solvent, ν_j is the number of ions in one molecule of salt, Z is the

charge of an ion, $\mathring{b}_j$ is the ionic radius, No is the Avogadro constant, k is the Boltzman constant, T is the absolute temperature. The result calculated from Eq. (2) was given in Table 1. It shows that the calculated data are much higher than the experimental ones. It is obvious that this theory can not correlate the experimental data quantitatively.

2. Internal pressure theory. The equation given by McDevit and Long is [3]

$$k_s = \frac{V_1^o(V_s-V_s^o)}{2.303\beta_0 RT} = \frac{V_1^o}{2.303RT}\frac{\partial Re}{\partial Cs},$$ (3)

where V_1^o and V_s^o are partial molar volumes of non-electrolyte and electrolyte at infinite dilution, V_s is molar volume of pure (liquid) electrolyte, β_0 is the compressibility of pure water, P_e is the "effective pressure" exerted by a salt in solution, R is the gas constant.

The calculated result from Eq. (3) is shown in Table 1 also. From Table 1 it can be seen that the calculated values are higher than the experimental ones by a factor of two to three. When a factor $\frac{r}{r+r_n}$ is multiplied to the right side of Eq. (3), the result is improved very much, where r is the mean ion radius of the salt and r_n is the radius of the non-electrolyte molecule. The calculated values are in close agreement with the experiments.

Table 1. Comparison of electrostatic theory (E.T.) and internal pressure theory (I.P.T.) with the experiments (25°C)

Salt	k_s(exp.)	k_s(cal.)		
		E.T.	I.P.T.	
			without $\frac{r}{r+r_n}$	with $\frac{r}{r \cdot r}$
LiCl	0.268	1.08	1.15	0.220
NaCl	0.323	0.787	1.60	0.341
KCl	0.283	0.639	1.28	0.301
RbCl	0.277	0.602	1.15	0.281
CsCl	0.261	0.561	0.958	0.245
NH_4Cl	0.178	0.614	0.511	0.123

3. Scaled particle theory. According to this theory, the salting effect constant of a slightly soluble non-electrolyte of small molecule in 1 1 salts solution at 25°C is given by [4]:

$$k_s = k_\alpha + k_\beta + k_r ,$$ (4)

$$k_\alpha = 2.15\cdot10^{20}(\sigma_3^3+\sigma_4^3)-2.47\cdot10^{-4}\phi_0+\sigma_1[6.45\cdot10^{20}(\sigma_3^2+\sigma_4^2) +$$
$$+ 1.34\cdot10^{28}(\sigma_3^3+\sigma_4^3)-4.23\cdot10^4\phi_0]+\sigma_1^2[6.45\cdot10^{20}(\sigma_3+\sigma_4)+$$
$$+ 4.01\cdot10^{28}(\sigma_3^2+\sigma_4^2)- 1.32\cdot10^{36}(\sigma_3^3+\sigma_4^3) - 4.17\cdot10^{12}\phi_0] ,$$ (5)

$$k_\beta = -1.85\cdot10^{14}(\mathcal{E}_1/k)^{1/2}[\alpha_3^{3/4}z_3^{1/4}\frac{(\sigma_1+\sigma_3)}{\sigma_3^3}+\alpha_4^{3/4}z_4^{1/4}\frac{(\sigma_1+\sigma_4)^3}{\frac{3}{4}}]+$$

$$+6.26\cdot10^{17}\phi_0(\mathcal{E}_1/k)^{1/2}(\sigma_1+\sigma_2)^3+ 4.00\cdot10^2\frac{\phi_0\alpha_1}{(\sigma_1+\sigma_2)^3} ,$$ (6)

$$k_r = 0.016 -4.34\cdot10^{-4}\phi_0,$$ (7)

where $\mathcal{E}_1/k$ is the energy paramater of solute, σ_j is the hard sphere diameter of a particle j, α_j is the polarizability, z_j is the total

155

number of electrons in an ion, Φ_0 is the apparent molar volume of the salt at infinite dilution, subscripts 1, 2, 3 and 4 are the solute (extractant D2EHPA in this paper), solvent (water), cation and anion respectively.

The values calculated from Eqs. (6) to (8) are shown in Table 2. From it we can see that the calculated results are much higher than the experimental values. It points out that the S.P.T. must be improved for the polar non-electrolyte molecule with large size, such as, D2EHPA.

Thus the model of Hu and Prausnitz [5] is applied in this paper, and all types of interactions between particles in solution are considered by the authors, such as Lennard-Jones potential with dipole-dipole and dipole-induced dipole contributions for molecule-molecule interaction and that with additional ion-induced dipole and ion- dipole contributions for ion-molecule interaction. The new equation of k_p is

$$k_p = 9.06 \cdot 10^{17} \left(\frac{\varepsilon_1}{k}\right)^{1/2} (\sigma_1 + \sigma_2)^3 \phi_0 - 2.67 \cdot 10^{14} \left(\frac{\varepsilon_1}{k}\right)^{1/2} \left[\alpha_3^{3/4} z_3^{1/4} \left(\frac{\sigma_1 + \sigma_3}{\sigma_3}\right)^3 + \right.$$
$$\left. + \alpha_4^{3/4} z_4^{1/4} \left(\frac{\sigma_1 + \sigma_4}{\sigma_4}\right)^3\right] + 6.05 \cdot 10^{-2} \frac{\phi_0 \alpha_1}{(\sigma_1 + \sigma_3)^3} + 1.79 \cdot 10^{34} \frac{\phi_0}{(\sigma_1 \cdot \sigma_2)^3} \times$$
$$\times (5.49 \cdot 10^{-23} \mu_1^2 + \alpha_2 \mu_2^2) - 3.22 \cdot 10^{35} \left[\frac{\alpha_3 \mu_1^2}{(\sigma_1 + \sigma_3)^3} + \frac{\alpha_4 \mu_1^2}{(\sigma_1 + \sigma_4)^3}\right] - 5.783 \cdot 10^{25} \times$$
$$\times \left(\frac{\mu_1^2}{\sigma_1 + \sigma_3} + \frac{\mu_1^2}{\sigma_1 + \sigma_4}\right) - 3.570 \cdot 10^{12} \left(\frac{\alpha_1}{\sigma_1 + \sigma_3} + \frac{\alpha_2}{\sigma_1 + \sigma_4}\right). \tag{8}$$

Eqs. (5), (7) and (8) give a new expression of k_s. In this calculation we used the packed factor to estimate the hard sphere diameter and energy parameter of D2EHPA. The calculated result, which is given in Table 2, shows that the result is improved greatly.

Table 2. Comparison of scaled particle theory with the experiments

Salt	k_s(exp.)	original* S.P.T.	k_s(cal.) improved S.P.T.**				
			I	II	III	IV	V
LiCl	0.268	0.563	0.253	0.238	0.484	1.36	0.465
NaCl	0.323	0.807	0.432	0.328	0.474	1.79	0.523
KCl	0.283	0.734	0.466	0.357	0.466	2.26	0.471
RbCl	0.277	0.579	0.283	0.247	0.306	2.41	0.259
CsCl	0.261	0.596	0.361	0.317	0.260	2.76	0.458
NH$_4$Cl	0.178		0.451			3.37	

* The parameters in calculation are: σ_1=10.17Å, ε_1/k=57.4k and Pauling's radii. ** The parameters in calculation are: σ_1=8.8Å, $\varepsilon_{1/k}$=136.9k, I,II,III,IV and V mean that the ion radii are Pauling's, Gourary-Adrian's, Goldsmidt's Latimer's and Weddington's radii.

The data in Table 2 show also that the difference among the values calculated from different ion radii is significant. Among them the Gourary-Adrian's radii are the best and the Latimer's radii are the worst for this calculation.

4. Pitzer theory. The Pitzer equation is widely used to calculate the activity coefficient of electrolyte. We expand Pitzer equation $/6/$ to calculate the activity coefficient of D2EHPA. From this theory the activity coefficient of D2EHPA (HA) can be given by

$$\ln r_{HA} = 2(\lambda_{HA,M}m_{M^+} \ _{HA,Cl}m_{Cl^+}\lambda_{HA,H}m_H)+6(\lambda_{HA,M,Cl}m_{M}m_{Cl} + \tag{9}$$
$$+\mu_{HA,H,Cl}m_{H}m_{Cl}+\mu_{HA,M,H}m_{M}m_{H}),$$

where m is the molal concentration, λ and μ are the bi-particle and triparticle interaction parameters respectively.

Eq. (9) can be simplified to

$$\ln r_{HA} = A+Bm_s + Cm_s^2, \tag{10}$$

where m_s is the concentration of salt. A is a constant, which is independent of the kind of salt, and when pH=2, A=0.209. B and C are constants for each salt, they are obtained by regression of the experimental data (see Table 3).

Table 3. Parameters in simplified Pitzer equation ($25^{\circ}C$)

Salt	B	C
LiCl	0.600	$-6.90 \cdot 10^{-3}$
NaCl	0.754	$-1.25 \cdot 10^{-2}$
KCl	0.644	$-1.63 \cdot 10^{-2}$
RbCl	0.634	$-2.17 \cdot 10^{-2}$
CsCl	0.584	$-1.79 \cdot 10^{-2}$
NH_4Cl	0.390	$-9.54 \cdot 10^{-3}$

Because the extraction of salt is prevented, we have

$$r_{HA} = \frac{m_{HA}}{m_{HA}^{\bullet}}, \tag{11}$$

where $m_{HA}^{\bullet}$ and m_{HA} are the solubility of D2EHPA in pure water and in salt solution. The above equations show that the Pitzer theory can be used to predict the solubility of extractant in aqueous phase.

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Aqueous phases in the extraction systems are multicomponent as a rule.in order to predict the out-salt effect in extraction processes it is necessary to calculate the extractant activity in the presence of electrolytes, i.e. out-salt effects are closely related to problems of the multicomponent solution theory.

The osmotic theory of the mixed isoactive solutions of electrolytes,which was realized on the base of Zdanovsky's law:

$$\sum_{i=1}^{n=i} \frac{m_i}{m_i^*} = 1 \qquad (1)$$

allows to calculate the thermodynamic properties of the multicomponent concentrated aqueous solutions using corresponding properties of the binary solution.

Isoactive mixing of the electrolyte solutions with different ions is followed by ion exchange and formation of quaternary aqueous-salt system, the equilibrium of this system can be wxpressed by:

$$\underset{1}{AM} + \underset{4}{BN} \rightleftharpoons \underset{2}{AN} + \underset{3}{BM} . \qquad (2)$$
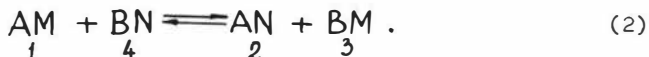
If mixed electrolytes contain cations of the same charge and with approximately equal sizes and character of water ion interaction and anions of equal charge and nature then the system will have approximately equal quantity of four salts.The increasing of difference between electrolytes (type and chemical nature) leads to the prevailing presence of one from the two pairs of salts.

In the present paper we consider two methods based on the osmotic theory of the mixed isoactive solutions of electrolytes.These methods based on the different conceptions of the standard state concern investigation of quaternary water-electrolyte systems of halides and nitrates of alkaline metals of two opposite compositions: $AM - BN - H_2O$ and $AN - BM - H_2O$.

It was noted [1,2] that the parabolic shape of the water isoactivate for mixed electrolyte solutions without common ions was only coused by the ion exchange.

It is general acception that electrolytes are completely dissociated in the standard state.As a result the standard state of any ion is independent from co-ion and thus the thermodynamic equilibrium constant (equation 2) is equal 1.The parabolic equations [3,4] for the calculation of thermodynamic parameters of the quaternary

158

aqueous-salt systems have been obtained, taking into account the ion exchange.We found [2], that in mixed solutions of alkaline metals halides and nitrates without common ions there were practically no interactions, except ion exchange.Therefore disagreement of experimental and theoretical values of thermodynamic parameters is in general the result of the alteration in the ion exchange equilibrium.

Taking into account the deviations Δ in Zdanovsky law determined by isopiestic investigations of the mixed concentrated solutions of alkaline metals halides and nitrates the concentrations of all four components can be determined as M_i - experimental values of concentration of two mixed electrolytes in isopiestic conditions, $m_1 = M_1 - p$, $m_2 = m_3 = p$; $m_4 = M_4 - p$, where p - a concentration of the second pair of electrolytes, formed due to ion exchange. We calculate the activity constant using equation (3), which was obtained for the present standard state:

$$lg\, \gamma_i = lg\, \frac{\nu_i\, m_i^* \gamma_i^*}{\sum \nu_i\, m_i} - (1-X)^2 lg\, \frac{a_1^*\, a_4^*}{a_2^*\, a_3^*} . \qquad (3)$$

The calculations indicated that $m_1 \cdot m_4 = m_2 \cdot m_3$ and $\gamma_1 \cdot \gamma_4 = \gamma_2 \cdot \gamma_3$ i.e. both the concentration constant and the constant which is caused by the change of activity coefficients are equal 1.But the deviations Δ are different for different systems and the largest Δ refers to LiCl + KNO$_3$ $\rightleftharpoons$ LiNo$_3$ + KCl system.

One can formally suppose that four undissociated salts which represent the individual components with their own standard state are in equilibrium.This equilibrium can be characterized by constant K

$$K_e = \frac{a_2 \cdot a_3}{a_1 \cdot a_4} = K_m\, K_\gamma \qquad (4)$$

Following Zdanovsky's law without taking into account the deviation Δ it is possible to calculate the concentration of each component: $m_1 = M_1 - q$; $m_2 = m_3 = q$; $m_4 = M_4 - q$, where q - the change of the concentration because of equilibrium shift.In this case the activity coefficients of the component in the mixed solutions would be determined by Mikulin law:

$$\gamma_i = \frac{\nu_i\, m_i^* \gamma_i^*}{\sum \nu_i\, m_i} . \qquad (5)$$

Then

$$K_\gamma = \frac{a_2^*\, a_3^*}{a_1^*\, a_4^*} . \qquad (6)$$

The obtained values of the ion exchange constants for the electrolyte systems under investigation are in the mutual agreement.It

159

should be noted, that being independent from the way of formation of the electrolyte system, the equilibrium is shifted to the direction of the pair of less soluble salts.It was confirmed by comparison of experimental and calculated values for solution density, using concentration of all four components or concentration of only two mixinh electrolytes with different ions.

Since both constants of the equilibrium (2) and deviations Δ characterize the shift of equilibrium in the system under study then the correlation between them should exist (Fig.1).

Since the deviations Δ_φ depend on water activity, the parameter d in equation (2) is related to abscessa

$$\Delta_\varphi = X(1-X)(e\,a_w + d) . \qquad (7)$$

Fig.2 shows the correlation of $\Delta_{\varphi*} = \varphi_1^* + \varphi_4^* - \varphi_2^* - \varphi_3^*$ with constants of ionexchange equilibrium.The more difference between two pairs of electrolytes, the greater the shift of equilibrium in the system, and it is always in the only direction: to the same pair of salt and independent from the way of formation of the system.
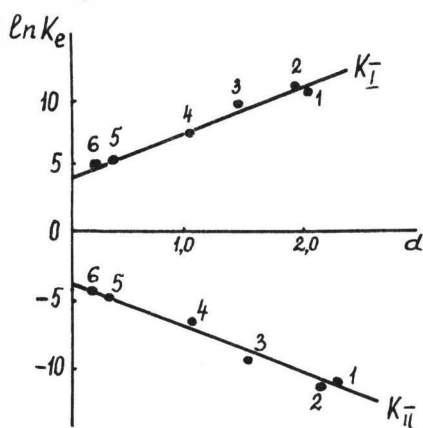
Fig.1. Correlation between constants of ionexchange equilibrium in the quaternary aqueous-salt multial systems and deviations of experimental values of osmotic coefficients from calculated values
1 – LiCl + KNO$_3$ $\overset{K_I}{\underset{K_{II}}{\rightleftharpoons}}$ LiNO$_3$ + KCl;
2 – LiBr + KNO$_3$ $\rightleftharpoons$ LiNO$_3$ + KBr;
3 – LiNO$_3$ + CsCl $\rightleftharpoons$ LiCl + CsNO$_3$;
4 – LiCl + NaNO$_3$ $\rightleftharpoons$ LiNO$_3$ + NaCl;
5 – LiBr + KCl $\rightleftharpoons$ LiCl + KBr;
6 – CsCl + KBr $\rightleftharpoons$ CsBr + KCl
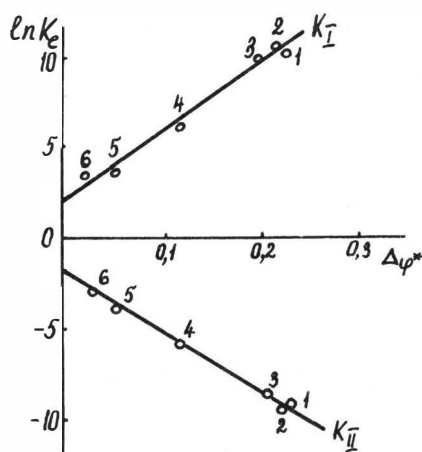
Fig.2. Correlation between constants of ionexchange equilibrium in the quaternyry aqueous-salt multial systems and differences of summes of isopiestic osmotic coefficients for two pairs electrolytes a_w = 0,9600

Fig.3 presents isoactivaties of water in the mixed systems $LiNO_3 - KCl - H_2O$ (1) and $LiCl - KNO_3 - H_2O$ (2).In both cases the experimental points are below of parabolic line (negative deviations of $\Delta_{1/m}$) The sign and magnitude of this deviations are the same (K = 1).In contrast to thermodynamic constant of equilibrium (2), containing complete information about equilibrium shift, the deviations Δ_φ and $\Delta_{1/m}$ do not permit to determine the direction of this shift.At the same time, devia-

Fig.3. Isotherms-isobars of water in mixed solutions of electrolytes $a_w = 0.9299$

tions of the experimental data from linear dependence for two opposite combinations of electrolytes have different sighns and values as well.They are related to the ion exchange and shift of the ion equilibrium.It means that deviations allow to determine the pair of the electrolytes in the direction of which the ion equilibrium was shifted. The analysis of the Fig.3 shows, that equilibrium in the present system would be shifted to $LiNO_3$ and KCl, independently on the pair of electrolytes formed the system.Mixing LiCl and KNO_3 is accompanied by ionexchange and essential shift of the equilibrium resulting in the formation of new pair of salts.It leads to considerable deviations of experimental data from linear dependence taking into account only additivity of properties for mixed electrolytes.Mixing the pair electrolytes of the opposite combination doesn't lead to any change, and hence the deviations are small.

The similar results have been obtained for other systems under investigation.

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Summarization of experimental data files through the use of the
simplest approximating equations is an important part in their syste-
matization. In accordance with the Linear free energy relationships
(LFER) concept $[1,2]$ the equilibrium constants for extractions due to
anion-exchange reactions:

$$\overline{RX} + Y^- \underset{\longleftarrow}{\overset{K_X^Y}{\rightleftharpoons}} \overline{RY} + X^- ;$$ (1)

neutralization reactions:

$$\overline{R_3N} + HY \overset{K_{HY}}{\rightleftharpoons} \overline{R_3NHY};$$ (2)
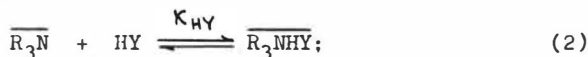
ion-associates formation:

$$R_4N^+ + A^- \overset{K_{ass}}{\rightleftharpoons} \overline{R_4NA}$$ (3)
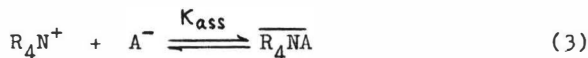
can be defined by equations:

$$\lg K_X^Y = \mathscr{æ} (\Delta G_Y^* - \Delta G_X^*),$$ (4)

$$\lg K_{HY} = a + b \cdot \Delta G_Y^*,$$ (5)

$$\lg K_{ass} = a' + b' \cdot \Delta G_A^*,$$ (6)

where ΔG^* are the parameters of anion hydration[*), $\mathscr{æ}$, a , a', b ,
b' are the parameters, which are steady for individual extraction
system series (a "series" denotes a number of extraction systems
which differ only by anions; the difference between the series lies
in the nature of a cation-extractant and a diluent, the composition
of an aqueous phase, component concentrations etc.)

The algorythm and the OPAG (Evaluation of hydration parameters)
program have been developed $[2]$ which permit evaluating of $\Delta G^*, \mathscr{æ}$,
a , a' , b , b' by the regression analysis and predicting extraction
constants using the available extraction constants for some anions.

Initial specifications are in the form of a matrix of logarythms
for the extraction constants $\lg K_{ij}$ ($i \in N$, $j \in M$; where "N" is the
number of anions and "M" is the number of extraction system series)
and the partially preset vector of a hydration parameter ΔG^*.

Solution of the problem of estimating prediction errors has allow-
ed designing and opting for the most effective sequence of statisti-
cal procedures.

The following stages should be emphasized in the algorythm:

[*) Values of ΔG^* for 92 anions are tabulated in $[2]$.

1. Refinement (mutual coordination) of individual repers (initial values) of ΔG^* under the assumption, according to the LFER concept, of linearity between lgK_{ij} in individual series (j) and of the fact that the most probable value for the ΔG_i^* repers is the mean of the parts falling on regression curves.

2. Evaluation of the experimental data spread about a regression curve (residual dispersion) as well as that of the ΔG^* reper dispersions predicted by a regression curve.

3. Evaluation of dispersion of the ΔG_i^* repers (the reper dispersion, $\hat{G}_i^2$) predicted by regression equation in some series.

4. Indirect evaluation of unknown values of ΔG_i^* and their spreads due to the regression equation derived from the equations (4)-(6):

$$\Delta G_i^* = \hat{\beta}_0 + \hat{\beta}_1(lgK_{ij} - \overline{lgK}_{ij}); \quad i=1,2,\ldots,N; \quad j=1,2,\ldots,M; \qquad (7)$$

where $\overline{lgK}_{ij}$ is the mean of the series. The latter procedure consists of two steps[*]. The first one involves series with the number of repers $n_{ij} \geq 2$; the indirect mean estimates of ΔG^* (the first generation estimates) thus obtained are used at the second step for new series and the second generation estimates[**].

5. Prediction of unknown lgK_{ij} parameters from equation (7) and evaluation of the prediction accuracy. Based upon real parameters $\hat{\beta}_1$, $\sum_i (lgK_{ij} - \overline{lgK}_{ij})^2$ and known equations [3] the root-mean spread of the lgK_{ij} estimates predicted can be given

$$\hat{G}_{tj} = \frac{\hat{G}_j}{\hat{\beta}_1} \left[1 + \frac{1}{n_j} + \frac{(lgK_{ij} - \overline{lgK}_{ij})^2}{(lgK_{ij} - \overline{lgK}_{ij})^2} \right]^{1/2}, \qquad (8)$$

where n_j is the number of independent pairs of experimental lgK_{ij}, ΔG_i^* in the j-series, $\hat{G}_j$ is the ΔG_i^* residual root-mean deviation estimated in the j-series.

The maximum deviation of lgK predicted from lgK_{ij} measured with the error of δ_{ij} is equal to

$$\Delta_{ij} = \sqrt{(\hat{G}_{ij} \cdot t_\alpha)^2 + \delta_{ij}^2},$$

where t_α is the Student factor and $\alpha = 0.05$.

The experimental data matrix involving extraction constants for 92 anions and 92 extraction system series (559 values of lgK in total) were originally processed on a computer using the OPAG program [2]. Unknown lgK values amounting up to $\sim 93\%$ of the completed matrix were estimated ($\widehat{lgK}_{ij}$).

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[*]The number of steps can be more than 2 at the adverse data sets.
[**]The weighted least-square method and the weighted averaging is used for the second generation estimates.

As a check upon the estimated accuracy of prediction experimental lgK for 47 anions in 16 series (86 in total) published later and not covered by [2] were used [4].

The histogram of the prediction errors for these additional systems is shown in fig. 1.
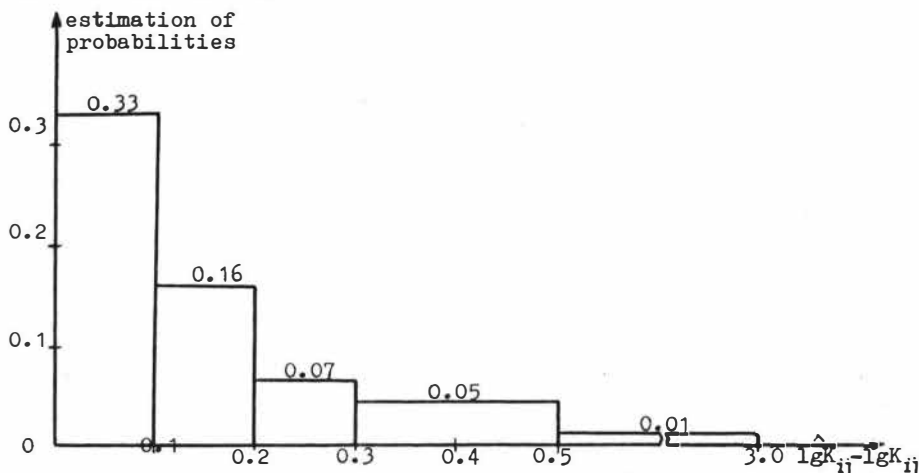
Fig. 1. Histogram of prediction errors for 86 additional experimental systems

It is shown that among the 86 lgK values 80 (93%) proved to be within the accuracy estimated: the 3 (3.5%) spread is due to rough experimental errors and only 3 (3.5%) is not attributable to external reasons.

Thus, the LFER concept ensures summarization of high quality for experimental extraction constants. The spread of predicted and experimental data primarily results from experimental errors ($\delta_{ij} = 0.5$[5]). In many cases errors of prediction can be less than experimental errors. High accuracy and reliability of estimation with OPAG (as evidenced in series with a good proportion of experimental lgK) makes it unnecessary to determine unknown lgK values from a great number of experiments. Requirements for the lgK prediction accuracy governed by a particular application . If, for instance, an acceptable level of the estimated root-mean error is assumed to be $\sigma_{ij\ acc.} = 0.2$ a fraction of lgK which does not require experiments for the 92 x 92 file will account for $\sim 30\%$ ($\sim 1.2 \cdot 10^5$) systems. At $\sigma_{ij\ acc.} = 0.3$ constants for $\sim 50\%$ or $\sim 2.0 \cdot 10^5$ systems are predicted with an acceptable accuracy.

OPAG is not only cost- and time-effective, it is also suitable in optimal designing experiments for determination new extraction constants.

As criteria of optimum use can be of:

-quantity of constants additionally estimated (with a preset accuracy) at the preset number of experiments;
-an error of estimation of constants for given systems etc.

Moreover, comparison between estimated and experimental data enables to reveal rough experimental errors.

At the present time quite a number of new experimental lgK values for both univalent and multivalent anions has been published which makes it possible to increase the format of the initial data matrix up to N = 235 and M= 287. In the nearest future conclusive results will be available upon processing new file with a modified OPAG2,which permits to predict lgK for any of $\sim 10^7$ extraction systems (~ 40000 combinations of 235 ΔG^* values taken 2 a time, involved into each of 287 series) and to calculate root-mean errors of estimation for each of them. The summarization efficiency i.e. the ratio of the number of constants represented to that of parameters, approaches $\sim 10^4$.

Preliminary results have shown the linear correlation between α' and $\varkappa$ for the anion-exchange reaction of the type (1) when the X^--anion connected with quadrary ammonium base is the same and equation (4), consequently, can be rearranged to:

$$ \lg K_X^Y = \alpha'' + \varkappa \; \Delta G_Y^* , $$

For different X^- -anions the correlation forms rays coming, at first approximation, from the origin of coordinates at different angles. The possibility of the secondary summarization offers promise for an additional reduction of approximating parameters.

In conclusion it should be noted that OPAG has also been successfully used for summarization the file of constants for the organic compounds "physical" distribution between water and various organic diluents (90 diluents for 370 compounds) using an empirical parameter VR^* (diluent effect) [6].

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The thermodynamical interphase distribution constant for a given molecular form is an important extraction system characteristic. The distribution constant (DC) value depends on the properties of distributed species as well as those of both phases. It depends on the Gibbs free energy variation assotiated with resolution of a molecular form in its transfer from one phase (an aqueous layer) to another one (an organic layer). Estimating DC was the subject of many works. At present, we know of two most general patterns governing DC variations, (i) the additivity rule for logarithms of DC (increment approaches [1]) and (ii) linear relations like $lgK_D = A + B IS^*$ where IS^* is the parameter of a solvent non-specific solvation suggested by V.S.Shmidt, B is the parameter of a distributed substance, and A is the logarithm of the distribution constant between water and a standard solvent [2]. Both patterns are claimed to derive from the principle of linear relations for free energy variations (PLRFEV). They are complemantary to each other, for the first one accounts for the contribution to DC from distributed species and the second one for solvent affects. (Although B values are no less interesting, the IS^* ones have historically, especially at the initial stage, been the major interest.) We analyzed a large number (1500) of DC values from the point of view of their compliance with the patterns mentiones above. The compounds studied included various organic analytical reactants and chelates. As a result we have found new patterns that may be of interest for both theory and practice of extraction and that do not follow habitual linear relations. Our purpose was to obtain a form of generalized expressions for the standard chemical potential of a substance such that would embrace both approaches mentioned above and new patterns discovered by us.

First we studied solvent effects. Determining patterns of IS^* variations is an important task requiring an analysis of a large array of IS^* values. To increase the number of IS^* values we compared available ones with various energy parameters such as the Snider $\mathcal{E}^o$ parameter used in adsorption chromatography, the δ_o Hildebrand parameter which, by definition, depends on free energy variations nonlinearly, water solubility in organic solvents (Fig. 1), adhesion tension at a liquid/quartz glass interface, optical absorption bands of solutions of mesityl oxide (500 nm), acetone (265 nm), palladium di-n-butyldithiophosphate (295 nm), and antraquinone (300 and 325 nm), and mer-

cury tension at mercury/solvent interfaces. The dependences of these parameters on IS^* are either linear or contain two intersecting linear regions. These data have enabled us to increase the number of IS^* values from 43 known ones to 160 and determine the IS^* value for water, 12 ± 2. We have also been able to show that for a given homologous series, IS^* values depend linearly on the number of carbon atoms in homologues (this has been checked for molecules containing up to 5-10 carbon atoms) the diference in IS^* for neighbour members depending substantially on the nature of the functional group present (it correlates linearly with the functional group dipole moment). The IS^* vs. n_C dependence for alcohols can be extrapolated to a value of about 12 for water.

Fig. 1. Water distribution constant as a function of IS^* in water/organic solvent systems. 1 - Octane, 2 - heptane, 3 - hexane, 4 - cyclohexane, 5 - carbon disulphide, 6 - carbon tetrachloride, 7 - tetrachloroethylene, 8 - p-xylene, 9 - ethyl benzene, 10 - toluene, 11 - chlorobenzene, 12 - benzene, 13 - dichloroethane, 14 - methylene chloride, 15 - chloroform, 16 - 2-nitropropane, 17 - diethyl ether, 19 - 2,2-trimethylpentanol-3, 18 - diisopropyl ether, 20 - isobutanol, 21 - n-butanol

At the second stage we have studied cintributions to DC from distributed substances. The homologous difference has been found to be approximately constant in the IS^* range of -1.1 to 6.5. In other words, the $lgK_D(IS^*)$ straight lines are parallel to each other for homologues of the same series. This is in agreement with the observation that the homologous difference depends only slightly on the solvent nature and the nearest functional environment of the CH_2 group. The following controversy arises. In fact, linear $lgK_D(IS^*)$ dependences describe the transfer of a substance from a standard solvent to another organic solvent. We can substitute water for the latter (its IS^* value is now known). The free energy variation should then be equal to zero independently of the nature of a sustance (the transfer from water to water), and we have $A = -B\, IS^*(H_2O)$, that is the straight lines should intersect each

167

other at a certain point, although they should be parallel to each
other for homologues according to what has been said above. To re-
concile the physically clear conclusion of intersection of straight
lines at one point with the observation of their parallelism we
should reject the idea that the dependences are linear over the whole
range of IS^* variations: at a certain IS^* value they are bound to de-
viate from linearity, all of them tending to the point corresponding
to water. There are examples. For copper(II) 2-methyloxyquinolinate,
benzoyl acetone, 1-nitroso-2-naphtol, and 2-nitroso-1-naphthol, the
inflection point corresponds to IS^* of 4.5, for lead(II) dithizonate
and copper(II) and scandium(III) 8-oxyquinolinates it is 5-6, and for
thenyl trifluoroacetone it is 7.5. Beyond the inflection point the
correlation is often spoiled. Treating data on the distribution of
carboxylic asids and the solubility of hydrogen and methane in vari-
ous solvents has allowed us to determine characteristic homologous
difference variations: toluene ($IS^* = 1.8$), 0.66 ± 0.08; benzene
(2.3), 0.66 ± 0.08; chloroform (4.5), 0.61 ± 0.06; diethyl ether
(6.0), 0.45 ± 0.1; iso-butanol (9.6), 0.45 ± 0.1; methanol (11.5),
0.37 ± 0.2, and water (12), 0 (by definition). Thus the dependence
$A = -B \, IS^*$ cannot hold because of the CH_2 group properties and there-
fore no unified solvent scale from heptane to water can be construc-
ted such that linear relations for DC of organic substances be obser-
ved within its frame. On the other hand, the linearity holds with
many inorganic FG (functional groups) and compounds (e.g. water). Ma-
thematically, this is expressed by the empirical equation $(A-n_C 0.55)/$
$/B = -IS^*(H_2O)$ where n_C is the number of carbon atoms in a distributed
substance, and 0.55 is an average carbon atom increment (homologous
difference), Fig. 2. We only came across a single deviation from this
equation, with copper(II) acetyl acetonate, and the axperimental data
themselves were controversal in that instance. The observed patterns
can be described by adopting the following mathematical expression
for the standard chemical potential of substance i in medium j:

$$\mu^o_{ij} = SP^h_i \, MP^h_j - T \, SP^s_i \, MP^s_j + \mu^o_{iv} \, ,$$

where SP is the substance parameter, MP is the medium parameter (for
vacuum, $MP_v = 0$), μ^o_{iv} is the standard chemical potential of a substance
under vacuum, and T is the absolute temperature. The first two terms
in this expression would be natural to associate with the enthalpy
and entropy contributions to the potential as is indicated by the su-
perscripts. This conclusion is directly substantiated by the data on
limiting thermodynamic functions of disolving a number of homologues
in various solvents. These data are, however, not numerous enough to
serve as conclusive evidence. Nevertheless the suggested mathematical
formalism describes inflection points, makes it possible to deduce the

dependence shoun in Fig. 2, and explains constant homologous differen-
ces for distributed substances and variability of homologous differen-
ces for IS* (the parameters SP_j and MP_j for the same substances can be
related to each other through vaporization thermodynamic functions).
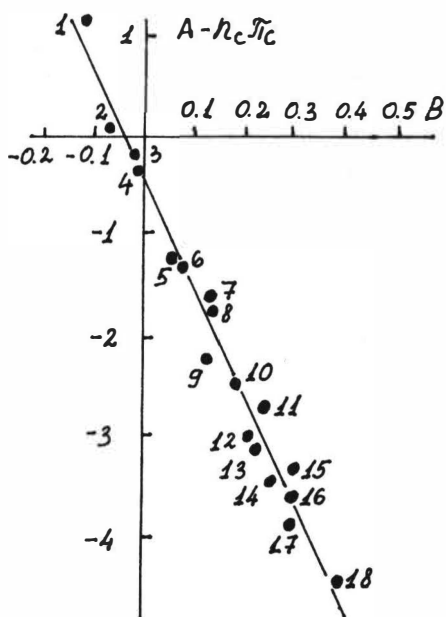
Fig. 2. Parameter B as a function of $A-n_c\widehat{\pi}_c$ where $\widehat{\pi}_c$ is the homolo-
gous difference for the water - standard organic solvent system,
IS* = 0: 1 - alkanes, 2 - alkyl benzenes, 3 - ethers, 4 - esters, 5
- ketones, 6 - nitroalkanes, 7, 8, 9 - primary, secondary, tertiary
amines, respectively, 10 - o-chlorophenol, 11 - beta-diketones, 12
- 8-alkyloxyquinolinates, 13 - nitroxyl tracers, 14 - alcohols, 15
- p-chlorophenol, 16 - 8-alkylmercaptoquinolinates, 17 - carboxylic
acids, 18 - nickel dimethyl glyoximate

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The term "binary extraction" is used to denote acid and salt (hydro-
xide) extraction processes by the salts of organic acids and organic
bases. The extraction of some salts by the carboxylates of amines and
quaternary ammonia bases was studied by J.Devis and R.R.Grinstead [1],
M.L.Naphtanovich and V.L.Heifetz [2], T.Sato et.al. [3]. But all these
works didn't contain the broad analysis of the major regularities of
the process of binary extraction and possibilities of its application.
The processes of binary extraction of acids and salts can be written
(with the example of organic salts of QAB - quaternary ammonia bases)
as follows:

$$mH^+_{(aq)} + B^{m-}_{(aq)} + mR_4NA_{(o)} \underset{K_{M_m B}}{\overset{K_{H_m B}}{\rightleftharpoons}} (R_4N)_m B_{(o)} + mHA_{(o)} , \quad (1)$$

$$mM^{n+}_{(aq)} + nB^{m-}_{(aq)} + mnR_4NA_{(o)} \underset{K_{M_m B_n}}{\rightleftharpoons} n(R_4N)_m B_{(o)} + mMA_n_{(o)} . \quad (2)$$
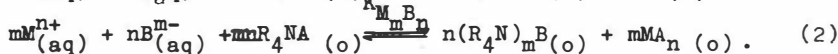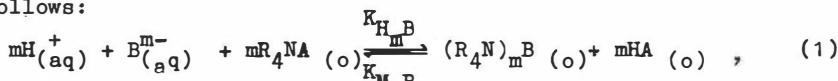
As one may see from the equations (1,2) the binary extraction is cha-
racterized by the transition of cation and anion of the extracted com-
pound in stoichometric ratio from aqueous to organic phase similar to
extraction by the neutral extractants and contrary to the cation-ex-
change and anion-exchange extraction, when the ions between the phases
exchange stoichometrically. On the other hand, contrary to addition
reaction (as is the case in extraction by neutral extractants), in bi-
nary extraction exchange reaction takes place. Consequently, in spite
of the fact that binary extraction is specified by formation of the
same extracted compounds, as in the cation-exchange and anion-exchange
extraction, the major regularities of distribution differ principally
from those for the systems with ion-exchange and neutral extractants.

Acid binary extraction. Activity coefficients of organic phase com-
ponents being constant the isotherm of distribution of acid $H_m B$ is de-
scribed by the equation

$$C_{H_m B (o)} = \overline{K}^{1/(m+1)}_{H_m B} C^{m/(m+1)}_{R_4NA(o)} C_{H_m B(aq)} \gamma_\pm (3)$$
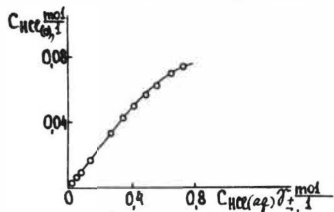
As you may see from the Fig.1, the initial
part of binary extraction isotherm is line-
ar (independent from basicity of the acid)
unlike the isotherm of acid extraction by the
neutral extractants. On account of that the
binary extractants are effective in small
concentrations region of the extracted acids
($D_{H_m B}$=const), where the distribution coef-
ficients essentially decrease in systems
with the neutral extractants.

Fig.1. HCl extraction by
o,1M di(2ethylhexyl)di-
thiophosphate tetraoctyl-
ammonia in toluene

When the ratio of protons and anions of mineral acid in aqueous or organic phases is not stoichometric the expression for the anion distribution coefficients has the form

$$\lg D_B = \lg \overline{K}_{H_m B} + m\lg C_{R_4 NA(o)} - m\lg C_{HA(o)} - mpH . \quad (4)$$

With the constants $C_{R_4 NA(o)}$ and $C_{HA(o)}$ linear dependences $\lg D_B$ on pH with $tg\alpha$ equal to -m are obtained, i.e. the basicity of extracted acids (Fig.2). The dependence of $\lg D_B$ on pH is most important, because they inform us about the extraction and stripping conditions and also about the efficiency of separating different mineral acids (extraction series). The anion distribution during the binary extraction differs from their distribution during anion-exchange extraction, when D_B in the broad region of pH practically doesn't change (Fig.3).
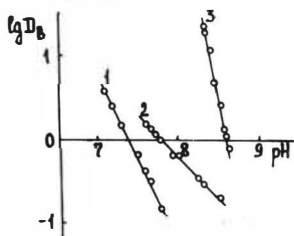
Fig.2. H_2SO_4(1), HCl(2) and $H_4[Fe(CN)_6]$(3) extraction by 0.1M 4-tretbutylphenolate tetraoctylammonia in toluene

From eq.(4) it follows that the extractant concentration, as usual, influences the distribution coefficient. Unlike the other classes extraction, the shift of extraction equilibrium in the systems with binary extractants is achieved by the change in the concentration ratio of two extracted compounds, for example, by increasing concentration of organic acid (Fig.4) or of the mineral salt QAB in organic phase (Fig.5).
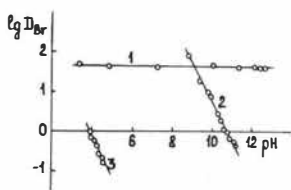
Fig.3. Br-ion distribution in systems with 0.1M solutions of bromide (1), 4-tretbutylphenolate (2) and caprylate (3) tetraoctylammonia in toluene $(C_{SO_4^{2-}} = 1M)$
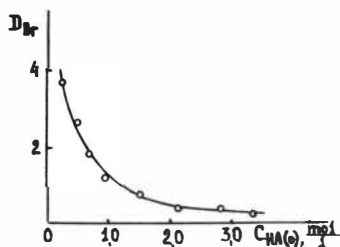
Fig.4. HBr extraction by 0.1M caprylate tetraoctylammonia solution in toluene depending on the caprylic acid concentration

The analysis of the equation, connecting the binary extraction constant of the acid $K_{H_m B}$ with physical-chemical constants of simpler processes (constants of distribution K_{HA} and dissociation K_a of the

171

organic acid, of the anion exchange of the anions of the mineral K_{B-OH} and organic K_{A-OH} acids)

$$K_{H_mB} = \frac{K_{HA}^m}{K_a^m} \frac{K_{B-OH}}{K_{A-OH}^m} \quad (5)$$

shows, that for the same binary extractant, the value K_{H_mB} is determined by the value of K_{B-OH}^m. Thus the acid extraction series $HReO_4 > HJ$, $HSCN >$ $HBr > HCl > HF$ (Fig.6) corresponds to the wellknown anion-exchange series for
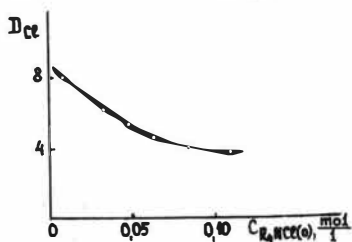
Fig.5. HCl extraction by 0.1M caprylate tetraoctylammoni$_a$ in toluene depending on R_4HCl concentration

QAB salts. The dependence of lg D_B on pH for HF is unusual due to incomplete dissociation of HF in aqueous solution. The given dependence can be used to define acid dissociation constant of extracted acid from the data of distribution in systems with binary extractants.
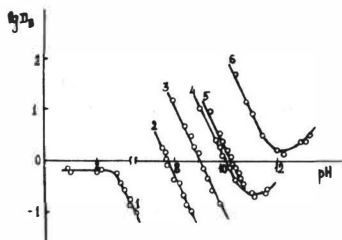
Fig.6. HF(1), HCl(2), HBr(3), HSCN(4), HJ(5) and $HReO_4$(6) extraction by 0.5M 4-tretbutylphenolate tetraoctylammonia solution in presence of 1.5M 4-tretbutylphenol
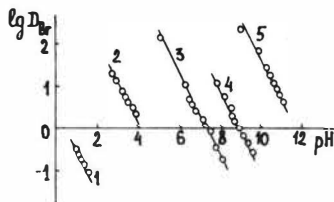
Fig.7. HBr extraction by 0.1M tetraoctylammonia salts solutions in toluene: di(2-ethylhexyl)phosphate (1), caprylate (2), 2-brom-4-alkylphenolate (3), 4-tretbutylphenolate (4), 2-tretbutyl-4-ethylphenolate (5) in presence of 0.3M of the corresponding acids

An important advantage of binary extraction is the possibility of varying extraction properties of extractants when using the organic cations or organic anions of different nature. During binary extraction research of HCl, HBr and HJ one showed, that extraction power of the binary extractants (organic salts of QAB and amines) increases in tetraoctylammonia salts series: di(2-ethylhexyl)dithiophosphate < di(2-ethylhexyl)phosphate < n-caprylate < d,d -dialkylmonocarboxylate < 2-brom--4-alkylphenolate < 4-tretbutylphenolate < 2-tretbutyl-4-ethylphenolate. This series, mainly, corresponds to the decrease of acid dissociation constant of organic acids (Fig.7). The binary extractants on the basis of alkylphenolates are mostly efficient in acid extraction - they

172

gield high distribution coefficients when extracting acid from neutral and alkaline solutions. In forming the R_4NA molecule steric effects can play an essential part for the binary extractants formed by organic acids with close values of K_a. Here due to decrease of K_{A-OH} (see eq.5) K_{H_mB} constants in the systems with sterically hindered anions increase, as, for example, in extracting by 2-tretbutyl-4-ethylphenolate tetraoctylammonia (Fig.7) compared to 4-tretbutylphenolate tetraoctylammonia. The analogous data were obtained in systems with $\prec,\prec$-dialkylmonocarboxylate QAB compared to caprylate QAB. The usage of organic cations of various nature and structure provides the additional possibilities to influence the properties of binary extractant.

Distribution in systems with binary extractants can be affected by factors which have not been considered before. For example, the dependences 4 and 6 in the Fig.6 are curve-linear, which is specific for the transition from acid binary extraction to salt binary extraction. H-bonds of organic acids with mineral and organic QAB salts influence essentially the extraction equilibrium. NMR-^{1}H and IR-spectroscopy and extraction data showed that interaction in the series of tetraoctylammonia salts enhances : $R_4NReO_4 < R_4NJ < R_4NBr < R_4NCl$ in accordance with the decrease of anion ion radius (Fig.8). The composition of the
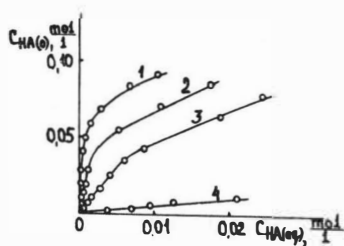
Fig.8. The phenol distribution between 0.04M chloride (1), bromide (2), iodide (3) tetraoctylammonia solutions in CCl_4, pure CCl_4 (4) and 0.5M potassium salts solutions
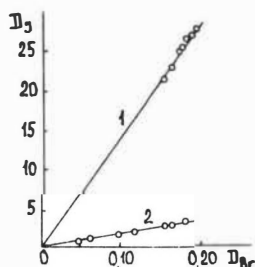
Fig.9. J^-- and Br^--distribution in systems with 0.1M solution of tetraoctylammonia salts (1) and 0.5M solution of potassium salts, 2 -the same's in presence of 0.3M 4-tretbutylphenol

formed adductors R_4NA and HA (as well as $(R_4N)_mB$ and HA) depends on the type and structure of organic acids and their anions. Using the theory of ideal associated solution we carried out the quantitative description of HCl and HBr extraction by 4-tretbutylphenolate tetraoctylammonia. Formation of H-bonds $(R_4N)_mB$ with HA in most cases causes the decrease of separation coefficients of anions during acid binary extraction, compared to the anion exchange data in systems with mineral QAB salts (Fig.9). This defect can be eliminated by binding the forming organic acid with electron-donor neutral extractants. Thus,
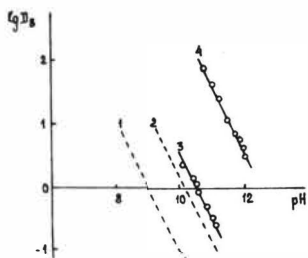
Fig.10. HBr(1,3) and HJ(2,4) extraction by 0.1M 4-tretbutylphenolate tetraoctylammonia solution in toluene in presence of 0,3M 4-tretbutylphenol (1,2); in presence of 0.35M octadecylamine (3,4)
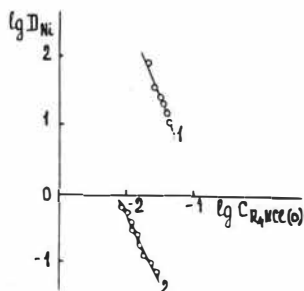
Fig.11. The dependence of D_{Ni} on R_4NCl concentration during the binary extraction of $NiCl_2$ by $\measuredangle,\measuredangle$ -dialkylmonocarboxylate (1) and di(2-ethylhexyl)phosphate (2) tetraoctylammonia

the separation coefficients of halogen-hydrogenous acids in systems with binary extractants with add of primary amine increase to 1-3 orders (Fig.10).

Salt binary extraction. Cation and anion distribution coefficients during the binary extraction of salts is expressed in form of equations:

$$D_M = \frac{C_{MA_n(o)}}{C_{M^{n+}(aq)}} = K_{M_mB_n}^{1/m} \frac{C_{B^{m-}(aq)}^{n/m}}{C_{(R_4N)_mB(o)}^{n/m}} \cdot \frac{C_{R_4NA(o)}}{} \cdot (6) \qquad D_B = \frac{C_{R_4N_mB(o)}}{C_{B^{m-}(aq)}} = K_{M_mB_n}^{1/n} \frac{C_{M^{n+}(aq)}^{m/n}}{C_{MA_n(o)}^{m/n}} \cdot C_{R_4NA(o)}^{m} \cdot (7)$$

The dependence D_{Ni} on $C_{R_4NCl(o)}$, which illustrate the influence of ratio between change of two extracted compounds, in organic phase are shown in Fig11. As one can see from equations (6,7), the cation distribution coefficients depend on anion concentration, and anion distribution coefficients depend on cation concentration of the extracted salt, which is an other difference of binary extraction from ionexchange processes. Thus, cation and anion distribution coefficients are interconnected, and the tangent of the slope angle of the dependence of lgD_M on $lg\, D_B$ is equal to the ratio of the charges of the cations and anions (Fig.12). Fig.13 presents the data on extraction of nitrate by di(2-ethylhexyl)dithiophosphate tetraoctylammonia essential influence of $C_{NO_3^-(aq)}$ on D_M.

The expression of interconnection of salt binary extraction constant with the physical-chemical characteristics of initial systems with organic acids and mineral salts QAB has the form:

$$K_{M_mB_n} = \frac{K_{HA}^{mn} K_{M-H}^m K_{B-OH}^n}{K_a^{mn} K_{A-OH}^{mn}} . \qquad (8)$$

From equation (8) followes, that during extraction of the salts with the same anions, the sequence of extraction must be in accordan-
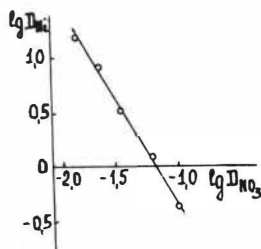
Fig.12. The dependence of $\lg D_{Ni}$ on $\lg D_{NO_3}$ during the extraction by 0,25M di(2-ethylhexyl)dithiophosphate tetraoctylammonia solution in toluene

Fig.13. Cu(1), Zn(2), Ni(3), Co(4), Ca(5) nitrate extraction by 0,2 M di(2-ethylhexyl)dithiophosphate tetraoctylammonia solution in toluene

Fig.14. NiJ_2 (1), $Ni(NO_3)_2$ (2), $NiCl_2$ (3), $NiSO_4$ (4) extraction isotherm by 0.25 M di(2-ethyl)-dithiophosphate tetraoctylammonia solution in toluene

ce with the values of metal-hydrogen exchange constant K_{M-H}, i.e. with the cation-exchange extraction series for the initial organic acid, which is confirmed experimentally: $Cu(NO_3)_2 \gg Zn(NO_3)_2 > Ni(NO_3)_2 > Co(NO_3)_2 \gg Ca(NO_3)_2$ (Fig.13). The extraction series, obtained from the results on binary extraction of Ni salts with different anions (Fig.14): $NiJ_2 > Ni(NO_3)_2 > NiCl_2 > NiSO_4$ coincides with the anionexchange extraction series for QAB salts.

Studying the influence of binary extractant composition its extraction power with reference to $NiCl_2$ we obtained the series: n-caprylate $> \measuredangle, \measuredangle$ -dialkylmonocarboxylate>di(2-ethylhexyl)phosphate>di(2-ethylhexyl)dithiophosphate tetraoctylammonia, qualitatively corresponding to the enlargement of K_a (see eq. 8).

Thus in the systems with binary extractants the use of the qualities of initial ionexchange extractants (efficient separation) is combined with new ways of process control. The formation of stable R_4NA salt makes the stripping easier.

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In the typical chelate extraction process of metal ions, the
extraction process can be explained simply by considering the
following two key steps, i.e. (a) the neutral chelate formation
between the metal ion and the acidic chelating agent in an aqueous
phase and (b) the partition of the extractable chelate into an
organic phase. The separation efficiency of two metals, M and M',
with a chelating agent HA is simply shown as the ratio of the
corresponding extraction constants K_{ex}/K_{ex}'. The K_{ex} is the two-
phase mixed constant and rewritten as $\beta_{MA_n} P_{MA_n} K_{HA}^{-n} P_{HA}^{-n}$, where β
is overall formation constant of metal chelate, P the partition
coefficient, and K the protonation constant of chelating agent.
However, despite the great advance of coordination chemistry on
chelate formation in the aqueous solution, we have not enough
information on the liquid-liquid partition of the metal chelate.
It is a surprising fact that we can not find any quantitative
description on the liquid-liquid partition of the extractable
chelate in authenic literatures on the solvent extraction chemis-
try. We have carried out a systematic study on the solvent effect
governing the partition of nonelectrolytes including metal
chelates and discussed quantitatively the regularity of partition
coefficients of the homologous series of aromatic compounds and
different types of chelates into a series of organic solvents [1-
3][4-10].

In the present paper, it is demonstrated that the partition
coefficients of the neutral chelates MA_n of metal ion M^{n+} with an
acidic chelating agent HA are largely influenced by the central
metals and the chelating ligands. To understand the role of the
central metal ions, it is necessary to compare the partition
coefficients of metal chelates of the central metal ions which
have quite similar chemical natures such as oxidation state and
electronic configuration. The solvent effect on the partition
coefficient is also discussed by the aid of the solution theory,
and finally the role of the partition coefficient in the separa-
tion efficiency of metals will be discussed.

The extraction equilibrium of a metal ion, M^{n+} with an acidic chelating agent, HA, can be expressed as follows by using the partition coefficient of the neutral chelate MA^n, P_M, the overall formation constant of $MA_n^{(3-q)+}$ in the aqueous phase, β_q

$$D = P_M \beta_n [A^-]^3 / (1 + \Sigma \beta_q [A^-]^q) \tag{1}$$

The extraction of scandium(III) as an example with 0.1 M Hacac in various organic solvents was carried out and the plots of the logarithms of the distribution ratios against the logarithms of the acetylacetonate (acac) concentrations in the aqueous phase are given in Fig. 1. In the solvent systems of heptane and 1-octanol, the distribution ratio increases with an increase in the acetyl-acetonate concentration and reaches a limiting value in the high concentration region of acetylacetonate. This suggests a stepwise formation of the chelates, $Sc(acac)^{2+}$, $Sc(acac)_2^+$, $Sc(acac)_3$, in the aqueous phase. The partition coefficients in other solvents
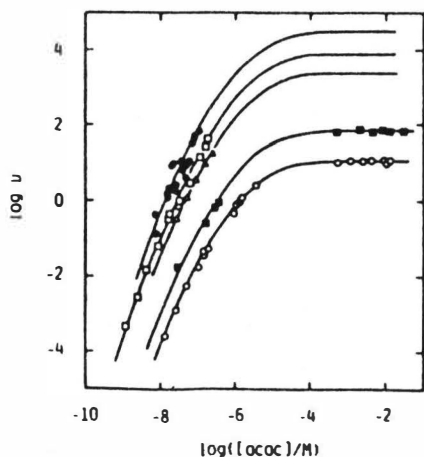
Fig. 1. Log D vs. log [acac], [Hacac]$_{init}$ = 0.1 M, pH 1.7 - 8.2. ○ 1, △ 2, □ 3, ● 4, ■ 5. The numbers correspond to those in Table 1
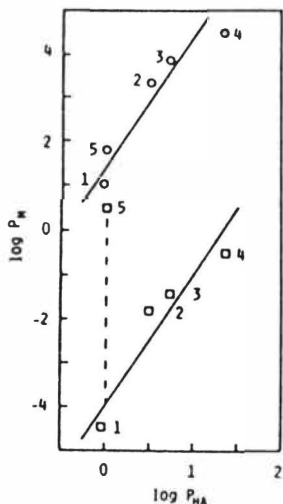
Fig. 2. Log P_M vs. log P_{HA}. ○ Sc(acac)$_3$, □ Y(acac)$_3$

systems, where a plateau region of log D cannot be measured experimentally, were determined by the least-squares fitting using K_1, K_2, and K_3 obtained in the heptane system. The extraction constants were calculated and listed in Table 1. The solid lines in Fig. 1 are drawn using these equilibrium constants and are in good agreement with the experimental plots. The log K_{ex} for the

scandium(III) chelate is much larger than that for the yttrium-
(III) chelate in all solvent systems. It is obvious that the
difference in K_{ex} can be attributed to the difference not only in
the formation constant but also in the partition coefficient.

The following simple but important relation has been derived
based on the solubility parameter concept[1,2],

$$\log P_M = \frac{V_M}{V_{HA}} \log P_{HA} + Const. \tag{2}$$

where V denotes the molar volume, and the molar volume ratio $V_M/$
V_{HA} is about three in the tris chelate. Figure 2 shows the corre-
lation of P_M against P_{HA} for scandium(III) and yttrium(III)
chelates. Plots for nonpolar solvents lie close to the straight
line with a slope of 3. A quite large deviation for the 1-octanol
system with yttrium(III) chelate is observed. A specific solute-
solvent interaction in this system may be responsible.

Figure 3 shows the plots of log K_{ex} in the benzene system
against the reciprocal of the ionic radii(r) of rare earth(III).
A clear regularity is found, that is, the extraction constants
linearly increase with increasing in 1/r. As was mentioned above,
the extraction constant is an apparent constant involving the
partition coefficient and the
formation constant of the metal
chelate, hence log P_M and log β_3
are ploted against 1/r in Fig. 3.
Both the partition coefficients
and the formation constants also
increase with increasing in 1/r.
A clear correlation between the
partition coefficient and the
formation constant can be observed.
The partition coefficients in-
crease with increase in the forma-
tion constants, that is, higher
the formation constant of the

Fig. 3. Log K_{ex}, log P_M, and log β_3
vs. ionic radii.
1, Sc; 2, Y; 3, La; 4, Nd; 5, Sm;
6, Tb; 7, Tm; 8, Lu

Partition coefficients and extraction constants of $M(acac)_3$ at 25°C

Number	Solvent	$Sc(acac)_3$		$Y(acac)_3$	
		log P_M	log K_{ex}	log P_M	log K_{ex}
1	Heptane	1.041	-5.87	-4.459	-17.03
2	Carbon tetrachloride	3.372	-5.21	-1.809	-16.05
3	Benzene	3.891	-5.39	-1.439	-16.38
4	Chloroform	4.499	-6.67	-0.531	-17.36
5	1-Octanol	1.835	-5.27	0.498	-12.27

chelate, higher the partition coefficient. The extraction constants of rare earth(III) with acetylacetone linearly increase with increasing in the reciprocal of their ionic radii. The difference in the extraction constants among rare earths(III) is attributed to the difference not only in the formation constants but also in the partition coefficients of the extractable chelates. An important contribution of the partition coefficient together with the formation constant to the extraction and separation efficiency of metal is quantitatively evaluated.

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In the recent years more and more solvating neutral
ligands like macrocyclic crown compounds have been investiga-
ted with the intention to find new specific extractants. Lipo-
philic crown compounds are efficient extractants for metal ions
due to their pronounced complex-forming properties and selec-
tive solubilities. The complexation and extraction behaviour
can be systematically influenced by various modifications of
their structure. Today an application of crown compounds as
extractants is limited by their complicated and expensive
synthesis. Corresponding open-chain structure analogues of the
crown compounds, which are not so expensive and easier obtain-
able by synthesis show in a qualified sense similar properties
but in some cases specific differences. Some compounds of this
type like nonionics, an industrial produced type of detergents,
are available on a large scale.

It is the topic of the present investigations to charac-
terize and to compare the extraction properties of different
crown compounds - crown ether 1, thia- and azacrown compounds
2, bis(crown ether)s 3, lariat ethers 4 - as well as of struc-
ture analogous open-chain compounds 5.

The selectivity of crown ethers 1 for alkali and alkaline
earth metal ions depends to a high degree on the hole-size
cation-diameter relationship. However there are a lot of
further factors, which can influence or change the resulting
separation possibilities. On the one hand, the separation fac-
tor for two metal ions can be changed in dependence on the
extractant concentration, if both of them form structural
different metal complexes (crown ether:metal = 1:1 and 2:1,
resp.). The extraction of sodium and potassium nitrate with
benzo[15]crown-5 is a typical example. On the other hand,
bis(crown ether)s, having two crown ether units in one molecule
extract cations larger than the hole size of the crown as sand-
wich complexes, and in consequence the selectivity of extrac-
tion for such metal ions is increased. This effect could be

X = S, NR

1 **2** **3**

X, Y, Z = O, S, NR

RX $\left(Y \right)_n$ ZR
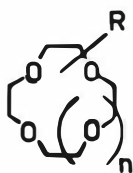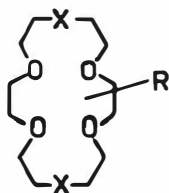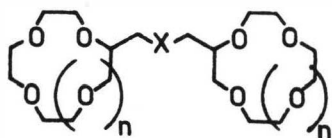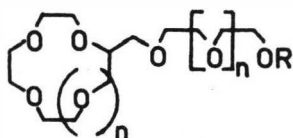
4 **5**

shown using new alkylene or arylene bridged carbonylhydrazones
of formylsubstituted benzocrown ethers [1].

Lariat ethers **4** offer - due to the introduction of additio-
nal ligator atoms on a flexible side-chain - favourable possi-
bilities to obtain an optimal coordination sphere for a defined
metal ion. However our extraction investigations with lariat
ethers did not show such an effect of structure optimization.
First of all, the presence of the flexible side-chain prevents
the formation of sandwich complexes with big cations. In con-
sequence the selectivity order corresponds to the hole-size
cation-diameter relationship.

A high superiority for crown ethers **1** in comparison to the
corresponding open-chain oligoethylene glycol dialkyl ethers **5**
results from their considerably higher stability constants for
alkali and alkaline earth metal ions caused by the so-called
macrocyclic effect, which leads to essentially higher extrac-
tion yields for these elements. The extraction of open-chain
compounds is unambiguously improved when the number of oxygen
donor atoms increases and is considerably influenced by the
size of alkyl substituents too [2].

The extraction properties are changed considerably, if sulfur or nitrogen are introduced as donor atoms. Corresponding to Pearson's HSAB-concept soft metal ions, like silver, palladium, gold, mercury, are favourably extracted, whereas the extraction efficiency is decreased in the case of hard alkali and alkaline earth metal ions. Generally the extraction equilibria with nitrogen containing compounds are complicated, because additional interactions of the nitrogen ligator atoms are important too /3/. Quite opposite conclusions in comparison with the only oxygen containing extractants can be deduced from the extraction behaviour of nitrogen or sulfur containing cyclic and open-chain compounds for transition metal ions /3, 4/. In these cases only small differences have been obtained. The nitrogen and sulfur ligator atoms dominate as coordination centres and a macrocyclic effect does not appear. The graduations of extraction properties of open-chain compounds can be interpreted by the aid of molecular models, in which are included the coordinative saturation and stereochemistry of the metal ion, the magnitude of the possible chelate rings and the complexing capability of the potential donor atoms.

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The extraction of alkali and alkaline earth metal ions with benzo-
-15-crown-5(B15C5) or dibenzo-18-crown-6(DB18C6) have been widely
studied. We have found that the extraction percentage of anions or
complexed anions ReO_4^- [1], , $InBr_4^-$, InI_4^- [2], and $AuCl_4^-$ can be gre-
atly increased with B15C5(or DB18C6) in the presence of potassium
salts according to the selective extraction of potassium ion by crown
ether. The extraction mechanism of these systems mentioned above have
been studied by slope method. In order to further elucidate the extrac-
tion mechanism and the coordinated properties of metal ions, the cry-
stal complexes of benzo-15-crown-5 potassium tetrabromoindate (III)[3],
hydrated dibenzo-18-crown-6 potassium tetrabromoindate(III) [4], hy-
drated benzo-15-crown-5 sodiam tetrabromoindate (III) [5], and benzo-
-15-crown-5 potassium tetraiododate(III) [6], corresponding to the
extracted complexes respectively have been synthesized and determined.

The extraction of trivalent rare earth ions with crown ether also
has been reported, but systematic studies about the extraction of
Sc^{3+} are almost lacking [7] Altough Sc^{3+} has small size, high elec-
tric charge and high hydration energy, preliminary experiments showed
that among the Sc^{3+} and rare earth ions, the distibution ratio of
Sc^{3+} was the maximum when picrate (pic$^-$) was used as a counter anion
and dichloroethane as a diluent. The seperation factors between Sc^{3+}
and Er^{3+}, Yb^{3+}, Y^{3+} respectively are 11, 8.9 and 12.9. In this paper
we have attempted to study systematically the mechanism by extraction
method and by determining the structure of crystal complex between
B15C5 and scandium picate.

Study of the extraction mechanism of scandium picrate by crown
ether

The percent extraction of Sc^{3+} from aqueous hydrochloric acid so-
lution by B15C5 remained constant when investigated as a function of
scandium ion concentration in the range 0-50µgSc$_2$O$_3$/ml,   and plot
of log $[Sc(III)]_o$ against log $[Sc(III)]_{aq}$ gave a straight line with
unit slope, thereby indicating that a monomeric Sc(III) complex has
been extracted into the organic phase. The extraction efficiencies
of scandium picrate by some crown ethers follow the order B15C5>
> DB18C6 > 12C4 and by some diluents follow the order $1.2C_2H_4Cl_2$>

$> C_6H_6 > CHCl_3$, subsequent studies were made using B15C5 as an extractant, dichloroethane as a diluent, and the concentration of Sc^{3+} was 20μg Sc_2O_3/ml.

The nature of the extracted complex was evaluated by measuring the distibution ratio of Sc^{3+} as a function of either pic^- or B15C5 (Fig. 1 and Fig. 2). Slope analysis of these data indicated that the main extracted species may be expressed as $Sc(pic)_2(B15C5)_{1.5}$. A (A refers to monovalent anion).

In order to identify A, the effect of Cl^- on the distribution ratio of Sc^{3+} has been examined. The result shows that D is almost independent of the concentration of Cl^-, this means that A can not be Cl^-. Some crystal with definite composition $Sc(pic)_3(B15C5)_2 \cdot 2H_2O.CH_3CN$ has been dissolved and pic^- concentration has been varied by adding Hpic into water. The plot of logD against logpic$^-$ shows a linear relation with a slope of 2, this indicates the presence of OH^- which may be derived from the hydrolysis of Sc^{3+}. As early mentioned the dominate form of Sc^{3+} is $Sc(OH)^{2+}$ at pH > 1 [8]. The time period necessary to establish the extraction equilibrium increased with the increase of pH value. Therefore the extracted complex can be represented as $Sc(OH)(pic)_2(B15C5)_{1.5}$. In the same way the composition of extracted complex has been found to be Sc(OH)(DB18C6). .$(pic)_2$ using DB18C6 as an extractant. Their conditional extraction constants are logKex = 5.69 and logKex = 3.45 respectively.
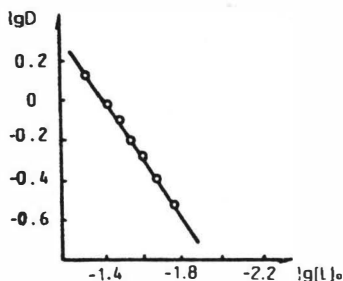
Fig. 1. Distribution ratio of Sc^{3+} versus concentration of B15C5 in the organic phase
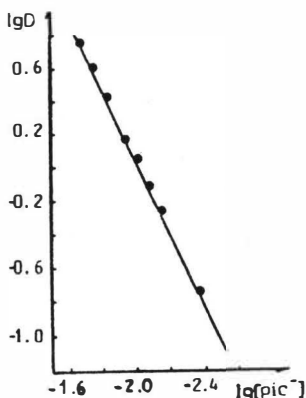
Fig. 2. Distribution ratio of Sc^{3+} versus concentration of pic^- in aqueous solution

Crystal structure of complex between scandium picrate and B15C5

The crystal of title compound corresponding to the extracted complex was first synthesized in the mixture of acetonitrile and ethanol. Its composition is shown to be $Sc(pic)_3 \cdot (B15C5)_2 \cdot 2H_2O \cdot CH_3CN$ by elemental analysis and colorimetry. The complex crystallizes in the triclinic space group $P\bar{1}$, with $r=2$. Lattice parameters are a=12.768(2), b=13.76(2), c=19.440(4), α =81.03(2), β =70,88(1), γ =70.71(2), V = 3042.58Å^3, D = 1.44g·cm^{-3}. X-ray structural work shows that Sc^{3+} is bound with three picrate anions and two water molecules. Each picrate ia a bidentate donor agent, which is attached to Sc^{3+} by two donor oxygen atoms of phenolic group and one nitro-group. The three bond angles of O-Sc-O are 67.5(2),74.6(2),70.7(2) respectively. The minimum distances between each oxygen atom of two coordinated water and two crown ether oxygen atoms of B15C5, i.e. O_5-O_{11}, O_5-O_{12}, O_4-O_{22} are 3.177Å, 3.2915Å, 3.1216Å and 3.2343Å respectively (Fig.3). This indicated that the two B15C5 associated with Sc^{3+} through the formation of hydrogen bond between coordinated water and ether oxygen atoms of B15C5.

The extraction result shows that scandium picrate can not be extracted into the organic phase if B15C5 is absent. It has been confirmed that the extracted complex contains hydroxy and the coordinated water may exist because of high hydration energy of Sc^{3+}. It is apparent from the study of the crystal structure that in the extrac-
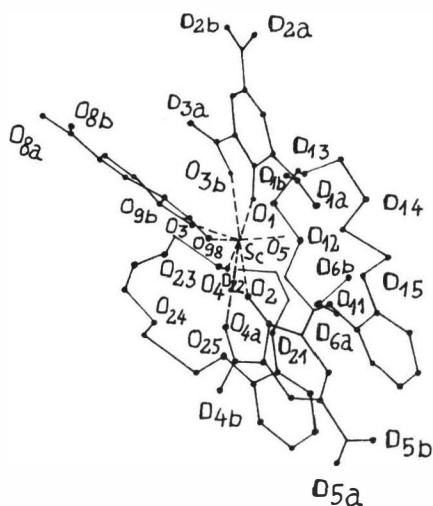
Fig.3. Unsymmetry unit in cell

ted complex B15C5 may associate with scandium picrate also through the formation of hydrogen bond between hydroxy or coordinated water and crown ether oxygen atoms. Thus a hydrophobic extracted complex is formed which can be extracted into organic phase effectively. This extraction mechanism indicates that the extraction efficiency is not related to the relative size of the metal ion and the crown ether cavity. Because 12C4 is more hydrophilic, it seems that hydrogen bond to form extracted complex between 12C4 and hydrated (or hydroxo) scandium picrate is impossible. Both of B15C5 and DB18C6 have better organophilic behavior. But the latter is sufficient bulky that it might pose steric problem on the formation of hydrogen bond, therefore the extraction efficiency of Sc^{3+} in the sequence of B15C5> DB18C6 > 12C4 may be explained satisfactorily.

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RELATIONSHIP BETWEEN THE FORMATION OF Ag(I) COMPLEXES
WITH HETEROCYCLIC BASES IN AQUEOUS SOLUTION AND THEIR
SUSCEPTILIBITY TO EXTRACTION

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The correlations have been studied between the extraction process
and the formation of Ag(I) complexes with imidazole as well as its al-
kyl derivatives (1-methyl-,2-ethyl-,1-propyl-) in aqueous solution.

Other systems, containing Ag(I) compounds with seven pyridine deri-
vatives (nicotinic acid amide, 3-hydroxy-,3-amino-,3-ethyl-,2,4-dime-
thyl-,2-amino-4-methyl-,2-amino-5-methyl-) have also been investigated.
All the investigations were carried out at 298 K, and the constant
ionic strength, $I = 0.5$, which was maintained with KNO_3 addition to
the solution. During the extraction of Ag(I) complexes of imidazoles,
2-methylbutanol and benzyl alcohol were used.

For the extraction measurements to be accomplished, the 6 cm^3 of
aqueous ($Ag(I) + HNO_3$) solution had been placed in calibrated test-tu-
be, then 6 cm^3 of the organic solvent added, and the content was being
shaken for ca 30 min in order to achieve a distribution equilibrium.
The pH and Ag(I) concentration in aqueous solution was determined spe-
ctrometrically, both before and after the extraction. Initial concen-
tration of Ag(I) was kept constant at the level of 0.01 mole per dm^3.

From those measurements, molar extraction percent, E%, partition
coefficient D, and equilibrial free basis concentration, $[L]$ were de-
termined. For each of the investigated systems, the molar fraction,
α_n, of individual complexes formed in aqueous solution were calcula-
ted from previously determined stability constants, β_n, according to
the equation

$$\alpha_n = \beta_n [L]^n / \sum_0^N \beta_i [L]^i .$$ (1)

Then, individual partition coefficients, P_n, were determined from the
relationship

$$D = P_1 \alpha_1 + P_2 \alpha_2.$$ (2)

The P_n values for extractable complexes are listed in Table 1.

Ligand	Benzyl alcohol		2-methylbutanol	
	P_1	P_2	P_1	P_2
Imidazole	-	9.2	-	1.0
1-methyl-imidazole	0.98	20.7	-	3.3
2-ethyl-imidazole	-	79.7	-	10.7
1-propyl-imidazole	-	66.6	-	12.2

The extraction process of Ag(I) complexes of pyridine derivatives
has been studied by means of quite new, extraction-potentiometric me-
thod which allows to determine individual partition coefficients, P_n,
more quickly.

Equilibrial ligand concentration, $[L]$, was calculated from pH value in aqueous phase, whereas the equilibrial Ag^+-ions concentration was found from E.M.F. value for the following concentration cell:

$$(+) \; Ag \; \left| \begin{array}{c} a \; M \; AgNO_3 \\ b \; M \; HNO_3 \\ (0.5-a-b) \; M \; KNO_3 \end{array} \right| \left| \right| \left| \begin{array}{c} 0.5 \; M \\ KNO_3 \end{array} \right| \left| \right| \left| \begin{array}{c} aqueous \\ solution \\ after \; the \\ extraction \end{array} \right| \; Ag(-)$$
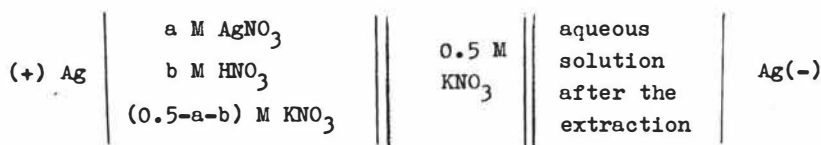
Basing on previously determined stability constants for $Ag(I)$ complexes of pyridine derivatives, the individual partition coefficient, P_n, values were calculated from the Leden function:

$$F_1 = \frac{\frac{c_{Ag^+}}{[Ag^+]} - 1}{[L]} = (1+P_1)\,\beta_1 + (1+P_2)\,\beta_2\,[L]. \tag{3}$$

The partition coefficient values for so investigated systems are listed in Table 2.

Ligand	benzyl alcohol		isobutyl alcohol		toluene	
	P_1	P_2	P_1	P_2	P_1	P_2
3-CONH$_2$Py	4.0	4.7	0	2.3	-	-
3-OHPy	13.6	25.1	6.2	6.3	-	-
3-NH$_2$Py	14.0	11.1	1.4	1.1	1.0	0
2-C$_2$H$_5$Py	12.6	253.0	31.8	36.3	0.6	0.5
2,4-(CH$_3$)$_2$Py	35.9	456.0	2.8	34.7	1.0	0.7
2-NH$_2$-4-CH$_3$Py	54.0	57.1	15.8	18.3	1.8	0.2
2-NH$_2$-5-CH$_3$Py	55.1	50.2	8.9	14.8	2.1	0.7

For imidazole or its derivative complexes it has been stated that the second $[AgL_2]NO_3$ complex undergo extraction with benzyl alcohol and 2-methylbutanol, and that P_2 values rises with the increase in alkyl group size. For pyridine derivative complexes investigated commonly two complexes ($[AgLS]NO_3$ and $[AgL_2]NO_3$, where S = solvent molecule) passed to the organic phase.

High extraction was observed for 2.4-dimethyl- and 2-ethylpyridine complexes. Benzyl alcohol proved to be the most efficient solvent for the $Ag(I)$ extraction in all the systems investigated.

SOLVENT EXTRACTION OF PICRIC ACID AND COMPLEX FORMATION IN ORGANIC PHASE WITH TRIOCTYLPHOSPHINE OXIDE

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The solvent extraction equilibrium of picric acid(Hpic) with trioctylphosphine oxide(TOPO) in cyclohexane and the spectrum of the organic phase which extracted the acid was studied at 298K. A certain amount of 1 mol dm^{-3} hydrochloric acid solution which contained 1×10^{-4} mol dm^{-3} to 1×10^{-3} mol dm^{-3} of Hpic was placed in a stoppered glass tube and the same volume of cyclohexane which contained TOPO was added. The two phases were vigorously agitated for 15 min and centrifuged. The amount of Hpic in the two phases was determined by spectrophotometry. The spectrum of the organic phase was measured over a wavelength range from 250 to 500 nm.

The distribution ratio of picrate can generally be written as

$$D = (\left[Hpic\right]_{org} + \left[Hpic(TOPO)\right]_{org} + \left[Hpic(TOPO)_2\right]_{org} + \ldots)/(\left[Hpic\right] + \left[pic^-\right])$$
$$= (Kd(1 + K_{1(org)}\left[TOPO\right]_{org} + K_{2(org)}\left[TOPO\right]_{org}^2)/(1 + Ka^*\{H^+\}^{-1}). \tag{1}$$

Here $Kd = \left[Hpic\right]_{org}/\left[Hpic\right]$, $Ka^* = \{H^+\}\left[pic^-\right]/\left[Hpic\right]$, and $K_{n(org)} = \left[Hpic(TOPO)_n\right]_{org}/(\left[Hpic\right]_{org}\left[TOPO\right]_{org}^n)$. The value obtained was $Kd = 0.15$ and $Ka^*\{H^+\}^{-1} = 0.71$ when the aqueous phase was 1.0 mol·dm^{-3} hydrochloric acid.

The distribution data at various TOPO concentrations were analyzed by using a least squares computer program on the basis of the assumption that;

$$\left[TOPO\right]_{init} = \left[TOPO\right]_{org} + \left[Hpic(TOPO)\right]_{org} + 2\left[Hpic(TOPO)_2\right]_{org} + \ldots \tag{2}$$

and that the extraction of hydrochloric acid with TOPO is only slight[1]. The constants obtained are listed in Table.

Summary of Association Constants

	$\log K_{1(org)}$	$\log K_{2(org)}$
Solvent Extraction	4.1	6.9
Spectrophotometry	4.2	6.7

Figure 1 gives the distribution ratio of Hpic as a function of the free TOPO concentration obtained by using Eq.2. The solid curve was calculated by introducing the values in Table 1 into Eqs.1 and 2. As seen from Fig.1, the data can be explained in terms of the free acid (Hpic), monosolvated(Hpic(TOPO)), and disolvated(Hpic(TOPO)$_2$) species in the organic phase.

Figure 2 gives the spectrum of the organic phase which extracted Hpic with TOPO. For the apparent molar extinction coefficient, the following equation can be written;

$$\varepsilon_{ap}[Hpic]_{org,total} = \varepsilon_0[Hpic]_{org} + \varepsilon_1[Hpic(TOPO)]_{org}$$
$$+ \varepsilon_2[Hpic(TOPO)_2]_{org}, \tag{3}$$

$$\varepsilon_{ap} = (\varepsilon_0 + \varepsilon_1 K_{1(org)}[TOPO]_{org} + \varepsilon_2 K_{2(org)}[TOPO]_{org}^2)$$

$$/(1 + K_{1(org)}[TOPO]_{org} + K_{2(org)}[TOPO]_{org}^2), \qquad (4)$$

Fig.1

TOPO/Cycl ohxane - 1mol/ HCl aq
$[Hpic]_{total} = 10^{-4}$ mol/l = const

log D

−4   −3   log[TOPO]$_{total}$

Fig.2

a. $[TOPO]_{total} = 1.02 \times 10^{-4}$,
$[Hpic]_{total} = 2.69 \times 10^{-5}$, mol/l

b. $[TOPO]_{total} = 1.02 \times 10^{-2}$,
$[Hpic]_{total} = 2.68 \times 10^{-5}$, mol/l

Absorbance

200   300   λ / nm 400   500
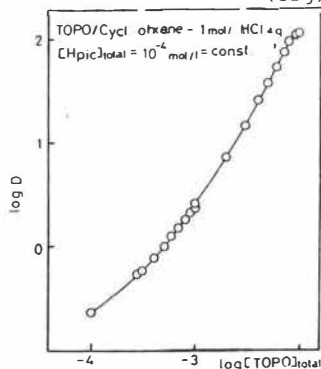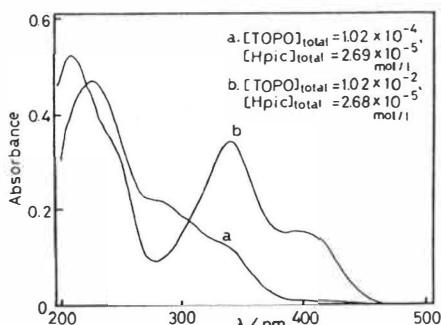
The data were analyzed on the basis of Fig.2 and 4 by using the least squares computer program. The value of association constants obtained from these spectrophotometric data are listed also in Table.

Figure 3 gives the calculated molar extinction coefficient of the monosolvated and disolvated species by using Eq.4 as a function of the free TOPO concentration.
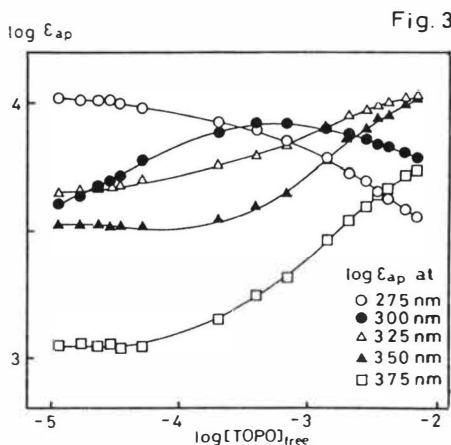
log ε_{ap}

Fig. 3

log ε_{ap} at
○ 275 nm
● 300 nm
△ 325 nm
▲ 350 nm
□ 375 nm

−5   −4   −3   −2
log[TOPO]$_{free}$

As seen from Table, the association constants obtained from the solvent extraction data agree with those obtained from the spectrophotometric data.

The spectrophotometric data indicate that the monosolvated species should approximately be regarded as an adduct in which Hpic combines with TOPO by a hydrogen bond while the disolvated species should be regarded as an ion pair in which a charge transfer occures and the pic$^-$ species combines with the $H(TOPO)_2^+$ species electrostatically. As seen from Fig.3, the shape of absorption spectrum is very much affected by TOPO. For this reason, even when the total picrate concentration is the same, the color of the organic phase which extracted the acid could be different when the TOPO concentration is different.

The extraction of Hpic into the non-polar solvent in the present study is different from that into 4-methyl-2-pentanone in which a part of the acid dissociates in the organic phase [2].

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At present complexones are widely used in chromatography for the
separation of REE,in analytical chemistry as masking agents and,to a
smaller extent,in extraction processes as a main separating agent.Such
complexones as EDTA, NTA and DTPA possess high selectivity and their
use in nonselective extraction systems can be very efficient.Each
complexone has its own pH range of the complexation of lanthanides
(Fig.1),which may vary depending on the composition of the aqueous
phase and conditions.As a rule some fixed pH value is used,it is sta-
bilized by a respective buffer or a full complexone capacity is used
over the pH range of the full complexation (Fig.2).The latter conditi-
on provides for a high capacity of the separation process and excludes
the necessity to stabilize the pH value.In this case,the separation
process occurs by the exchange mechanism.When choosing an extraction
system one can encounter four cases: 1. The extractant is selective/
the complexone is nonselective.The selectivity of the extraction sys-
tem is determined solely by the extractant itself (Fig.3,1). 2. Both
the extractant and complexones are selective and have the same shape
of the dependence of the constants of the formation of solute compou-
nds and those of complexation on the lanthanide atomic number.The ex-
traction system is nonselective.(Fig.3,2).Two agents supress each
other. 3. The extractant is nonselective/the complexone is selective.
The selectivity of the system is determined only by the complexone
(Fig.3,3). 4. The extractant is selective,but it has a reverse order
of the dependence of extractability of lanthanides on their atomic
number;the complexone is selective and has the direct order of the
dependence of complexability of lanthanides.(Fig.3,4).The selectivity
of the extraction system is the maximum one.

These two latter extraction systems are of interest for the separ-
ation of lanthanides in the presence of complexones.Neutral phosphor-
organic solvents (TBP, phosphonates etc.),naphthenic acids and carbo-
nic acids of the fatty series should be referred to the group of extr-
actants with low selectivity.The first two are most efficient during
the separation of REE of the yttrium subgroup,since for yttrium lanth-
anides a small inversion of the values of distribution coefficients is
observed.Nitrogen containing extractants exhibiting a reverse depen-
dence of the distribution coefficients on the atomic number of lantha-
nides.However,these extractants are more selective for cerium elements
and the field of their effective application is limited by the tasks

of radiochemistry.We have been using complexones in extraction proces-
ses of REE separation since 1959 $/1-4/$.During this period we have for-
mulated main requirements to such systems.The maximum value of the
separation coefficient of a chosen extractant (S) equal to the pro-
duct of the separation coefficient and the ratio of the values of
stability constants of complexonates of feed components $\beta = S.K_{LnI}/K_{LnI}$
can be achieved at a high complexation degree of solute componets in
the aqueous phase (Fig.4).

From the practical viewpoint it is more convenient to employ compl-
exones using their full capacity,when there is an excess of feed comp-
onents and the pH value providing for the high complexation degree in
the aqueous phase.The advantage of these conditions is,that we can
carry out the separation process over a wide pH range.To maintain a
high complexation degree in the aqueous phase,beside the chosen pH
value,we must also have relatively high values of distribution coeffi-
cients of feed components for the extractant,when the complexone is
absent,since only in this case the concentration of the part of dis-
tributed substances free from complexation is low (Fig.5).

Table 1,2 show the values of separation coefficients for a number
of extraction systems with complexones.Systems on the basis of EDTA
for the separation of elements of the yttrium subgroup of lanthanides,
for which the choice of the extractant is rather unambiguous, are of
the greatest practical value.The system with EDTA is comparable with
phosphororganic compounds by its selectivity and other working parameters
(concentration in the orga-nic phase 60-80 g/l REE and 25-30 g/l in the aqueous
phase at the EDTA concen-tration being 0.15 M.At pH values lower than 5-5.5
there are practically no

Table 1.Values of separation coefficients
for binary mixtures of lanthanides
of the cerium subgroup

REE pairs	Carbonic acids C_7-C_9		Naphthenic acids	
	DTPA	NTA	DTPA	NTA
Pr-Ce	2.90	2,70	3.65	2.95
Nd-Pr	2.0	2.30	2.05	2.25
Pm-Nd	2.25	2.15	2.10	2.40
Sm-Pm	2.05	1.95	2.04	2.00
Sm-Nd	4.60		4.3	4.80
Eu-Sm	1.22	1.3	1.2	1.25

kinetic limitations,it takes 1-2 minutes for the exchange equilibrium
to be established(Fig.6,7).Typical examples for various classes of ex-
tractants are presented in Fig.8-11$/2-6/$.In the case of carbonic acids
the pH of the complexation should be lower than the pH of the extrac-
tion of lanthanides with carbonic acids.The total content of REE in
the system should be higher than the total capacity of the complexone
and that of carbonic acid soap to avoid kinetic difficulties.Extrac-
tion systems in the presence of complexones can be successfully empl-
oyed in all the cases as an alternative process for chromatography and
as an independent method of separation with general extraction advan-

tages.When organizing the separation processes the main difficulty,as
in the case of chromatographic processes,is related to the necessity
to regenerate a complexone and to organize the backward REE flow from
the raffinate outlet.To remove REE from complex compounds one can use
acids and metal cations,which have the values of complexation const-
ants close to or a little higher than for separated elements (Fe^{3+},
Cu^{2+}, Ni^{2+} etc.).In contrast to usual extraction systems extractant
has a higher loading than the aqueous phase.

Table 2. Values of separation coefficients
of binary mixtures of yttrium REE during
their extraction with TBP and TOPO in
the presence of EDTA

Lanthanide pairs	TBP-0.4M REE-6M NH_4NO_3 0.15M EDTA	0.5M TOPO in xylene-0.4M $Ln(NO_3)_3$ 0.15M EDTA	
		without salt-ing out agent	4M NH_4NO_3
Tb-Co	1.9-2.3	-	1.9
Dy-Tb	1.6-1.9	2.0	2.1
Ho-Dy	1.9-2.5	2.3	2.5
Er-Ho	1.9-2.5	3.4	3.3
Tm-Er	1.7-2.4	-	1.7
Yb-Tm	2.5-3.5	-	4.0
Lu-Yb	2.0-2.4	-	-

In the present paper we do not consider any peculiar features of using
complexones in preparative radiochemistry.For example,the nessecity of
using buffer elements during the separation of small quantities of ra-
dioactive elements in exchange systems of higher capacity.Since the
use of complexones is more efficient when separating elements of the
yttrium subgroup,then we must take into account,that this subgroup
usually constitutes less than 5% of the total sum of feed elements.
Hence,in this case one can use efficiently various unsteady processes
(fraction counterflow and different variants of the full reflux method)
for obtaining group concentrates and individual lanthanides.

Fig.12 presents as an example the data on the purification of Yb
from the admixtures of the neighbouring elements Lu and Tm by the
full reflux method in the extraction cascade with an additional mixer,
included in the chain of extraction cells to increase the capacity of
the system.When the extractant volume (W),expressed in a relative value
to the volume of the additional mixer(W/A) and equal to 8-9 relative
volumes,is passed through the extraction cascade,the purity of Yb
increases by 4 orders of magnitude,i.e the final content of admixtures
constituted less than 5.10^{-4}%.In this case the extraction system with
100% TBP containing 50 g/l REE,-0.15 M EDTA-6 M NH_4NO_3, pH=4-5 was
used.The initial REE concentrate contained 78% Yb, 6-7% Tm and
and 15% luthetium.
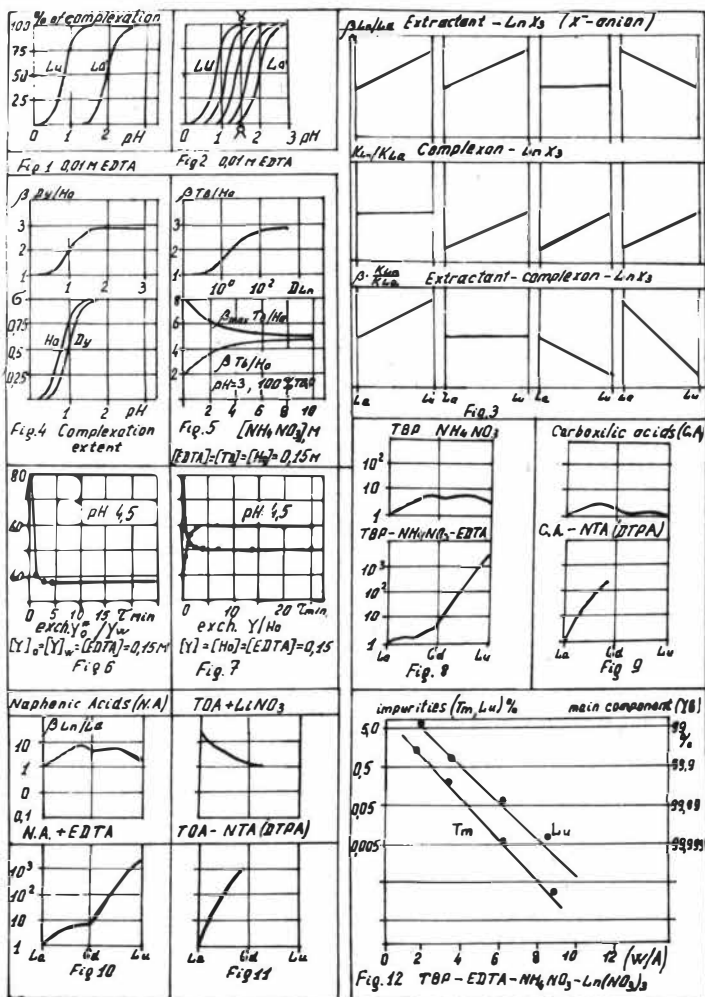
Fig.1-12. Main regularities of the extraction of lanthanides in extraction systems with complexones

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COORDINATION CHEMISTRY OF DI(2-ETHYLHEXYL)PHOSPHORIC ACID
SALTS IN EXTRACTION PROCESSES

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The wide use of di(2-ethylhexyl) phosphoric acid (D2EHPA , HX in
formulas) determined the interest in the composition and structure of
complexes formed in the extracts. Besides, some of these complexes may
act as extracting agents which complicates the extraction picture.
The organic phase in the D2EHPA extraction contains, in the general
case, a mixture of partially hydrated neutral and acid salts of D2EPA
and to understand the entire picture of the extraction it is necessary
to study separately the states of neutral salts in nonequeous organic
solvents and their interaction with water and H_2X_2 molecules and also
the hydration of acid salts. To achieve this we performed an IR, elec-
tron, and NMR^{31}P spectroscopic study of the structure of neutral salts
Mx (M- alkali metals and NH_4^+),MX_2($M-Mg^{2+},Ca^{2+},Ba^{2+},Co^{2+},Ni^{2+},Cu^{2+}$,
Zn^{2+}),VOX_2 and their hydration in $CCl_4,C_6H_6,n-C_6H_{14}$ as well of the
composition, structure, hydration of acid di(2-ethylhexyl)phosphates
of $Co^{2+},Zn^{2+},Zr^{4+},Hf^{4+}$.
Neutral and, in some cases, acid salts formed by D2EHPA , both in
nonequeous solvents and in the presence of water, tend to polymerize
to form associates of a complex structure. The various features of
these associates are a result of diversity of the modes in which the
POO groups coordinate to the metal cations.
The following types of mono-, bi-, and tridentate coordination of
the POO-groups to the cations M were found

$$\underline{I} \quad {>}P{\overset{\nearrow O}{\diagdown O-M}} \qquad \underline{II} \quad {>}P{\overset{\nearrow O-M}{\diagdown O-M}} \qquad \underline{III} \quad {>}P{\overset{\nearrow O}{\diagdown O}}{>}M \qquad \underline{IV} \quad {>}P{\overset{\nearrow O\diagdown}{\diagdown O\diagup}}{\overset{M}{M}} \quad .$$
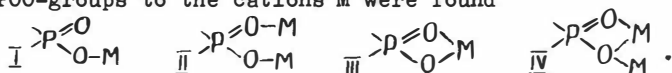
In nonaqueous solutions of neutral alkali metal salts type I-III
coordination takes place. LiX solutions give rise only to long-chain
linear polymers $(LiX)_p$ (type II). In the series of salts NaX, KX,RbX,
CsX the amount of the linear polymers $(MX)_p$and the average degree of
polymerization p drop (terminal type I POO-groups appear) while the
fraction of the monomeric molecules with type III POO-groups sharply
increases. In contrast to alkali metal carboxilates, there is no equa-
lization of the multiplicity of the phosphorus-oxygen bonds of the
POO-groups in the studied salts.
Transition metal salts MX_2 form in solutions linear polymers (in the
case of CuX_2 only at high salt concentrations) in which the cation is
in a distorted tetrahedral ligand field. $(ZnX_2)_p$ and $(CoX_2)_p$ molecules
with p of about 4 contain non-equivalent chelate terminal POO-groups
of the type III_1 and III_2 differing by the degree of equalization of
the phosphorus-oxygen bonds multiplicities (index 1 denotes that the
bonds are to a large extent equalized, index 2 shows that one bond

is largely of a double character while the other is mainly a simple bond). NiX_2 (in contrast to CoX_2) and also CuX_2 give rise, in diluted solutions, to cyclic tri- and tetramers with type IV POO-groups similar to those described in [1] for Cu(II)dioctylphosphinate. Due to this the coordination number (CN) of Ni^{2+} and Cu^{2+} increases to 6. Rearrangement of the linear polymers $(CuX_2)_p$ to cyclic tri- and tetramers at C_{CuX_2} from ~ 0.3 to0.05 mol/l(in terms of the monomer) was studied in [2]. Beyond this concentration interval, linear cyclic(up to $5\cdot 10^{-3}$ mol/l) species prevail. The VOX_2 salt produces only dimers over the concentration range from $5\cdot 10^{-3}$ to 0.5 mol/l.

<u>Hydration of neutral salts.</u> In contrast to $(CuX_2)_p$ and $(NiX_2)_p$ the linear polymers $(ZnX_2)_p$, $(CoX_2)_p$ and the $(VOX_2)_2$ dimer do not coordinate water molecules due to coordination saturation of their Zn^{2+}, Co^{2+}, and VO^{2+} cations. Hydration of $(CuX_2)_p$ molecules in CCl_4 was studied using differential IR spectroscopy. The spectra of CuX_2 solutions containing different amounts of water were measured relative a nonaqueous solution, with the reference cell thickness chosen so as to compensate for the spectrum of non-hydrated $(CuX_2)_p$ species. It was found that in 0.05 molar solutions of CuX_2 in CCl_4 with up to 0.03 mol/l of water, the H_2O molecules enter into cyclic associates with the molar ratio $CuX_2:H_2O=3:2$. The structure of these associates is discussed. With further increase in C_{H_2O} a mixture of water-containing cyclic associates of different composition is formed and the amount of hydration increases. In solutions at equilibrium with water the average composition of the water-containing associates is close to $(CuX_2 \cdot 2H_2O)_4$ but even under these conditions 10 to 30% of CuX_2, depending on the solvent, exist in the form of nonhydrated associates.

Hydration of cyclic molecules $(NiX_2)_p$ (P= 3÷4) in CCl_4 was studied at the molar ratios $n=H_2O/NiX_2$ from 1 to 11 (at equilibrium with water). With the increase in n from 0 to 2 the electronic spectra of the solutions show a systematic increase in the rates of $^3A_{2g}(F)\text{-}^3T_{2g}(F)$, $^3A_{2g}(F)\rightarrow^3T_{1g}(F)$, and $^3A_{2g}(F)\rightarrow^3T_{1g}(P)$ transitions corresponding to the Ni^{2+} cations in an octahedral ligand field while the molar absorption coefficient of the $^3A_{2g}(F)\rightarrow^3T_{1g}(P)$ transition sharply decreases from 23 to 10 l·mol/cm. This implies that the H_2O molecules are coordinated directly to the cations displacing the POO oxygen atoms from the first coordination sphere. At n = 2÷6   the first coordination sphere of Ni^{2+} is successively filled with water molecules while the POO-groups are all displaced into the second sphere, each POO group being connected to the H_2O molecules through hydrogen bonds (HB). At n=6÷11 the number of water molecules in the outer sphere of Ni^{2+} gradually increases and they concentrate in the center of the micelle. Thus, the micelle structure consists of a core of H_2O molecules bonded to each other through HB's,   which is surrounded by a shell of

hydrated molecules $Ni(H_2O)_6^{2+}$ and a next shell of POO-groups attached through HB's to the protons of the water molecules. Owing to such a structure, the micelle molecule is able to capture CoX_2 molecules when Co(II) is present in the aqueous phase of the extraction system. At high NiX_2/CoX_2 molar ratios almost all of the cobalt enters into the micelles where it acquires an octahedral environment whereas in the absence of Ni^{2+} the tetrahedral forms $(CoX_2)_p$ remain unhydrated.

Hydration of alkali metal salts gives rise to inverse micelles similar to $(NiX_2 \cdot 11H_2O)_p$. Hydration of alkaline metal salts decreases in the series: BaX_2 (inverse micelles) $< CaX_2 < MgX_2$ (no hydration).

Acid salts. When HX is added to solutions of ZnX_2 and CoX_2 its molecules first coordinate to the terminal III_1 and III_2 groups of the linear $(MX_2)_p$ polymers producing non-equivalent acid groups V_1 and V_2 _[3]_

$$\underline{V}_1 \quad \underline{V}_2 \quad \overline{VI}$$
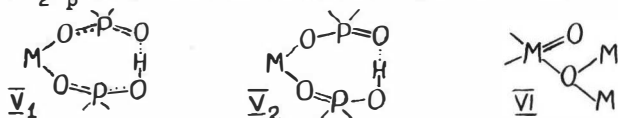
with the polymerization degree of the $(MX_2)_p$ oligomers remaining unchanged and only a large excess of HX results in HX coordination to the middle (bridging) POO-groups of the polymer, a procees which leads, in the end, to complete monomerization and formation of coordinatively saturated $M(HX_2)_2$ molecules with two V_1 groups which are uncapable of coordinating water.

Acid salt polymers $MX_2(HX_2)_2$ (M= Zr,Hf) in decane contain, in the presence of of an excess of HX, a large number of non-equivalent POO-groups of which types II, III_1, IV, V_1, V_2 were identified _[4]_.

In the real extraction systems with D2EHPA all of the above processes occur simultaneously. The equations such as

$$M^{2+}_{(aq)} + 2H_2X_2 \text{ (o)} \rightleftharpoons M(HX_2)_2 \text{ (o)} + 2H^+_{(aq)}$$

often used to describe the ion exchange equilibria in such systems are certainly too simplified. In many cases the extraction selectivity is determined by factors not included in these equations. For example, with increasing temperature the octahedral hydration environment of Co^{2+} becomes unstable preventing the cation from entering into the mixed micelles which leads to a considerable improvement of the separation factor for Co/Ni.

Extraction with D2EHPA salts. Solutions of CuX_2 in CCl_4, C_6H_6, and n-C_6H_{14} extract chlorides and bromides of alkali metals and NH_4^+ _[5]_ and also $BaCl_2$ and CuX_2 from their aqueous solutions by an acceptor mechanism to form complexes MA (M = K,Rb,Cs,NH_4^+) and $[M(H_2O)_m]^{n+}A_n^-$ (M = Li,Na,Ba,Cu) where A^- is the complex anion $[(CuX_2)_4Hal]^-$, Hal = Cl, Br. Such a mechanism is possible due to the presence in the extracting agent of the metal cation (Cu^{2+}) – an electron acceptor. The structure

of A^- was established by IR and EXAFS spectroscopy. The halogenide-ion lies in the center of a tetrahedron of 4 copper atoms to which it is bonded by waek Cu-Hal bonds. In scheme A the curved lines represent bidentate bridging POO groups and each second acid residue is conventionally shown as a tridentate one since one of its two POO groups is coordinated to Cu^{2+}. Scheme B shows the coordination environment of Cu^{2+}.

A

B
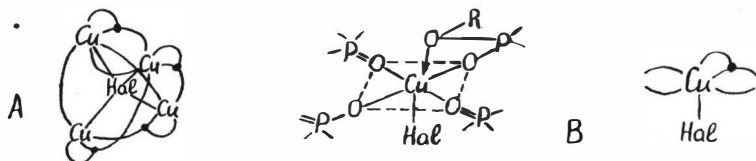
The MA salts form in organic solvents contacting and solvate-separated ionic pairs whereas in the $M(H_2O)_m^{n+}A^-$ salts the first coordination sphere of the M^{n+} cations is completely filled with water molecules attached to the POO groups of A^- through HB´s.

The acid salts $MX_2(HX_2)_2$ (M= Zr,Hf) extract much better than HX itself, HNO_3, Fe^{3+}, Eu^{3+}, and Sc^{3+} from nitrate media /4/. The extraction of HNO_3 with the salts of Zr(IV) and Hf(IV) proceeds by the acceptor mechanism according to the equilibrium

$$M\overset{O}{\underset{O}{\diagdown}}P\diagup + HNO_3 \rightleftharpoons M\overset{O-P=O}{\underset{O\cdots N\cdots O}{\diagdown}} ,$$
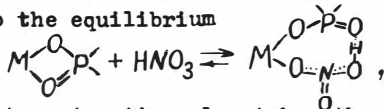
and only at high C_{HNO_3} values its extraction also takes the usual coordination path involving addition of HNO_3 through a proton to the P=O groups of the $MX_2(H_2X_2)$ salts.

$HfX_2(HX_2)_2$ solutions extract Fe(III) from solutions with C_{HNO_3} = 0.01-6 mol/l in the form of complex cations $FeNO_3^{2+}$ and $Fe_2(NO_3)_4^{2+}$ (by cation exchange mechanism) and neutral dimer $Fe_2(NO_3)_6$. The extraction of Fe(III) with acid di(2-ethylhexyl)phosphate of Zr(IV) is somewhat different. The extracted species are $Fe(NO_3)_2^+$ and $Fe_2(NO_3)_6$. The structure of these forms was established. The salts of Zr(IV) and Hf(IV) extract Eu(III) as $Eu(NO_3)^{2+}$ and $Eu(NO_3)_2^+$.

Thus in the extraction with D2EHPA it should be taken into account that the cation exchange extraction products may themselves act further as extracting agents. There are reasons to believe that the coordination chemistry of systems with D2EHPA is in many respects similar to that of the systems with phosphinic and phosphonic acids.

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The use of anion effects is one of the routs of extraction system
improvement for separation and purification of elements. In certain
cases by the replacement of a salt anion it is possible to achieve
tenfold or even hundredfold increase of its distribution coefficients
(D) using traditional extractants [1-4]. Some results are presented in
Fig. 1, 2.
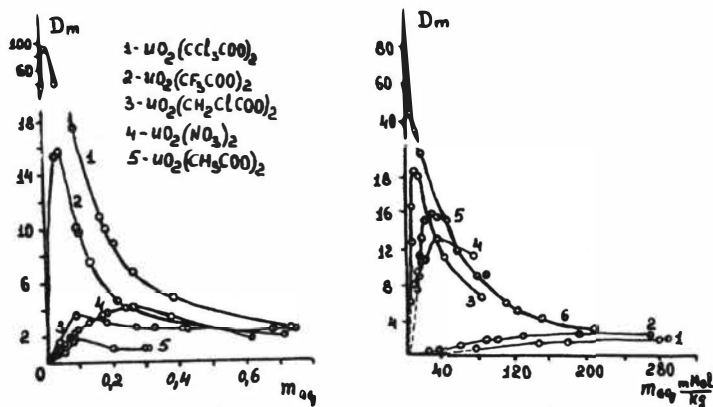
Fig. 1. Dependence of distribution coefficients of salts (TBP) on
their concentration in aqueous phase (mole/kg) at 25 °C
Fig. 2. Dependence of distribution coefficients of trichloroacetates
(TBP) on their concentration in aqueous phase at 25 °C. 1 - strontium;
2 - barium; 3 - yttrium; 4 - lanthanum; 5 - europium; 6 - uranium (VI)

The present report summarizes the results of the series of investi-
gations of salts (mainly uranyl salts) with halogenacetic acids in
ternary systems salt - water - extractant (diethyl ether (DEE) and
tributil phosphate (TBP)) at 25 °C. Fig. 3 shows examples of the obta-
ined reciprocal solubility diagrams for these systems. The totality of
known phase diagrams salt - water - extractant obtained at room tempe-
rature can be reduced to four types (Table 1). The diagrams of the
first type are wellknown [5-7] and were believed typical for the sys-
tems in question. They are characterized by the presence of a "triple"
point, i. e. the region in which a three-phase equilibrium is observed,
(Fig. 3 a, e). Essential difference of the second type diagrams from
diagrams of the first type consists in inverse dependence of salt so-
lubility on water concentration in the system (Fig. 3 f). For diagrams
of the third type the formation of a closed binodal curve is observed.
"Triple" point is nonexistent (Fig. 3 b). Fourth type is a variant of
the third one (Fig. 3 d).
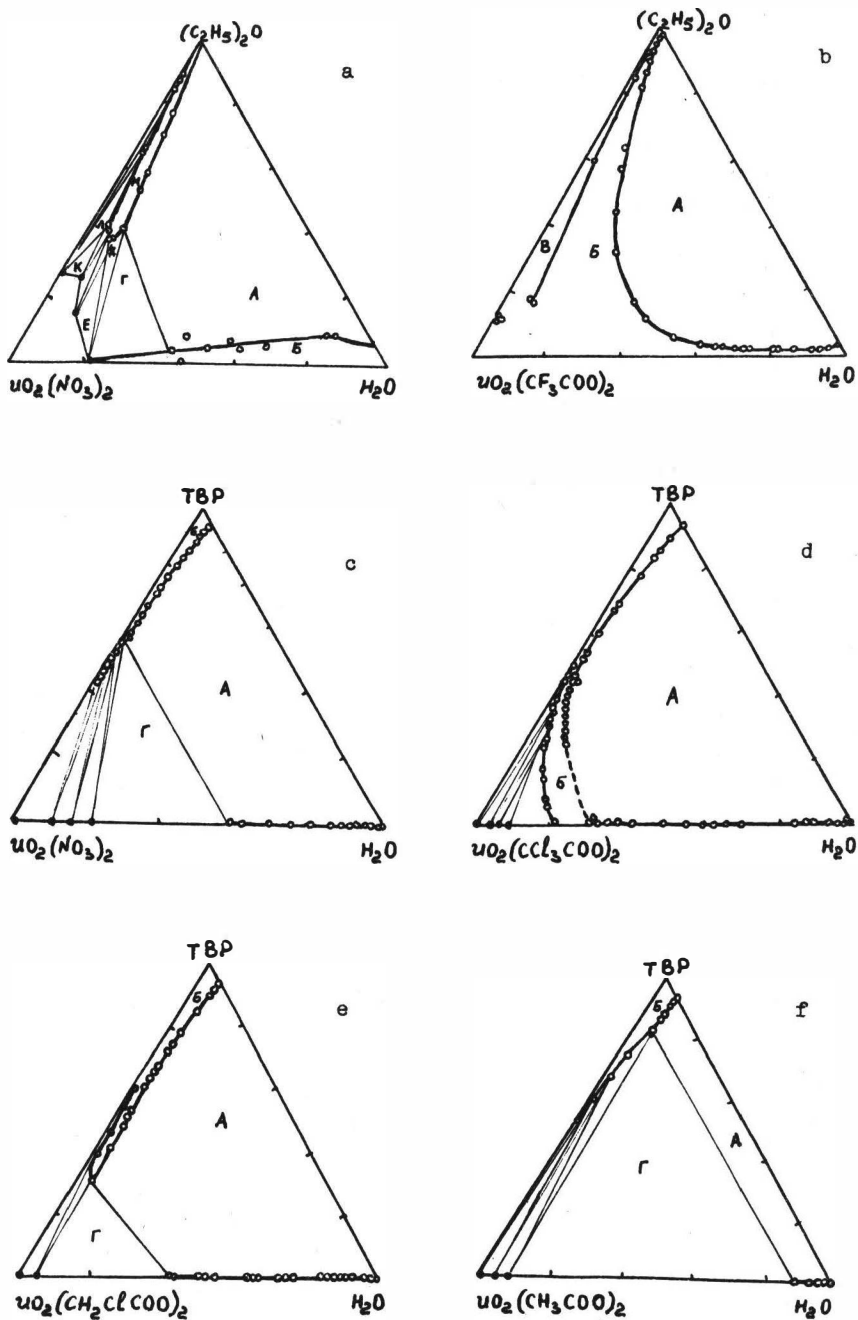
Fig. 3. Phase diagrams of ternary systems salt – water – extractant at 25 °C

The group of systems salt - water - extractant with the closed binodal curve is rather numerous, though in the case of similar systems such a phenomenon earlier was thought to be untypical. The analysis of Table 1 leads in particular to conclusion about the relationship between the phase diagram character and the properties of anion at the fixed cation and extractant. Halogenacetate-ions are convenient series for the investigations of relationship between salt characteristics and electron-donor ability of anions.

Table 2 presents the hydratation and solvatation numbers of halogenoacetates and nitrate of uranyl at the extraction by DEE and TBP. The tendency to the closed binodal curve formation correlates with hydratation number and is connected with electron-donation ability. Deviations are explained satisfactory by differences in solvatation numbers which seems to be connected with steric effects.

The data presented show that the connection of anion characteriztics with salt extraction ability is ambiguous. Nevertheless,

Table 1. Types of phase diagrams of the systems salt - water - extractant at 25 °C

Type	System
I	$UO_2(NO_3)_2$ - H_2O - ethers UO_2Cl_2 - H_2O - DEE $UO_2(ClO_4)_2$ - H_2O - $(n \cdot C_4H_9)_2O$ $UO_2(CH_2ClCOO)_2$ - H_2O - TBP $Sr(CCl_3COO)_2$ - H_2O - TBP
II	$UO_2(NO_3)_2$ - H_2O - C_4H_9OH $UO_2(NO_3)_2$ - H_2O - TBP $UO_2(CH_3COO)_2$ - H_2O - TBP
III	$UO_2(ClO_4)_2$ - H_2O - DEE $UO_2(CCl_3COO)_2$ - H_2O - DEE $UO_2(CF_3COO)_2$ - H_2O - DEE $UO_2(CH_2ClCOO)_2$ - H_2O - DEE $UO_2(C_6H_5SO_3)_2$ - H_2O - TBP $Sm(CCl_3COO)_3$ - H_2O - TBP
IV	$UO_2(CCl_3COO)_2$ - H_2O - TBP $UO_2(CF_3COO)_2$ - H_2O - TBP

Table 2. Characteristics of a series of hydrate-solvate complexes of uranyl salts

Salt	H^D_{14}	Hydratation number		Solvatation number	
		DEE	TBP	DEE	TBP
$UO_2(NO_3)_2$	0.4	4 [5]	-	3.6 [13]	2 [7]
$UO_2(CF_3COO)_2$	2.0	9.4 [8]	3.2 [4]	1.7 [12]	2 [10]
$UO_2(CCl_3COO)_2$	2.6	8.1 [8]	8.2 [4]	1.7 [12]	1 [9]
$UO_2(CH_2ClOO)_2$	4.6	6.4 [8]	1.9 [4]	1.7 [12]	1 [10]
$UO_2(CH_3COO)_2$	6.7	-	-	-	1 [11]

p. 129

taking uranyl carboxylates as an example, the possibility of a more accurate evaluation of the influence of anion electron-donor ability on the extractability of salts is demonstrated. At present the Edwards parameter is most universal and widely used characteristic of electron-donor ability of anions. As can be seen from Fig. 4 within the limits of uncertainty 5-7 kJ/mole this parameter really reflects the change of donor-acceptor interaction energetics in a series of halogenoacetates and halogenoacetic acids [15]. However, appreciable deviation in
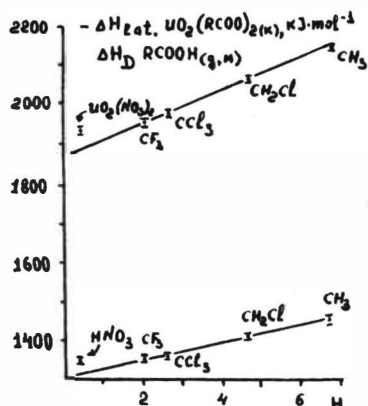
case of nitrate-ion allows us to affirm that at extension of the number of compared anions even for relative evaluation of electron-donor ability corrections should be introduced in Edwards scale.

Fig. 4. Dependences of salt lattice enthalpies and enthalpies of acid dissociation in gas on Edwards parameter

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STUDIES ON THE INFLUENCE OF DIFFERENT ANIONS ON EXTRACTION OF NEODYMIUM WITH DI(1-METHYLHEPTYL)METHYL PHOSPHONATE

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Di(1-methyl-heptyl)methyl phosphonate

$$CH_3-\underset{O}{\overset{P}{\|}}-\left[O-\underset{CH_3}{\overset{|}{C}H}-(CH_2)_5CH_3\right]_2 ,$$
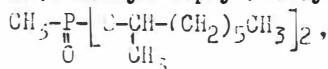
whose trade name is P-350, was developed in the sixties in China as an efficient neutral organophosphonate extractant. Although it finds wide application in industry for separation of light rare earths, investigation into extraction mechanism are nearly unknown [1]. Presented in this report is the determination of thermodynamic constants for the extraction of $Nd(NCS)_3$, $Nd(ClO_4)_3$ and $Nd(NO_3)_3$ with P-350. A comparison is made between the structures of the extracted complexes and the corresponding solid complexes using triphenyl phosphine oxide as a model molecule of P-350, and the IR data of the saturated organic phases and the solid complexes have been discussed as well.

The thermodynamic researth on extraction systems. The distribution ratios have been determined for the extraction of neodymium salts with P-350 for various P-350 concentrations using either kerosene or hexane as diluents, and using either NaNCS, NaClO_4 or NaNO_3 as salting out agents. The extraction reactions may be represented as follows:

$$Nd^{3+} + 3A^- + n(RO)_2CH_3P=O_{(o)} \rightleftharpoons NdA_3 \cdot n(RO)_2CH_3P=O_{(o)}$$

$$K_{ex} = \frac{[NdA_3 \cdot n(RO)_2CH_3P=O]_0}{[Nd^{3+}][A^-]^3[(RO)_2CH_3P=O]_o^n} = \frac{D}{[A^-]^3[(RO)_2CH_3P=O]_o^n} ,$$
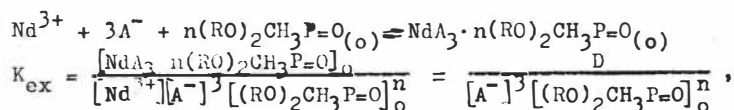
where A^- designates NCS^-, ClO_4^- or NO_3^-. Kex is the concentration equilibrium constant, and D is the distribution ratio. Then we have:

log D = log Kex + n log [(RO)_2CH_3P=O]_o + 3 log [A^-]

The unknowns Kex and n can be solved through slope analysis. Data show that the ratios of P-350 to Nd are equal to 3 for the extracted complexes, and the differences among the extraction equilibrium constants for the various systems for a given diluent are large. The value of K_{NCS^-}, $K_{NO_3^-}$ or $K_{ClO_4^-}$ is 50.56, 0.401 or 0.220 respectively.

According to the thermodynamic equation $\Delta G^o = RT \ln K$, the change or Gibbs free energy of extraction can be calculated. By using a direct static measurement with a Calvent calorimeter, the changes of enthalpy of all these extraction reactions have been obtained [2]. Consequently, the entropy changes can be calculated. The results are listed in Table 1. It can be seen that the extraction reaction of $Nd(NCS)_3$ with P-350 is the only reaction which reacts spontaneously under standard state conditions, while the other two have positive free energy changes ΔG^o. On the other hand, they are all exothermic reactions. Among them, the extraction reaction of $Nd(ClO_4)_3$ with P-350

is worthy of notice, since it has a remarkably large absolute value of ΔH^o. All of the entropy changes are negative, that is, the disorders of the systems are relatively decreased after reaction.

Table 1. The thermodynamic parameters of the extraction reactions

System	ΔG^o,KJ/mol	ΔH^o,KJ/mol	ΔS^o,J/mol K
P-350(hexane)-Nd(NCS)$_3$	-9.719	-29.92	-67.78
P-350(hexane)-Nd(ClO$_4$)$_3$	3.752	-74.31	-261.9
P-350(hexane)-Nd(NO$_3$)$_3$	2.265	-22.69	-83.68

IR spectra. Hexane solutions of P-350 saturated with Nd(NCS)$_3$, Nd(ClO$_4$)$_3$ or Nd(NO$_3$)$_3$ and the respective solid complexes of triphenyl phosphine oxide (KBr window) were examined for infrared absorption in the range of 400-4000 cm^{-1} by a Nicolet 7199B FTIR spectrometer. The characteristic absorption bands of the phosphoryl in these systems are listed in Table 2. The data show that these characteristic bands have been shifted towards lower wave number after coordination in either the saturated organic phases or in the solid complexes. It is very interesting that the perchlorate system have relatively large shifts in comparison with the other systems. This fact indicates that the structures of liquid saturated organic phase and the corresponding solid complexes are somewhat similar even though they are not exactly the same in composition. This phenomenon agrees well with the observation on the quarternary ammonium salt systems studied previously in our laboratory [6].

Table 2. Characteristic absorption bands of the P=O

Complex in hexane	Band of P=O, cm^{-1}	$r_{P=O}$ shift	Complex in KBr	Band of P=O, cm^{-1}	$r_{P=O}$ shift
P-350	1247.2		Ph$_3$P=O	1190.0	
A*	1183.9	63.3	D	1153.5	36.5
B	1177.3	69.9	E	1138.4	51.6
C	1184.5	62.7	F	1149.1	40.9

*A = Nd(NCS)$_3$.3(P-350)		B = Nd(ClO$_4$)$_3$.3(P-350)
C = Nd(NO$_3$)$_3$.3(P-350)		D = Nd(NCS)$_3$.4(Ph$_3$P=O)
E = Nd(ClO$_4$)$_3$.4(Ph$_3$P=O)		F = Nd(NO$_3$)$_3$.2(Ph$_3$P=O).C$_2$H$_5$OH

It is noted that the ratios of P-350 to Nd in hexane solution are lower than that for triphenyl phosphine oxide to Nd in solid complexes shown in Table 2. This may be caused by the replacement of P-350 by water while maintaining the same coordination number and the structure of the respective solid complexes. This is supported by the IR spectra of the saturated organic phases, in which strong broad bands appear in the region around 3300 cm^{-1}.

Discussions. In the cases of the extraction of $Nd(NCS)_3$, $Nd(ClO_4)_3$ and $Nd(NO_3)_3$ with P-350, the reactions have the same Nd^{+3} cation, but have anions of differing size, of which ClO_4^- is the largest. Thus the reaction involving ClO_4^- has the largest hollow enthalpy and the smallest hydration enthalpy. Besides these two terms, the structure of the extracted complex in the perchlorate system has another peculiarity. It is known that the $Ph_3P=O$ is not bonded with a neutral molecule, but with a $Nd(ClO_4)_2^+$ cation in the solid state complex [4]. This cation has a relatively stronger attraction for the phosphoryl oxygen than either of the neutral molecules $Nd(NCS)_3$ [3] or $Nd(NO_3)_3$ [5]. It has been observed experimentally that the [$Nd(ClO_4)_2 \cdot 4 Ph_3P=O$]$^+$ cation, in comparison with the other two complexes, has the shortest $Nd-O_p$ bond length and the largest shift in IR spectra after coordination of the phosphoryl oxygen. This produces a more favorable condition in the exothermal reaction. This is why the largest exothermal heat has been observed in the extraction of $Nd(ClO_4)_3$ with P-350.

Acknowledgement

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EXTRACTION PROPERTIES OF TBP - URANYL NITRATE DISOLVATE

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Aqueous nitric acid solutions of uranyl nitrate in the presence of
solid salt of uranyl nitrate and equilibrated organic solutions of tri-
n-butyl phosphate (TBP) represent an upper limit to concentration of
uranium in the aqueous and organic phases at a given temperature and
contain minimum "free" TBP in the organic phase. The solutions at equ-
ilibrium with the solid salt can be considered as standard ones.

On extraction of nitric acid in such systems, as it was previously
found [1], the ratio of TBP - to uranyl nitrate concentration with
increasing HNO_3 concentration in the aqueous phase remains stable and
in close to 2, in spite of increasing concentration of nitric acid in
the organic phase up to the values exceeding the concentration of ura-
nium in the organic phase. Water is co-extracted with nitric acid. It
has been proposed that the TBP - uranyl nitrate disolvate exhibits
some specific extraction properties. In this work the extraction beha-
viour of actinoids and monoacids in such systems is examined at 20 °C.

On extraction of uranyl nitrate from nitric acid solutions in the
presence of chloride ion, the co-extraction of chloride ion with ura-
nium is observed (Fig. 1), whereas in the absence of uranium the dis-
tribution coefficient of chloride ion is by two orders of magnitude
lower. The ratio between the distribution coefficients of chloride ion
(D_{Cl^-}) and nitrate ion ($D_{NO_3^-}$) is a stable value equal to 0.33 ± 0.5.

Proceeding from the experimental results on co-extraction of chlo-
ride ion with uranyl at variable concentrations of chloride and nitrate
ions, one can suppose that chloride ion extracted according to the
following reaction: $UO_2(NO_3)_2(TBP)_{2(org.)} + nCl^-(aq.) \rightleftharpoons$
$\rightleftharpoons UO_2(NO_3)_{2-n}Cl_n(TBP)_{2(org.)} + nNO_3^-(aq.)$.

At low concentration of chloride ion n is 1 and then from the equa-
tion follows the constant ratio of $D_{Cl^-}/D_{NO_3^-}$; at concentration of
chloride ion exceeding that of nitrate ion n is equal to 2.

The co-extraction of chloride ion with uranyl nitrate is similar to
the co-extraction of pertechnetate ion with uranyl nitrate [2].

Bromide, fluoride, azide and thiocyanate ions have the analogous
behaviour in this case. However, on co-extraction of azide and thiocy-
anate ions the situation becoms more complicated because of extraction
of the corresponding acids by TBP. But on increase of uranium concent-
ration in the organic phase the extraction by "free" TBP is decreased
and in the presence of the solid salt of uranium anion exchange pro-
cess takes place (Fig. 2). The concentration of azide and thiocyanate
ions in the organic phase is by several times higher than the concent-
ration of sum acids in the organic phase, i. e. the anions are comple-
tely bound with uranium disolvate.
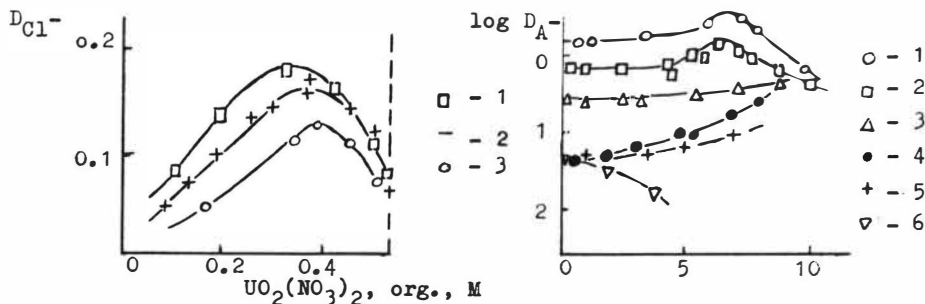
Fig. 1. Co-extraction of chloride ion with uranyl nitrate in 30 % TBP in CCl_4. Concentration of nitric acid in aqueous phase: 1 - 0.5 M; 2 - 1.0 M; 3 - 3.0 M

Fig. 2. Co-extraction of anions by 30 % TBP - CCl_4 in the presence of $UO_2(NO_3)_2$ salt. 1 - SCN^-; 2 - N_3^-; 3 - TcO_4^-; 4 - Cl^-; 5 - Br^-; 6 - F^-

In Fig. 3 the extraction of tetravalent actinoids tracers into TBP saturated with uranium in the presence of solid uranyl nitrate is shown. This dependence differs significantly from the extraction of actinoids into the "free" TBP and is described by the equation: $\log D_{An} = B \cdot N + C$, where D_{An} - distribution coefficient of tetravalent actinoid at the constant concentration of uranium and HNO_3 in the aqueous phase, N - atomic number, B and C - constants.

In order to determine salting-out properties of uranyl nitrate, the experiments were conducted on the extraction of plutonium from aqueous nitric acid solutions at different ratio between the concentrations of magnesium nitrate and uranyl nitrate. This ratio was adopted in such a manner that at the constant concentration of nitric acid in the aqueous phase the water activity and activity coefficients of uranium and plutonium were unaffected and were equal to those in the system with the solid salt of uranyl nitrate.

The activity coefficients were calculated according to [3]. The salting-out properties of uranium-magnesium system should be steady at variable content of uranyl nitrate. So, the ratio of An (IV) distribution coefficients and uranyl nitrate in such a system should be also constant taking into account the formation of corresponding disolvates in the organic phase. As it is seen from Fig. 4, in the case of Pu (IV) this does not take place. Fig. 4 shows, that the ratio between the distribution coefficients of plutonium and uranium on extraction from uranium-magnesium systems with permanent salting-out effect and on extraction from the systems without magnesium nitrate (with variable salting-out) is practically the same over the whole investigated range.

The ratio of distribution coefficients seems to depend not on the salting-out properties of the aqueous phase, but on the interaction of
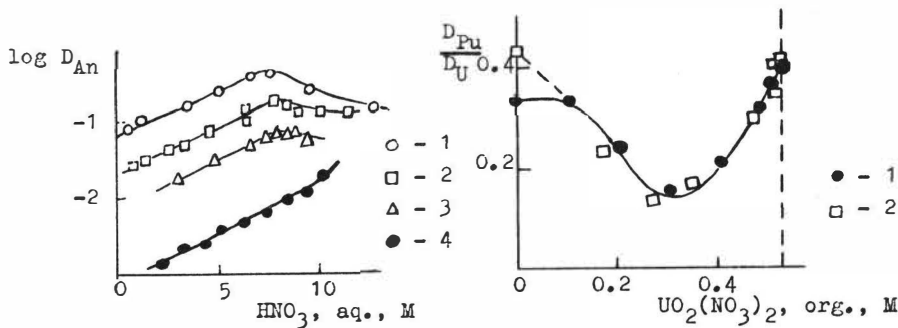
Fig. 3. Distribution of tetravalent actinoids between nitric acid so-
lutions and 30 % TBP - CCl_4 in the presence of $UO_2(NO_3)_2$ salt. 1 - Pu;
2 - Np; 3 - U; 4 - Th
Fig. 4. Dependence of the ratio of Pu (IV) and U (VI) distribution co-
efficients on uranium concentration in 30 % TBP - CCl_4 2 M HNO_3.
1 - $UO_2(NO_3)_2$ - HNO_3; 2 - $UO_2(NO_3)_2$ - $Mg(NO_3)_2$ - HNO_3 under permanent
salting-out effect

actinoids in the organic phase, since the data obtained point to on
preferable salting-out of plutonium in comparison with uranium. More-
over, on initial portion of the curve (Fig. 3) the decrease in ratio
of distribution coefficients is evident and this is testimony to the
relative displacement effect of uranyl nitrate in the organic phase
which may result from the specific exchange reactions between uranium
and plutonium solvates. As for the range of higher uranium concentra-
tions shown in Fig. 4, it should be taken into consideration that the
tetravalent actinoids are prone to the formation of anion complexes
and this tendency decreases in the following sequence: Pu, Np, U, Th.
It can be supposed that the anion exchange properties of TBP - uranyl
nitrate disolvate lead to extraction of actinoids in the form of anion
complexes, as in the case of their extraction by amines.

The formation of the anion complexes of tetravalent actinoids on
their extraction by TBP - uranyl nitrate disolvate may be responsible
for increasing ratio of distribution coefficients with increased ura-
nium concentration (Fig. 4) and for dependence nature (Fig. 3).

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Extraction of metal ions from aqueous nitric acid solutions with
zirconium di-2-ethylhexyl phosphate complexes conforming with the
$ZrA_4(HA)_2$ gross-composition where A is an anion ofdi-2-ethylhexylphos-
phoric acid (D2EHPA) is significantly impaired with the growth of nit-
ric acid concentration in the aqueous phase. In literature this fact
is explained by both the salting out effect of the acid and a decreas-
ed probability of hydrogen ion exchange in HA molecules that solvate
zirconium in $ZrA_4(HA)_2$, for ions of a metal extracted with an increase
of the hydrogen ion concentration in the aqueous phase. This explanat-
ion is similar to the existent concepts of the influence of the aque-
ous phase acidity on the metal extraction with acid extractants,
D2EHPA, in particular. In this case the intensification of extraction
of metals with D2EHPA that is in the solvate shell of zirconium com-
plexes as compared to free D2EHPA is ascribed to higher acidic proper-
ties of D2EHPA molecules that enter into the composition of $ZrA_4(HA)_2$
complexes [1].

The validity of this explanation of the extraction intensification
does not seem convincing, since the suggested increase of pK_a for sol-
vating D2EHPA molecules cannot alter the conditions of the ion exchan-
ge and competition between hydrogen ions and a metal being extracted
in the presence of nitric acid. At the same time, in nitric acid ext-
raction from aqueous solutions using $ZrA_4(HA)_2$ complexes in an organic
phase A^- anions can be displaced and substituted by NO_3^- anions to form
mixed complexes, that have no extraction ability for ions of a metal
being extracted.

To determine the exact composition and partial concentration of
zirconium di-2-ethylhexyl phosphate complexes in the organic phase
following its contact with the aqueous solution of nitric acid and
strontium and to establish the mechanism of nitric acid and strontium
extraction with zirconium di-2-ethylhexylphosphate complexes we have
studied the ^{14}N and ^{31}P $-\{^1H\}$ NMR spectra of the extraction system
consisting $ZrA_4(HA)_2 - C_{10}H_{22}-H_2O-HNO_3-Sr$ as dependent on the concent-
ration of its components. It is possible to observe the ^{14}N NMR spect-
ra only for extracts that were in contact with an aqueous solution,
containing more than 5 mole/l nitric acid. At the lower acid concent-
rations of the aqueous solution the ^{14}N NMR signals in the organic
phase are not observed due to the influence of the nitrogen- 14 quad-
rupole relaxation on the NMR line width of NO_3^- anions that are present

in zirconium complexes and are likely to be characterized by a signi-
ficantly lower symmetry of the electric field on the nitrogen nucleous
having a quadrupole moment as compared to free NO_3^- anions.

Fig.1 shows typical $^{31}P - \{^1H\}$ FT NMR spectra obtained using gated
broadband decoupling from protons for the extraction system consist-
ing ZrA_4 $(HA)_2 - C_{10}H_{22}-H_2O-HNO_3$. At the concentration ratio
$z = [NO_3^-]/[Zr^{4+}] \leqslant 1$ in the organic phase one observes an intensive peak
of ZrA_4 $(HA)_2$ complexes with a chemical shift $\delta_2 = -7.46\pm0.02$ ppm and
three weak peaks with the relative intensities of 2,5 and 6% and che-
mical shifts $\delta_1 = -5.45\pm0.02$, $\delta_3 = -9.07\pm0.02$ and $\delta_4 = -13.36\pm0.02$ ppm
respectively, which are likely to be due to polynuclear zirconium
di-2-ethylhexyl phosphate complexes with the ZrA_4 $(HA)_2$ gross-composit-
ion. For a peak with the chemical shift δ_2 the relative intensity of
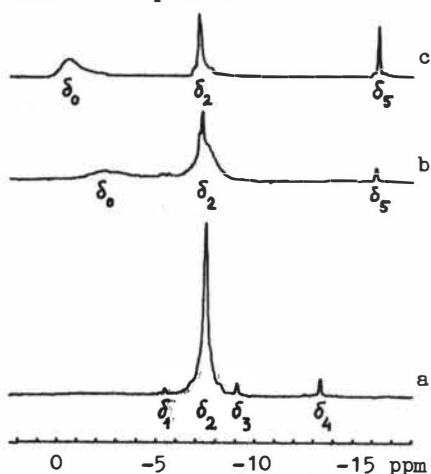
Fig.1. 36,44 MHz $^{31}P-\{^1H\}$ FT NMR
spectra of $ZrA_4(HA)_2-C_{10}H_{22}-H_2O-$
HNO_3 at different ratios z:
a - 0.07, b - 1.4, c - 2.63

which is 90%, one does not observe
separation into multiplets corres-
ponding to non-equivalent ligands in
ZrA_4 $(HA)_2$ complexes because of a
quick intracomplex exchange of li-
gands, although a little asymmetry
of the observed ^{31}P NMR lineshape
can be due to unresolved ^{31}P peaks
of A^- anions and solvating HA mole-
cules in the complexes.

At the concentration ratio z > 1
the ^{31}P peaks with the chemical
shifts δ_1, δ_3 and δ_4 disappear while
the peak with the chemical shift δ_2
decreases in intensity, is a little
displaced to the low-field region
and separated at least into two com-
ponents. Simultaneously in the ^{31}P
NMR spectrum there appears a free
D2EHPA peak the chemical shift of

which depends on the concentration of nitric acid in the organic phase
and a peak with the chemical shift $\delta_5 = -16.13\pm0.02$ ppm. The intensities
of the free D2EHPA peak (δ_0) and the peak with the chemical shift δ_5
increase with growthing the ratio z, in this case the peak with the
chemical shift δ_5 is a little displaced to high-field, e.g.,
$\delta_5 = -16.36\pm0.02$ ppm at z=3.31. These changes in the spectrum with in-
creasing the concentration ratio z evidence not only to the displace-
ment of A^- anions and their substitution by NO_3^- anions zirconium com-
plexes and the formation of mixed complexes and appearance of free
D2EHPA in the organic phase but also to the non-equivalence of organo-
phosphorous ligands in the mixed complexes, $ZrA_{4-x}(NO_3)_x(HA)_2$, one of

which is characterized by the chemical shift δ_5 and is not displaced out of the complex by NO_3^- anion even at the concentration ratio $z \approx 4$ in the organic phase. This ligand is likely to show a bidentatic bond with a complexing ion as a result of which its chemical shift is more than by a factor of two higher in the absolute value than those of the rest ligands in mixed complexes, $ZrA_{4-x}(NO_3)_x(HA)_2$.
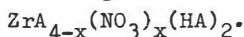
The relative intensities of peaks in the $^{31}P-\{^1H\}$ NMR spectra for free D2EHPA and ligands of zirconium complexes were used to determine the P number of organophosphorous ligands in mixed zirconium complexes as dependent on the z concentration ratio in the organic phase and to calculate the partial concentrations of mixed complexes by the equation: $P = 6p_0 + 5p_1 + 4p_2 + 3p_3$, where p_0, p_1, p_2 and p_3 are relative partial concentrations of $ZrA_{4-x}(NO_3)_x(HA)_2$ complexes at x=0,1,2 and 3, respectively. Fig.2 shows partial concentrations p_x and the P number of organophosphorous ligand in zirconium complexes as dependent on the z concentration ratio in the organic phase. The calculated dependence of P agrees well with the experimental data obtained from the analysis of peak intensities in the $^{31}P-\{^1H\}$ NMR spectra of nitric acid extracts (fig.1).

Fig.2. Dependences of the P number of organophosphorous ligands and partial concentrations p_x in $ZrA_{4-x}(NO_3)_x(HA)_2$ complexes on the ratio z: 1 - x=0, 2 - x=1, 3 - x=2, 4 - x=3, 5 - experimental, 6 - calculated by equation $P = 6p_0 + 5p_1 + 4p_2 + 3p_3$

When extracting strontium from nitric acid solutions containing 0.7 mole/l strontium nitrate with a monomolar solution of D2EHPA in decane, containing 0.125 mole/l $ZrA_4(HA)_2$ complexes, the strontium concentration in the organic phase depends on the nitric acid concentration of that phase and decreases with increasing the acidity of the aqueous solution of strontium. Fig.3 shows the typical ^{31}P NMR spectra obtained without proton decoupling for the extraction system, consisting $D2EHPA-C_{10}H_{22}-H_2O-HNO_3-Sr$. Three peaks of this spectrum belong, respectively, to free D2EHPA ($\delta_0 \simeq 0$ ppm), $ZrA_4(HA)_2$ complexes ($\delta_{Zr} = -7.56 \pm 0.02$ ppm) and zirconium-strontium complexes ($\delta_{ZrSr} = -10.4 \pm 0.02$

Fig.3. ^{31}P NMR spectra of D2EHPA-$C_{10}H_{22}$-$\overline{Zr-H_2O}$ (a), D2EHPA-$C_{10}H_{22}$-Zr-H_2O-Sr (b) and D2EHPA-$C_{10}H_{22}$-Zr-H_2O-Sr-HNO_3 (c-g) at different concentrations HNO_3 in the aqueous phase: c - 0.01, d - 0.05, e - 0.1, f - 0.5, g - 1.0 mole/l
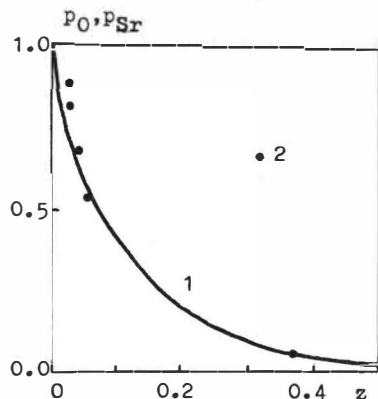
Fig.4. Dependences of relative partial concentrations p_0(1) of $ZrA_4(HA)_2$ complexes and the extracted strontium p_{Sr}(2) on the ratio z

ppm). With the growth of the strontium concentration in the extract the peak intensity with the chemical shift δ_{Zr} decreases, the peak intensity with the chemical shift δ_{ZrSr} increases while the sum of the intensities of these peaks remains constant. The data suggest the extraction of strontium into the organic phase to be performed with $ZrA_4(HA)_2$ complexes in which two hydrogen ions of D2EHPA molecules solvating ZrA_4 complex are substituted by one ion of Zr^{2+} to form $Zr \cdot A_4 \cdot SrA_2$ complex. The comparison between the dependences of the p_0 relative partial concentration of $ZrA_4(HA)_2$ complexes and the p_{sr} extracted strontium concentration on the z concentration ratio (fig.4) points to their symbatic behaviour and permits conclusion to be drawn that strontium ions are extracted only with $ZrA_4(HA)_2$ complexes while mixed complexes do not show any extraction ability for strontium. Hence, the nitric acid influence on strontium extraction with zirconium di-2-ethylhexyl phosphate complexes shows up as a decrease of the partial concentration of $ZrA_4(HA)_2$ complexes in the organic phase and in the end they determine the extraction ability and capacity of an extractant.

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Introduction. The formation of lanthanide(Ln(III)) complexes with the
organic reagent acetylacetone (HAa) has been studied with a liquid-liquid
extraction technique using trace amounts of radioactive lanthanides and the
AKUFVE-LISOL technique. The extraction is poor with a maximum distribution
ratio (D) between the organic and aqueous phase of 0.05(Nd) - 1.3(Lu) at 1 M
HAa. The cause of this low extraction, which also holds for trivalent acti-
nides, is surprising in comparison to how well the tetra- and hexavalent
actinides are extracted, and therefore worth investigating, considering its
importance in nuclear fuel reprocessing. Also a better understanding of the
coordination chemistry of the lanthanides can be achieved.

Experimental equipment. The AKUFVE is a continuous solvent extraction
apparatus developed a long time ago [1], while the LISOL is a recent detector-
system [2], now coupled to the AKUFVE. LISOL stands for LIquid Scintillation
On-Line. The new system has made it possible to investigate complexation more
thoroughly and with much higher precision than before. Thus the AKUFVE-LISOL
is able to measure distribution values between 10^{-5} and 10^5, and at as high
pH as 9. The principle of the technique is a continuous withdrawal of a small
fraction of the streaming liquid, aqueous or organic, to which a strong acid
to supress sorption and a scintillation cocktail is added. After mixing of
the liquids, they are fed to a scintillation detector arrangement.
   The most prominent features of the LISOL is that when most other measuring
systems fail because of problems with memory effects at high sorption levels,
the LISOL can be used for measurements at very high sorption levels with no
significant effect on the measured D-value. Moreover, the technique is almost
independent of the radioactive decay scheme of the used nuclide. The limita-
tion is the quenching problem, which can be severe for certain systems [3];
this can, however, be corrected for in most chemical systems.

Chemical conditions. The complex formation of acetylacetone with the lan-
thanides has been studied in a two-phase system with 0.1 - 4 M HAa in
benzene/ 1 M Na(H)ClO$_4$ in water at pH 3-9.
   The organic phase consisted of distilled HAa dissolved in washed benzene
and the aqueous phase was prepared using NaClO$_4$ of analytical grade. The ra-
dioactive lanthanides were prepared by .neutron activation of the pure oxides
(>99.999%) and the radiochemical purity was checked by gamma spectrometry.

No radiochemical impurity could be detected. In all experiments the concentration of lanthanides was between 10^{-4} and 10^{-6} M, and the temperature was kept at 25°C. The experiments were made in an inert nitrogen atmosphere.

For each lanthanide three different sets of experiments were done. (i) The first set consisted of extraction with 1.0 M and 3.0 M original concentration of HAa in the organic phase. The pH was varied between 3 and 9. Each extraction curve contained about 40 points. (ii) For better understanding of the complexes formed in the organic phase, a second set of experiments were performed, where the $[Aa^-]$ was kept constant but the HAa-concentration in the organic phase was varied. This is easily done by on-line addition of small amounts of H^+ or OH^- to keep pH constant in the continuous AKUFVE system. (iii) To account for the quenching, a third set of experiments were done under the same conditions, but this time no radioactivity was added to the AKUFVE. The activity was instead added to the strong acid used for the LISOL sorption supression, the same amount for each phase, and the ratio of measured counts in the two phases was recorded and used for correcting the measured D-values.

At the high pH required (pH ≤ 9) for the extraction, hydrolysis and mixed complexes can not be excluded. By using available literature data [4,5] and the extrapolation technique described in ref. [6], the contribution of each of these other complexes to the total complexation was estimated. It was found that these other species could be neglected compared to the simple $LnAa_y$-species (y=1 to 4). In the organic phase an adduct formation of HAa to the $LnAa_3$-complex is indicated. Taking the above mentioned into consideration, the model equation for the Ln(III)-extraction will be:

$$D = \frac{P_3\beta_3[Aa^-]^3(1+ka_1[\overline{HAa}]+ka_2[\overline{HAa}]^2)}{1+\beta_1[Aa^-]+\beta_2[Aa^-]^2+\beta_3[Aa^-]^3+\beta_4[Aa^-]^4} \qquad , \qquad (1)$$

where β_n is the equilibrium constant for formation of $LnAa_n^{3-n}$ ($\beta_n=[LnAa_n^{3-n}]/[Ln^{3+}][Aa^-]^n$), P_3 is the distribution constant for $LnAa_3$ between the organic and the aqueous phase and ka_n is the adduct formation constant for the $LnAa_3(HAa)_n$ complex in the organic phase. Upper bars refer to the organic phase.

At equal phase volumes, the free ligand concentration, $[Aa^-]$, is

$$[Aa^-] = \frac{Ka[\overline{HAa}]_0}{[H^+]+P_{HAa}\cdot[H^+]+Ka} \qquad , \qquad (2)$$

where $P_{HAa}=4.5$ and $Ka=10^{-9.0}$ at 25°C and 1 M $NaClO_4$, and $[\overline{HAa}]_0$ is the original concentration of HAa in the organic phase.

Results and discussion. The experimental data were fitted to eqn. 1 with a least squares program (simplex method), where the weighted error square sum was minimized. From the fitting it was concluded that the first formation constant β_1 could not be evaluated with any high accuracy. Since our β_1-values agreed with those of Grenthe et al [7], and since their technique for obtaining β_1 is more accurate than ours, we have used their β_1-values in our evaluation of the other constants. The literature value for β_1 adjusted to 1 M Na(H)ClO$_4$ and the values of β_2, β_3, β_4, P$_3$ and ka$_1$ are listed in Table 1.

Table 1. Equilibrium constants of lanthanide acetylacetonates

	$_{60}$Nd	$_{61}$Pm	$_{62}$Sm	$_{63}$Eu	$_{65}$Tb	$_{67}$Ho	$_{69}$Tm	$_{71}$Lu
log β_1	5.21	5.30	5.50	5.78	5.93	5.96	6.00	6.14
log β_2	8.87	9.20	9.30	9.79	10.00	9.93	10.43	10.58
log β_3	11.86	12.23	12.59	13.12	13.34	13.31	13.82	13.91
log β_4	13.57	14.07	14.31	14.97	15.26	15.24	15.66	15.70
log P$_3$	-3.5	-2.8	-2.2	-1.7	-1.4	-1.0	-0.35	-0.05
log ka$_1$	2.6	1.9	1.3	0.71	0.62	0.54	0.25	0.12
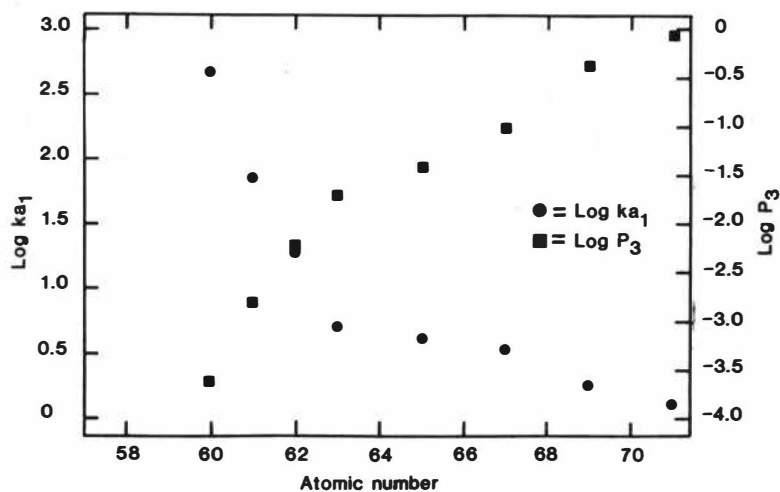
Figure 1. The distribution constant P$_3$ for LnAa$_3$ and the adduct formation constant ka$_1$ for LnAa$_3$·HAa versus atomic number

The β_n-values show an increase with increasing atomic number (Tab. 1), as expected due to the lanthanide contraction which increases the metal charge density and thus also the strength of the electrostatic bond to the acetylacetonate oxygen atoms. The fourth complex $(LnAa_4^-)$, though not earlier reported except for $_{63}Eu$ [6], is clearly indicated in our investigation.

That the value P_3 for the distribution constant of the $Ln(Aa)_3$-complex is low is probably because the extracted species contain 2 or 3 water molecules which makes them rather hydrophilic. It can be compared with the coordinatively saturated $PuAa_4$, which has a P_4 of about 400 [8]. This supports that an adduct complex can be formed in the organic phase, one HAa replacing two H_2O.

From the distribution of the uncharged complex (P_3) in Fig. 1, it can be seen that there is a break around atomic number 63 (europium). This is also shown in the adduct formation constant ka_1. It may be explained by the fact that the coordination number of 8 is reached around atomic number 63, and from then on the organic phase equilibrium is dominated by the reaction $LnAa_3(H_2O)_2 + HAa \rightleftharpoons LnAa_3HAa + 2H_2O$.

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Ions of d-electron 4th period metals can transfer from aqueous
sulphate solutions into the organic phase containing carboxylic acid
as an extraction reagent following two different extraction mecha-
nism: cation-exchange mechanism which is described by equations of
single and multiple equilibria models; hydratation-solvation mecha-
nism the nature of which is extraction of ion pairs composed of hyd-
rated and solvated hydrogen cation and complex metal anion.

The occurence ranges of the two different extraction mechanisms
are separated with the extraction minimum (Fig.1). The position of
the extraction minimum and the occurence ranges of the two extracti-
on mechanisms depend on the composition and the physicochemical pro-
perties of the aqueous phase (pH, the kind of metal ion and its com-
plexformative properties, etc.). In the cation-exchange area the ex-
traction process is much more effective than within the area in which
metal ions transfer into the organic phase following the hydratation-
solvation mechanism. Within the two areas the extraction of particu-
lar metal ions is considerably varied, which is indicated by the va-
lues of partition coefficients D and concentration constants of the
extraction K_{ex}. Within the occurence range of the cation-exchange me-
chanism the metal ions complexes, the compositions of which were de-
termined by partition methods, occur in the organic phase as solvated
or non-solvated monomers, eg. $MnAr_2$, ZnR_2; as dimers, eg. $(CuR_2 \cdot 2HR)_2$,
$(MnR_2 \cdot HR)_2$, $(CrR_2 \cdot 2HR)_2$ or as trimers, eg. $(FeR_3)_3$, $(FeAr_3)_3$, where:
R - radical of alyphatic acid, Ar - aromatic acid radical (Table).

It was pointed out that some discrepancies in the interpretation
of the experimental data can be eliminated by replacing·little accu-
rate graphical methods with analytical methods as well as by accura-
tely defining some basic assumptions of single and multiple equilib-
ria models with particular regard to the functions describing the ex-
traction process.

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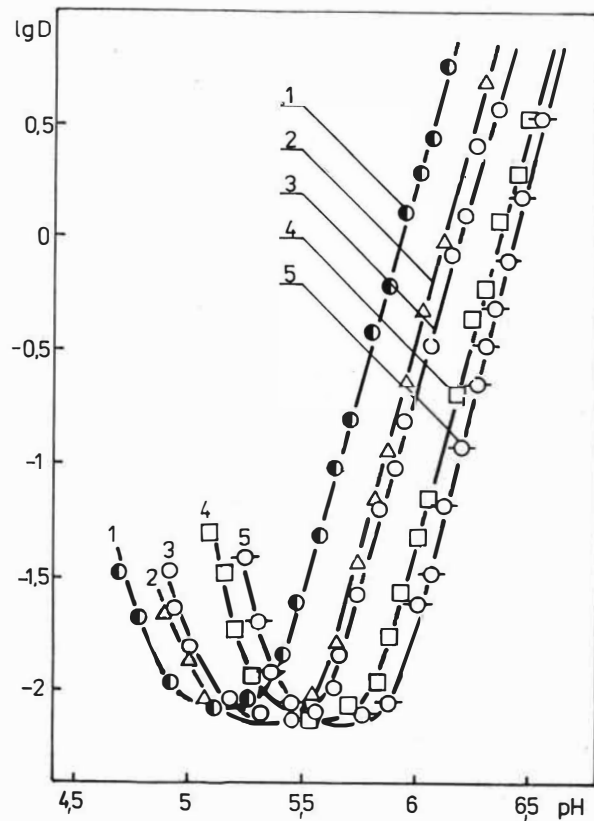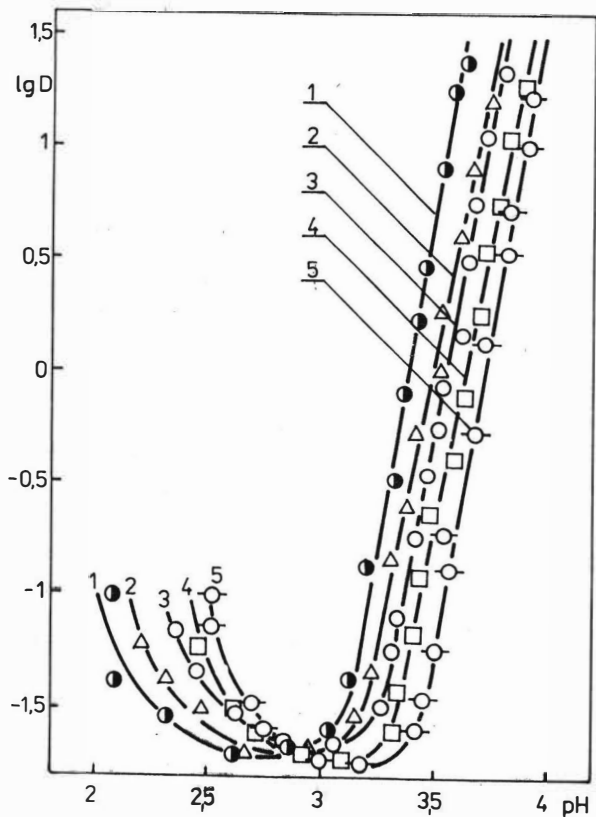
Fig.1. Extraction of Cr(III) (a) and Mn(II) (b) with hexanoic acid (0.6 M)
Metal conc.: $1 - 5 \cdot 10^{-2}$; $2 - 1 \cdot 10^{-2}$; $3 - 5 \cdot 10^{-3}$; $4 - 1 \cdot 10^{-3}$; $5 - 5 \cdot 10^{-4}$ M

Metal	Complexes		opt pH		R,%	
	HR	HAr	HR	HAr	HR	HAr
Sc(III)	Butanoic acid in isoamyl alcohol [1], isobutyl alcohol [2]	$H_3\left[Sc(Hal \cdot C_8H_5O_3)_3 \cdot H_2O\right]$ Hal = Cl, Br [3]	3.0 [1] 3.5 [2]	3.0[3]	99-100	99[3]
Ti(III)	$\left[(TiO^+)(R^-)\right]_\infty$ [4] R = C_8	Salicylhydroxyoxime acid [5]	4.5-5.0 [4]	-	100 [4]	97-100
V(IV)	$\left[VO(OH)R(HR)\right]_2$ R = C_8 $VO(H_2O)_3R_2$ R = C_2-C_8	-	-	4.2-6.8	>1	80-98
Cr(III)	$(CrR_3 \cdot 2HR)_2$ R = C_6-C_{10}	-	3.5-4.0	-	99	-
Mn(II)	$(MnR_2 \cdot 2HR)_2$ R = C_6-C_{10}	$MnAr_2$ Ar = $C_6H_5COO^-$	5.5-6.5	5.0	92	20
Fe(III)	$(FeR_3)_3$ R = C_6-C_{10} $(FeR_3 \cdot H_2O)_3$ [6]	$(FeAr_3)_3$ Ar = $C_6H_5COO^-$	1.8-3.0	2.5-3.5	98	100
Co(II)	$CoR_2 \cdot 2HR$ R = C_6-C_{10}	no extr.	5.5-6.5	-	90	0
Ni(II)	$NiR_2 \cdot 2HR$ R = C_6-C_{10}	no extr.	5.5-6.5	-	90	0
Cu(II)	$(CuR_2 \cdot 2HR)_2$ R = C_6-C_{10}	$(CuAr_2 \cdot 2HAr)_2$ Ar = $C_6H_5COO^-$ o-$CH_3C_6H_4COO^-$	3.5-4.5	4.0 5.0	90	98
Zn(II)	-	$ZnAr_2 \cdot 2HR$ Ar = $C_6H_5COO^-$	-	5.0	-	65

ACCEPTOR EXTRACTION OF URANYL SALTS WITH MIXTURES OF
ORGANOPHOSPHORIC ACIDS WITH NEUTRAL ADDITIVES

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The extraction of uranium with mixtures of organophosphoric acids
(HX) (di-2-ethylhexyl phosphoric acid (D2EHPA) and di-2-ethylhexyl
dithiophosphoric acid (D2EHDTPA), amyl-2-ethylhexyl phosphoric acid
(A2EHPA), diheptyl phosphoric acid (DHPA) with neutral additives L
(TBP, triphenyl phosphine oxides (TPPO), tri-isoamyl phosphine oxides
(TAPO), diphenyl sulphoxides (DPSO) and dioctyl sulfoxides (DOSO),2-
nonylpyridine-N-oxide (2-NPO))exhibit, along with the widely known
synergic effect at low HX saturations with uranium , a new synergic
effect occuring after complete saturation of HX .

 Extraction with mixtures HX + L . A comparison of the extraction
isotherms of uranyl salts (nitrate, chloride, sulfate) with benzene
solutions of HX and mixtures of HX with L as to the synergic effects
in these processes permitted us to classify the observed extraction
dependences into three types (Fig. 1). First, the extraction of uranyl
nitrate with HX + L mixtures is superior to that with HX solutions
over the entire range of uranium concentrations (Fig. 1a). The second
type is characterized by the presence of two regions of synergic ext-
raction and a transitional (antagonistic) region the length of which
is determined by the nature
and concentration of L (Fig.
1b). This type is realized
in the extraction of uranyl
sulphate and chloride with
mixtures of D2EHPA with L.
The third type (Fig. 1c)
shows synergic extraction
only at high uranium con-
centrations and was estab-
lished for mixtures with
phosphinic and phosphonic
acids. A feature common to
all of these cases is an in-
creased uranium content in
the organic phase exceeding
considerably the maximum con-
tent achievable with the ca-
tion exchange mechanism (U:
: HX= 1:2) for high con-

Fig. 1. Types of dependences in the ext-
raction of $UO_2(NO_3)_2$ and UO_2SO_4(b,c) with
HX and mixtures of HX+L in benzene. (a)
1) 0.2M DOSO, 2) 0.28M D2EHPA , 3) mix-
ture(1)+(2); (b) 1) 0.3M D2EHPA, 2)-6)
mixtures 0.3M D2EHPA+0.5M L (2-TBP, 3-
-DOSO, 4-TPPO, 5- 2-NPO, 6- TAPO);
(c) 1 - 0.1M DHPA, 2 - 0.1M A2EHPA,
3-4 - mixtures 0.1 HX + 1M PSO (petro-
leum sulfoxides) (3-DHPA, 4-A2EHPA)

centrations of the uranyl salts. The form of the dependences in Fig.1 results from superposition of cation-exchange and noncation-exchange synergic effects.

Cation-exchange synergic effect. In the absence of L, the uranium extraction with acids(Fig. 1) changes in an antibate manner with their acidic properties: DHPA(pK_a=3.6) > A2EHPA (2.7) > D2EHPA(2.1) > D2EHDTPA(1.2) and analogously to the corresponding neutral compounds which is due to the predominantly covalent character of bonding in the formation of intracomplex compounds (ICC) of uranyl with HX. It can, therefore, be assumed that the acceptor power of the uranium atom (effective positive charge) in ICC has the opposite trend, i.e., it increases with increasing acidic properties of HX and with decreasing ICC stability. In accord with this, the synergic effect (S) for mixtures of HX with PSO (Fig. 2a) has the highes value for D2EHDTPA and the lowest value for DHPA. In a series of L (Fig. 2b) the effect increases (TAPO > 2NPO > DOSO > TPPO > TBP > DPSO) with increasing donor power of the oxygen atom in L (except for TPPO) characterized by the shift ΔV_{sym}(OH) of water in the IR spectrum upon the interaction of water with L in CCl_4 (the values of ΔV_{OH} are shown in the table) .

Fig. 2. Synergic effect in the uranium extraction with mixtures of HX with PSO (a) and D2EHPA with L (b). HX concentration - 0.1 M, uranium concentration - - 0.002M. a): (1) - D2EHDTPA, (2)-D2EHPA, (3) - A2EHPA, (4)- DHPA. b): (1)- TAPO, (2) - 2NPO, (3)-DOSO, (4)-TPPO, (5)-DPSO
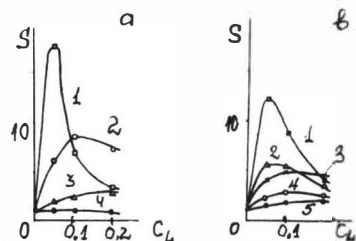
The synergic effect at low uranium concentrations (region 1 in Fig.1b) is due to formation of addition complexes $UO_2(HX_2)_2L$ for mixtures of D2EHPA with TBP [1] , DOSO , or substitutional complexes UO_2XHX_2L and $UO_2X_2 2L$ for more active TAPO [1] and 2NPO. As the uranium concentration increases this effect is replaced by the antagonistic one (region II) at U:HX ratio of 1:4 [2] which occurs as a result of the interaction of HX with L, an insufficient amount of HX to form a mixed complex, and other processes. In the second case, the high value of S and formation of substitutional complexes prevent occurence of the antagonistic extraction. On the contrary, the small values of S in the mixtures of A2EHPA and DHPA with PSO result in the antagonistic region being in this case the only one up to complete HX saturation (Fig. 1b).

Noncation-exchange extraction. In all of the systems shown in Fig.1 a sharp increase of the uranium content in the organic phase is observed after saturation of HX with uranium (the highest values of

U:HX are equal for UO_2SO_4 to 0.452 ± 0.003 (D2EHPA), 0.472 ± 0.012 (A2EHPA) and 0.456 ± 0.07 (DHPA); for UO_2Cl_2 they are equal to 0.500 ± 0.006 and somewhat higher for $UO_2(NO_3)_2$ in the case of D2EHPA). Judging by the presence of anions (inorganic) in the extract, the superstoichiometric extraction in region III is due to recovery of uranyl salts. The actual components of the synergic mixtures in the noncation-exchange extraction are polymeric salts $(UO_2X_2)_p$ and L (after reextraction of the uranyl salts with water the values of U;HX for the mixtures HX+PSO and UO_2SO_4 are equal to 0.459 ± 0.008 (D2EHPA), 0.462 ± 0.005 (A2EHPA), 0.462 ± 0.006 (DHPA), for mixtures of D2EHPA with TBP and DOSO this value is equal to 0.448 ± 0.003 and 0.440 ± 0.008, for these mixtures and UO_2Cl_2 it is equal to 0.500 ± 0.006, almost coinciding with the above values). The regularities of the noncation-exchange extraction of the uranyl salts confirm the coordination nature of the new effect: the effect increases with decreasing dehydration energy of the uranyl salt anions ($NO_3^- > Cl^- > SO_4^{2-}$) strictly according to the values of ΔV_{OH} with the change of L and with decreasing ICC stability with the change of HX. Under optimum conditions the value of S reaches 10^2.

The analogy of the synergic action of the acid and neutral compo — nents of the mixture in the extraction from diluted and concentrated solutions of uranyl salts indicates the same nature of these two effects both of which are determined by the acceptor properties of the uranium atom in monomeric $UO_2(HX_2)_2$ and polymeric $(UO_2X_2)_p$ complexes in the addition of, respectively, L and the coordination compounds of the uranyl salts with L due to the bridging anion.

Extraction with mixtures UO_2X_2 and L. A quantitative description has been made for uranyl sulfate which is not extracted by the individual components of the mixture taken separately. The UO_2X_2 salts in benzene solutions exist in the form of linear polymers whose uranium atoms are, according to Baes, coordinatively unsaturated. The addition of L and UO_2SO_4 to the $\{U\}$ units (acceptor centers) in the $(UO_2X_2)_p$ polymer is considered:

$$\{U\} \quad + \quad mL \quad \overset{K_m}{\rightleftharpoons} \quad \{U\}L_m, \qquad (1)$$

$$\{U\} + UO_2^{2+} + SO_4^{2-} + nL \quad \overset{K_n}{\rightleftharpoons} \quad \{U\}SO_4UO_2L_n . \quad (2)$$
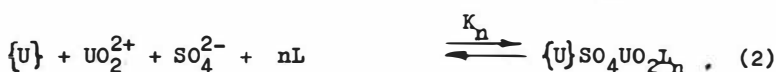
The stoichiometric coefficients in (1) and (2) and the extraction constant (table) were obtained by a computor processing of a large amount of data for the uranium concentrations from 0.1 to 2.5M, UO_2X_2 concentrations from 0.001 to 0.25M, and for L from 0.01 to 0.5 M (for TBP to 2M). A noticeable addition of L is observed for TAPO only ($m = 1$, $K_m = 130\pm 20$). In the case of saturated solutions and at high L concentrations it is possible that each $\{U\}$ unit will add even two

uranyl sulfate molecules. The qualitative dependences presented above for the mixtures HX+L at HX saturations are confirmed by the regularities observed in the extraction constant changes. In addition to this, as in the coordination extraction of uranium and other metals with neutral compounds, for different L there is a good linear correlation $lgK_1 = -1.60 +$

Table 1. Extraction constants of UO_2SO_4 with mixtures of uranyl di-2-ethylhexylphosphate with L (* and ** uranyl salts with DHPA and A2EHPA

L	ΔV_{OH}, cm^{-1}	$K_n = C_{UO_2SO_4}^{...}/a_\pm \cdot C_{UO_2X_2} \cdot C_L'$	
		$n = 1$	$n = 2$
DPSO	124	16 ± 2	
TBP	150	91 ± 8	590 ± 20
TBP*		25 ± 5	
DOSO	174	350 ± 50	
PSO		324 ± 16	880 ± 30
PSO**		64 ± 9	320 ± 50
PSO*		350 ± 40	
TPPO	196	480 ± 50	
2 NPO	224	$(2.5 \pm 0.2) \cdot 10^3$	$(5.8 \pm 0.2) \cdot 10^4$
TAPO	240	$(2.9 \pm 0.2) \cdot 10^4$	

+ 0,0234 ΔV_{OH}(the correlation coefficient 0.99) (L as mixtures with uranyl di-2ethylhexylphosphate).

The NMR (^{31}P) and IR data are consistent with addition of L and $UO_2SO_4L_n$ to coordinatively unsaturated uranium atoms in the polymeric chain according to the scheme.

$$\text{a} \qquad \text{b} \qquad \text{c} \qquad \text{d}$$
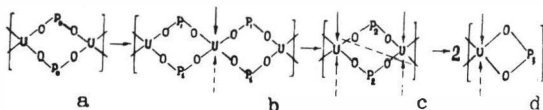
The polymeric chain with the bridging POO-group is retained upon addition of L (except for TAPO) and $UO_2SO_4L_n$ (concentration of the terminal units "d" is small). The numbers of the occupied and free uranium atoms in the chain determined experimentally from the integral intensities of P_0, P_1, P_2 and P_3 signals in NMR spectra were found to coincide with those calculated for a chaotic distribution of the molecules along the chain indicating an independent behaviour of the units. Conclusions based on a thermodynamical analysis, about the stoichiometry of the extraction and an insignificant addition of L are confirmed by quantitative determination of the number of units occupied by uranyl sulfate from NMR data (their ratio to the analytic UO_2SO_4 concentration in the extract is 1) and by the IR based concentration of the bound L (TBP). The bands present in the IR-spectra and their similarity with the IR spectra of some dimeric sulfate complexes indicate addition of $UO_2SO_4L_n$ to $\{U\}$ via a bridging sulfato group.

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EXTRACTION OF COPPER SALTS WITH A MIXED EXTRACTANT

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Copper salts can be efficiently extracted from dilute aqueous so-
lutions by a mixed extractant, e.g. one composed of a long-chain car-
boxylic acid (2-ethyl caproic acid) and a long-chain tertiary amine
(trioctyl amine) in a diluent of low polarity. The structure of the
copper obtained with the aid of a mixed extractant differs completely
from the kind of compound resulting from extraction by means of each
extractant singly. The different structures and associated reactions
in the cases in point are:

(a) With 2-ethyl caproic acid alone (a liquid cationic extractant)
this reaction may be expected:
$$\overline{4R'COOH} + 2Cu^{++} \longrightarrow \overline{[(R'COO-)_2Cu^{++}]_2} + 4H^+. \tag{1}$$
The dimer formed in the organic phase shows a strong absorbance at
680nm, which pertains to copper carboxylate.
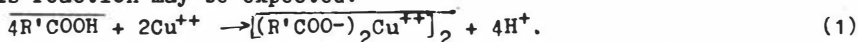
(b) In the case of copper chloride extraction with an anionic exchan-
ger (for example with trioctylamine HCl, a liquid anion exchanger):
$$\overline{2R_3NH^+Cl^-} + CuCl_4^= \longrightarrow \overline{(R_3NH^+)_2CuCl_4^=} + 2Cl^- \tag{2}$$
the organic phase shows a strong absorbance at 425nm, which is typi-
cal for the tetrachloro cuprate ion.
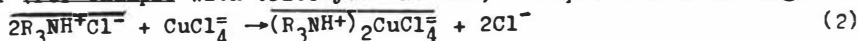
(c) With a mixed extractant consisting of (a) and (b) and a diluent a
species is formed that differs markedly from both (a) and (b), an ab-
sorbance at 725 nm being observed. The following reaction is tentati-
vely suggested:
$$\overline{4R_3N} + \overline{2R'COOH} + CuCl_2 \rightleftharpoons \overline{(R'COO-)_2Cu^{++}(R_3N)_2} + 2R_3NH^+Cl^-. \tag{3}$$
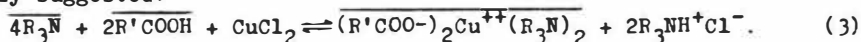
This reaction is easily reversed by shaking the organic phase with
pure water - in contrast to case (a), in which the reaction can be re-
versed only by the addition of an acid, and to case (b), which requir-
es the addition of a base.

Some relevant experiments were carried out in order to verify the
changes occurring in the organic phase:
1) Distribution ratios of copper chloride in the presence of increas-
ing chloride concentrations in the aqueous phase - for the case of
R_3N alone and for the mixed extractant.

2) Spectral shifts (in the visible region) occurring in the organic phase when the tertiary amine is added to copper carboxylate.

3) Changes in the carbonyl stretching vibration is the I.R. region - of the carboxylate alone compared with that of the mixed extractant.

4) NMR spectra of copper chloride in the mixed extractant show that both the two methylenic protons of the amine and the acid are shifted - as a result of copper binding.

5) Efforts are now being made to crystallize a mixed complex of copper amine acetate, the structure of which can be determined by X-ray crystallography.

The particular attractiveness in the application of mixed extractants lies in the facts that extraction - of copper in the case investigated - is enhanced, that the pH of the aqueous solution remains unchanged, and that it is simple to return the copper to the aqueous solution by reextracting with water.

The copper may be taken as a model for the other transition metals, which can also be efficiently extracted into mixed extractants of the type described.

From an investigation of the experimental data obtained with the different methods a common model evolved on the following lines:
The liquid exchangers form a pseudo-micellar phase, in which the organic ions and water are dissolved. Reversed micelles comprising both functional groups are formed, in which the polar heads are directed inwards, while the aliphatic chains are directed outwards. The number of reversed micelles per unit volume is a function of the salt concentration.

The volume of the micelles remains constant in the temperature range, 12-32 deg.C. and is independent of salt concentration. The electrical conductivity of the salt-loaded organic phase is the result of a combination of thermio micelle-micelle collisions and ion transfer due to the external electrical field.

In most instances the findings obtained with one method confirmed those due to another. These findings assist in understanding the driving force of the reaction and in an efficient planning of its applications.

A DIRECT EVIDENCE OF SYNERGISTIC EXTRACTION EFFECT - STUDIES
ON SYNERGISTIC EXTRACTION OF NEODYMIUM WITH HPMTFP AND Ph_3PO

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1-Phenyl-3-methyl-4-acyl-pyrazolone-5 are effective extractants
for metal ions. They are more easily to be synthesized and more ef-
fectively to be used in metals extraction than HTTA. Usually, syner-
gistic extraction effect can be hopefully observed when they are used
with some kinds of neutral ligands to extract metal ions. In this
paper the synergistic extraction system of 1-phenyl-3-methyl-4-tri-
fluoracetyl pyrazolone-5 (HPMTFP) and triphenyl phosphine oxide
(Ph_3PO) has been investigated, and the crystal and molecular structure
of the extracted complexes have been determined by four circle single
crystal diffractometer, therefore, a direct evidence of synergistic
extraction effect has been obtained.
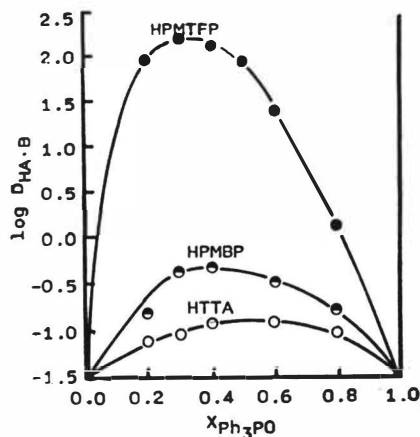
I. The synergistic extraction of
Nd with diketones(HA) and $Ph_3PO(B)$:
Under the conditions of $25\pm0.5^{\circ}C$,
$C_{Nd^{3+}}=1\times10^{-3}M$, pH 3.81 and the
total concentration of extractant
$C_T=C_{HA}+C_B=1.0\times10^{-2}M$, the total dis-
tribution ratio D_T is determined,
for the various mole fraction of
Ph_3PO $X_B=C_B/C_T$. In this case, D_T is
known as $D_{HA\cdot B}+D_{HA}+D_B$. D_{HA} and D_B
were deducted from D_T. Plotting
$\log D_{HA\cdot B}$ vs. X_B, a synergistic
extraction digram was obtained as
shown in Fig.1, and the equilibrium
constants were shown in Table 1.
It can be seen that the larger the
acidity of diketone is, the more
drastic synergistic effect can be
observed.

Fig.1. Synergistic extrac-
tion of neodymium
with HPMTFP and
Ph_3PO

Table 1. The synergistic extraction equilibrium constants of
neodymium with diketones (HA) and Ph_3PO (B)

HA:B	$\log D_{HA\cdot B}$			$\log K_{HA\cdot B}$		
	HPMTFP	HPMBP	HTTA	HPMTFP	HPMBP	HTTA
7:3	2.217	-0.355	-1.057	4.563	0.747	-0.318
6:4	2.092	-0.321	-0.945	4.209	0.735	-0.239
4:6	1.380	-0.494	-0.946	4.179	0.677	-0.045
Average				4.317	0.720	-0.201

II. The crystal and molecular structure of the extracted complexes:
It was reported previously that the ratio of Nd to HPMTFP is equal to
3 in the extracted complex when HPMTFP was used to extract rare earths
/1/. The single crystal of the extracted complex of the Nd(PMTFP)$_3$
2H$_2$O has been synthesized, and the crystal and molecular structure
has been determined by single crystal X-ray diffraction techniques
/2/. The crystal is monoclinic with space group P2$_1$/c, a=17.799(9),
b=12.661(6), c=18.691(7) Å; ß=102.71°, V=4108.8 Å^3 and Z=4. The cen-
tral Nd atom is coordinated by 8 oxygen atoms, six of them are from
three PMTFP$^-$ groups, and the rest two are provided by two water mole-
cules. The oxygen atoms take a square antiprism arrangement around
the Nd.

Experimental results show that the synergistically extracted com-
plex Nd(PMTFP)$_3$·2Ph$_3$PO is triclinic with space group P$\bar{1}$, a=12.880(4),
b=13.649(7), c=21.670(5) Å; α=93.14(3), ß=91.63(2), γ=115.99(4), V=
3413.6 Å^3 and Z=2. In the complex, Nd atom is coordinated by eight
oxygen atoms, and the polyhedron keeps the same geometrical configura-
tion as that in Nd(PMTFP)$_3$·2H$_2$O /3/.

Table 2. The comparison of the selected bond lengths in the
extracted complexes

Bonds	Nd(PMTFP)$_3$ 2H$_2$O		Nd(PMTFP)$_3$ 2Ph$_3$PO	
	lengths(Å)	average value	lengths(Å)	average value
Nd-O$_w$	2.571(10)	2.555(10)		
	2.539(9)			
Nd-O$_p$			2.359(2)	2.375(2)
			2.391(2)	
4th-position	2.503(8)		2.480(2)	
Nd-O	2.378(10)	2.444(10)	2.477(2)	2.485(2)
	2.452(10)		2.499(2)	
5th-position	2.379(7)		2.420(2)	
Nd-O	2.326(10)	2.364(11)	2.342(2)	2.356(3)
	2.388(11)		2.312(3)	
4th-position	1.229(14)		1.267(4)	
C-O	1.247(15)	1.239(15)	1.206(4)	1.235(4)
	1.241(13)		1.223(4)	
5th-position	1.275(13)		1.262(5)	
C-O	1.310(20)	1.322(20)	1.272(4)	1.254(5)
	1.380(20)		1.227(4)	

The comparison of the selected bond lengths are listed in table 2.
Data show that Nd-Op bond is shorter than Nd-O$_w$ bond evidently. It is
the result of the bigger coordination capability of Ph$_3$PO as compared
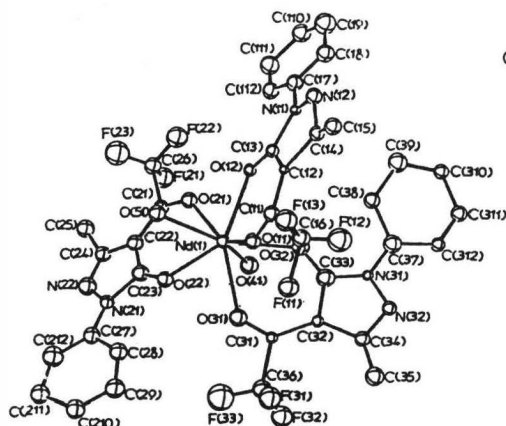
Fig.2. The molecular structure of $Nd(PDTFP)_3 \cdot 2H_2O$
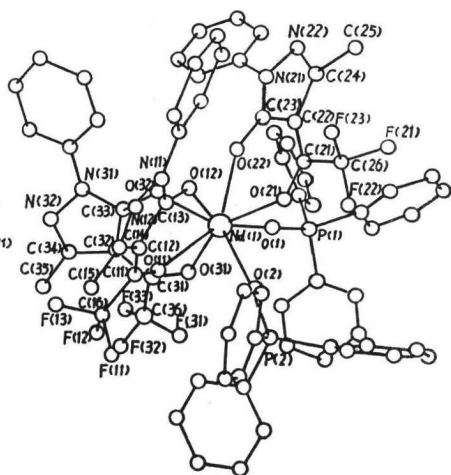
Fig.3. The molecular structure of $Nd(PDTFP)_3 \cdot 2Ph_3PO$

with that of the water molecule. The rest of the six Nd-O bond can be separated into two sets, the Nd-O bonds which close to CF_3 group are longer than those which located at 5th-position of the pyrazolone. On the other hand, the C-O bonds which close to CF_3 group are shorter than those which located at 5th-position of the pyrazolone. This fact may be caused by the stronger negativity of the CF_3 group.

III. Conclusion. A direct evidence of synergistic extraction effect in the system of $HPMTFP-Ph_3PO-Nd(NO_3)_3$ has been obtained. The replacement of the two water molecules in the extracted complex by the two hydrophobic Ph_3PO molecules leads to the synergistic extraction effect. The increase of the solubility of the extracted complex in the organic phase results in the increase of the log K from -4.63 (log K_{HA}) to 4.32 (log $K_{HA \cdot B}$).

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A considerable part of literature on extraction is allotted to the advantages of metal extraction mechanism, however, is not enough developed [1,2]. Due to experimental difficulties of metal complexes stoichiometry identification in solutions containing mixtures of phosphororganic compounds (POC), while interpreting results of extraction equilibrium, the conclusions of composition and relative concentration of complexes forming in the organic phase are often based on speculative conceptions.

It was the object of the present work to establish stoichiometry and concentration of associates existing in such extraction systems as di-2-ethylhexylphosphoric acid (D2EHPA) - tributylphosphate (TBP) (trioctylphosphinoxide (TOPO)), as well as complexes formed after extraction of uranium (VI) from sulphuric acid solutions. For this purpose the NMR spectrometric investigations of extracts and model solutions of the D2EHPA-TBP(TOPO)-UO_2SO_4 system (CCl_4 as solvent) were carried out. ^{31}P NMR spectra were recorded with CXP-100 Bruker spectrometer. As a standard the 80% H_3PO_4 was used.

In studying the mechanism of phosphororganic extractants coordination they took into account hypothesis that in bond-forming by the quardri coordinated phosphous atom its 3d-orbitals take part. It was established for D2EHPA, TBP and other phosphates containing PO_4-group that complex formation may be accompanied by screening intensification of a phosphorus atom due to filling out its 3d-level by $2p\pi$-$3p\pi$ electrons of the oxygen atoms, which do not participate in bonds formation with an electron acceptor, e.g. $\tilde{\delta}\,^{31}P$ (NaD2EHP)= -0.3ppm, $\delta\,^{31}P$ (TBP HNO_3)= -2.5ppm ($\delta\,^{31}P$(D2EHPA)= 1.9ppm, $\delta\,^{31}P$(TBP)= 0.5ppm).

Study on molecular association in the extraction system D2EHPA - TOPO has shown that equilibric existence of such complexes as TOPO 2D2EHPA, TOPO D2EHPA and D2EHPA 2TOPO takes place in CCl_4 solution depending on the component relative contents in the mixture. In this case the formation of hydrogen bond between D2EHPA and TOPO is accompanied by ^{31}P signal shift of the acid towards the strong field region. Similar measurements of the electron screening of D2EHPA and TBP functional groups of the phosphorus atom let us deduce that the acid-base interaction is practically absend in this system.

Figs. 1 and 2 show ^{31}P NMR spectra of the simulated systems $UO_2(D2EHP)_2$ (uranyl di-2-ethylhexylphosphate) - TBP (fig.1) and $UO_2(D2EHP)_2$ - TOPO (fig.2), analysis of the chemical shift variations

and the relative integral intensity of phosphorus signals made of these spectra allows to determine the stoichiometry and the contents of forming componds. The cited data show that in a solution containing uranyl D2EHPhosphate and neutral phosphororganic base the neutral POC
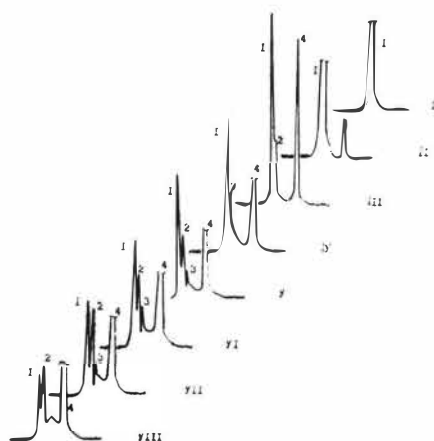
Fig.1. ^{31}P NMR spectra of the simulated TBP-UO_2(D2EHP)$_2$ system upon ingredient proportion: 1 - 0, II - 0.4, III - 0.8, IV - 1.7, V - 3.3, VI - 5.0, VII - 6.7, VIII - 10.0

(NPOC) molecules take part in an additional solvation of salt molecules. Stability and stoichiometry of the new-formed solvates depend to a great extent on electrodonating ability of the phosphororganic base (TBP or TOPO). In the case of UO_2(D2EHP)$_2$-TBP system a comparatively low stability (k≅ 20) of UO_2(D2EHP)·TBP and UO_2(D2EHP)$_2$·2TBP complexes is the reason that a greater part of UO_2(D2EHP)$_2$ salt and TBP molecules are in a noncoordinated form in the solution (fig.1). A use of TOPO as solvating additive leads to the complete shift of equilibrium towards formation of UO_2(D2EHP)$_2$·TOPO (k≅ 10^2) and UO_2(D2EHP)$_2$·2TOPO (k ⩾ 10^4) complexes

$$UO_2(D2EHP)_2 + nS \rightleftharpoons UO_2(D2EHP)_2 \cdot nS \qquad (n=1,2) .$$
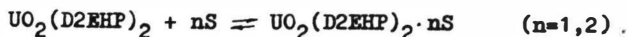
At that the appearance of signal in ^{31}P NMR spectra of UO_2(D2EHP)-TOPO system in a strong field region (-1.0ppm) and its integral intensity symbate variation regarding solvates concentration allows to suppose existence of complexes in a state of two tautomeric forms

$$UO_2(D2EHP)_2 \cdot nTOPO \rightleftharpoons [UO_2 \cdot nTOPO]^{2+}(D2EHP)_2^{2-}, \text{ where } n=1,2 ;$$

with covalent and ion bonded D2EHPA acid residues. In the presence of TOPO excess an increase of the medium polarity leads to intensification of exchange between ionic and molecular forms of $UO_2(D2EHP)_2 2TOPO$ complex and to simultaneous increase in the ionic form part $[UO_2 2TOPO]^{2+}$ $(D2EHP)_2^{2-}$ (fig.2).
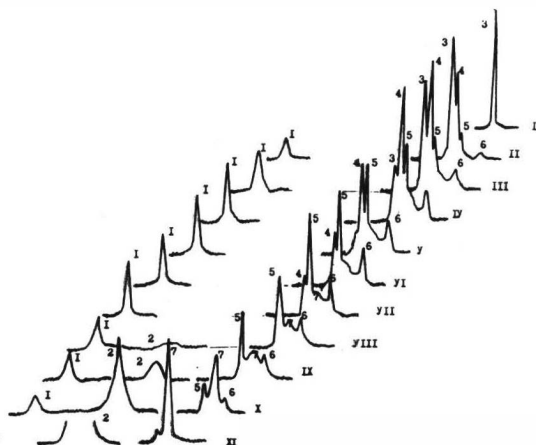
Fig.2. ^{31}P NMR spectra of the simulated $TOPO-UO_2(D2EHP)_2$ system upon ingredient proportion: I - 0, II - 0.3, III - 0.5, IV - 0.7, V - 0.8, VI - 1.0, VII - 1.3, VIII - 1.7, IX - 2.0, X - 3.3, XI - 5.0, XII - 10.0

As compared with simulated systems in real extracts prepared by shaking of the organic phase with the uranyl sulfate water solution (pH=2, $[U(UI)] = 20g/dm^3$) some differences in ^{31}P NMR spectra are observed only for D2EHPA-TOPO. In this case beside the main extractable U(VI) forms typical for simulated systems ($UO_2(D2EHP)_2 \cdot TOPO$ and $UO_2(D2EHP)_2 \cdot 2TOPO$ solvates) one can also observe formation of $UO_2(HSO_4)_2 \cdot 2TOPO$ and $UO_2(D2EHP)(HSO_4) \cdot 2TOPO$ complexes.

Fig. 3 shows ^{31}P NMR spectra of $UO_2(D2EHP)_2$- D2EHPA system, the analysis results of chemical shifts and phosphor signals integral intensity variations which were further used to interpret ^{31}P NMR spectra of real extracts with different uranium (VI) equilibric concentration in the organic phase. It was established that D2EHPA molecule polarization owing to P=O group coordination to uranyl ion leads to
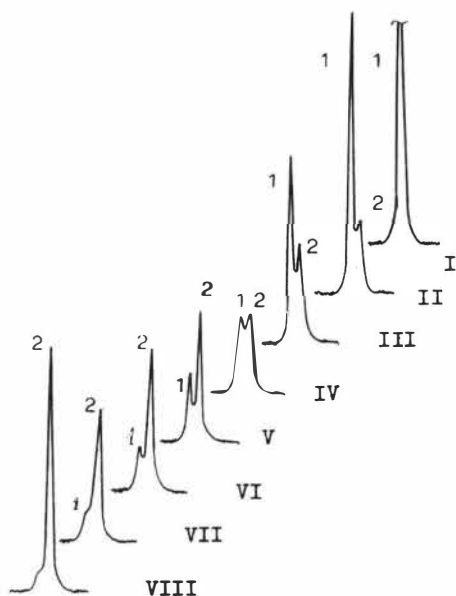
231

intensification of its protondonating properties and as a result to formation of a strong hydrogen bond with phosphoryl group of acidic uranyl D2EHPhosphate residue.

$$\begin{array}{c} (OR)_2 \qquad\qquad (OR)_2 \\ \stackrel{O\; =\; \overset{\|}{P} - O}{\underset{O\;\rightarrow\;P=O}{H}}\;\cdots\; UO_2\cdots\; \stackrel{O\;-\;\overset{\|}{P}\;=\;O}{\underset{O\;=\;P\;\leftarrow\;O}{H}} \\ (OR)_2 \qquad\qquad (OR)_2 \end{array}$$
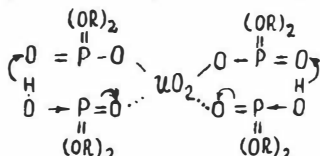
The latter is the reason of decrease of the D2EHPA active concentration in the solution and decrease of the extracting ability of the organic base. The presence of a neutral base in the extraction system leads to blocking of the coordination center for free D2EHPA molecules to uranyl ion, to the increase of the active acid concentration resulting in additional uranyl D2EHPhosphate molecules solvation and formation of UO$_2$(D2EHP)$_2$·nS type complexes and as a result to extraction of the additional quantities of U(VI) into the organic phase. On the whole synergistic extraction process equilibrium depending upon basicity and concentration of solvating additive can be expressed by the following scheme:

$$\nu_1 UO_2SO_{4\text{в}} + \nu_2 HR_o \rightleftharpoons \frac{\nu_2}{4} UO_2R_2\cdot 2HR_o + \frac{\nu_2}{4} H_2SO_{4\text{в}} + (\nu_1 - \frac{\nu_2}{4})UO_2SO_{4\text{в}}, \quad (1)$$

$$\nu_1 UO_2SO_{4\text{в}} + \nu_2 HR_o + \frac{\nu_2}{3}S_o \rightleftharpoons \frac{\nu_2}{3}UO_2R_2\cdot S\cdot HR_o + \frac{\nu_2}{3} H_2SO_4 +$$
$$+ (\nu_1 - \frac{\nu_2}{3})UO_2SO_4, \quad (2)$$

$$\nu_1 UO_2SO_{4\text{в}} + \nu_2 HR_o + \nu_2 S_o \rightleftharpoons \frac{\nu_2}{3} UO_2R_2\cdot 2S_o + \frac{\nu_2}{3} H_2SO_{4\text{в}} +$$
$$+ (\nu_1 - \frac{\nu_2}{3})UO_2SO_{4\text{в}}. \quad (3)$$
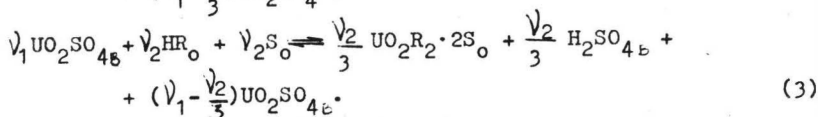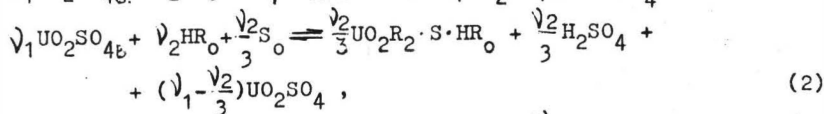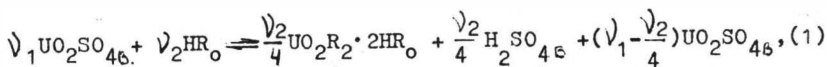
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INFLUENCE OF NaOH OR TRIETHANOLAMINE (TEA) ON THE EXTRACTION OF | 1-47 |
THENOYLTRIFLUOROACETONE (TTA) IN SINGLE-PHASE EXTRACTION

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Introduction: the extraction of metal ions in conventional liquid-liquid ex-
traction is a function of the pH of the aqueous phase, regardless of the base em-
ployed, unless secondary complexation takes place. In Single-Phase (SP) extraction
[1] we have observed that this does not hold true, and this study investigates the
role of the base on the variation of the percent of metal ion extracted. Fe, Co,
Cu [1,2], Cr, Mn [3], Y, La, Pr, Eu and Gd [4] have been quantitatively extracted and
some good separations obtained. The technique consists of preparing, initially,
an SP solution made up of water, containing the metals ions to be extracted, an
organic solvent immiscible with water, containing the complexing agent, and a third
solvent miscible with both water and the primary organic solvent [1]. After the
acidity of the SP solution is adjusted, an excess of water is added to promote both
phase separation and extraction. The organic extract contains the chelates formed.
The need for controlling the SP solution acidity (an aquo-organic medium of low di-
electric constant) led us to propose an arbitrary working scale of pH, denominated
pHSP, which varies, of course, with the solvents employed and with their relative
ratios in the SP solution. The pHSP is measured with a combined (glass and calomel)
electrode. After calibrating the pHmeter with standard aqueous solutions, the elec-
trode is immersed in the SP solution and the reading is taken as the pHSP. In or-
der to prevent hydrolysis of some metal ions during the preparation of the SP so-
lution, the aqueous phase is generally acidified with a few drops of concentrated
acid. After preparation of the SP, the desired pHSP is then obtained by the addi-
tion of a base. Variation of the % E and of the shape and position of the ex-
traction curves have been observed, due to the use of different inorganic bases
(viz. ammonia and borax [1]), but not to the extent of affecting the separation
factor of any pair or group of metal ions. However when triethanolamine (TEA) was
used [3], drastic modifications were observed. In the separation of La from Eu

Fig. 1

Single-Phase
Extractions curves
of La and Eu

Addition of:
NaOH: x
TEA: o
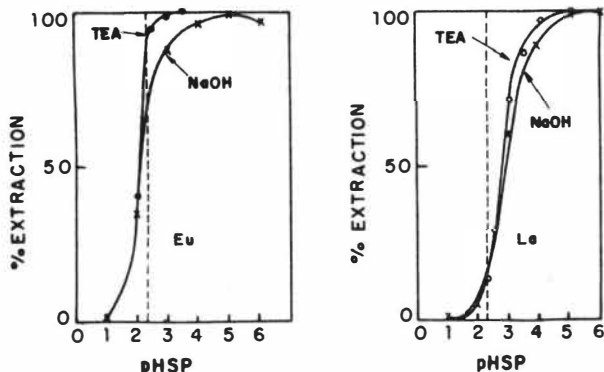
using TTA, the form of the extraction curves changed significantly. Depending on
the base employed (NaOH or TEA), the separation factor could be doubled [4].

Results and Discussion: Table 1 shows the percentage of extraction of Ni using the
system: methylisobutylketone (MIBK), ethanol, water, TTA, when diverse bases are
used to regulate the pHSP.

Table 1. Single-Phase extraction of Ni with TTA using diverse bases to regulate
acidity. Ratio (v/v) Mibk:ethanol:water:5.0:7.5:2.0

pHSP	% Extraction of Ni				
	NaOH	NH_4OH	MEA	DEA	TEA
2.0	0	0	2	6	4
3.0	5	23	32	41	49
4.0	45	69	71	74	80

MEA: Monoethanolamine   DEA: diethanolamine

From these results and the shape of the extraction curves of La and Eu (Fig. 1) one
finds an indication of a region of pHSP where the effect of TEA toward the complexa-
tion is a maximum, i.e. between pHSP 2 to 3. Natural a priori assumptions were: (1)
different degrees of hydrolysis; (2) adduct formation (i.e. metal/TTA/base); (3)
formation of an intermediate complex which would more easily react with TTA and
(4) the possibility that the base itself could form extractable species. Experi-
ments showed that none of these effects, by itself, could account for the results.
Tests showed that TEA, in the absence of TTA, does not extract Ni at all, so this
possibility can be ruled out. According to possibilities (2) and (3) an excess of
neutralized TEA added to the SP solution should increase the % E. The results are
presented on Table 2.

Table 2. Single-Phase extraction of Ni with TTA as a function of neutralized TEA
added (1 M solution of TEA, pH 7.0)

pHSP regulated with	% Extraction of Ni				
	ml of neutralized TEA added:				
	0.0	0.5	1.0	1.5	2.0
NH_4OH	23	19	19	23	19
TEA	49	29	34	24	29

These results are quite intriguing: for NH_4OH the %E practically does not change,
while for TEA it clearly decreases with added TEA. Data was also obtained showing
that if the Ni species are added after regulating the pHSP, TEA still promotes a
higher percentage of extraction than NH_4OH, which shows that the hydrolysis problem,
if there is any, is a minor one. Mixtures (v/v) of NH_4OH and TEA show an almost
linear relationship between the % TEA present in the mixture and the increase in %E.
This means that the TEA effect is purely additive, which should be expected for the
case of adduct formation, but not for the presence of an intermediate complex that
would be formed and disrupted without relation to stoichiometry.

At this point of our investigation it was decided to check whether there could

be any influence from the kind of base employed toward the chelate itself. SP solutions containing 10^{-5} M TTA were prepared, the pHSP was set to 1.0 with HNO_3 and then raised to several different values with either NaOH or TEA (here NaOH was used so that the results would be compared with the data of Zebroski [5]).

Spectra were taken down to 330 nm since, below this, the absorption of MIBK and HNO_3 is too high. Reference solutions were without TTA. Fig. 2 presents the spectra obtained, and the differences in shape relative to the two bases employed is noteworthy. Since evidence of the species present might appear below 300 nm, spectra were also obtained, from 200 to 400 nm, of SP solutions of cyclohexane, ethanol, water (acidified with HCl), with TTA. Two of these spectra are presented in Fig. 3. According to Zebroski [5], King and Reas [6] and Healy et alli [7], these spectra can be assigned to the hydrate form of TTA, plus, possibly, to small amounts of the enol form. Assuming that in the SP solutions (with either MIBK or cyclohexane) TTA is present in the initial acid solution largely as the hydrate, one can follow what is happening in the spectra of Fig. 2 in the range from 300 to 400 nm. At pHSP 1.0, there is no base present. As NaOH or TEA are added, the absorbance decreases. With the continuing addition of NaOH it continues to decrease. One can suggest the formation of more hydrate, which has a lower absorptivity in this region [5], at the expense of the enol form present in solution. This is a sound possibility, since the bases are added as aqueous solutions. On the other hand when TEA is added, there is an increase in absorbance above pHSP 2.0 and although the solutions are still acid, this means conversion of the hydrate to enol and/or enolate ion, the reacting species in metal ion complexation.

Conclusion: denoting by B: any of the nitrogenated bases, and by HTTA the protonated TTA species, the following equations may be formulated:

$$B: + H^+ \rightleftharpoons B:H^+ \qquad (1)$$

$$B: + HTTA.H_2O \rightleftharpoons [B:H^+TTA^-] \ I + H_2O \qquad (2)$$

$$I \rightleftharpoons B:H^+ + TTA^- \qquad (3)$$

$$TTA^- + H^+ \rightleftharpoons HTTA \ (enol) \qquad (4)$$
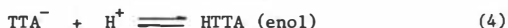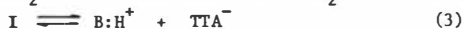
It has been reported [5] that the rate of conversion of the hydrate to enol is a slow one, although the reverse reaction is quite fast. The above equations could explain why B: produces enough enolate ion to be observed in the spectra and also to react with the metal ion at lower acidities. (I) probably does not react with the metal ion (Ni in the case) for, as the results in Table 1 show, the increase in the concentration of neutralized TEA $(B:H^+)$ leads to a decrease in the extraction of Ni. This is evident from equation (3), in which the equilibrium is shifted to the left, preventing the formation of enough TTA^-. Depending on the strengh of the nitrogenated base, the concentration of B: varies accordingly: the weaker the base, the larger the concentration of B:, and the greater the amount reacting with the hydrate to form species (I). The strongest effect of TEA is around pHSP 2-3. This may be a characteristic of this base, and MEA and DEA, as well as other bases not studied here, could show a stronger effect in other pHSP ranges. This indicates new and interesting separation studies to be undertaken.
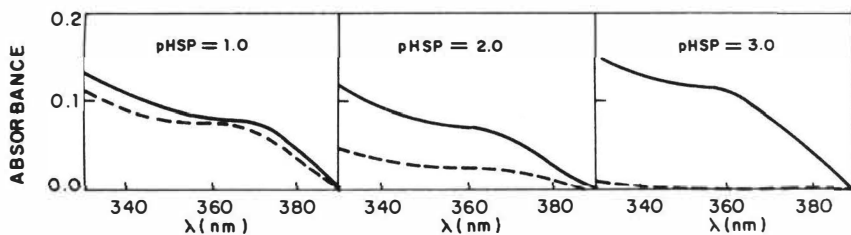
Fig. 2. Spectra of SP solutions of 10^{-5} M TTA.
System MIBK/ethanol/water.
NaOH: - - -   TEA: ------
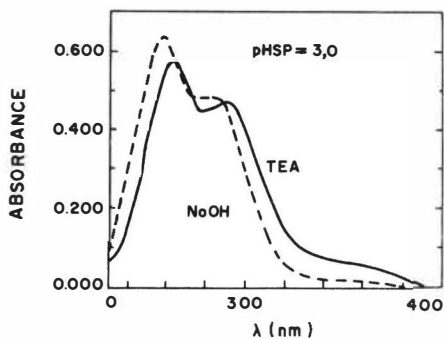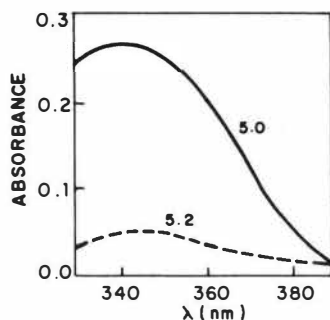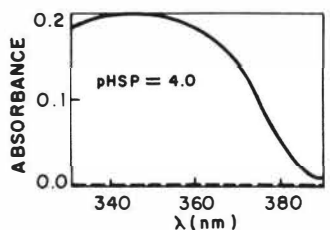
Fig. 3. Spectra of SP solutions of 10^{-5} M TTA.
System cyclohexane/ethanol/water.
NaOH: - - -   TEA: ------

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THE LOW-GOVERNED NATURE OF ASSOCIATION (MICELLATION) OF
DIALKYLPHOSPHATES IN WATER AND ORGANIC PHASES AND THEIR
MANIFESTATION IN THE PROCESS OF METAL EXTRACTION WITH
DIALKYLPHOSPHORIC ACIDS

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Difficulties of the quantitative discription of metal extraction
by dialkylphosphoric acid (DAPA) at molar ratio of metal to acid near
to saturation are explained by considerable extracting form associa-
tion in extracts. It is more often supposed that coordination poly-
mers to be formed. But some facts contradict the polymer theory [1-
-4]. There, di-n-butyl- and di(2-ethylhexyl)phosphate of copper in
anhydrous solvents are in a polymeric form. But while saturation with
water the associates $Cu_4(DAP)_8 \cdot hH_2O$, where $h=4\div8$ depending on nature
of salts and a solvent, arise. These transformations are accompanied
by sharp decreasing of viscosity. Dialkylphosphates extract water and
electrolytes into the organic phase. Table 1 gives some examples of
previously called acceptor extraction [1].

Similar effects are known
for some micellating SASs.
Accoding Eicke, water and
electrolytes solubiliza-
tion with micelles of re-
versed type is quantita-
tivly explained by the el-
ectrostatic theory [5].
Biphilic nature of DAP
anions and strain of the
chelate rings in complexes

Table 1. Solubilization of water and
electrolytes by di(2-ethylhexyl)phos-
phate and di-n-butylphosphate solution

System	H_2O : M	X : M
$CuA_2-C_7H_8-5,5M$ NaCl	3 : 2	1 : 8
ZnA_2-CCl_4-4M KCl	–	1 : 10
$CoA_2-CCl_4-6,2M$ KJ	–	1 : 20
$CdR_2-C_7H_8-H_2O$	1 : 2	–
$CoR_2-C_7H_8-4M$ KCl	3 : 2	1 : 30
$NiR_2-C_7H_8-H_2O$	11 : 1	–

may lead to decreasing of solution free energy mostly because of mic-
ellation. The micellation it self may cause special regulars of metal
extraction by DAPA and extraodinary effects of coextraction.

In this work we study the micellation of di-n-butyl- (MA_2) and di-
(2-ethylhexyl)phosphates (MR_2) with number of cations ($Co^{2+}, Ni^{2+}, Cu^{2+},$
Cd^{2+}, Zn^{2+}) in water and extracts and also the regulars of their dis-
tribution in water and organic solvent (n-heptane, toluene, tetrach-
loromethane etc.) under $V_o:V_w=1:1$ and $25^\circ C$. The procedure of experi-
ment is described in detail in [3,4].

According to conductometric and tensiometric dater the DAPA in
water are ionogen micellation SASs (MSASs). Critical micelle concen-
trations (CMC) of MA_2 depend but little on counter-ion and are in the
range of $(5\div7)$ $10^{-2}M$. CMC of EHPA salts change to some extend in the
row of cations but don't exceed 5 $10^{-4}M$, table 2.

The shift equilibrium method, noted in table 2, was worked by fin-
ding the concentration dependences of the turbidity of solutions

containing the surplus of counter-ion M^{2+} and variable quantities of R^-. The CMC in pure salt solution was found from the parameters of pseudophase micellation model equation [6]:

$$lg(CMC) = -lgK_m - K_g lg(M^{2+}),\qquad(1)$$

with K_m - a micellation constant,
K_g - bounding parameter of counter-ion with micelle.

Table 2. CMC of $M(BHPA)_2$ in water (10^{-4})

Method	Salt				
	ZnR_2	CuR_2	CdR_2	CoR_2	NiR_2
Shift equlibrium	0,32	0,8	2,2	3,2	3,5
Condactivity	-	0,68	2,4	3,8	-
Surface tension	-	-	-	3,2	3,7
Turbidity	-	-	2,6	-	-

Experimentally there were revealed three types of distribution isotherm, namely oleophilic (0), hydrophilic (H) and amphiphilic (A) MSASs. Their characteristic features are shown in Fig.1. The ZnA_2 distribution lead to big micelle formation in organic phase (inertia radius (R_g) according to dispersion of Roentgen rays data * equals 20nm). NiA_2 becaus of its small extractability forms micelles only in water, $R_g=30$nm. It is charachteristic for CuA_2 to have big associats in water $(R_g=22$nm) and small ones in extracts $(R_g=1$nm).
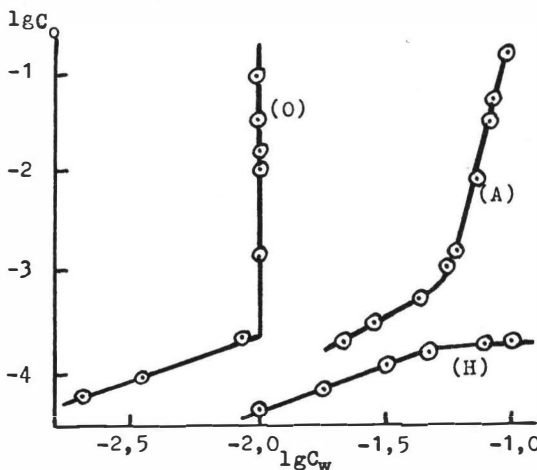
Fig.1. The dibutylphosphates of Zn(0), Cu(A), Ni(H) distribution in H_2O - CCl_4-system

The distribution isotherms of oleophilic and hydrophilic MSASs can be easily explained by the pseudophase micellation model in organic and water phases correspondinly. The distribution isotherms of amphiphilic MSASs are difficult to expain. From point of view of pseudophase model it is extraodinary that the CuA_2 extraction sharply increases within the bounds of its CMC in water (CMC_w). This type of isotherm can be discribed by the empirical equation:

$$C_o = K (C_w - CMC_w),\qquad(2)$$

with K - a constant.

* Experimental by A.I. Golovanov.

238

We may think that extraction isothermes classification is of general character. The same phenomenon can be noticed in the process of distribution of cetylpyridinium bromide (CPB) between water and n--octanol and heptane mixtures (Fig.2). With increasing of solvent agent the isotherm type changes. The curves breaks, like in the previous example, can be found not far from CMC of cetylpyridinium bromide in water wich was found by potentiometric method. This in water saturated with n-octanol, CMC equals $4,8 \cdot 10^{-4}$M and corroborates with the break of curve 1. The curves 2 and 3 break at concentrations different from CMC not more 1,5 times. The equation (2) is right for upper parts of these cuves.

The distribution ratios of EHPA salts are described by equation (3):

$$D = C_o/(K^{-1}C_o + CMC_w) , \quad (3)$$

wich is derived from the equation (2). Some examples are given in Fig.3. If toluene is substituted for another nonpolar solvent the character of curves remaines the same. The stoichiometry of the salts in experiment was in the limits of $1:2^{\pm}0,02$. Bisides, microadmixtures soluble in water were washed from MR_2 until the distribution ratios became constant. In all the experiments water phase had pH 6,5 ÷7. It indicates that the two-phase hydrolysis is weak. It is shown by special experiments that M:R ratio around CMC equals 1:2 within the analysis errors.

It is noted, accoding to R_g, that the micelles in organic phase are small: 4,5 (ZnR_2); 3,1 (CdR_2); 1,7 (NiR_2); 1,5(CoR_2);
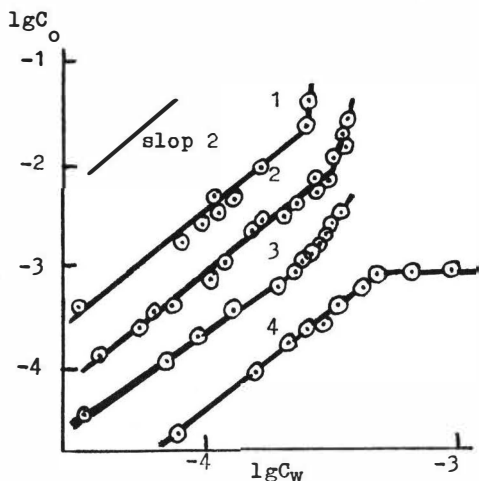
Fig.2. CPB extraction with heptane accoding to volume fraction of n-octanol:1-0,5; 2-0,3; 3-0,2; 4-0,1
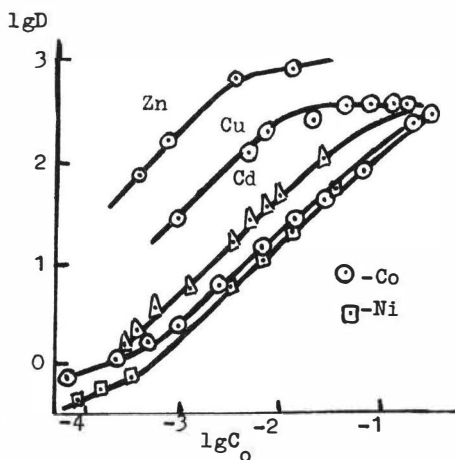
Fig.3. The EHPA salts distribution in $C_7H_8-H_2O$-system. The lines — are from the equation (3)

239

1 nm (CuR_2). Besides, the micellar character of organic phase is shown by the spasmodic deviation from Beer's low in toluene extracts absorptivity, at CoR_2 concentration $5 \cdot 10^{-4}$M (λ =288nm). Obviocely it is a CMC of CoR_2 in toluene phase. In Fig.3 it is seen that the curve 4 breaks just at this concentration. Probably the curve breaks in accordance with the change from coordinating to micellar distribution mechanism.

CMC of MR_2 in water calculated by equation (3)accord with then independent valuations, see Table 2 and 3. There is a liniar correlation between extractivity and micellation ability of EHPA salts. It is well-defind in the CMC area, when the equation is fulfild:

$$D = C_0/CMC_w .$$ (4)

Table 3. CMC (10^{-4}M) of EHPA salts accoding to distribution between water and organic solvent data

ZnR_2	CuR_2	CdR_2	CoR_2	NiR_2
		Toluene		
0,04	0,3	2,0	3,5	5,0
		n-Heptane		
0,22	1,0	-	4,0	-

Amphiphilic MSASs, which have smaller CMC in water are extracted better. Extraction of such SAS molecules to micelles "phase" is somewhat similar to extraction into nonpolar solvent phase.

The results of investigation show that during the quantitative description of metal extraction with DAPA it showed be borne in mind the possibility of its micellar association, both in organic and water phases.

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The extraction methods are of high importance for the separation
of products of nuclear reactions.

Phosphine oxides or quarternary ammonium salts are successfully
used for quantitative extraction of lanthanides (REE) and transpluton-
ium elements (TPE) from concentrated salt solutions or for separation
of these elements. A high selectivity of TPE- and REE-extraction with
trioctylphosphine oxide (TOPO) towards fission products and other
elements is reached when strong complexing agents such as diethylene-
triaminopentaacetate (DTPA) and lactic acid are added. Investigations
on the extraction properties of TPE and REE with TOPO-DTPA-lactic
acid and Aliquat 336 using various salting-out agents have been carri-
ed out earlier [1]. In the present work a possibility of theoretical
elucidation of the experimental material is discussed.

These extraction systems, which are of a very complicated chemical
composition with high concentrations, do not submit any exact thermo-
dynamic analysis. Therefore empirically methods have a high importance
for the derivation of functional dependences. The salting-out action
of cations is widely discussed, and it is pointed out that the salting-
out effect depends on the cation charge and radius or on cation hydra-

tion etc. [2,3]. An advantage must give the use of the parameters, quantitatively determining the influence of ions on the solvent property. For such a parameter we consider the so-called micro-viscosity of ions - the viscosity of the water layers around an ion. These values which characterize the total influence of the ion on the solvent are calculated in the present for a high number of cations [4] (Table 1). They are comfirmed by experimental data on electrolytic conduct-ivity, on Samoilov activation energy (ΔE), on NMR-results

Table 1. Viscosities of the first hydration shells (microviscosities) of some cations

Cation	$\eta_i \ 10^4$ (kg m^{-1}s^{-1})
Li$^+$	30.02
Cs$^+$	5.20
Mg^{2+}	44.42
Mn^{2+}	32.15
Co^{2+}	38.89
Ni^{2+}	36.98
Cu^{2+}	41.13
Zn^{2+}	34.65
Cd^{2+}	26.55
Pb^{2+}	20.43
Al^{3+}	76.61
Ce^{3+}	29.93

and on the $B^{\pm}$ - coefficient of Dole-Jones-equation /5/. Besides, the microviscosity being a kinetical property, it is very sensitive to slightest changes of properties of the solvent system. Thus it can be expected that the microviscosity must correctly reflect the salting-out effect of ions.

Fig.1 and 2 indicate the experimental dependences of partition coefficients K_d for REE and TRE from the microviscosity η_i of salting-out cations (Al^{3+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}) in the extraction systems HNO_3-TOPO/benzene and DTPA-lactic acid-TOPO/benzene. REE and TRE are in microconcentrations. At the concentrations of salting-out cations of 0.5 mol/l and 0.2 mol/l a regular dependence of partition coefficients from η_i is obtained. The efficiency of salting-out agent increases with an increase in the microviscosity.
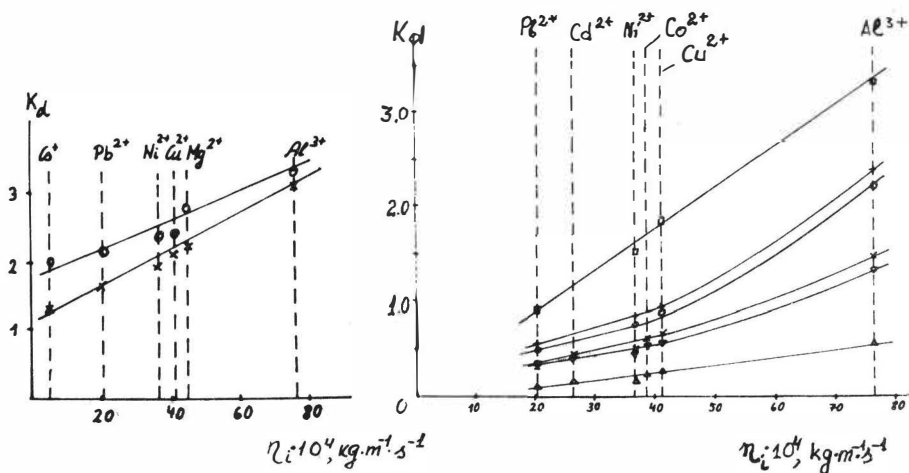
Fig.1. Distribution ratio K_d as a function of microviscosity η_i
organic phase: 0.1 mol/l TOPO in benzene
aqueous phase: (o) Sm, 0.3 mol/l HNO_3; 0.2 mol/l salting-out cations. (x) Tb, 0.3 mol/l HNO_3; 0.5 mol/l salting-out cations

Fig.2. Distribution ratio K_d of Am (+), Cf (□), Ce (▽), Sm (o), Tb (x), Tm (△), as a function of η_i
organic phase: 0.1 mol/l TOPO in benzene
aqueous phase: 0.07 mol/l DTPA, 1 mol/l lactic acid, 0.5 mol/l salting-out cation

Further on the extraction of scandium was investigated. The data listed in Table 2 show, that in extractions with TOPO in the system DTPA - lactic acid the dependence of K_d from η_i is practically linear.

Fig. 3. Distribution ratio K_d of Ce (*) and Eu (•) as a function of η_i
organic phase: 40% Aliquat 336
                in Xylene
aqueous phase: 0.02 mol/l HNO_3,
0.5 mol/l salting-out cations
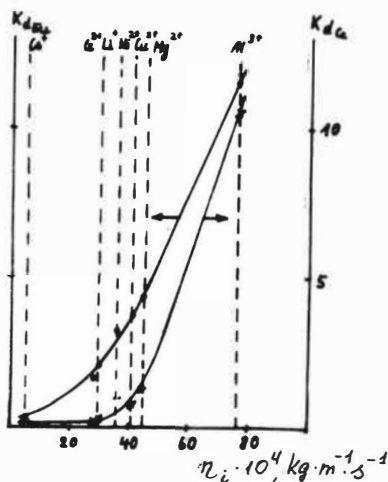
Table 2. Extraction of Sc^{3+} from DTPA - lactic acid solutions by 0.1 mol/l TOPO in benzene

Salting-out cation (i) (0.5 mol/l)	$\eta_i \cdot 10^4$ (kg m^{-1}s^{-1})	K_d	$\dfrac{\eta_{Al^{3+}}}{\eta_i}$	$\dfrac{K_{d(Al)}}{K_{d(i)}}$
Al^{3+}	76.61	0.76	1	1
Cu^{2+}	41.13	0.40	1.86	1.9
Co^{2+}	38.89	0.37	1.99	2.0
Ni^{2+}	36.98	0.35	2.07	2.2
Zn^{2+}	34.65	0.34	2.12	2.2
Pb^{2+}	20.43	0.19	3.75	4.0

The results obtained in investigation of REE extraction with quarternary ammonium salt Aliquat 336 are illustrated on the example of extraction of Ce^{3+} and Eu^{3+} and presented in Fig. 3. It is seen that in comparison with TOPO the same dependence is obtained using Al^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Li^+, Cs^+ and even Ce^{3+} as salting-out agent.

Thus, we can conclude that it is possible to use the microviscosity for the explanation of salting-out action of cations.

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Extraction equilibrium is known to be a special case of phase equili-
bria. The analysis of the data published in the literature reveals
that both theoretical and experimental aspects of the extraction prob-
lem haven't mostly been investigated from the point of view of hetero-
geneous equilibria. A specified character of phase equilibrium hasn't
generally been taken into account either. But with the rapid develop-
ment of the chemistry of extraction and with the wide use of extracti-
on methods in different branches of industry today there arises a pro-
blem of adequate description of phase equilibria in extraction systems.

This paper deals with our method of mathematical description for
liquid-liquid (L-L) and liquid-liquid-solid (L-L-S) equilibriums. Equ-
ations for estimating phase fields, the position of connod on the site
of layering and the composition of the critical solution have been de-
rived (1,2). This approach has been realized in a set of computer pro-
grams.

Fig.1 shows the calculated phase diagrams L-L, L-L-S in nitric acid-
water-acetylacetone and strontium chloride-water-n-butyl alcohol sys-
tems.

The method is used to evaluate the phase state for the systems con-
taining inorganic acids (hydrochloric, nitric, sulphuric, phosphoric,
boric), salts of alkali and alkali-earth metals, water and neutral ex-
tracting agents (ketones, alcohols, N, N-dialkylamides).

It has been found that the phase diagrams for the systems with ke-
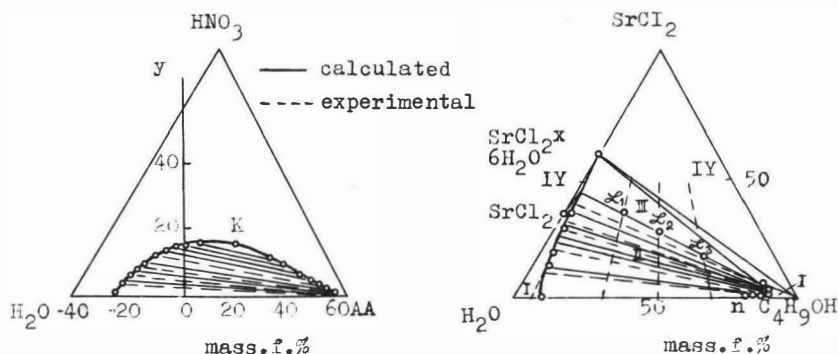
Fig. 1. The phase diagrams of the systems: a) nitric acid-water-ace-
tylacetone, b) strontium chloride-water-n-butyl alcohol

244

tones (aliphatic ketones $CH_3COC_nH_{2n+1}$ where $n=2,4,6$, diketones, cyclic ketones) are characterized by L–L equilibrium and can be classified as simple systems with one binary layering on the side of water–ketone without solubility isotherms showing an interaction (Fig. 1a).

The investigation of the dependence of intercalation sites of the systems on the ketone character shows that the structure and size of the intercalation field are influenced by carbon radical length of the ketone. It has been established that the size of the intercalation field and the presence of cyclization ketone in the molecule, on the one hand, and the secondary ketone group, on the other, are related.

In acid–water–dialkylamide systems the phase states are also determined by the binary layering on water–amid side.

The phase diagrams for the systems containing alkali and alkali-earth salts are more complex. They are characterized by L-L-S equilibrium and by patches of crystallized water–free salts, as well as crystalline hydrates having one or several water molecules (Fig. 1b). The size of the phase fields is greatly influenced by the nature of the salt distributed.

The phase diagram for the extraction system in question enables us to come to the conclusion concerning the distribution of all the components in the system, determine the composition of co-existing phases and calculate distribution coefficients.

The acid distribution isotherms for HCIO, HNO_3, H_2SO_4, H_3PO_4, and H_3BO_3 show similar relationships both in the systems with ketones and with dialkylamides.

The extraction behaviour of the salts having similar radii but different charges has been investigated for the systems with alkali and alkali-earth salts, for example, Li and Mg, Na and Ca, etc. The data obtained show that for lithium and magnesium chlorides one can observe a steep slope (up) of the distribution isotherms, especially in the higher concentration range. The isotherms for the distribution of sodium chloride and calcium chloride differ widely. For sodium chloride this relationship changes smoothly while in the case of calcium chloride we have an almost linear initial part and a sharp maximum for high concentration range. The distribution isotherms are close to each other and the higher salt concentration of the solution won't change them much. No definite dependence of the salt extraction constant on the radius and charge of the cation has been found.

It was established from the phase diagrams that for the systems studied the acids and salts produce a salting-out effect on the solibility of extracting agents in water. This salting-out effect is estimated by calculating the salting-out constants by Sechenov equation:

$$lg \ s_o/s = KC,$$

where s_0 and s are the solubilities of the extracting agent in water and salt solution respectively and C is the concentration of the salt in mole/l.

The values of the salting-out constants show that the measure of the decrease of extracting agent solubility is closely related to the nature of the salt distributed (Fig. 2).
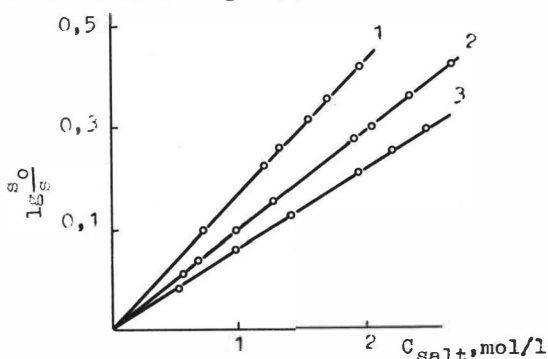
Fig.2. The solubility of n-butyl alcohol in electrolyte solutions: $1 - Sr(NO_3)_2$, $2 - Ca(NO_3)_2$; $3 - Mg(NO_3)_2$

Using the phase diagrams we can obtain the composition of the extracted complexes. Taking into account a considerable interface water distribution for the systems studied we assume the formation of non-stoichiometric hydrate-solvates. The extraction equilibrium is described by Eq(1)

$$K^T = \frac{m^{-2}}{a} \exp^{\nu} \left[h_{\pm}(1-a_w) \right] = K_{eff} \exp^{\nu} \left[h_{\pm}(1-a_w) \right], \quad (1)$$

$$\ln K_{eff} = \ln K^T - h(1-a_w), \quad (2)$$

where $\bar{m}$ is the salt concentration in the organic phase, a is the salt activity in the water phase, a_w is equilibrium water activity and ν - is electrolyte stoichiometric coefficient.

Eq. (1) and (2) require the analysis of the relationships of K_{eff} to a_w which in case of the validity of the assumption concerning the nonstoichiometric ion hydration of the completely dissociated electrolyte must be linear and the angular coefficients must be equal to some average quantity of water molecules h hydrating the complex to be extracted when $a_w = 1$ (3).

It can be seen from Fig.3 that the relation of $\ln K_{eff}$ to a_w is linear for most systems. For such systems the extraction equilibriums are expressed by Eq.(1). The values of the parameters are given in Table.

246
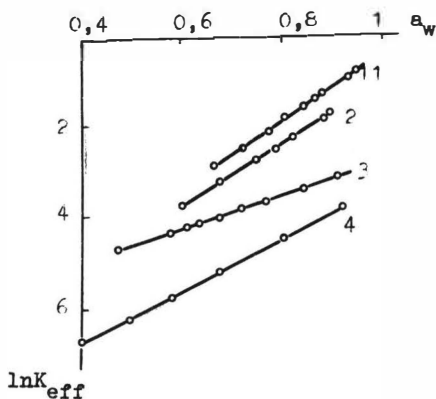
Fig.3. The relationship of lnK
to a_w during the extraction of
nitric acid with ketones:
1 - MBK, 2 -MCH, 3 -AP , 4 -MHK

The extraction of salts with n-butyl alcohol

Salt	h	lnK^T	Salt	h	lnK^T
LiСl	2,82	4,97	$MgCl_2$	1,54	10,23
NaCl	6,74	4,72	$CaCl_2$	2,38	5,20
KCl	1,72	3,88	$BaCl_2$	1,86	10,46
RbCl	6,47	2,82	$Mg(NO_3)_2$	0,77	6,61
$LiNO_3$	4,02	1,59	$Ca(NO_3)2$	0,53	6,20
$NaNO_3$	2,48	2,53	$Ba(NO_3)2$	1,54	3,06

Thus, based on the data given above the conclusion is made that the
approach we suggest in this paper is more informative than the routine
methods as it enables us to estimate the whole statics of the extrac-
tion process and to determine the composition of the co-existing pha-
ses without isolating the phases and investigating them separately.

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In extraction system, mineral aqueous solution is usually used
as aqueous phase. The mostly used ways to increase extraction
efficiency are to find effective extractants or to use synergism.
However, the ways to change the properties of aqueous phase are
seldom considered. Hala 1 pointed out that the metal ions extra-
ction and separation will be improved obviously if using the mi-
xed aqueous-organic media, i.e., putting some water-miscible or-
ganic solvents into aqueous phase. This phenomenon is very impo-
rtant to theoretical studies and applications of extraction che-
mistry.

    In the present study, a very important system of nuclear fuel
extraction,i.e., the extraction of uranyl sulphate by TOA has
been chosen to study the distribution ratio change of uranium
with the addition of CH_3OH, CH_3CH_2OH, etc., into the aqueous pha-
se. The above-mentioned sytem belong to ion-association extrac-
tion system. The physical properties of aqueous phase greatly
affect the static electricity association, the stability of ex-
traction complex and the mass transfer course.

    1. Effect of water-miscible organic solvents on the distribu-
tion ratio
    The extraction system is 1.91×10^{-3} M UO_2SO_4-0.5 M $(NH_4)_2SO_4$-V%
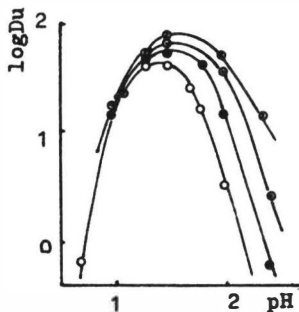
Fig.1.log Du-pH for CH_3OH Fig.2.log Du-pH for DMSO
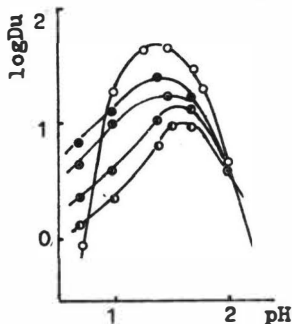
V%: o--0%, ●--5%, ⊙--10%, ◉--15%, ◐--20%

organic solvent/0.060 M TOA-n-C_6H_{14}. The distribution ratio for
the U(VI) extraction by TOA from aqueous phase containing metha-
nol, ethanol, acetone, dioxane, DMSO, THF,DMF, glycol, acetoni-

trile, etc., at various pH values are shown in Fig.1 and 2(only for CH_3OH and DMSO systems, the others are similar).

From the results above, it can be seen that methanol, ethanol, acetone, dioxane, THF and acetonitrile make distribution ratio increase. The greatest $\Delta Du \%$ can reach 10^3 or even more. But DMSO, DMF and glycol make distribution ratio decrease a dozens of times. The extensive study on this phenomenon can be applied efficiently to extraction and separation of uranium.

2. The concerntration change of stepwise complexes of $UO_2(SO_4)_i^{2-2i}$ in polar phase

To explain the mechanism how organic solvents affect extraction, the formation of complex $UO_2(SO_4)_i^{2-2i}$ in aqueous phase, the change of dielectric constant, the polarity of solvent and interface tention should be discussed.

In polar phase, the complexing reaction between UO_2^{2+} and SO_4^{2-} still exists, i.e.,

$$UO_2^{2+} + i\, SO_4^{2-} \rightleftharpoons UO_2(SO_4)_i^{2-2i},$$

but the stability constants in water are $\log K_1 = 1.73$, $\log K_2 = 0.85$, $\log K_3 = 0.86$, however, in aqueous solution containing 20% CH_3OH, $\log K_1 = 3.88$, $\log K_2 = 1.60$, $\log K_3 = 1.72$ (estimating values). On the basis of these data, the mole percentage of stepwise complex ions can be calculated. When pH=1, the amount of complex ion $UO_2(SO_4)_3^{4-}$ is greater than or equal to 50%. while at the same condition in water, the amount is only 3%. When pH= 1.6, the amount of $UO_2(SO_4)_3^{4-}$ is not less than 80%, which is favourable to extraction equilibrium.

3. Relation between the distribution ratio of extraction and the dielectric constant of polar phase

The addition of some solvents such as methanol, ethanol, acetone, dioxane brings about a considerable decrease of dielectric constant ε and increase of distribution ratio of uranium. It is apparent that ε is the predominant factor to affect Du in the above systems. The plots of $\log Du$ vs. $1/\varepsilon$ at various pH values are shown in Fig.3 and 4 (only for methanol-water and acetone-water systems, the others are omitted). It is clear that at smaller $1/\varepsilon$ values or smaller amounts of organic solvents the staight lines appear, which are basically parallel. This can be explained with the following formula of distribution ratio.

At first, we suppose the process of ion association extraction is

$$R_3NH^+(a) + L^-(a) \xrightarrow{\text{Ktr}} R_3NH^+(o) + L^-(o)$$

$$\xrightarrow{\text{Kip}} R_3NH^+L^-(o) \tag{1}$$
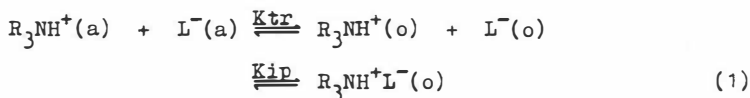
Which includes two parts, i.e., mass transfer between two phases and ion association. According to Born equation, the change of standard free energy in the course of mass transfer as follows
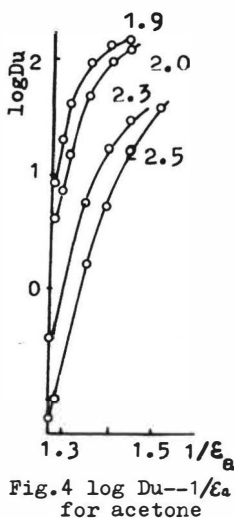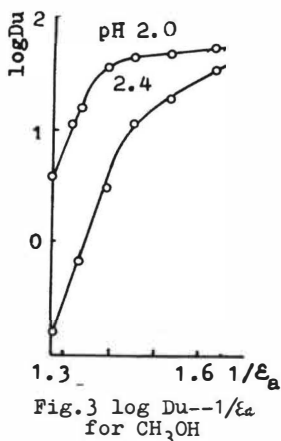
$$G^0 = \frac{Ne^2}{2}\left(\frac{Z_+^2}{r_+} + \frac{Z_-^2}{r_-}\right)\left(\frac{1}{\varepsilon_o} - \frac{1}{\varepsilon_a}\right), \quad (2)$$

where Z_+, r_+ and Z_-, r_- represent the valence, radius of cation and anion respectively, ε_o and ε_a denote the dielectric constant of organic and aqueous phase respectively. ε_a is usually very great, therefore $\Delta G^0 > 0$, which is unfavourable for mass transfer course. Additionally, according to Fuoss equation, the ion association constant is

$$\ln K_{ip} = \ln \frac{4Na^3}{3000} + \frac{|Z_+ Z_-|e^2}{akT}, \quad (3)$$

where a is the distance between center of cation and anion. The total extraction reaction constant K_d is the product of above-mentioned two parts, i.e.,

$$\log K_d = \log (K_{tr} K_{ip}) = \log K_{tr} + \log K_{ip}$$

The extraction reaction we chosed is

$$UO_2(SO_4)_3^{4+} + 4R_3NH^+(o) = (R_3NH)_4 UO_2(SO_4)_3$$
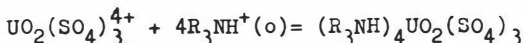
$$K_d' = \frac{\left[(R_3NH)_4 UO_2(SO_4)_3\right]_o}{\left[UO_2(SO_4)_3^{4-}\right]\left[R_3NH^+\right]_o^4} = \frac{Du}{\left[R_3NH^+\right]_o^4} = K_d \cdot P,$$

where P is the factor concerning the partion coefficient of extraction.

$$\log Du = \log K_d' + 4\log\left[R_3NH^+\right]_o. \quad (4)$$

Fig.3 log Du--1/ε_a for CH_3OH

Fig.4 log Du--1/ε_a for acetone

Supposing $A = \log\frac{4a^3 N}{300} \cdot P$, $B = \frac{4e^2}{2.303\ akT}$, $C = \frac{Ne^2}{4.606RT}\left(\frac{1}{r+} + \frac{16}{r-}\right)$,

$\log Du = A + (B - C)/\varepsilon_o + C/\varepsilon_a + 4\log\left[R_3NH^+\right]_o$

This formula indicates the relation between Du and ε_o, ε_a. When ε_o and the last item of formula are basically constant, log Du is linear to $1/\varepsilon_a$. ε_o increases with increasing the amount of organic solvent in polar phase. Furthermore, the last item, i.e., the decrease of free extractant concerntration affects Du. So, Du increases gradually. However, acetone and dioxane etc. do not act on TOA, so Du rises over a wide range of concerntration.

4. Effect of the polarity of solvent upon distribution ratio

The Du decrease caused by the addition of DMSO, DMF, glycol is attributed to that the solvents have great polarity and can form hydrophilic solvate with UO_2^{2+}, which is unfavourable for the formation of $UO_2(SO_4)_3^{4+}$. The polarity seties of solvents (reference solvent CCl_4) is following: $CH_3CN < (CH_3)_2CO < $ dioxane $ < CH_3OH < H_2O < THF < DMF < DMSO$.

5. Effect of interface tention on extraction

We have measured the relation between interface tention of various non-aqueous solvents the amount of organic solvents with the falling-drop volume method.

The surface tention of alcohol-water, acetone-water, dioxane-water systems decreases rapidly. This leads to a decrease of the free energy of extraction, which is favourable to extraction. On the contrary, the surface tention of DMSO-water, DMF-water, glycol-water systems change little. So, the extraction process is not affected greatly.

6. Extraction mechanism

The mechanism of extraction for uranyl sulphate by TOA in polar phase is the same as that in the absence of organic solvents. We have chosen the polar phase containing different V% of acetone, DMSO, methanol etc. at pH=2.30, and plotted log Du as a function of $\log(TOA)_o$. The figure shows that the line slopes are approximate to those without organic solvents. Finally, on basis of brief identification by Infra-red and Ultraviolet spectra, we infer that solvents in organic phase do not participate the formation of extraction complex.

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Purification of pesticide polluted effluent waters from pestici-
de production plants is one of the most severe ecological problems
in these factories. Waste waters usually contain up to 1,5% of ac-
tive substances organic solvents and surface active agents.

At the moment, several technologies are used in solving these
problems: - temperature and chemical treatment of effluent waters,
followed by flocculation or flotation; - adsorption on activated car-
bon; - various distillation processes; - pyrolysis (incineration) of
contaminated waters.

In order to obtain information on technical and economic aspects
of supercritical fluid extraction, as applied to separation of ac-
tive substances and organic solvents from pesticide polluted efflu-
ent waters, some separation experiments were performed.

Preliminary experiments show that this process could be, an effi-
cient method for purification of organic contaminated waters in fu-
ture. Based on these experiments, a rough comparison of economic
data was performed.

Supercritical Fluid Solvents. Supercritical fluids are good sol-
vents, comparable to liquid gases. The solvent capacity of liquid
gases is largely attributed to their density $\boxed{1}$. The density may be
varied over a wide range by small changes of temperature and pressu-
re. Near the critical temperature small variations of temperature
and pressure correspond to large changes in density and thus in sol-
vent power. Furthermore, supercritical fluids can be completely se-
parated from the extract by pressure and temperature changes $\boxed{2}$.

The list of substances that have been proposed as supercritical
solvents is limited $\boxed{3}$: carbon dioxide, ethylene, ethane, nitrous
oxide, propane and higher alkanes, methanol, acetone, toluene, py-
ridine and water.

Near the critical point the latent heat of evaporation is also
low, so a simple separation of extract and solvent with low energy
consumption is feasible. Supercritical fluids show favorable trans-
port properties, namely, low viscosities, high diffusion coeffici-
ents and good thermal conductivity $\boxed{4}$.

The most used gas is carbon dioxide because it introduces no
possible health hazards. It is also nonflammable, non-corrosive,
inexpensive, readily available in high purity, and it has a criti-

cal temperature conveniently a little above ambient so that it is easily handled and removed from the products.

Phase Equilibrium Thermodynamics. The prediction of the solubility of a liquid component in a supercritical gas is more difficult than for the solid - supercritical fluid problem, because the supercritical fluid dissolves in the liquid and alters its properties. In solid - supercritical fluid system the solubility of fluid in the solid is negligible and only the fluid phase need to be considered [5].

Several authors have studied the mutual solubilities of the carbon dioxide system [6,7].

Ternary system which have been investigated experimentally include: carbon dioxide with water-organics [8,9] ethane solvent with water-alcohols [10] and ethylene solvent with water organics [11]. Successful attempts to qualitative and quantitatively modelling of liquid - supercritical fluid systems using the Peng-Robinson [9,10] and the Redlich-Kwong equations of state [12] have been performed. The interaction constants used in these equations have been determined from binary solubility data.

Separation of Organics from Aqueous Solutions. In our lecture a short review on separation of non-polar impurities from aqueous solutions [13], extraction of flavouring components from liquids with sub-critical CO_2 [14] and extraction of other soluble substances (alcohols etc) will be presented [15,16].

In our experimental work on treatment of pesticide polluted waters by supercritical extraction process small scale experiments were performed by model solutions of commercially available pesticides. The experiments were performed at $40^{o}C$ and 150 Bar. Extraction time was 50 minutes.

The analysis of raffinates shows that in the sample of: - Aniten DS - the decline of fluorenol content is 11,2%; - Betanal Am-11 - the decline of COD (Chemical oxgen demand) is 22,0%; - Lasso EC - the decline of COD value is 21,0% and the decline of content of alachlor in water is 30,0%; - Volaton 500 EC - the decline of COD value is 9,5%.

Conclusion. Preliminary results of treatment of pesticide polluted waters with supercritical CO_2 show that this separation process could be an effective method also in industrial scale. To optimize this process, further experements, especially in countercurrent extraction column, should be carried out.

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EXTRACTANTS

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Although solvent extraction technology had its beginning more than 100
years ago, it owes a significant amount of its present prominence as a
separation technique to its successful application with actinide elements.
Solvent extraction plays a vital role in actinide separation, recovery and
purification. The use of thorium, uranium and plutonium and other actinides
in nuclear energy programs has led to the rapid development of many new
solvent extraction processes that display simplicity, selectivity and speed.

The scientific literature abounds with articles on new solvent
extractants [1-6]. While many of the reagents are only of academic
interest, several types of extractants show promise in improving actinide
recovery, separation or purification. In the last decade, American and
Russian workers have evidenced much interest in the potential application
of certain neutral and acidic bifunctional organophosphorus compounds in
actinide separations. Triggering this interest is the ability of some
carbamoylmethylenephosphorus (CMP) and carbamoylmethylenephosphine
oxide compounds to extract trivalent actinides from strong nitric acid
solutions, a property which distinguishes them from monofunctional
organophosphorus compounds [5].

Because CMP strongly extracts actinides and lanthanides, and does not
extract more than 40 other elements from 5-7 M nitric acid, the extractant
has been found useful for an americium recovery and purification process
[7]. Dihexyl-N,N-diethylcarbamolymethylphosphonate is sorbed on a
non-ionic macroreticular resin and used in an extraction chromatography
mode. The process effectively separates and purifies americium from
impurities such as aluminum, calcium, chloride, copper, fluoride, iron, lead,
magnesium, plutonium, potassium, sodium and zinc.

Using solvent extractants sorbed onto a solid (extraction
chromatography) is well known [7]. The technique combines the attractive
properties of solvent extraction (high selectivity, fast rates, high loading
capacities, etc.) with the advantages of column adsorption and ion exchange
(applicability to the treatment of very dilute solution, ease of liquid/solid
phase separation associated with lack of serious problems, such as crud
formations and solvent losses into the aqueous phase, ease of handling and
simplicity of equipment, etc.)

Recently some additional advantages have been reported using the
technique for actinide recovery [8]. The system uses solid supports, such as
styrenedivinylbenzene beads, polyurethane foam, activated carbon, etc.,
loaded with a solid solvent extractant, such as
octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). The
extractant (without diluent) is equilibrated with the support at a
temperature just slightly above the melting point of the extractant. In
addition to efficient sorption of ionic actinide species, polymeric species of

plutonium (IV) are also effectively removed from aqueous mineral acid solutions by the solid extractant-solid support. The actinide loaded material is removed from the column and incinerated, leaving the plutonium in the residue for further recovery.

The advantages of the technique are as follows: (1) The CMPO removes actinides in all oxidation states as well as actinide polymers. (2) The purity of the extractant is not critical since no back extraction step is needed. Thus acid hydrolysis or radiation damage to the reagent should not be a problem, and solvent clean-up steps and solvent pollution problems are eliminated. (3) No diluent is needed, only an inexpensive and combustible support material. (4) The process yields high recoveries and has a high concentration factor.

Besides the importance of the solvent extractant selection in the above "extraction chromatography-incinceration stripping" process, the proper support is vital to the success of the system. The support must have a high capacity for the extractant and must maintain that capacity during use. Bleeding of the extractant can, however, be prevented by having a small amount of support material free of extractant at the end of the column. The extraction kinetlcs of the extractant-support must also be comparable to a liquid-liquid system. Finally, the complete combustion properties of the support material are important to provide an ash free residue. The process could also be designed to use the waste heat during the combustion step in other process steps such as initial drying or activation of the support.

A recent study [9] has suggested the best candidate column material for tertiary plutonium recovery is trioctylphosphine oxide (TOPO) sorbed on Amberlite XAD-4 non-ionic resin (20-50 mesh); the recommendation was based on the following: (1) TOPO has a high capacity for plutonium with consistently lower effluent concentrations than other materials tested, (2) although TOPO cannot be satisfactorily eluted with typical reagents, acid digestion or incineration can be used with a consequently large concentration factor of the plutonum recovered, and (3) TOPO removes plutonium (IV) polymer from nitric acid, whereas anion exchange resins do not sorb polymer.

Several inexpensive support materials for sorbing TOPO were evaluated since the use of Amberlite XAD-4 would have an economic impact on the tertiary process since the support is used only once. The following sorbents were tested for TOPO capacity: 1) "Cotton" filler material from the Micro-Wynd II filter cartridge supplied by AMF CUND Division, Meriden, Connecticut; 2) "cord" material from the Micro-Wynd filter; 3) Micro-Klean II filter cartridge also supplied by AMF; 4) typical polystyrene-type packing material which was washed with methanol, dried, frozen and ground to 20-50 mesh; 5) two different sources of polyurethane sponge packing material, washed with methanol; 6) 3M pillow material; 7) Amberlite XAD-4, 20-50 mesh, non-ionic resin supplied by Rohm and Haas Co.; 8) household sponge; and 9) treated peat, described in Ref.10.

In the work, flint-glass Pasteur pipets (5.7mm i.d. x 14cm), containing a small amount of glass wool at the bottom, were washed with acetone, dried, and tared. Weighed sorbent materials were placed in the columns (6-8cm high), which were then heated for one hour at 60°C, cooled and tared. The

support volumes ranged between 1.5 and 2.0 ml. All of the columns were then heated to 60°C and about 5 ml of molten TOPO (60°C) was passed through each of the columns. The columns were kept upright for one hour at 60°C, then cooled and weighed. Finally, 100 ml of 7M nitric acid was passed through each of the columns. Again, the columns were dried and weighed. Control columns containing the glass wool and support material, but not contacted with TOPO, were also processed along with the TOPO columns. These were used to determine the weight loss or gain by the support material during the heating and nitric acid washing steps.

Table I. Summary of TOPO Capacity of Support Materials

Support Material	Bulk TOPO Capacity g/ml	Washed TOPO Capacity g/ml	Capacity Loss on Wash(%)
Polyurethane 1	0.61	(a)	(a)
Polyurethane 2	0.58	0.57	2
Amberlite XAD-4	0.41	0.41	0
3 M Pillow	0.38	0.37	3
Micro-Klean	0.32	0.32	0
"Cotton"	0.30	0.21	30
Treated Peat	0.30	0.27	10
Household Sponge	0.28	0.13	54
"Cord"	0.25	0.19	24
Polystyrene	0.15	0.10	33

(a) decomposed.

Table 1 summarizes the results of the highest capacity supports. The values are an average of at least three determinations. The average standard deviation of the determinations was ±5%. Scrutiny of the capacity data shows that polyurethane sponge material (Source 2) has the highest capacity with only 2% loss of TOPO after passing 50 column volumes of nitric acid through the column. Not only is a high TOPO capacity support material required for the tertiary plutonium recovery process, but the TOPO must be retained by the support material after large volumes of 7 M nitric acid are passed. The polyurethane sponge material meets these requirements. Furthermore, a small amount of unloaded support could be placed at the exit of the column to sorb any TOPO physically removed from the support. The polyurethane material also has excellent liquid flow characteristics; the column back pressure is very low, just as with using 20-50 mesh resins.

More work is needed to compare polyurethane on a larger scale in comparison with the second best material, Amberlite XAD-4. However, since there could be stability problems with polyurethane foam contacted with strong nitric acid solutions, a study of the safety hazards associated with using the polyurethane materials should be a first priority. It should be emphasized that there are many different types of polyurethane foams, some of which are more stable than others [11]. This was observed in this work. The first source of TOPO loaded polyurethane sponge, washed with

nitric acid, decomposed at $50^{\circ}C$; the same material with no TOPO did not decompose, however.

We are continuing to test other inexpensive natural and waste materials for use as combustible solvent extractant supports, such as Victorian brown coal, rice hulk ash, waste wool, etc. Furthermore, we are looking at other hydrometallurgical applications and extractants. For example, in the uranium ore process, an inexpensive and impure amine reagent, which strongly extracts uranium, could be used to reduce costs and avoid phosphorus contamination to the incinerated residue opposed to using an organophosphorus extractant. A column operation may also be replaced by a moving conveyer bed or other novel technique for ease of extraction-incineration stripping.

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Macrocyclic polyethers or crown-ethers form stable complex extracts
with the metal ions,whose radii correspond to the size of the macrocycle
(Structural Correspondence Principle (SCP).

This review concerns the application of SCP for explaining size-se-
lective extraction processes of metal salts from aqueous solutions into
the organic solutions of functionanalysed crown-ethers of different spa-
tial and electronic structure. According to the data of X-ray analysis,
crown-ethers form the inclusion compounds,arranged in a "guest-host"
type fashion with the ions of alkali and alkaline earth metals(AM and
AEM), as well as the ions Pb^{2+},Hg^{2+},H_3O^+, which have been used as the
main object of study. As a measure of the extractive ability of crown-
-ethers extraction constant values ($\widetilde{K}$) or distribution coefficients(D)
of nitrates of metals(concentration 1g/l) have been chosen from nitric
acid solutions into 0,1 M solutions of crown-ethers in chloroform at
$25 \pm 0,1^{o}C$.

The increase of the size of the macrocycle and oxygen atomic number
in it from4-in derivatives of 12-crown-4 to 8-in derivatives of 24-
crown-8 was established to result in the selective increasing D some
elements in the following serieses:

12-crown-4 $Li^+ \varkappa Na^+ > Ca^{2+} > K^+ > Rb^+ \approx Cs^+ > Mg^{2+}$ Sr^2 Ba^{2+}
15-crown-5 $K^+ \approx Ca^{2+} > Na^+ > Rb^+ \approx Cs^+ > Li \approx Mg^{2+}$ Sr^{2+} Ba^{2+}
18-crown-6 $Sr^{2+} > Ba^{2+} > K^+ \gg Ca^{2+} \approx Cs^+ \approx Rb^+ > Na^+ > Li^+ \approx Mg^{2+}$
21-crown-7 $Rb^+ > K^+ > Cs^+ > Na^+ > Sr^{2+}$
24-crown-8 $Cs^+ > Rb^+ > K^+ \gg Sr^{2+} > Ba^{2+} > Na^+ > Li^+$
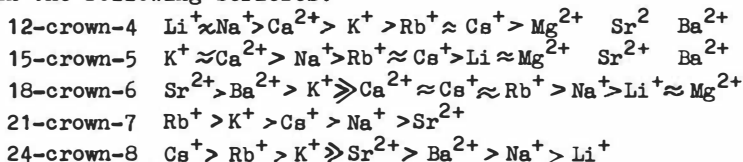
It is to be noted,that these serieses are not absolute,since the
extraction order of elements may vary mainly with the acid-salt compo-
sition of aqueous solution, tape of anion, substituents of macrocyclic
ring,solvent and temperature of the process $\begin{bmatrix} 1-3 \end{bmatrix}$.

Nevertheless,one can draw the conclusion,that the selectivity of
extraction of AM and AEM moves towards more large cations with the inc-
reasing the size of the macrocycle,that conforms to SCP. However,it
should be taken into consideration the fact,that inner cavity sizes of
free "uncomplexed" crown-ether essentially differ from the size of the
complexed macrocycle and therefore the conformation macrocycle mobility
becomes the determining factor in forming the stable complex compou-
nds $\begin{bmatrix} 4,5 \end{bmatrix}$.

Table 1 gives the data on crown-ether extraction DC18C6 and DB18C6 of
40 metals, differing in ion radius(r) and effective charge. It was
found, that for singly charged ions $\widetilde{K}$ is a linear function of comple-

xation constant of (K) ions with crown-ethers in water:

DC18C6 $\tilde{K}=0,182K-2,0$ (I)

DB18C6 $\tilde{K}=0,0273K-0,01$ (2)

$\tilde{K}_{DC18C6}=6,27\tilde{K}_{DB18C6}+2,6$ (3)

This means, that in the common cases, the stability of forming complexes determines the extractive ability of macrocyclic compounds. The comparison of the reported data shows, that SCP is not suitable for explaining the ion reactivity with a differnt charge[6]. This suggestion may be confirmed by a series of examples (Table 1), but we'll consider only one of them. For ions with the similar radii(0,90--0,99 Å) but differing in the charge:

Na^+ $\tilde{K}=3,0$ Ca^{2+} $K=0,75$,

Y^{3+} $\tilde{K}= <10^{-2}$, Pu^{4+} $K = 2223$,

the value $\tilde{K}$ varies by more than 5 orders of magnitude.

Comparing ion radii and $\tilde{K}$ for singly charged ions, one can draw the conclusion, that the most stable complexes form Tl^+ and K^+ and thus the optimal size of such ions for the derivatives of 18-crown-6 is in the range 2,88-2,66Å. For doubly charged ions maximum extraction occurs for Pb^{2+} and Hg^{2+} with the diameter 2,20-2,42 Å , for triply charged ions-for Pu^{3+} and La^{3+} with the diameter 2,00-2,30Å and finally for Pu^{4+} and Np^{4+}

Table 1. The maximum extraction constant values($\tilde{K}$) of nitrates of metals from the nitric acid solutions by DB18C6 and DC18C6 solutions in chloroform

ION	Radius r,Å	Extraction constant values. $\tilde{K}$	
		DB18C6	DC18C6
Li^+	0,60	0,095	0,015
Na^+	0,96	0,20	3,0
K^+	1,33	1,35	22,5
Rb^+	1,48	0,28	3,75
Cs^+	1,69	0,06	1,2
Ag^+	1,26	10^{-2}	31,5
NH_4^+	1,42	0,11	2,4
Tl^+	1,44	8,0	51
H_3O	-	0,026	0,56
Mg^{2+}	0,65	$<10^{-3}$	0,45
Ca^{2+}	0,99	$<10^{-3}$	0,75
Sr^{2+}	1,13	$<10^{-3}$	72
Ba^{2+}	1,35	$<10^{-3}$	27
Zn^{2+}	0,74	$<10^{-3}$	$<10^{-3}$
Cd^{2+}	0,97	$<10^{-3}$	$<10^{-3}$
Hg^{2+}	1,10	$<10^{-3}$	300
Pb^{2+}	1,21	$6,0$	9600
Cu^{2+}	0,92	$<10^{-3}$	0,3
Fe^{2+}	0,75	$<10^{-3}$	$<10^{-3}$
Mn^{2+}	0,80	$<10^{-3}$	$<10^{-3}$
Co^{2+}	0,72	$<10^{-3}$	0,015
Sc^{3+}	0,81	$<10^{-3}$	0,08
Y^{3+}	0,93	$<10^{-3}$	10^{-2}
La^{3+}	1,15	$<10^{-3}$	0,6
Ac^{3+}	1,11	$<10^{-4}$	$<10^{-3}$
Al^{3+}	0,50	$<10^{-4}$	$<10^{-4}$
Ga^{3+}	0,62	$<10^{-4}$	$<10^{-4}$
In^{3+}	0,81	10	-
Bi^{3+}	-	-	0,15
Fe^{3+}	0,53	$<10^{-4}$	$<10^{-4}$
Eu^{3+}	0,98	$<10^{-4}$	$3,6\cdot10^{-4}$
Cm^{3+}	0,99	$<10^{-4}$	$1,3\cdot10^{-3}$
Am^{3+}	1,00	$<10^{-4}$	$6,3\cdot10^{-4}$
Pu^{3+}	0,92	$<10^{-5}$	4,8
Np^{4+}		0,075	170
Pu^{4+}		0,17	2223
UO_2^+		0,062	0,72
PuO_2^+		0,012	4,3
NpO_2^+		0,016	3,3
NpO^{3+}		$3,3\cdot10^{-3}$	0,06

this value equals 1,80-1,84Å   This does not mean,that with the increasing ion charge one should use as extragents the macrocycles

of still decreasing size (15-crown-5, 12-crown-4) since the principles of changing energy of compression of these macrocycles,depending on the distance and energy of ion solvation are differant here and the resultant effect,determining the complexes stability may be lower, than in the case of a larger size of 18-crown-6. By analogy,one can consider the derivatives of 18-crown-6, where the introduction of substituents of the same size of macrocycles results in a change of its hardness and thus a series of anomalies is observed in the metal extraction by functionanalysed crown-ethers. This suggestion may be confirmed by the example of the extraction of AM and AEM by various derivatives of 18-crown-6 (Table 2).

At the invariable size of macrocycle and due to the introduction of aromatic and cycloaliphatic substituents, values $\widetilde{K}$ increase by two orders for AM, for AEM-by four orders and for lead-even by more than five orders.

Table 2

Extraction constant values($\widetilde{K}$) of nitrates of AM and AEM and lead from 0,1 M solutions of the nitric acid into 0,1 M solutions 18-crown-6(18C6), dibenzo-18-crown-6 (DB18C6),benzocyclohexyl 18-crown-6(BC18C6) and dicyclohexyl 18-crown-6 (DC18C6) in chloroform at $25\pm$ 0,1°C.

Crown-ether	Li^+	Na^+	K^+	Rb^+	Cs^+	Sr^{2+}	Ba^{2+}	Pb^{2+}
18C6	$<10^{-4}$	$4\cdot10^{-3}$	0,18	0,060	0,030	-	-	-
DB18C6	$1,6\cdot10^{-3}$	$3,3\cdot10^{-3}$	0,23	0,049	0,062	0,01	0,01	0,016
BC18C6	0,018	0,020	0,95	0,019	0,092	10,6	8,2	49,6
DC18C6	0,030	0,72	14,6	3,1	0,72	270	131	4232

At the constant atomic number of macrocycle and due to increasing its size in the serieses:DB18C6 < DB20C6 < DB22C6 and DC18C6 < DC20C6 < DC22C6 at the extraction of AM and AEM, one can observe decreasing of the values D for all elements, K and Sr selectivity losses and a drop of the separation factors β, especially for pairs K/Na and Sr/Ca (Table 3).

This means,that it should be taken into account the effective inner cavity size,decreasing in the studied serieses of crown-ethers and resulting in the change of selectivity rather than the total size of macrocycle.

Table 3
Distribution coefficients (D) of nitrates of AM and AEM at extraction from 1,0M solutions of nitric acid into 0,025M solutions of crown-ethers in chloroform at $25 \pm 0,1^{\circ}C$

Crown-ether	Distribution coefficients, D						Separation factor, β	
	Li^+	Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	K/Na	Sr/Ca
DB18C6	$0.4 \cdot 10^{-4}$	$8.3 \cdot 10^{-4}$	$9.2 \cdot 10^{-3}$	$0.7 \cdot 10^{-2}$	$2.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	11	0.04
DB20C6	-	$5.7 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	$<1 \cdot 10^{-4}$	0.9	0.66
DB22C6	-	$6.2 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$	$5.1 \cdot 10^{-3}$	0.9	<0.01
DC18C6	$6.5 \cdot 10^{-4}$	$12.5 \cdot 10^{-3}$	0.23	$6.0 \cdot 10^{-3}$	4.3	2.1	18	7160
DC20C6	$3.2 \cdot 10^{-4}$	$7.7 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	$1.25 \cdot 10^{-2}$	$3.5 \cdot 10^{-4}$	$<1 \cdot 10^{-4}$	0.6	0.07
DC22C6	$3.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$	$5.75 \cdot 10^{-3}$	$7.2 \cdot 10^{-4}$	$<1 \cdot 10^{-4}$	1.4	0.13

Thus, the formation of functionanalysed derivatives of macrocycles due to the introduction of additional substituents one can rise the selectivity of extraction. It becomes the most important direction of search of size-selective extragents for separation of the elements with the similar chemical properties. Within the framework of this study, more than 50 different structures of cyclic and acyclic polyethers, containing aromatic, aliphatic and cycloaliphatic fragments in molecules have been studied. The introduction of additional substituents into phenyl and cyclohexyl rings of crown-ethers made it possible to receive a series of perspective structures with alkyl, α-oxyalkyl and acyl radicals, whose extractive ability increases significantly, when the substituents with the normal structure are used.

Distribution of cations depends on the length of hydrocarbon radical in a series from ethyl to dodecyl, reaching maximum for amyl radicals and the number of such radicals in crown-ether molecule.

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ELECTRONIC STRUCTURE, CONFORMATIONAL FEATURES AND
EXTRACTION CAPACITY OF CROWN ETHERS

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The extraction capacity of organic agents is mainly determinate by
stability of their metal complexes. The aim of this work is to investi-
gate complexation features of a number of crown-ethers (CE) on the ba-
sis of theoretical calculations and structural and thermodynamical data
analysis. Object of the investigation have been chosen the following
polyethers: 18-crown-6 (18C6); dibenzo-18-crown-6 (DB18C6); 3',3''-di-
chloro-DB18C6; 3',3''-dinitro-DB18C6; 3',3''-dialkyl-DB18C6.

1. Let's consider metal cation (M^{n+}) complexation process with li-
gand (L) in the solvent (S)

$$(M^{n+})_s + (L)_s \longrightarrow (ML)_s^{n+} , \qquad (1)$$

as a set of the following stages: cation (I) and agent (II) desolvata-
tion, agent conformational transformation (III), agent-cation interac-
tion (IV), complex solvation (V). In this case the complexation energy
is determined as a sum of the terms:

$$E_c = E_I + E_{II} + E_{III} + E_{IV} + E_V .$$

Conformational transformation energy has been calculated by molecular
mechanics method using MM2 programm [1] . The energy of ion-molecular
and intermolecular interactions ΔE has been calculated by the method
[3] based on perturbation treatment:

$$E = E_{es} + E_{pl} + E_w , \qquad (2)$$

where the electrostatic term E_{es} is determined from the molecular elec-
trostatic potential (MEP) of the agent, the polarization term E_{pl} -
from the experimental chemical bond polarizabilities of the interaction
systems. Corrected on the molecular charge distribution [2] the poten-
tial functions "exp-6" have been used in order to calculate van-der-
Waals energy term E_w in (2). Solvation energy was calculated either by
means of (2) in framework of the discrete cluster model, or Monte-Carlo
method, or from experimental data.

2. Information about coordination metal polyhedron obtained from X-
ray data has been used for cation-ligand interaction energy calculations
Optimal ligand geometry in the complex has been determined from confor-
mational calculations by MM2 programm.

Hydrogen and carbon atomic positions were refined and oxygen atomic
positions were fixed in these calculations. For "flexible" 18C6 two con-
formations were analyzed; observed in K^+, Rb^+, Cs^+ - complexes D_{3d} -
conformation and observed in Na-complex C_1 - conformation [4] . For
"hard" DB18C6 and its analogues C_2-conformation CE have been analyzed [5].
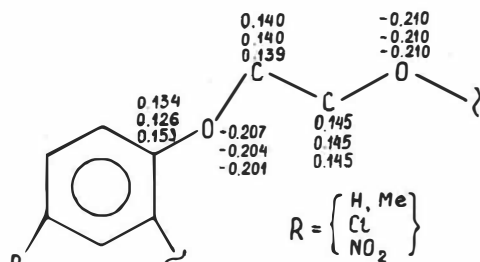
Fig.1. Charge distribution in DB18C6 and its
dichloro-, dinitro-, dialkyl-substituted

In quantum chemical and energy calculations geometry CE obtained from
conformational calculations has been used. Atomic charges resulting
from CNDO/2 quantum chemical calculations make up - 0.210 e for 0, 0.140
e for C and - 0.02 e for H atoms [6] . Benzene rings in DB18C6 decrease
the charges on neighbour oxygen atoms, but they don't change the charges
on the distance oxygen atoms. Electronegative groups Cl and NO_2 in ben-
zene rings also exert the same influence (Fig.1). Alkyl substituents
almost don't influence charge distribution in macrocyclic ring of DB18C6.
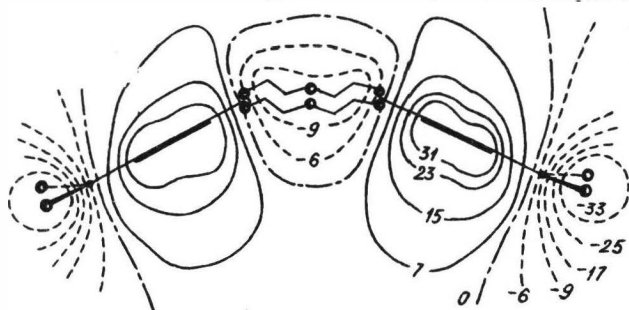
Fig.2. MEP distribution in 3',3''-dinitro-DB18C6
Line values - in 1kcal/mol

Using quantum chemical calculations data MEP distribution in CE has
been built by means of "MOLP" programm [7] . Within the cavities this
distribution is characterized by the region of negative value of MEP
with zero line as two-side crater (Fig.2). Cation is fixed in the cavi-
ties centre where MEP value is minimum. Negative MEP region on the mole-
cule border are found for dichloro- and dinitro- derivatives of DB18C6
and correspond to superfluous negative charge on the electronic acceptor
substituents.

Calculated according (2) cation-CE interaction potential curves are
shown in Fig.3. Minimums in these curves agree with equilibrium distance
between the cation and the average-square plane of oxygen atoms in DB18C6.
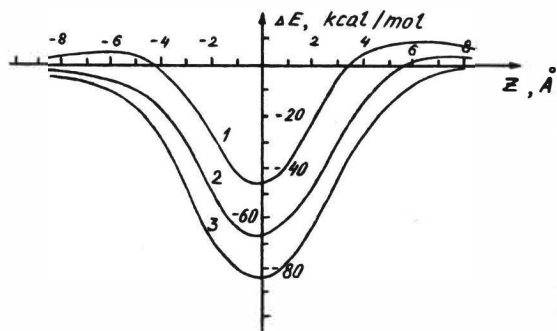
Fig.3. Potential curves
the interaction K⁺ with
DB18C6 (1),
dichloro-DB18C6 (2),
dinitro-DB18C6 (3),
Axis Z is ligand symmetry
axis

3. Investigation of the DB18C6 and dialkyl-DB18C6 complexes with K^+
and Na^+ hydration effects have been carried out by Monte-Carlo method
for clusters, which include CE complexes with cation and 125-140 water
molecules. It's shown, that addition of the alkyl radicals result in th
partial desruption of the hydrogen bond of water and increase of the
complex hydration energy.

4. In terms of above selectivity model of 18C6 complexation with al-
kali cation in the water has been analyzed. E_I was approximated by ex-
perimental values of the cation hydration energy. Complex hydration
energy has been calculated within the framework of discrete model for
the cluster, including ligand, cation and 2-5 water molecules (Table1).
Data from tables 1, 2 demonstrate, that the experimental selectivity
set is reproduced if energies of all stages are used; a priori removal
of any stage from calculation resultes in serious errors.

5. The influence of substitutes on CE complexation process is exami-
ned on the example of DB18C6, dichloro-, dinitro- and dialkyl-DB18C6.
According to experimental data the stability of dialkyl- DB18C6 comple-
xes with alkali metal decrease with the increase of alkali chain from
Me to Oct [8] . The same decrease of the complex stability constant are
found for dichloro- and dinitro-derivatives of DB18C6 [9] . The analysi:
carried out in the framework of the above model, show different reasons
decrease in the case in question. The influence of electron-acceptor
(Cl, NO_2) substituents connected with decrease of cation-ligand interac-
tion energy (Fig.3). Decrease of the dialkyl-DB18C6 complexes stability
is associated with hydrophobic interaction of CE, which become stronger
with increase of the alkyl chain size. Thus, decrease of different term
E_c result in the same effect — decreasing total complexation energy, an
hence, decreasing of complex stability.

Table 1. Complexation 18C6 and alkali cations energy balance,(kcal/mol)

Cation	E_I	E_{III}	E_{IV}	E_V	$E_I + E_{IV}$	$E_I + E_{III} + F_{IV}$	E_c'
Na^+	98.4	6.7	-111.9	-4.8	-13.5	-6.8	-11
K^+	80.6	0.0	- 88.9	-24.0	- 8.3	-8.3	-32
Rb^+	75.5	0.6	- 82.6	-20.0	- 7.1	-6.5	-26
Cs^+	67.8	0.3	- 66.3	-17.0	1.5	1.8	-15

Table 2. As to analysis of the 18C6 selectivity

Criterium of selectivity	Selectivity set
E_{IV}	$Na^+ > K^+ > Rb^+ > Cs^+$
E_{III}	$K^+ \approx Cs^+ \approx Rb^+ > Na^+$
$E_I + E_{IV}$	$Na^+ > K^+ > Rb^+ > Cs^+$
$E_I + E_{III} + E_{IV}$	$K^+ > Na^+ > Rb^+ > Cs^+$
$E_I + E_{III} + E_{IV} + E_V$	$K^+ > Rb^+ > Cs^+ > Na^+$
Experimental data [9]	$K^+ > Rb^+ > Cs^+ > Na^+$

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The 4'-substituted B15C5 derivatives 1a-c and the bis(crown ether)s
2a-d, 3a and 3b have been synthesized by reaction of carboxylic acid
hydrazides with 4'-formylbenzocrown ethers [1,2,3] ,(see Fig. 1).
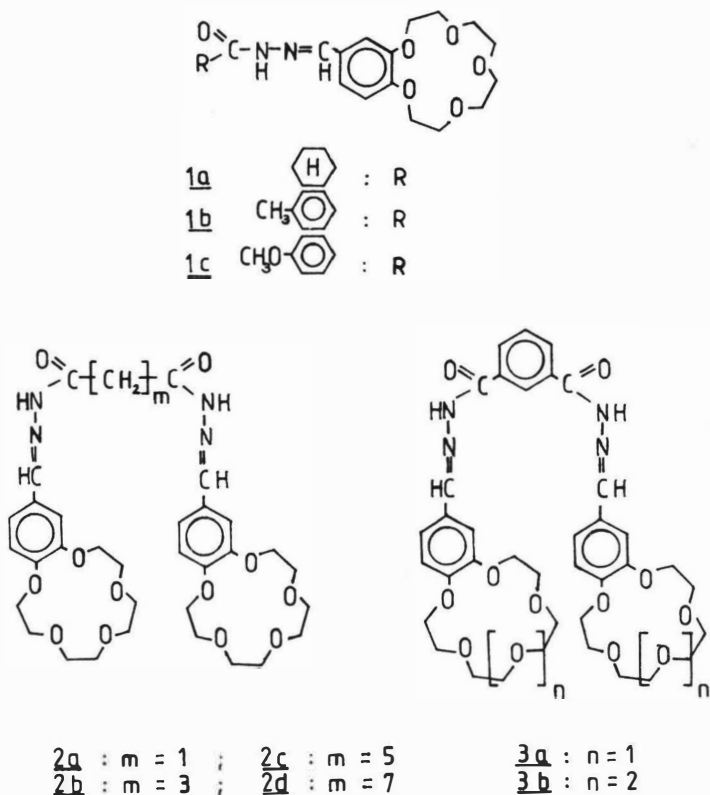
Fig.1. Representation of used crown ether derivatives

The extraction properties of macrocycles in the system metalnitrate
or metalchloride-picric acid-H_2O / ligand-$CHCl_3$ have been radio-
metrically obtained by measuring of the appropriate γ -radiation rate
of the radionuclides [4].
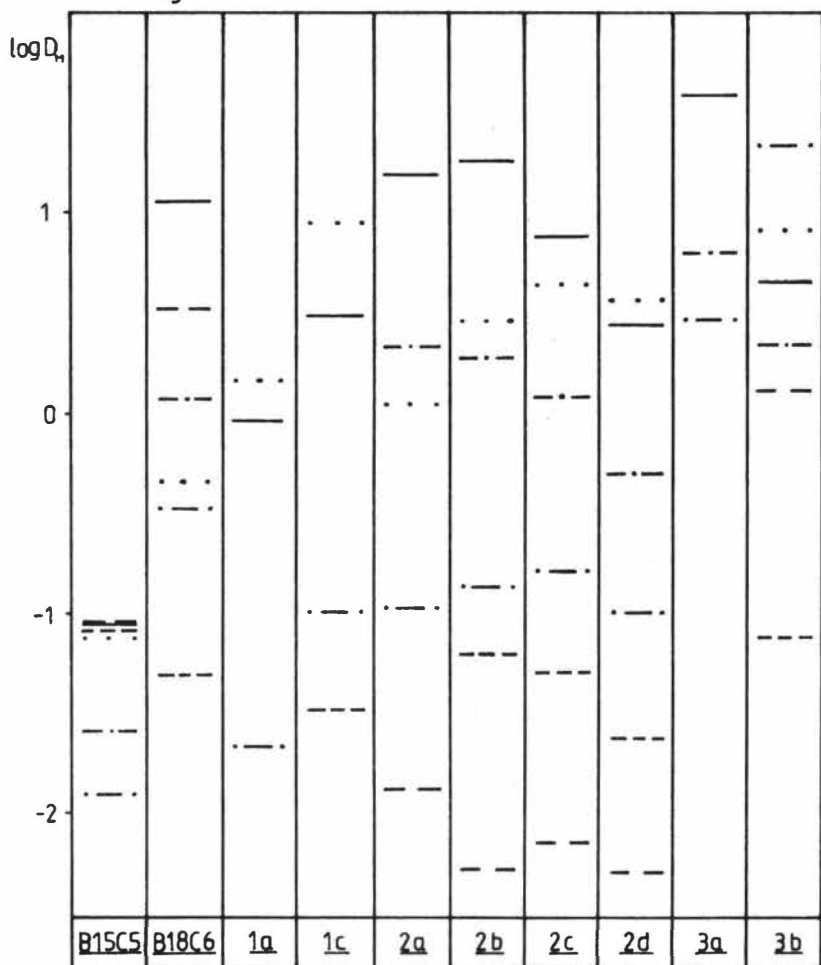
Fig.2. Extraction of alkalimetals, strontium and silver with mono-
and bis(crown ether)s

In Fig.2 the extraction values (log D_M) for Na^+, K^+, Rb^+, Cs^+,
Sr^{2+} and B15C5, B18C6, 1a, 1c, 2a-d and 3a,b are given.
The obviously better extraction of potassium by the substituted

benzocrown derivatives 1a and 1c is remarkable in comparision with B15C5.

As expected the compounds 2a-d proved to be potassium-selektive extraction agents. The introduction of a rigid arylenbridge increases the log D_M-values in the extraction of alkalimetal cations in comparision with aliphatically bridged bis(crown ether)s; it doesn't lead to any increase of potassium-selectivity.

The bis(crown ether) 3b of B18C6-type turned out to be a cesium-selective extraction agent.
The extraction-selectivities of 2a-d, 3a and 3b can be reduced to the influence of the bis(crown ether) effect [5].

The high log D_{Ag}-values received during the extraction of silver cations are remarkable. A coordinative correlation of silver cations to the nitrogen atoms of the hydrazone group is supposed.

Furthermore, we investigated the potassium- and cesium-selectivity of the bis(crown ether)s by means of the separation factor , given by

$$\alpha = \frac{D_K, DC_s}{D_M}$$

It was possible to determine the composition of the formed complexes by conductometric titration for the cations K^+, Rb^+, Cs^+ and Ag^+ [6,7].

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SYNERGIC EXTRACTION OF METALS WITH 4-ACYLPYRAZOL-5-ONES AND CROWN ETHERS

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Crown ethers are interesting complexing agents particularly towards alkali and alkaline earth metals which can be selectively extracted in the presence of sufficiently hydrophobic anions like picrate (1), di dodecylnaphtalene sulfonate, bis (2-ethylhexyl) phosphate (2), hexachloroantimonate (3). Accordingly, in a previous paper (4), we reported the extraction of the ion pair $\overline{KE^+, Co(PMBP)_3^-}$ with E = 18C6 type crown ethers and HPMBP = 1-phenyl-3-methyl-4-benzoylpyrazol-5-one. In the absence of K^+, a synergic extraction of cobalt with the HPMBP-E mixture was also found. This fact was explained by the formation of $\overline{Co(PMBP)_2E}$ species. The present paper deals with the extraction of divalent transition metals M^{2+} (M = Cu, Co, Zn, Cd) with mixtures of HPMBP and various crown ethers of different cavities (B15C5, DB18C6, DB24C8 - B, DB = benzo, dibenzo) from aqueous media of 1.0M ionic strength fixed by LiCl, NaCl, KCl, CsCl, $NaNO_3$ or $Ba(NO_3)_2$.

Extraction equilibria. The extraction of divalent metals M with HPMBP can be represented by the following equilibrium :

$$M^{2+} + 2\ \overline{HPMBP} \xrightleftharpoons{K_{2,0}} \overline{M(PMBP)_2} + 2H^+, \tag{1}$$

where the overlined symbols refer to the organic phase. In the presence of crown ethers E, a synergic extraction is generally observed. it can be represented by the two following equilibria depending on the alkali or alkaline earth cations B^{n+} in the aqueous phase and the crown ether employed :

$$M^{2+} + 2\ \overline{HPMBP} + \overline{E} \xrightleftharpoons{K_{2,1}} \overline{M(PMBP)_2E} + 2H^+ \tag{2}$$

and / or

$$nM^{2+} + 3n\ \overline{HPMBP} + \overline{E} + B^{n+} \xrightleftharpoons{K_{3n,1}} \overline{BE[M(PMBP)_3]_n} + 3nH^+ \tag{3}$$
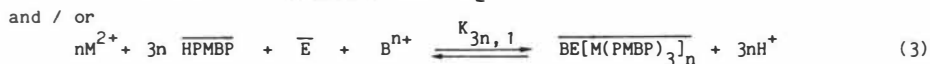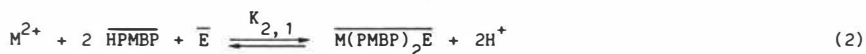
The slopes of the experimental distribution curves log D_M vs pH (with $D_M = \overline{[M]}\ [M]^{-1}$) together with the experimental values of [B] allow the determination of the relative importance of equilibria (2) and (3). From equilibria (1) and (2), it follows the synergic complex formation equilibrium (4).

$$\overline{M(PMBP)_2} + \overline{E} \xrightleftharpoons{K_s} \overline{M(PMBP)_2E} \tag{4}$$

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Table 1

Extraction of Co^{2+} by HPMBP + E in chloroform

crown ether	electrolyte	extracted species	$\log K_{2,1}$ or $\log K_{3n,1}$	
B 15C 5	LiCl	$Co(PMBP)_2E$	-4.8	
	NaCl		-4.8	
	$NaNO_3$		-4.7	
18C6	LiCl		-4.1 (5)	
DC 18C6B	LiCl		-4.3 (5)	
DB 18C6	LiCl		-4.9	
DB24C8	LiCl		-4.6	
	KCl		-4.6	
	CsCl		-4.5	
B 15C 5	KCl	$KECo(PMBP)_3$		-7.05
18C6	KCl			-7.4
DB 18C6	KCl			-6.9
DB 18C6	$BaNO_3$	$Co(PMBP)_2E$	-4.7	
		$+ \quad BaE[Co(PMBP)_3]_2$		-14.2

Table 2

Extraction of M^{2+} by HPMBP + DB 18C6 in chloroform

electrolyte	extracted species	$\log K_s$	or $\log K_{3,1}$
$NaNO_3$	$Cu(PMBP)_2$	-	-
$NaNO_3$	$Zn(PMBP)_2E$	1.95	-
$NaNO_3$	$Co(PMBP)_2E$	2.1	-
$NaNO_3$	$Cd(PMBP)_2E$	2.6	-
KNO_3	$Cu(PMBP)_2$	-	-
KNO_3	$Zn(PMBP)_2E$	1.95	-
KNO_3	$KE Co(PMBP)_3$	-	-6.9
KNO_3	$KE Cd(PMBP)_3$	-	-8.6

Results and Conclusions. The extraction constants of the mixed species $\overline{M(PMBP)_2E}$ and $\overline{BE[M(PMBP)_3]_n}$ $K_{2,1}$ and $K_{3n,1}$, as well as the formation constants of the adducts $M(PMBP)_2E$ have been determined at 25°C. They are summarized in the tables 1 and 2.

The analysis of distribution data shows that the composition of extracted species in organic phase depends on the electrolyte cation. For LiCl, NaCl, CsCl, $NaNO_3$, the extracted species are of the $\overline{M(PMBP)_2E}$ type. For KCl, the extracted

species are $\overline{KEM(PMBP)_3}$ when the crown ethers are B15C5, 18C6, DC18C6, DB18C6 (crown ethers with a good correspondence between their cavity sizes and the K^+ diameter) and for M = Co or Cd (metals with a sufficient stability of the $M(PMBP)_3^-$ anion). When E = DB24C8 (a crown ether with a large cavity) only species of the $\overline{M(PMBP)_2E}$ type are extracted. The formation constants of the $\overline{M(PMBP)_2E}$ adducts follow the order Cd > Co > Zn. They are not very sensitive to the cavity size of the crown ethers, which shows the external binding of the $\overline{M(PMBP)_2}$ complexes. They increase only slightly with increasing the number of oxygen atoms in the cycle and decrease with increasing the electron withdrawing strength of the crown ether substituents (18C6 > DC18C6 > DB18C6 - DC = dicyclohexyl). With $Ba(NO_3)_2$ as electrolyte, the distribution curves analysis fits with the co-extraction of $\overline{Co(PMBP)_2E}$ and $\overline{BaE[Co(PMBP)_3]_2}$. No synergic effect was observed in the extraction of copper from the different aqueous media in the presence of the various crown ethers.

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Phosphorus-containing podands (PCP) form stable complexes with ions
of alkali metals, and in numerous cases are not worse in efficiency
than crown-ethers[1]. The presence of phosphoryl groups in the molecu-
les of those compounds permits to expect their interesting extraction
properties.

In the present work the extraction of inorganic acids (HNO_3, $HClO_4$,
HCl) and alkali metals perchlorates by several PCP of various structu-
res was studied: $(RO)_2P(O)(CH_2)_n(OCH_2CH_2)_mO(CH_2)_nP(O)(OR)_2$,
n=I, m=0(I); n=I, m=I(2); n=I, m=2(3); n=I, m=3(4); n=2, m=0(5);
n=2, m=I(6); $R=C_5H_{II}(I \div 6)$, $R=C_6H_{I3}(5)$;
$R_2P(O)CH_2OCH_2CH_2OCH_2P(O)R_2$, $R=C_8H_{I7}(7)$;
$(RO)_2P(O)CH_2CH_2CH_2P(O)(OR)_2$, $R=C_5H_{II}(8)$.

These compounds were synthesized using the Michaelis-Beccker reac-
tion, proceeding from dialkylphosphites and dihalogenated ethers. In
all cases, the extraction properties of podands were compared with the
similar properties of bis-phosphonate (8), not containing oxygen atoms
in the bridge fragment.

Nitric acid is extracted via solvate mechanism. On the extraction
isotherms of nitric acid with 0.I M solution of PCP in toluene (fig.I)
at acid concentration of least 5 M, a rising area is noted, correspon-
ding to the accumulation of solvates of composition I:I and I:2 :

$$H^+ + NO_3^- + S_0 \rightleftharpoons (S \cdot HNO_3)_0 \qquad (I)$$

$$H^+ + NO_3^- + (S \cdot HNO_3)_0 \rightleftharpoons (S \cdot (HNO_3)_2)_0 \quad (2)$$

The coordination occurs only via oxy-
gen atoms of phosphoryl groups. This
explains the absence of noticeable
effect of the structure on the shape
of isotherms in this area.

On increasing of HNO_3 concentra-
tion in aqueous phase ($X_{HNO_3} > 7$ M) a
transfer to organic phase of solvates
$(HNO_3)_n$ S (n>2) is noted. The shapes
of isotherms in this area definitely
proves the participation of ether
oxygen atoms in the formation of hy-
drogen bond with the HNO_3 molecules.
The increase of the number of ether

Fig.I. The extraction iso-
therms of nitric acid with
0.I M solutions of podands
in toluene

oxygen atoms leads to the increas of the extraction capacity of podands.

The studies of the effect of diluent on the extraction of nitric acid showed that in the area of lower solvate extraction the degree of

nitric acid extraction increases in the octane – carbon tetrachloride – toluene – chloroform series. In the area of formation of higher solvates with composition I:I and I:2 an inverse dependence is noted (fig.2).

The extraction of $HClO_4$ and HCl with phosphorus-containing podands proceedes via hydrate-solvate mechanism. Structural changes in the PCP molecules have little effect on the distribution of those acids.

In studies of the extraction properties of phosphorus-containing podands in the row of alkali metals perchlorates a dependance of PCP extraction capacity on the molecule structure was found. Besides the high extraction capacity of podands in respect to lithium perchlorate, the distribution coefficients of perchlorates of other alkali metals in the sodium – potassium – rubidium series increase with the increase of number of oxygen atoms in polyether fragment. Table 1 lists the negative logarithms of distribution coefficients of alkali metals perchlorates between the aqueous phase and .0.1 M solution of PCP in initrobenzene.

Extraction of alkaly metals perchlorates with 0.1 M solutions of PCP in nitrobenzene

PCP	-log D			
	Li$^+$	Na$^+$	K$^+$	Rb$^+$
I	I.96	2.37	2.24	2.04
2	I.7I	2.26	I.62	I.64
4	I.59	I.79	I.03	I.I0
5	I.44	2.3I	2.49	2.73
6	I.60	2.03	I.58	I.59
7	0.55	I.40	0.97	0.97
8	I.28	2.52	2.45	2.30

Fig.2. The extraction isotherms of nitric acid with 0.I M solutions of podand 5 (R=C_6H_{I3}) in diluents: I – octane, 2 – carbon tetrachloride, 3 – toluene, 4 – chloroform

Reference

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| | 2-7 |

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INTRODUCTION

The potential of polyethers as the new generation of specific
extracting agents for metal ions has been markedly enhanced by
the introduction of polyethers which bear a pendant ionizable
group[1]. By attachment of lipophilic groups the solubility of
ionizable polyethers in the aqueous phase could be remarkable
reduced. In such molecules, novel bifunctional complexing agents
are created by the combination of an ionizable group with an ion-
-binding polyether chain or polyether ring. These ionizable poly-
ethers possess a distinct adventage over neutral polyethers in that
transfer of cations from an aqueous phase into an organic medium
does not require the concomitant transfer of the aqueous phase anion[2].

By varying polyether part of a molecule, the size of lipophilic
part and its attachment site, and the kind end number of ionizable
groups, the specific and extremely selective carriers of metal
ions can be elaborated[3-9].

We now present results on competitive solvent extraction and
liquid membrane permeation of alkali and alkaline earth cations from
aqueous solutions by series of lipophilic and ionizable acyclic
polyethers of varying molecular structure.

RESULTS AND DISCUSSION

A new series of monoionizable acyclic polyethers 1-10 have now
been prepared and utilized as carriers for competitive solvent extra-
ction and membrane permeation of alkali metal cations from aqueous
solutions. All studied polyethers possess the same lipophilic group,
i.e. decyl group. Polyethers 1-4 have the same acidic groups, i.e.
carboxylic groups, and the same terminal groups i.e. benzyl groups.
They differ in numbers of polyether oxygens. Results of competitive
solvent extraction of alkali metal chlorides from aqueous solutions
into chloroform solutions of acyclic polyethers 1-4 give the follo-
wing selectivity orders: $Li^+ \gg Na^+ > K^+ \approx Rb^+ \approx Cs^+$ for 1, $Li^+ \gg Na^+ > K^+ \approx$
$Rb^+ \approx Cs^+$ for 2, $Li^+ > K^+ \approx Na^+ \approx Rb^+ \approx Cs^+$ for 3, and $Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$ for 4.

$n\text{-}C_{10}H_{21}$ — (aromatic ring) — O — $\left(\text{CH}_2\text{CH}_2O\right)_n$ — OX, with Ac substituent on ring
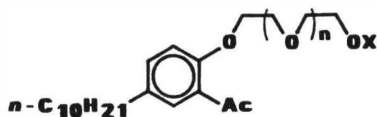
Ac	X	n			
		0	1	2	3
-COOH	(benzyl) CH_2-	1	2	3	4
-COOH	-H	5	6	7	8
-COOH	$-CH_3$	9			
-P(O)(OH)OEt	(benzyl) CH_2-	10			

The Li^+/Na^+ selectivity ratio was 4.8 for 1, 3.1 for 2, 2.3 for 3, and 2.5 for 4, respectively. The maximum metal loading into the organic phase was 85% for 1, 90% for 2, 103% for 3, and 63% for 4. All of these acyclic polyethers are selective for Li^+. With the lithium cation diameter (1.48 Å) appears to best fit the pseudo-cavity formed upon complexation. This indicates that probably not all of the oxygen atoms are involved in the complexation process. The lower selectivity is observed as the ethylene oxide chain increases. This can be explained in terms of a tendency of these polyethers to wrap equatorially around the cation with the acid group positioned axially.

The next serie of studied acyclic polyethers (5-8) comprises compounds with hydrogen as the terminal group. The loading of metal in the organic phase varies from 72 to 95% but selectivity is much poorer. Compounds 5-7 are all selective for Li^+ with Li^+/Na^+ selectivity ratio equal to 1.6 for 5, 1.9 for 6, and 1.4 for 7. Polyether 8 was selective for K^+. The change in the best extracted metal from Li^+ to K^+ proves a "head-to-tail" cyclization through hydrogen bonding for 8.

Comparizing the acycic polyethers 1-4 and 5-8 one can suppose that the terminal end groups have an influence on the selectivity of acyclic polyethers. Change from the benzyl to the hydrogen atom end group leads to a decrease of selectivity but has no market effect on extraction efficiency.
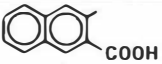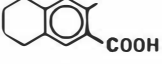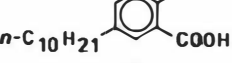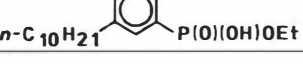
To verify this hypothesis, competitive solvent extractions with 9 were conducted. This extractant is closely related to 1 and 5 but has a terminal methyl group. In this case Li^+ was again the best extracted metal and the Li^+/Na^+ selectivity ratio was 2.9. This is an intermediate value between the values obtained for 1 and 5.

Since the best selectivity for lithium was observed for polyether with two oxygen atoms in polyether chain and with benzyl end group, the last polyether (10) possessed both these groups but instead of carboxylic group bore the diphosphonic acid monoethyl ester group. In this case lithium was still the best extracted metal but the Li^+/Na^+ selectivity ratio equaled only 3.0.

The transport of alkali metal cations through bulk liquid membranes by ionizable acyclic polyethers 3 and 4 was also examined. Selectivity order from the competitive transport from aqueous solutions   across a chloroform liquid membrane by 3 and 4 was $Li^+ > Na^+ \approx K^+ \approx Rb^+ \approx Cs^+$ in both cases. Both compounds exhibited preferences for Li^+ transport but 3 had a slightly higher lithium selectivity.

$$XO \frown O \frown_n OX$$

X	n				
	0	1	2	3	4
![naphthalene]COOH	11	12	13	14	15
![decalin]COOH	16	17	18	19	
$n\text{-}C_{10}H_{21}$![benzene] COOH	20	21	22	23	
$n\text{-}C_{10}H_{21}$![benzene] P(O)(OH)OEt	24	25	26	27	

Dionizable acyclic polyethers 11-27 were utilized as carriers in competitive solvent extraction of alkaline earth cations from aqueous solutions [10,11] . Acyclic polyethers 11-15 are dinaphtoic acid analogues. Neither 11 nor 12 possessed sufficient solubility in chloroform to be utilized in the solvent extraction studies. Polyether 13 was very selective for barium (Ba^{2+}/Ca^{2+} = 250) while polyethers 14 and 15 exhibited poor selectivity.

The polyether dicarboxylic acids 16-19 are tetralin acid analogues. For 16, 18, and 19 the extraction selectivity orders were $Ca^{2+} > Ba^{2+} > Sr^{2+}$ (with no Mg^{2+}), $Ba^{2+} \gg Sr^{2+} \approx Ca^{2+}$ (with no Mg^{2+}) ,and $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$, respectively. Extractant 18 shows excellent selectivity for $Ba^{2+}(Ba^{2+}/Sr^{2+}$ = 50). Loading and selectivity of 17 was very poor.

Last serie of acyclic polyether dicarboxylic acids was this with n-decyl salicyl group (20-23). For compounds 20-23 no detectable Mg^{2+} was extracted and 22 exhibits excellent selectivity for Ba^{2+}. Com-

278

pounds 20, 21 and 23 which have two less, one less, and one more ethy-
lenoxy units than 22 possessed the lower Ba^{2+} selectivity. Replacing
carboxylic group in compounds 20-23 with diphosphonic acid monoethyl
esters (24-27) give worse solvent extraction results. For all four
complexing agents, Ca^{2+} and Ba^{2+} were preferable extracted over the
Sr^{2+} and Mg^{2+}.

CONCLUSIONS

From the results presented it comes that a specific and very selec-
tive cation carriers for liquid-liquid extraction and liquid membrane
separations could be evaluated by varying the molecular structure of
lipophilic and ionizable acyclic polyethers.

We have found that some of studied monoionizable acyclic polyethers
were very selective in lithum separation. For example, the Li^+/Na^+
selectivity ratio for polyether 1 was 4.8, while this ratio for lithium
over other alkali metals was 12. These results are little worse in
comparision to those obtained for crown ether carboxylic acids[12].
Main adventage of manoionizable acyclic polyethers versus ionizable
crown ethers is that syntheses of first are much cheaper and simpler.

Results of competitive solvent extraction of alkaline earth cations
from aqueous solutions into chloroform by dionizable acyclic poly-
ethers show that these compounds can be good complexing agents. Some
of them are very selective for barium. For example, the Ba^{2+}/Ca^{2+}
selectivity ratio for polyether 13 was 250.

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In the extraction of metals, β-diketones such as thenoyltri-
flouroacetone are extensively used [1]. Acyl pyrazolones have
been found to be promising reagents for the extraction of metals
from acidic media [2-6]. In the present study, the potential of
3-phenyl-4-acetyl-5-isoxazolone(HPAI) and 3-phenyl-4-benjoyl-5-
isoxazolone (HPBI) for the extraction of Mn(II), Fe(II), Co(II),
Ni(II), Cu(II), Zn(II), and Cd(II) has been investigated. Chlo-
roform was used as solvent for extraction in case of HPBI. Methyl
isobutyl ketone was uaed as solvent with HPAI, as the ligand was
soluble in this solvent to a greater extent than other organic
solvents. Solid complexes of these metals with HPAI and HPBI
have been isolated and studied [7,8]. In common with other β-di-
ketones (like acyl pyrazolones), acyl isoxazolones exist in keto
and enol forms (Fig.1).

The extraction behaviour of each element as a function of pH
in aqueous solution is shown in figs. 2 and 3. Quantitative ext-
raction of Fe(II) was
observed in the pH range
1.5-8.0 with HPAI and in
the pH range 2.5-7.0
with HPBI. Both the
ligands showed quantita-
tive extraction of Ni(II)
and Co(II) from pH 3.0-
9.0. The notable feature
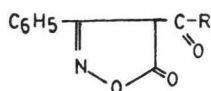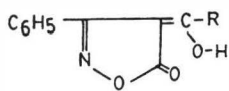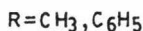
Keto   enol

$R=CH_3,C_6H_5$

Fig.1

in the extraction of Ni(II) is a shorter equilibration time as
compared with acyl pyrazolonea [9] or other β-diketones. Zn(II)
showed a sharp rise in extraction (fig.3) in the region of pH 4.0-
6.0 with HPBI and can be quantitatively extracted from solutions
of pH 5.5-8.0. Maximum extraction of Zn(II) (80%) was observed
over the pH range 6.0-7.0 with HPAI, then the extraction decrea-
sed at higher pH (9.0), where only 30% of Zn(II) was extracted.
Fig.2 shows a sharp rise in the extraction of Mn(II) from pH 8.0
by HPAI and the quantitative extraction into the organic phase
was observed at higher pH values. Below pH 6.0, no appreciable

quantity of Mn(II) was extracted. Maximum extraction of Mn(II) (95%) was observed over the pH range 8.0-9.0 with HPBI. The extraction of Cu(II) was quantitative in the pH range 2.5-8.0, then decreased at higher pH values and at pH 9.0 only 80% of Cu(II) was extracted. Cd(II) was extracted to the extent of only 25% at a pH of 8.8 with HPAI and 90% with HPBI in the pH range 8.0-9.0.

In order to understand the mechanism of extraction and the composition of complexes formed, plots of distribution coefficient ($\log K_d$) against pH at a fixed ligand concentration, and against log of ligand concentration at a constant pH would be valuable (figs. 4 and 5). The plots were linear with a slope of ~ 2 indicating the release of two H^+ ions and the involvement of two molecules of ligand during the extraction process. It can be inferred from these results that the main equilibrium involved in the extraction process may be represented as

$$M^{2+}_{aq} \;+\; 2\, HA_{org} \rightleftharpoons MA_{2\ org} + 2\, H^+_{aq}, \qquad (1)$$

where HA represents the ligand HPAI and HPBI. Extraction constant (also called equilibrium constant) for this process is given by

$$K_{ex} = \left[MA_2\right]_{org} \left[H^+\right]^2_{aq} / \left[M^{2+}\right]_{aq} \left[HA\right]^2_{org} . \qquad (2)$$

If it is assumed that MA_2 concentration is negligible in the aqueous phase, the distribution ratio is given by

$$K_d = \left[MA_2\right]_{org} / \left[M^{2+}\right]_{aq}. \qquad (3)$$

From (2) and (3) we have

$$\log K_{ex} = \log K_d - 2 \log \left[HA\right]_{org} - 2\ pH . \qquad (4)$$

The values of extraction constant ($\log K_{ex}$) were calculated from (4), using the experimental values of K_d, HA and pH. The $\log K_{ex}$ values calculated for the extracted metals are compared with those of the corresponding systems using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyltrifluoroacetone (HTTA) and are given in Table-1. It is clear from the table that the extraction of metals occurs at lower pH values with HPAI and HPBI than HPMBP and HTTA. Cd(II) and Mn(II) are, however, exceptions, where the extraction occurs at higher pH values with HPAI. The results obtained in theae investigations demonstrate that
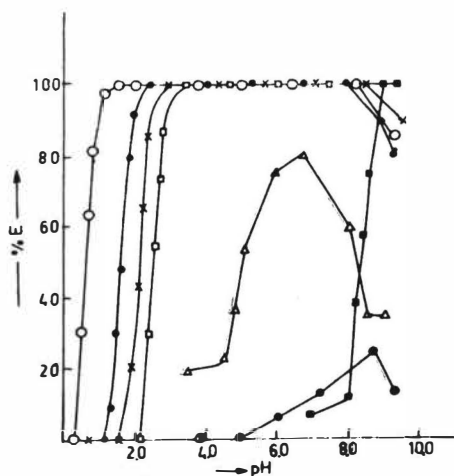
Fig.2. Plot of pH vs %E
O-Fe(II) ; ●-Cu(II); x-Ni(II); □-Co(II);
△-Zn(II); ■-Mn(II);●Cd(II) with
0.01M HPAI
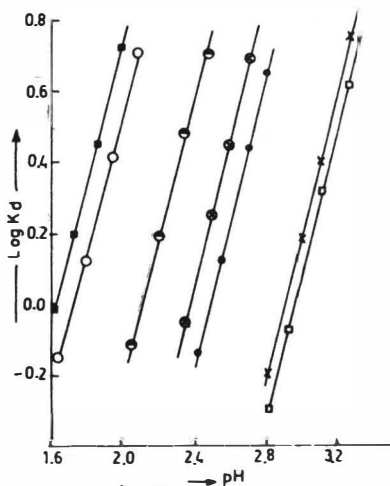
Fig.4. Plot of log K_d vs pH
O-Cu(II)-HPBI;●-Co(II)-HPAI;
●-Ni(II)-HPAI; x-Fe(II)-HPBI;
□-Co(II)-HPBI; ●-Ni(II)-HPBI;
■-Cu(II)-HPAI
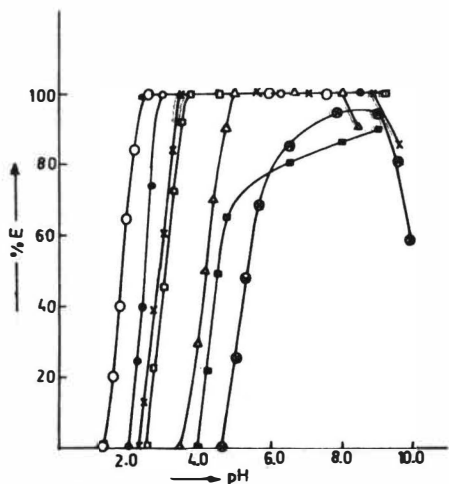
Fig.3. Plot of pH vs %E
O-Cu(II);●-Ni(II); x-Fe(II); △-Zn(II);
■-Cd(II);●-Mn(II);□-Co(II) with 0.01M-HPBI
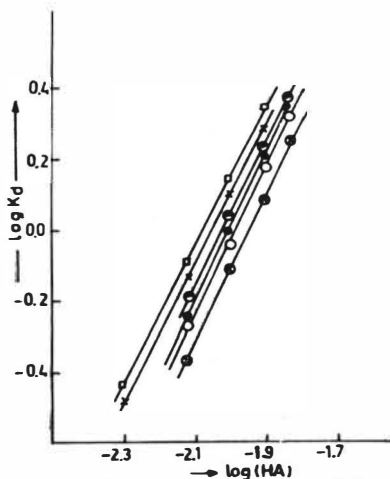
Fig.5. Plot of log K_d vs log[HA]
O-Mn(II)-HPAI;●-Fe(II)-HPAI;
●-Cu(II)-HPBI;□-Zn(II)-HPAI;
●-Co(II)-HPBI; x-Ni(II)-HPBI

282

Table 1. Comparison of Extraction Constant values $(\log K_{ex})$
of metal chelates of HPAI and HPBI with HPMBP and HTTA

Metal	Ligand			
	HPAI	HPBI(a)	HPMBP(b)	HTTA (c)
Mn(II)	-12.63	-6.63	-8.10	-10.07
Fe(II)	+ 2.57	-1.74	—	—
Co(II)	- 1.10	-1.88	-7.25	-6.80
Ni(II)	- 0.51	-0.89	-4.22	-8.60
Cu(II)	+ 0.75	+0.52	-0.70	-1.28
Zn(II)	- 5.89	-4.36	-6.18	-8.13
Cd(II)	only 25% extraction	-4.92	-9.70	-11.4

a) present work   b) ref. 10,11   c) ref. 12,13

acyl isoxazolones represent a new group of promising chelating
reagents for solvent extraction studies.

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4-Acyl-1-phenyl-3-methyl-pyrazol-5-ones are exellent metal extractants [1] and excel most of acyclic-ß-diketones. A further improvement of the extraction qualities especially of thio-philic metal ions is observed if oxygen as donor atom is sub-stituted by sulfur [2]. In the same way 4-phenylhydrazono-1-phenyl-3-methyl-pyrazol-5-thione forms stable chelates with non-ferrous and noble metals [3,4] and exhibits good extraction qualities.

It seems interesting to compare these different ligands which all contain the pyrazolone systems

$$CH_3 - \underset{\underset{\underset{C_6H_5}{\overset{|}{N}}}{\overset{\parallel}{N}}}{\overset{}{C}} \!\!-\!\!\!-\!\!\!- \underset{\underset{C \equiv X}{\overset{|}{C}}}{CH} - R$$
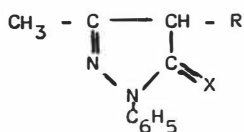
	R	
I	Benzoyl-	O
II	Thiobenzoyl-	O
III	Benzoyl-	S
IV	Phenylhydrazono-	S
V	Phenylhydrazono-	O

The extraction of zinc with these ligands was chosen to evalu-ate the stability constants of the complexes from the extracti-on curves. To determine the distribution ratios the AKUFVE-technique with ^{65}Zn was used [5]. The calculations [6] were ma-de with the acid of a computer programme "MIQUA" following the equations.

$$\frac{1}{D} = \frac{1 + \beta_1 \cdot c_L + \beta_2 \cdot c_L^2}{K_{D,Ml_2} \quad \beta_2 \cdot c_L^2},$$

$$c_L = \frac{c_{L,total}}{c_{H^+}} \cdot \frac{K_{A, HL}}{K_{D, HL}}.$$

For the ligands studied the sequence of $pH_{0.5}$ values was found as

$$III < II < I < IV < V.$$

The distribution coefficients of the ligands (chloroform/water) needed for the calculation of the stability constants of the complexes were taken from literature data. In the case of

ligand IV the distribution was measured in strongly alkaline so-
lution; therefore a correction of hydroxide concentration by ac-
tivity coefficients [8] was necessary.

The evaluated data are collected in table 1.

The comparison of the stability constants of the zinc comple-
xes with differently substituted pyrazolones and thiopyrazolones
shows that complexes with O,S- or S,N coordination exhibit simi-
liar stabilities, but are more clearly stable than those with
O,O-coordination. This result corresponds to the thiophilic cha-
racter of zinc.

The O,S ligands II, III ($pH_{0,5} < 2,5$), therefore, are better
extracting agents than the O,O ligand I ($pH_{0,5} = 4,8$).

Table 1. Stability constants of zinc complexes with
different derivatives of pyrazolone, evaluated from
distribution data in the chloroform/water system

Ligand	$\lg \beta_1$	$\lg \beta_2$	$\lg \dfrac{K_{D,HL}}{K_{A,HL}}$
I	2,94 [7]	6,56 [7]	
	2,85	8,26	8,30 [2]
II	8,36	16,48	9,82 [2]
III	6,84	16,09	8,67 [2]
IV	8,83	16,51	14,70

+) System benzen/water

4-Phenylhydrazono-1-phenyl-3-methyl-pyrazol-5-thione IV shows
a similiar complex stability like the ligands with O,S ligator
atoms II, III . But there are distinct differences in the aci-
dity which determines the extraction behaviour. From NMR spectra
it is known that compounds IV and V are NH acids. The pK_a va-
lues in ethanol/water (1:1) are for the pyrazolone V 8,7 and 7,7
for the thio compound IV. Corresponding to this fact the extrac-
tion of d-metals studied here runs off at lower pH values with
the S,N ligand.

Table 2. Extraction of d-metals with 4-phenylhydrazono-
1-phenyl-3-methyl-pyrazol-5-thione IV and -one V

Extractant	$pH_{0,5}$			
	Cu^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}
IV	4,35	6,70	6,85	7,15
V	6,8	8,65	8,10	9,55

The lg D/pH diagrams prove the formation of 1:2 complexes.

Cobalt is extracted as the cobalt II compound, oxydation, often observed during chelation, does nut occur.

Cobalt II also exists in the solid complex as can be seen from magnetic measurements ($\mu_{B.M.}$ = 5,41).

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One of the most important direction for complexing compounds chemistry is composing such reagents that are not only effective but also highly selective. Regarding research for reagents with selective properties, amides of carboxylic acid with general formula $RC(O)NR'_2$ (R, R' - alkyl) present certain interest. The given compounds belong to the class of nitrocarbonyl-containing extragents of "neutral" type, their reactivity is conditioned above all by the charge of the oxygen of the carbonyl group.

The study presently carried out in regard of extraction ability of certain amides of carboxylic acids has shown that by changing the structure of substituents at the amide grouping - $C(O)N<$ one can provide ample opportunity for the solution of the problems concerning separation of elements by solvent extraction. The following parameters of amides as hydrolytic stability and radiation resistance, compatibility with organic diluents, solubility in aqueous media are also greatly dependant on the structure. In accordance to $/1-5/$, amides of carboxylic acids have no shortcomings typical to TBP and could be substituted for TBP in the solvent regeneration technology of nuclear fuel.

The present work goes forth with the study on reactivity of amides and gives data on the extraction of rare earth elements (REE), vanadium, molybdenum, rhenium, uranium, niobium, tantalum by NN-dibutylamide of acetic acid (DBAA), NN-dibutylamide of nonanic acid (DBNA), NN-dibutylamide of fatty synthetic acids of C_7-C_9 fraction (DFSA). The amides used in the study were synthesised by interaction of dibutylamine with chloride of acid of carboxylic acids. The aqueous solutions for REE, uranium, iron, molybdenum, vanadium, rhenium contained 1 g/l of the metal to be recovered and were obtained by dissolving corresponding salt samples: nitrates ofREE, uranyl chloride, ferric chlorine, $(NH_4)_6Mo_7O_{24}$, NH_4VO_3, NH_4ReO_4 in acids with required concentration. The initial solution for extraction of niobium and tantalum were prepared by dissolving matallic niobium and pentoxide of tantalum in the solution of hydrofluoric and sulphuric acids. The tests were conducted at $22\pm2°C$. The volumes ratio of aqueous and organic phases 1:1, the diluent - keresene.

The distribution coefficients (D) of REE in the oxidation degree 3+ at the DBAA extraction without diluent are not high (Table 1). The increasing acidity of the aqueous phase from 2N to 8N leads to decrease of D of rare earth elements. At that, samarium is displaying it to the utmost extent. As compared to erbium, ytterbium, yttrium, NN-dibu-

tylamide of acetic acid most preferentially extracts lanthanum, cerium, praseodymium, samarium and europium.

Presence of salting out one- and two-charge nitrate cations in the solution improves the recovery of metals by DBAA. Thus, by addition 50 - 200 g/l $NaNO_3$ or $Ca(NO_3)_2$ to 1N HNO_3 raises the distribution coefficient of cerium from 0.6 to 3.0 and from 1.0 to 4.1 accordingly.

Table 1. REE distribution coefficients at extraction by NN-dibutylacetamide

REE	HNO₃ concentration, N			
	2	4	6	8
La	0.20	0.200	0.12	0.10
Ce	0.21	0.20	0.22	0.10
Pr	0.20	0.29	0.24	0.12
Sm	0.30	0.24	0.20	0.10
Eu	0.16	0.17	0.11	0.07
Er	0.10	0.10	0.05	0.05
Yb	0.07	0.07	0.05	0.04
Y	0.10	0.10	0.04	0.03

T.2.Mo and Fe distribution coefficients at extraction by 1 mol/l DFSA

Met	HCl concentration, N				
	2	4	6	8	10
Mo	0.10	20	> 50	>50	22
Fe	0.7	≥ 180	≥ 180	≥180	>180

The study on the effect of hydrochloric acid concentration on extraction of vanadium, rhenium, uranium, molybdenum has shown that with raising acidity the extractability of these elements by DFSA increases reaching the extreme point of 6N HCl for vanadium, 6-8N HCl for rhenium and molybdenum, 6N HCl for uranium and then drops (Fig.1, Table 2). Iron is quantitatively transferred into the organic phase, starting from 4N HCl (Table 2).

The maximal recovery degree comprises 85% for vanadium, 97% for rhenium, 97% for uranium. Under similar
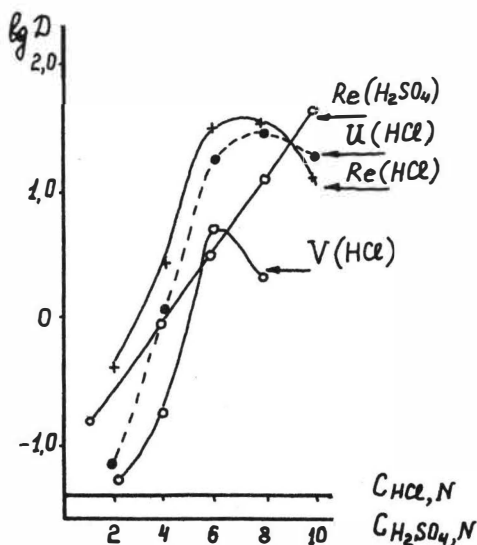
Fig.1.
Distribution coefficients of elements vs. aqueous phase acidity at extraction by 1 mol/l DFSA

conditions 1 mol/l TBP maximally extracts 75% vanadium. 92% rhenium, 96% uranium.

The influence of iron, sodium chloride and sodium sulphate on the rhenium extraction from the hydrochloric acid medium has been studied. The distribution coefficient of rhenium rises with incresing concentration of NaCl and SO_4^{--} ions. Varying iron concentration from 0.3 to 3 g/l in the model solution containing 100 g/l NaCl, 2N Hcl, 1 g/l Re practically had no effect on the distribution coefficient of rhenium, which testifies to insignificant ferrum 3+ competition for extragent.

The rhenium capacity of 1mol/l DFSA for the solutions with composition 100 g/l NaCl, 2N HCl, 1 g/l Re has been 1 g/l.

In distinction from hydrochloric solutions, the rhenium extraction out of sulphuric acid solutions is steadily increasing with raising acidity. In 10 N H_2SO_4 the distribution coefficient is 54 (Fig.1).

The experiments on extraction of niobium and tantalum with 1 mol/l DBNA, conducted on model solutions let one make a conclusion that while changing concentration of sulphuric acid in the initial solu tion from 4 N to 8 N the distribution coefficients of Nb and Ta increase. It testifies to the formation of well extractable complexes $HMeF_6 \cdot nB$, $H_2MeF_7 \cdot nB$ (Me = Nb, Ta, B - amide molecule) (Fig.2).
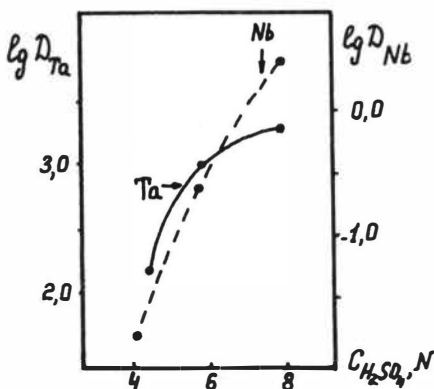
Fig.2. Distribution coefficients of Ta and Nb vs. H_2SO_4 concentration. Ta was extracted from solution:HF-1N, Ta-0.03 mol/l; Nb:HF-0.5N, Nb-0.02 mol/l
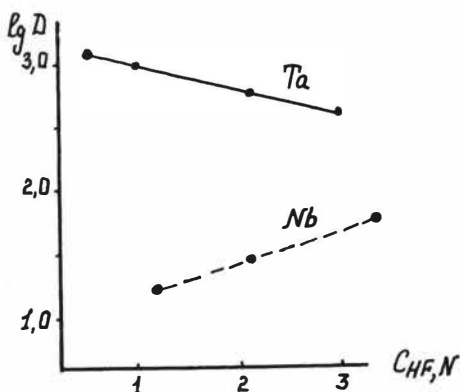
Fig.3. Distribution coefficients of Ta and Nb vs. HF concentration. Ta was extracted from solution: H_2SO_4-6N, Ta-0.03 mol/l; Nb: H_2SO_4-8N, Nb-0.02 mol/l

The extraction is considerably affected by hydrofluoric acid, which seems to be extracted by amide and serves, at the same time, as a complexing agent for tantalum (Fig.3).

Thus, the carried out studies have proved the potential ability to utilize amides of carboxylic acids for extractional concentration of rare earth elements as well as for recovery and separation of iron, rhenium, vanadium, molybdenium, uranium, niobium and tantalum. At tha the reactivity of amides to above elements is comparable to tributyl-phosphate, and in some cases exeeds it. The merit of the compounds of $RC(O)NR_2'$ ($R,R' \geq C_4H_9$) type is their low solubility in aqueous phase and stability in aqueous-organic phases.

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Diamides of carboxylic acids could be an alternative to the CMPO-TBP proposed in the TRUEX process to separate alpha emitters (including trivalent ones) from radioactive wastes solutions. Diamides are interesting economically because they are easy to prepare and to purify. They are completely incinerable and don't create new solid wastes. First investigations [1] permitted to select the number of carbons between the two functional groups; it appeared that malonamides offer the best possibilities because of their chelating effect. The generic formula of these compounds is RN(R')C(O)CH(R'')C(O)NR(R'); R and R' are alkyl or oxyalkyl radicals R'' is an hydrogen, alkyl or oxyalkyl radical.

Influence of the structure of the solvent on extractive properties.
As they act as chelating agents towards metallic cations steric effects are very important. It has been shown that a short R has a favorable influence on extractive properties. For instance good results have been obtained when R is a methyl and R' a butyl or an octyl group;see Table 1.Further improvements can be found by taking R" as a long alkyl or oxyalkyl radical instead of hydrogen as it can be seen in Table 2 on distribution coefficients of Am^{3+}.

Increasing the length of R" enhances the distribution coefficients; oxyalkyl radicals are better than alkyl ones. An optimum in the size of the oxyalkyl radical seems to be reached (d and e are not better than f which has two less carbons). Ramification has a weak influence (see d and e).

Extraction of acids. Extraction of $HClO_4$ and HNO_3 [2] has been studied using dimethyldioctylmalonamide (noted as L) diluted in tertio-butylbenzene or toluene for IR spectra. Distribution isotherm (t:23°C) of $HClO_4$ is given in Fig. 1 . It appears that there is a limit to organic $HClO_4$ concentration corresponding to a 1:1 amide to acid concentration ratio. Assuming that activity coefficients are constant in the organic phase and taking into acount the mean activity coefficient γ_{H+} of aqueous $HClO_4$ the equilibrium constant can be written as $K' = [\overline{HClO_4 \cdot L}]/\gamma_{H+}[HClO_4]^2[\overline{L}]$ where brackets indicate concentrations. Calculation for each point of the curve gives a constant value of 4.15 ± 0.15 for K'.

As it can be seen on the IR spectra given in Fig. 2 the N-C=O main stretching band at 1645 cm^{-1} is strongly affected by $HClO_4$:it

$[HClO_4] mol.l^{-1}$
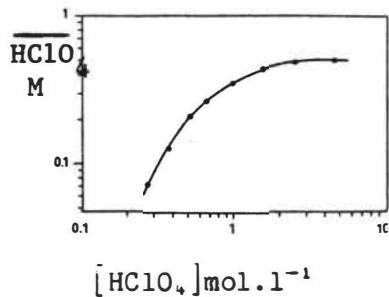
Fig. 1. Distribution isotherm of HClO
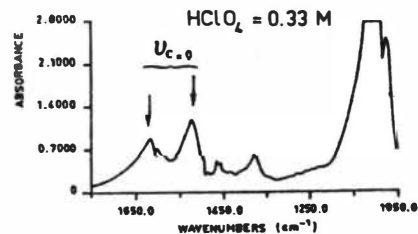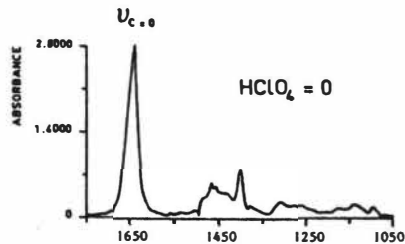
Fig. 2. IR spectra of 0.33M diamide in toluene

HNO_3 aq $mol.l^{-1}$
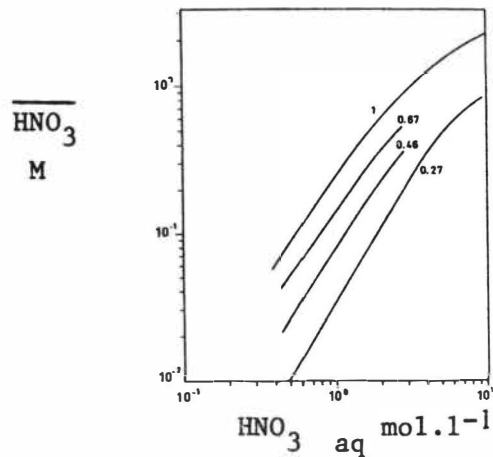
Fig. 3. Distribution isotherms of HNO_3 for various diamide concentrations

Table 1. Influence of the structure of the diamide on the Am^{3+} extraction coefficient (0.5 M diamide in benzene)

R	R'	$D_{Am(III)}$*
C_6H_{11}	C_2H_5	0.11
C_4H_9	C_4H_9	0.18
C_3H_7	C_8H_{17}	0.45
CH_3	C_4H_9	0.55
CH_3	C_8H_{17}	1.18
*D maximum.		

disappears and is replaced by two bands at 1615 and 1520 cm^{-1}. This fact is interpreted by two sorts of interaction with $HClO_4$: - a proton transfer to one $C = O$ with a 125 cm^{-1} energy shift and an intra molecular hydrogen bond with a 35 cm^{-1} energy shift. So the extraction $\underline{equilibrium}$ can be represented by the equation: $H^+ + ClO_4^- + \overline{L} \rightleftharpoons \overline{HL^{+-}ClO_4}$.

HNO_3 extraction isotherms are given Fig. 3 . For acidities lower than 5M extraction can be interpreted by the formation of three species in the organic phase $HNO_3(L)_2$, $HNO_3 \cdot L$, $(HNO_3)_2L$ with the equilibrium constants respectively noted $K'_{1,2}$, $K'_{1,1}$, $K'_{2,1}$. With the same asumptions on activities, the best fitting of the curve for $L = 0,27$ M gives the following values $K'_{1,2} = 0.64$; $K'_{1,1} = 0,14$; $K'_{2,1} = 0.0075$. IR spectra for various amounts of HNO_3 in the organic phase are given in Fig. 4 . The infrared pattern is more complicated than for $HClO_4$; at least four $C = O$ stretching band appear. The 1645 cm^{-1} one is attributed to free L. For small HNO_3 concentrations this band is slightly shifted because one HNO_3 is shared by two L and

Table 2. Influence of the substituant of the central carbon upon Am^{3+} distribution ratios aqueous phase HNO_3 5 M (organic phase: extractant 0.5 M in tertio-butyl benzene t = 20°C

N°	Various R''	$D_{Am}3+$
a*	C_6H_{13}	1.16
b	$C_2H_4-O-C_2H_5$	3.18
c	$C_2H_4-O-C_6H_{13}$	7.55
d	$C_2H_4-O-C_2H_4-O-C_8H_{17}$	9.43
e	$C_2H_4-O-C_2H_4-O-CH-CH_2-C(CH_3)_3$ C_2H_5	10.38
f	$C_2H_4-O-C_2H_4-O-C_6H_{13}$	11.14
* 10% decanol added.		
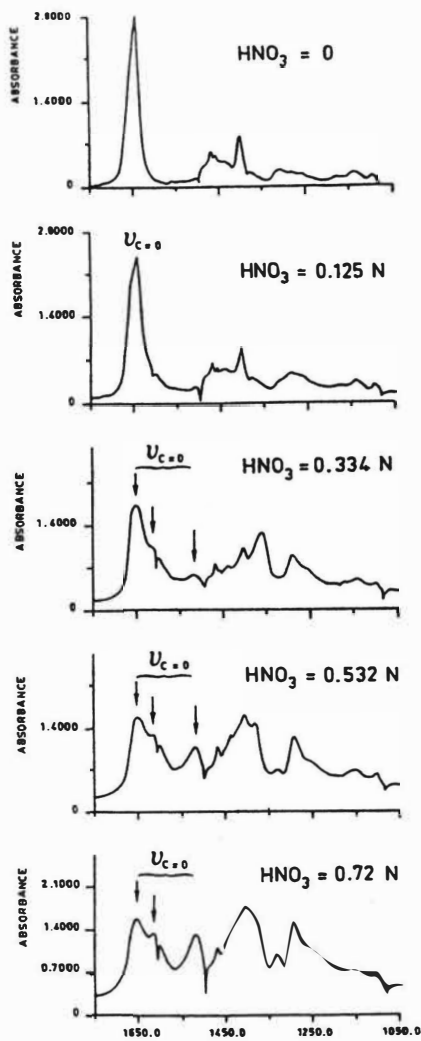
Fig. 4. IR spectra of 0.33M L with various amount of HNO$_3$ in toluene
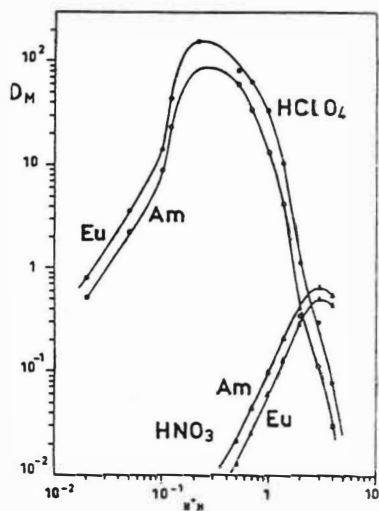
Fig. 5. Distribution coefficients of Am^{3+} and Eu^{3+} in HClO$_4$ and HNO$_3$

this interaction is weak. Two other bands at 1610 cm^{-1} and 1520 cm^{-1} are attributed respectively to HNO_3 L and $(HNO_3)_2$L. These C = O band shifts indicate that hydrogen bonds are present in the species HNO_3L_2 and HNO_3L, in the third species $(HNO_3)_2$L a proton transfer is found. This fact is due to a bonding of one HNO_3 to the other one which weakens 1st basicity and allows the proton transfer.

Extraction of metallic cations /3/. Extraction of americium and europium has been studied in HNO_3 and $HClO_4$ medium using dimethyldioctylmalonamide diluted in tertiobutylbenzene. Distribution coefficients are given in Fig. 5 , three important features can be observed:
- distribution ratios are much more higher in $HClO_4$ than in HNO_3 (which is due to higher lipophilic character of ClO_4^--ion),
- the maximum of D is obtained at lower acidities for extraction from $HClO_4$ because $HClO_4$ competes more strongly than HNO_3 for the coordination sites of the extractant,
- there is an inversion in the order of Am(III), Eu(III) extractibility. Probably ClO_4^- ions remain in the second coordination sphere.

Distribution ratios of Am^{3+} and Eu^{3+} have been studied as a function of L concentration in HNO_3 for neutral solutions; slopes of 4.03 and 4.15 for Am^{3+} and Eu^{3+} can be found. This indicates the following mechanism $M^{3+} + 3NO_3^- + 4L \rightarrow \overline{M(NO_3)_3L_4}$.

At higher acidities the curve is not a straight line, the linear part has a slope close to 2. Which is better represented by: $M^{3+} + 2L \cdot HNO_3 + NO_3^- \rightarrow \overline{M(NO_3)_3L_2} + 2H^+$. Saturation of a 0.3 M solution of amide in toluene by Nd^{3+} led to an organic phase with a /L/ /Nd/ ratio of 2.0. Studies of U.V.-visible spectra of the complex confirm that in neutral medium metal is bonded to two ligand molecules in the first coordination sphere. In more acidic medium only the two ligands in the inner sphere remain. For substituted malonamides (ex. with $R'' = C_6H_{13}$) variation of distribution coefficient of Am^{3+} as a function of L concentration is a straight line with a slope close to 2 (2.3).

Applied studies. Distribution coefficients of several metals of practical interest in the nuclear fuel reprocessing have been measured with substituted diamides. The values are given in Table 3
- Am^{3+} and Eu^{3+} are well extracted in 3 to 6 M HNO_3 solutions, they are easily backextracted in a weak medium,
- U(VI), Pu(IV) are easily extracted and can be backextracted but a complexing or reducing medium is needed to separate uranium from plutonium ,
- as in case of phosphoric extractants zirconium follows the actinides and must be separated by $H_2C_2O_4$ complexation,
- corrosion product Fe^{3+} is strongly extracted too,
- technetium (VII) is weakly extracted in the whole range of concentration of HNO_3 studied.

Table 3. Distribution coefficients of several metals in HNO_3-Extractant 0.5M in t-butylbenzene $T=20^{o}C$ $O/A=1-R"=C_2H_4-O-C_2H_4-O-C_6H_{13}$

$[H^+]$,M→	0,06	0,5	1	3	4	5
Am^{3+}		0.0012	0.0071	2.45	5.65	11.14
Eu^{3+}		0.0015	0.0043	1.19	3.14	6.73
Pu(IV)	0.09	1.89	8.16		184	
U(VI)	0.1	3.75	9.09	55.3		111
Zr(IV)			0.092	7.86		170.2
Zr(IV)			0.020	0.10		1.46
$+H_2C_2O_4$ Fe^{3+}		0.0062	0.01	0.35		66.2
Tc(VII)		0.719	1.095	0.88	0.767	0.751

A mixer settler experiment has been planned, in that purpose behaviour of neptunium has been studied using $(CH_3C_4H_9 NCO)_2-CH-C_2H_4-O-C_6H_{13}$ (which is less expensive to synthesize) the results are given in Table 4.

Table 4. Distribution coefficients of neptunium'VI)an (V)
$T = 20^{o}C$ $O/A = 1$. Extractant 0.5M in t-butylbenzene
$R" = C_2H_4-O-C_6H_{13}$

$[M^+]$, M →	0.5	1	2	3	4	5	6	7
Np(VI)	3.81	5.20	7.91	15.11	73.0	81.6	131	26.5
Np(V)	0.0198	0.029	0.430					

Neptunium(VI) is well extracted in 5 or 6 M HNO_3 it could be backextracted as neptunium(V) using 0.2 hydroxylamine in 0.1 M HNO_3 (plutonium is backextracted too as Pu(III) in that medium). Neptunium(V)is poorly extracted from a weak acidic medium, but in a strong acidic medium oxidation and disproportionation occur and Np(VI) and Np(IV) extraction displaces the equilibrium.

Conclusion. These studies have clearly shown the interest of pentaalkyl propanediamides for extracting ·emitters from wastes solutions in nitric acid medium. However it is not possible to select immediately a particular solvent for practical purpose, radiolytical stability must be checked and progress is to be done in economical synthesis. Theoretically, extraction mechanisms differ with the substituent of the central carbon and several studies must be done to elucidate that influence.

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At boron extraction by aromatic polyoxycompounds the necessary condition is the presence of positive ions in the system, which are a part of a composition of extractive anion complex of boron with reagent as antiions. I.e. with boron coextragates the equivalent quantity of the stated ions, that sharply lowers the selectivity of the process. One of the ways of prevention of such coextraction is the creation of extraction reagents in the molecule of which, along with the most reactive to boron hydroxylic groups, would be present the electrodonor, for example, amino, providing the formation of neutral coordinate saturated extractive compound. We synthesized reagents aminomethyl derivatives of alkylphenol, containing OH- and NH- groups in γ-position relative to each other.

In the report are cited the data on the studies of extraction properties towards boron of the representative of the stated type of compounds - 2oxy-5 - octylbenzylethanolamine (OBEA).

The cryoscopic measurements and IR-spectra investigation allowed us to establish, that OBEA independently on the concentration in weak-polar solvents, for example, benzene, is associated into dimers, whereas in strongpolar solvents - nitrobenzene exists mainly in a monomeric form.

The dependence of boron extraction by OBEA from pH of water solution (fig.) has for all the diluents an extremal character with maximum value of distribution coefficients D_B in the region of pH 5,0-7,5. At this it is typical, that the value D_B in optimum extraction condition is correlated with dielectric permittivity of the used diluents,decreasing in series: hexane > CCl_4 > benzene > heptanol > methylethylketone. The low values of D_B in the case of alcoholic solution OBEA, probably, are explained by the formation comparatively of strong symmetric hydrogen bond between the hydroxyl groups of alcohol and ethanol fragment of extractant that noticeably hampers its interaction with boron ions.

Boron reextraction from an organic phase is carried out by acidic as well as alkaline reagents. The highest degree of reextraction (to 75-80%) is achieved at a use of 3-4% of H_2SO_4 and NaOH ($[B]_0$ = 0,47g/L) solutions and Na_2CO_3 of the same concentrations reextragates boron per 55%.

Studied the effect of chlorides and sulphates of alkaline and alkaline earth metals on boron extraction. The presence of NaCl, KCl,Na_2SO_4 and $MgSO_4$ in water solution in quantities, that exceeding the boron content to 50-500 times by mass, practically does not influence on its extraction. The presence of the same quantities of $MgCl_2$ and $CaCl_2$ no-
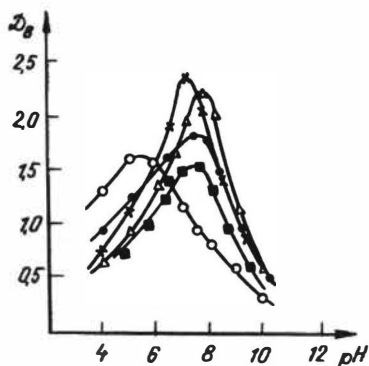
Depedence of boron extraction
by 0.4 M solution of OBEA in the
the organic diluents from pH

- • benzene
- x hexane
- o heptanol
- Δ CCl_4
- ■ methylethylketon

ticeably increases D_B, i.e. these salts have an effect of salting out. Such influence of the stated compounds well correlates with the character of the values change of their activities coefficients and water activity in the solutions of these salts. At the same time the analys of the phases after boron extraction has shown, that the ions of alkaline and alkaline earth metals do not coextragate into the phase of extractant, that, firstly, witnesses about the selectivity of boron extraction and, secondly, excludes the supposition of extraction proceeding by the mechanism formation of ionic associate, characteristic for aromatic polyols.

The role of proton in the extraction process has been studied by the potentiometric titration of H_3BO_3 and the extractant in mono - and two-phase systems by NaOH solution. The curves of the extractant titration in the absence and presence of boric acid differ little, it follows from the above, that at interaction of boron with reagent the change of protons number in the system do not occur and the correction of pH in the course of extraction is not required.

The stechiometry of the extraction is determined by the methods of an equilibrium shift, saturation and also at comparison of the calculated and experimental data for the measurement of extracts molecular mass, containing different quantities of boron. The molar ratio of boron: OBEA in the forming complex is equal to I:I, and besides, such composition is constant and does not depend upon the concentration of hydrogen ions in the system.

The confirming results as well as the information about the structure of the extractive compound were obtained at the investigation of a solid complex of boron with OBEA, obtained from the organic phase by specially worked out methods. The extracted compound represents by it-

self a noncrystalline substance of white colour with T_{ml}.=148-149°C.
The data of the elementary analysis, cryoscopy and thermogravimetry
meet the composition of the complex with an equimolar ratio of the
components and correspond to formula $C_{17}H_{28}O_3NB$. The study of NMR -
-spectra on nucieus ^{11}B has shown, that the resonant signal with a che-
mical shift $\delta_{BF_3 \, O(C_2H_5)_2}$ = -6,0 m.p. refers to tetracoordinated atom
of boron. The analogous result has been obtained at interpretation of
IR-spectra. The intensive absorption bands at 1100 and 940 cm^{-1} and
absence of characteristic for valent vibrations OH-group band in the
region of 3350-3300 cm^{-1} witnesses about bonding of tetracoordinated
atom of boron with the molecule of the reagent by means of placed in
it both oxygen atoms. A weak band at 3200 cm^{-1} in the spectrum of the
complex meets the valent vibration of NH-group and also may be assig-
ned to the excited by intramolecular bond of the valent vibrations of
OH-group in B-OH. It is worth to be noted, that the spectra of the so-
lution of the solid complex and corresponding extract in CCl$_4$ in the
region of band absorption of B-O bond are completely identical, that
proves the presence in both cases of the same chemical form of boron.

The bond of boron atom with phenolic hydroxygroup of the reagent is
being confirmed by the data of the potentiometric titration of benze-
neethanol solutions of OBEA and its compound with boron by Na OH solu-
tion. The dependence curve pH of the medium from the concentration of
titrant in the first case has a sloping character, resulted from the
interaction of sodium hydroxide with phenolic OH-group. An abrupt jump
on the titration curve of boron containing complex witnesses in favour
of the supposition about linking of the stated group by atom of boron.

For revealing of coorolination bond between atoms of boron and nit-
rogen in the studied compound was used the capacity of aromatic satu-
rated amines under the dissolution in water to increase pH due to
their basicity : $R_2NH+H_2O \rightleftharpoons R_2NH_2^+ + OH^-$. The comparison of the results
of the measurement of pH of water solution at contacting with it of
chloroform OBEA solutions and the complex with boron has shown, that
the presence of the former in an organic phase, as it was expected,
sharply increases pH of the medium and by growing of its concentration
rises the alkalinity of the solution. In the case of complex dissolu-
tion independently on its concentration pH of water solution practi-
cally remains constant, i.e. it does not reveal the main properties,
that gives us the ground to state the presence of a rather stable co-
ordination bond between the atoms of boron and nitrogen.

The following fact serves as a proof for it. It is established,
that the amines interact with chromium ions forming soluble in organic
solvents complexes, that is used for the extraction of Cr(VI) from su-

bacid solutions. OBEA also forms with $Cr_2O_7^{2-}$ the coloured compound in the sulfuric medium, extractable by chloroform. In the analogous conditions under utilization of chloroform solutions of boron containing complex OBEA the extraction of bichro-mate-ions is not observed. The latter may occur in the case of linking of non-fissed electron pair of nitrogen atom, that happens under its coordination with the boron.

$$H_{17}C_8 - \left\langle \bigcirc \right\rangle - O - B - O$$

with substituents: OH on B, and $CH_2 - NH - C_2H_4$
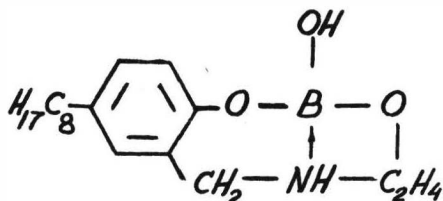
The following structure of boron compound with OBEA is expected on the basis of the investigation result.

Owing to coordination bond of the atom of boron with nitrogen in this compound is formed the chelate knot, which includes penta - and hexamembered cycles stabilizing the complex. As the dominating form of the existence of boric ions in water solution in the conditions of extraction is $B(OH)_3$, the formation mechanism of the stated extragatable complex can be described by the equation:

$$B(OH)_{3(w)} + NHR_2(OH)_{2(o)} \rightleftharpoons NH(RO)_2BOH_o + 2H_2O$$
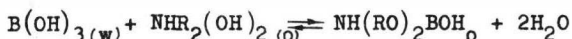
The analogous characteristics of the extraction capacity towards boron (high selectivity, favourable conditions of extraction) have been also obtained for a series of other representatives of aminomethyl derivatives of alkylphenol. All this with regard for synthesis simplicity in technological respect of the stated type of compounds allow us to consider them rather perspective extractants for the extraction of boron from hydromineral raw materials.

SOME POSSIBILITIES FOR IMPROVEMENT OF THE EXTRACTION
PROPERTIES IN MIXED EXTRACTION SYSTEMS
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The separation of mixtures of substances into individual components
is one of the major tasks of chemist or chemical engineer. A large num
ber of unit operations have been developped as tools for them in the
cases of separation problems involving liquids. In this field solvent
extraction has enjoyed increasing utility in the last several years.
It has u number of attractive features but its application is also re-
lated to some difficulties. The most important one is the fact that
the organic phase must contain a compound capable of interacting sig-
nificantly with the inorganic species to be extracted. Unfortunately
the functional groupings needed for this purposes also tend to increa-
se the interaction of the extractant compuond with water. One result
is a higher tendency of the latter to distribute into the aqueous
phase and be lost. That's why the application of extraction processes
to diluted solutions and wastewaters is not economically valuable.
Most of the extractants for industrial purposes such as Lix, ACORGA-
series, Kelex etc. provide a good selectivity and high extraction ra-
tes but are also very expensive. Others like different types fatty
acids are cheap and in some cases biodegradable but are still neglec-
ted because of their lower extraction rates, bad selectivity or other
specific problems. A way to improve the extraction properties of a gi-
ven extractant is its use in mixed extraction systems. Recently many
studies have been carried out with such systems in the field of metal
separation [1-5]. Generally the$_y$ represent mixtures of cationic or ca-
tionic and neutral extractants. Here a new type of solvent extraction
systems which consist of cationic and anionic extractants are descri-
bed. The few studies in this field have revealed their possibilities
to produce synergistic extraction and/or improve the extraction rates
[6-9]. In this paper the possibilities for improvement of the extrac-
tion properties of some acidic extractants are studied.

Experimental . The initial test work was performed on synthetic sulpha-
te solutions containing various metals alone or in mixtures. Later in
the test program experiments were performed on a model of real sulpha-
te wastewaters containing Cu, Zn and Mn. All the tests were carried
out in an AKUFVE 110 apparatus combined with an automatically opera-
ting system for pH control and regulation. The organic phase consis-
ted of an acidic extractant (D2EHPA or fatty acids C_{14}- C_{18} oleic frac
tion) and a basic extraotant (Primene JMT, Amberlite LA-1 or Alamine
336) in kerosene containing 2 volume per cent(v/O) tributylphasphate

as an emulsion inhibitor. In all cases ammonium hydroxide was used as pH correcting agent.

Results and discussion. Several effects due to the structure of the mixed systems were studied. At first it should be mensionned that the extraction of an inorganic species from an aqueous solution by a solvent is generally the result of one of two types of interaction. If the species extracted is a neutral copmound, solvation or complex formation with the extractant is usually involved, accompanied by at least partial loss of the hydration shell of the compound. The second common type of extraction is exactly analogous to conventional ion-exchange. The described system has elements common to both types of mechanisms discussed above – that is it extracts the ionic constituents of inorganic salts as separate species so that the result is extraction of"neutral"compound. That's why the use of mixed cationic-anionic extractant results in smaller quantities of pH correcting agent used to obtain a desired pH value. This can be illustrated by the results obtained when Ag, Cu, Cd, Zn, Co, Ni, Fe and Pb are extracted with the system - 10 v/O fatty acids C_{14}- C_{18} + 5 v/O Primene JMT without further pH correction. The data are compared in Table 1 to those obtained when only 10 v/O fatty acids are used and using the same initial pH and concentrations and it can be easily determined that

Table 1. Comparison between acidic and mixed extraction systems

N	Metal	Initial pH	Initial concen. mg/l	Primene JMT+ F.A.			F.A.		
				pH	Concen. mg/l	m	pH	Concen. mg/l	m
1	Ag	4,40	1000	3,19	41	23,40	3,00	987,6	0,012
2	Cu	3,55	735	4,61	23	30,95	2,78	73,5	9,00
3	Cd	4,74	670	4,94	314	1,13	3,67	616,0	0,14
4	Zn	5,05	251	5,03	35,2	6,13	3,62	206,0	0,14
5	Co	5,00	549	5,31	424	0,29	3,81	523,0	0,05
6	Ni	5,00	558	5,31	440	0,27	3,79	531,0	0,05
7	Fe	2,04	140	3,75	2,5	55,0	1,97	87,0	0,61
8	Pb	2,93	223	3,40	174	0,28	2,45	187,4	0,19

in most cases higher equilibrium pH values resp.distribution coefficients are obtained. In this manner the use of the new type of extractants leads to improvement of the extraction behaviour of the whole system.

In another series of experiments preliminarily saturated with 1n H_2SO_4 organic phase (10 v/O D2EHPA or 50 v/O fatty acids + 2 v/O amine of different type) was used to study the influence of the basic extractant on the distribution coefficients of various metal cations. From the plots of lg m vs pH the $pH_{0,5}$ values(pH at 50% extraction) were determined and given in Table 2. As it can be seen the e ffect depends on

302

on the composition of the mixed system and the type of the metal cati-
on extracted. The presence of the basic component leads in some cases
to considerable changes in the selectivity of the extractant towards
the metal cation. For example when copper is extracted 2 v/0 of amine
increase the distribution coefficient about 10 times but only 2,5 ti-
mes for zinc and even decreases its value for Mn. In this manner modi-
fying the composition a suitable selectivity can be obtained.

Table 2. $PH_{0,5}$ values for various mixed extractants

N	Metal	Fatty acids +				D2EHPA +		
		-	JMT	LA-1	Al.336	-	JMT	Al.336
1	Cu	4,10	3,70	3,70	3,70	2,11	2,70	2,52
2	Zn	5,15	5,00	4,95	5,00	1,56	1,52	1,36
3	Mn	5,65	5,82	5,50	6,00	2,62	2,36	2,23
4	Cd	4,70	4,65	5,05	4,70			

The third series of experiments were performed using a model of re-
al solutions containing 0,654 gZn/l, 0,603 gCu/l and 1,15 gMn/l and
either 10% D2EHPA or a mixed system - 10 v/0 D2EHPA+2 v/0 Alamine 336.

Plots of the separation coef-
ficients ß vs pH are presented
in Fig.1. As it can be seen
both Zn and Mn load higher in
the case of mixed extractant
system and in this manner the
decrease in Cu extraction le-
ads to improvement of the se-
lectivity.

As it was mentionned by
Mrnka, Yagodin and col. [7,8]
the presence of basic compo-
nent leads to enhancement of
the extraction kinetics. This
is supported by the results
performed using 1 g/l copper
solution and organic phase con
sisting of 10 v/0 fatty acids
+ 5 v/0 Primene JMT. Totaly
regenerated and preliminarily

Fig.1. Separation coefficients for
Cu, Zn, Mn system in the ca-
ses of acidic and mixed ex-
tractants

saturated with 1n H_2SO_4 organic phase were used and the results are
compared in Fig.2. As it can be seen in the case of low pH values
resp. low distribution coefficients a considerable increase in the ra-

te of extraction can be detected when saturated extractant is used. In the same time an increase in the rate of the process can be established when non-saturated extractant is applied. This can be attributed to the formation of water soluble amine sulphate which acts like a carrier for the extracted cations.

In conclusion it should be mentionned that the obtained results are a good illustration of the possibilities of this type of mixed extractant systems. Finally, because these systems use conventional acidic and basic components they form a basis for further development of selective extraction systems simply by the modification of the structure of the individual components of the extractant. Because of these features this type of sys tems may have considerable promise in extending solvent extraction further into the field of industrial processing of high volume, low cost materials.

Fig.2. Extraction rates in the cases of mixed extractant systems

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During the last decade, the problems of searching and synthesizing
new effective extragents were becoming still more urgent and important
due to the extensive employment of extractions in hydrometallurgy and,
besides, to an increasing bulk of low-grade and complex ores. And so,
special interest is acquired by the sulfur organic reagents owing to the
specific involvement of sulfur in complexations and to the existence of
rich natural resources of sulfur organic compounds. The range of indus-
trial extragents is insufficient to meet the processing requirements in
hydrometallurgy of rare, non-ferrous, and noble metals.A considerable re-
serve of sulfurous oils is available in the Soviet Union. Hence, the
effective extragents prepared on the basis of sulfur organic compounds
should allow research workers to solve the problems, both scientific and
technological, in such fields as hydrometallurgy, petroleum chemistry
and processing.

Petroleum sulfides. To prepare petroleum sulfides, the distillates
of West Siberian and Arlan oils were used, those containing up to 3-8wt.%
of organic sulfides. The sulfides were concentrated by extracting the
190-360°C diesel fraction with sulfuric acid (87wt.%) at room temperature
with an oil-to-acid ratio as 5:1. The sulfide concentrates yielded 5-6%
of the oil gross weight, those containing 12% of total sulfur and 10%
of sulfide sulfur. The petroleum sulfides consisted mainly of cyclic
sulfides irrespective of oil fields (Table 1).

Table 1

Structural and group compositions of 190-360°C fraction
sulfides of different oils, rel.%

Type of compounds	Oil fields		
	Arlan	West Surgut	Arlan
thiamonocyclanes	45.7	56.0	57.6
thiabicyclanes	21.0	16.6	21.0
thiatricyclanes	12.7	13.0	8.5
thiatetracyclanes	4.7	5.4	2.5
thiaindanes	4.7	3.3	3.2
dialkyl sulfides	6.9	3.1	3.7
alkyl cycloalkyl sulfides	2.3	3.2	3.1
alkylphenyl sulfides	1.4	-	0.5

The selective extraction and separation of noble metals (with soft acids according to PSHAB) demand such a class of sulfur organic compounds as those containing sulfur capable of revealing its donor properties and of forming an EDA-complex with the extracted metal. Different thioester derivatives and, hence petroleum sulfides, are considered the relevant compounds [1]. The extraction properties of petroleum sulfides have been studied in extractions of silver nitrates from 0.1 mol/l nitric acid solutions and of gold, .patinum, palladium, irridium, ruthenium, and mercury chlorides from hydrochloric acid solutions. The metals are extracted with petroleum sulfides to give the coordinatively solvated compounds $AcNO_3 \cdot Sq$, $PdCl_2 \cdot S_2$, $AuCl_3 \cdot S$, $PtCl_4 \cdot S_2$, $IrCl_4 \cdot S_2$, where S - petroleum sulfide. The extraction degree is about 99% for silver, gold, mercury, and palladium. At room temperature, the petroleum sulfides do not practically extract platinum metals from hydrochloric acid solutions due to the slowly proceeding saturation of chloride-ions for petroleum sulfides in the acid complexes of the said metals. Still. a temperature increase and the use of labilizing agents involved in redox reactions with the extracted metal promote the extraction of platinum metals to increase up to 70-95%.

By the extractivity to gold (III) chloride, the contribution of mesomeric and iduction effects of radicals at the sulfur atom have been estimated with respect to the sulfur extraction properties. With an increase in the electronic density on the sulfur atom, the sulfur donor properties become improved and the extractivity of compounds turns out higher as related to the noble metals. The extraction and stability of petroleum sulfide complexes are increased with the growing "softness" of cations Zn(II)<Cd(II)<Pb(II)<Cu(II)<Hg(II). Besides, there is observed a linear dependence between the values of stability constants (or extraction constants) and of the ion "softness" parameters by Clopman.

On the grounds of the results obtained for the extractivities of petroleum sulfides, they have been suggested as selective and effective extragents to extract and separate the noble metals (Au, Ag, Pd, Hg, Pt, Ir, Rh, and Ru).

Petroleum sulfides are also usefully employed as the extragents of noble metals in analytical chemistry to get their requirements [2].

Petroleum sulfoxides (PSO). To prepare water low-soluble PSO (thus applicable to extractions), one uses either the petroleum sulfide concentrates or the 260-360°C directly distilled fractions of high-sulfurous oils. The petroleum sulfides or distilled fractions are oxidized with hydrogen peroxide. In oxidation of sulfides to sulfoxides, the structure of oxidizable molecules has been found practically unchanged and so, the structural and group compositions of PSO are similar to those of

petroleum sulfides. Two donor atoms present in a sulfoxide molecule favour the extraction of metal salts of both hard and soft acids. Still, in most cases PSOs reveal themselves as hard bases. The extraction properties of petroleum and individual sulfoxides were investigated in extractions of various salts and acids [2-4]. There are formed both non-hydrated and hydrated solvates ($HNO_3 \cdot S$, $HReO_4 \cdot 2S$, $HCl \cdot hH_2O \cdot qS$) in extractions of acids with sulfoxides [3-4]. The metal extractions with sulfoxides proceed due to the formation of an electron-donor-acceptor-complex (EDAC) of metal salt with sulfoxides; the complex is extracted into an organic phase as it happens in extractions with tributylphosphate. The metal is coordinated via the SO-group oxygen, that being assertained by IR and NMR spectroscopies of the isolated complexes and of the extracts. The extractions of majority of metals from nitric and hydrochloric acid solutions have been investigated. The petroleum sulfoxides have been proved as effective extragents for extraction and separation of uranium, thorium, rare-earth elements, zirconium, hafnium, bismuth, antimony from nitric acid solutions, of arsenic, tin, bismuth, iron, copper, zinc, indium, gallium, zirconium, hafnium, molibdenum, tungsten, palladium, and platinum metals from hydrochloric acid solutions, of chromium and rhenium from sulfuric acid solutions, and of tantalum and niobium from fluoride sulfuric acid solutions.

On the basis of the data obtained for redox properties of PSO, they have been recommended as extragents of metal salts and acids from the solutions of 0.1-1.0V redox potentials. The lowered acid concentration in an aqueous phase and the decreased phase contact period result in the reduced degree of oxidation of sulfoxides to sulfones.

The uranyl nitrate extraction from 0.1 mol/l nitric acid solution has been taken as an extractivity probe to make the extraction series for sulfoxides and other neutral oxygen containing reagents. The basicity of oxygen containing extragents has been observed to correlate to their extractivity,

$$\lg \overline{K}_V = -11.88 + 5.6 \ pK_S$$

The strength of complexes, and hence the extraction, are increased with the lowered "softness" of the extracted metal. The petroleum sulfoxides are superior to tributylphosphate and inferior to phosphonates. As compared to the neutral phosphorous organic compounds (NPOC), the sulfoxide reveal their higher sensitivity to changes in extraction properties occurring due to an electron-negative substituent. Thus, an aliphatic radical (X=2.0) changed for a phenyl one (X=2.54) results in 17-times lower extraction with NPOCs and in 40-times lower extraction with sulfoxides for the same metals. Another specific difference of sulfoxides from NPOCs lies in the fact that their extractivity turns

out unpredictable by the IR spectral data. With the aromatic substituents introduced, the valency vibration frequency of SO-group is slightly increased, while in NPOCs it becomes well-pronounced. The enthalpy component has been proved to contribute to the increasing extractivity in a series from aliphatic to cyclic sulfoxides. In complexations, therefore, sulfoxides are more sensitive to structural peculiarities in molecular geometry than NPOCs [4].

Different aspects of lanthanide and actinide extractions have been considered with a mixture of organic acid - sulfoxide. The effectivity of lanthanide and actinide extraction and separation with the picrolonic acid - sulfoxide system varies with respect to the basicity of a neutral addition.

Thermodynamic aspects of the liquid-solid phase extraction have been studied for petroleum sulfoxides and tributylphosphate of rare-earth-element (REE) chlorides.

The metal transfer from solid-to-organic phase should be determined by the enthalpy component of metal chloride solvation with an extragent. As a result, in the course of competitive extraction the organic phase in enriched with the extracted complex of higher stability constant. The obtained data afford a series to represent the solvating ability of petroleum sulfoxides and tributylphosphate to metal chlorides (for extractions of anhydrous metal chlorides). The hydration degree of metal ion produces essential influence on the liquid-solid phase extraction. It has been demonstrated possible to separate alkaline and earth metal chlorides from lanthanide, and light lanthanide chlorides from the heavy ones. The effects of phase ratio, the hydration degree of extracted salts, temperature, the diluent and extracted component types have been investigated in liquid-solid phase extractions.

Our studies into extraction with petroleum sulfoxides have proved them to be promising extragents in extracting of a great number of radioactive, rare, disseminated, and non-ferrous metals, as well as of organic and inorganic acids.

Chromatographic studies of petroleum sulfoxides and sulfones as hadrocarbon solvents. Due to the ever increasing demand for pure hydrocarbons, special importance have acquired the extractive methods used to separate mixtures of various hydrocarbons. The gas-liquid chromatography has been known to serve an excellent method for estimating the selectivity of extragents-solvents and, in particular, of the solvents used to extract aromatic hydrocarbons. Petroleum sulfoxides have been investigated as promising extragents for the extraction of aromatic hydrocarbons and for the separation of parafins and olefins. The limiting activity coefficients $\gamma°$ have been calculated, and the

aelectivity values of PSOs and sulfones ($S = \gamma^\circ / \gamma^\circ_B$ rel. to benzene) have been found by the separation of various hydrocarbons possessing the same number of carbon atoms. The resulted values are summarized in Table 2.

Table 2

Hydrocarbon	PSO		P.sulfones		Hydrocarbon	PSO		P.sulfones	
	γ°	S	γ°	S		γ°	S	γ°	S
pentane	3.527	-	4.702	-	cyclohexane	2.690	2.31	3.678	3.07
hexane	3.721	3.20	5.398	4.51	methylcyclo-pentane	2.822	2.43	3.923	3.28
heptane	4.120	-	6.025	-					
octane	4.240	-	6.284	-	benzene	1.163	1.0	1.187	1.0
hexene-1	2.905	2.50	3.589	3.00	toluene	1.220	-	1.359	-
heptene-1	3.080	-	4.086	-	M-xylene	1.397	-	1.586	-
octene-1	3.246	-	4.456	-	P-xylene	1.281	-	1.546	-

According to Table 2, the most intensive turn out the interactions of aromatic hydrocarbons with PSO and sulfones to reveal a tendency to the formation of π-complexes of different strength degrees. Olefins are also capable of forming π-complexes. Still, the strength of these complexes and, consequently, the intensity of interactions are lower than those for aromatic hydrocarbons. The selectivity of petroleum sulfones is higher than that of PSOs due to the higher positive non-ideality of non-aromatic hydrocarbon solutions in petroleum sulfones.

Petroleum sulfones and sulfoxides may be also usefully applied to the quantitative absorption of sulfurous anhydride and nitrogen dioxide from industrial gases. With the employment of PSO as an adsorbent, the amount of absorbed O_2 reaches 0.55 g per 1 g of the absorbent.

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The studies presented were undertaken to investigate extraction and
complexation of rhodium (III) and ruthenium(III) chlorides with indivi-
dual aminosulfides and aminoketosulfides synthesized for the first time
in the Institute of Chemistry, USSR Acad.Sci.Bashkirian Branch. Our
objective is to search for some novel highly effective and selective
extragents of noble metals, and also to study complexing properties of
novel sulfur-nytrogen-containing polyfunctional reagents.

For more detailed understanding of a mechanism of extraction equili-
bria of aminosulfides and aminoketosulfides with noble metals, the com-
parison of the extraction results obtained to the content and composi-
tion data of complexes extracted is required, thus permiting to observe
complexations from common point of view. Proceeding from the ligand
coordination of donor atoms as determined by the complexing conditions,
the noble metal complexes with aminosulfides and aminoketosulfides were
extracted from acid and neutral media by direct and extraction methods.

Structural formulae, conventional and complete names of some reagents
studied are listed below :

Dibutylaminoethyloctylsulfide
(DEOS)
$$C_8H_{17}SCH_2CH_2N(C_4H_9)_2$$
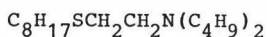
Piperydinoethyldodecylsulfide
(PEDS)
$$C_{12}H_{25}SCH_2CH_2N$$
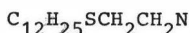
1-Phenyl-2-piperydinoethyl-
thiomethyl-1-propanone
(PPP)
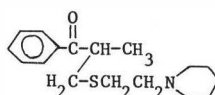
Bis(piperydinoethylthiomethyl)-
1-phenyl-1-ethanone
(BPP)
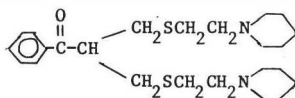
1,1,3,3-tetrakis(diethylamino-
ethylthiomethyl)-2-propanone
(TEP)
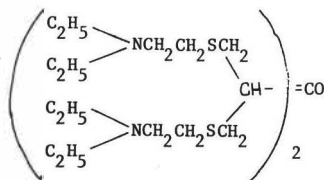
The rhodium (III) and ruthenium extractions from 0.1-3 mol/l hydro-chloride solutions by individual aminosulfides and aminoketosulfides we-re investigated. The optimum conditions of metal extractions were found i.e. phase contact times, aqueous phase acidities. The extraction iso-terms were recorded, the solvate numbers were evaluated. The total sum of the results obtained suggests that the rhodium (III) and ruthenium (III) extractions with the reagents from a strong acid medium have been carried out by the mechanism of interphase anion exchange with the con-comitant formation of ion associates, and those from weak acid ones (0.1 mol/l hydrochloride solutions) - by the involvement mechanism. It was shown that with the extractions from strong acid medium with amino-sulfides, the stage of ion associate formation proceeded rapidly (in contrast to aminosulfides). The rapid extraction procedure of the gi-ven metals alongside with some other metals of the platinum group, aminosulfides and aminoketosulfides, should be explained by a rapid in-volvement of sulfur atom extragents into the internal coordination sphere of metal ions due to a labile effect of amine nytrogen protonated atoms in the intermediate ion associates formed.

With extractions from the media similar to the neutral ones, the rea-gent nytrogen atoms are nonprotonated thus affecting the metal transfer to an organic phase. A comparison of rhodium (III) and ruthenium (III) extractions with aminosulfides and aminoketosulfides to those with other noble metals suggests a conclusion that the kinetic factor and aqueous phase acidity are of particular importance.

It is of interest to note that with the gold (III) and platinum (III) extractions the life time of intermediate ion associates is much longer. Proposed is the common equation of rhodium (III) and ruthenium (III) extractions with the reagents studied,

$$2RSCH_2CH_2NR_1 + [MeCl_5(H_2O)]^{2-} \longrightarrow \begin{array}{c} RSCH_2CH_2NR_1 \\ Cl \diagdown \downarrow \diagup Cl \\ Me \\ Cl \diagup \uparrow \diagdown H_2O \\ RSCH_2CH_2NR_1 \end{array} + 2Cl^-$$
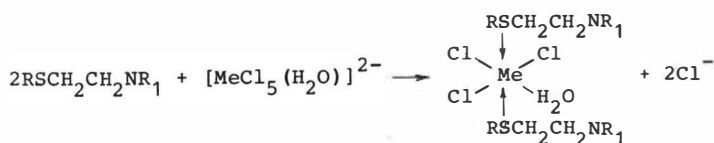
The extracted chloride complexes of the given metals were isolated and assigned. The results obtained confirmed the extraction mechanism proposed. The contents and properties of the extracted complexes and coordinated compounds isolated by a direct method were compared. In the course of our studies, a number of physical chemical analysis tech-niques were used, such as IR-, PMR-, and electron spectroscopies.

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Some kinds of organosulfur compounds are important extractants for noble metals. We have studied a kind of compounds with the structure of

$$R-S-(CH_2)_n-\overset{X}{\underset{\parallel}{C}}-Y \quad (R: \text{ Alkyl}; \; X: O, S; \; Y: OR, NR_2).$$

In this paper, we introduce ethyl dodecylmercaptoacetate (EDMA), which unlike other sulfur ethers, has no unpleasent odor and can be used as an extractant for palladium satisfactorily.

According to our previous reports, the reversed-phase paper chromatography using a solution of an extractant as the stationary phase can be used as a rapid and simple method to estimate the extractability of the extractant for metal ions [1-4].As the reversed-phase paper chromatography is similar in mechanism to liquid-liquid extraction, the smaller the Rf value in the Rf graph, the greater will be the extraction coefficient (D) of the extractant for the metal. Compare the Rf graphs shown in the periodic table, one can easily observe the extractive and selective abilities of the extractant for different metal ions. For EDMA,we used paraffin oil as a high boiling point solvent, and this solution was used as a stationary phase in reversed-phase chromatography.Different molarities of HCl and HNO$_3$ were used as the mobile phase. The Rf graphs of more than 30 matallic ions are shown in Figs1,2.
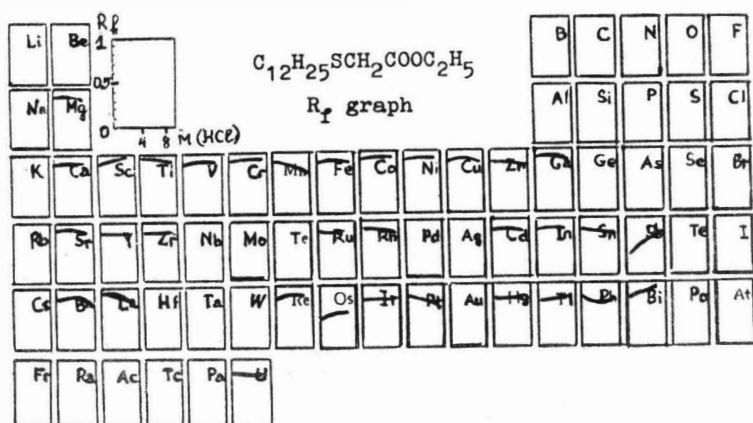
Fig.1. R$_f$ graph of metals using paraffin oil-EDMA as stationary phase and HCl as mobile phase

$C_{12}H_{25}SCH_2COOC_2H_5$
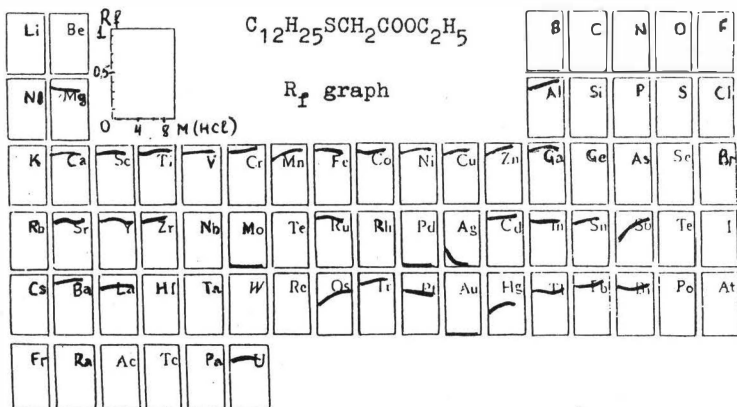
R_f graph

Fig.2. R_f graph of metals using paraffin oil-EDMA as stationary phase and HNO_3 as mobile phase

From the Rf graph, we can see that EDMA is an excellent extrac-tant for Pd^{2+} and Au^{3+}, and with low extraction coefficient for most of the metals such as Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Co^{2+} in HCl and HNO_3 system. We further studied the extraction behavior of EDMA for palladium.

(1) The percentage extraction (E %) of Pd^{2+} in different diluent are shown in Table I.

diluent	chloro-form	carbon tetra-chloride	toluene	cyclo-hexane	petroleum ether	kerosine
E %	81.5	99.3	99.9	98.5	98.8	98.7

[EDMA]=2×10^{-2}mole; [Pd^{2+}]=7.4×10^{-3}M; [HCl]=0.65M; t=28°c.

(2) Distribution coeffecient (D) of EDMA for different mo-larities of HCl are shown in Table II.

HCl(M)	0.1	0.6	0.9	1.3	2.0	2.8	4.3	6.4
log D	1.6	1.1	1.0	0.99	0.80	0.78	0.71	0.59

[EDMA]=2×10^{-2}M; [Pd^{2+}]=1×10^{-2}M; t=28°c.
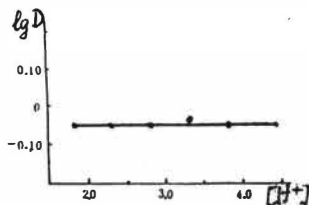
Fig.3. Relation between logD and $[H^+]$
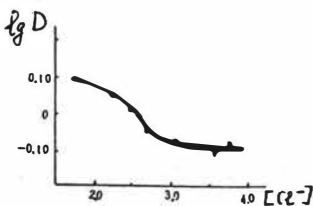
Fig.4. Relation between logD and $[Cl^-]$

The relation between log D and [H$^+$] or [Cl$^-$] are shown in Figs 3,4.

(3) The number of EDMA coordinate to Pd is determined by the method of molecular ratio (Fig.5). The ratio of EDMA to Pd is 2:1.

(4) The composition of extracted complex is also determined by the method of saturation. The ratio of EDMA to Pd is also 2:1.

(5) From Infrared spectrum, we can see that EDMA coordinates with Pd through the sulfur atom. (FIG.6)

$$[EDMA] + [Pd^{2+}] = 4\times10^{-3}M.$$
$$(HCl) = 2\ M,\ \ t = 15^{\circ}C$$
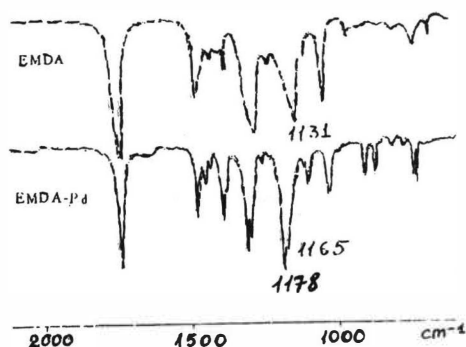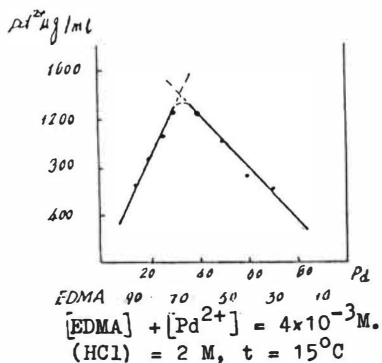
Fig.5. Extraction of Pd^{2+} with the change of molecular ratio

Fig.6. IR of EDMA and EDMA-Pd complex

(6) The solid extracted complex is obtained after recrystalization from toluene. It is an orange yellow crystal, m.p. 33°c. Its elementary analysis coincides with the formula PdCl$_2$ 2EDMA.

	Pd	Cl	C	H
determined	14.06	9.41	51.19	8.78
calculate	14.11	9.40	50.96	8.56

From the above discussion, we can see that EDMA can strongly extract palladium and the composition of the extracted complex is PdCl$_2$· 2EDMA.

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314

EXTRACTION OF METALS BY SULPHUR-CONTAINING ANALOGUES OF
MONO- AND POLYNUCLEAR PHENOLS

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Mono- and polynuclear phenols having two or several hydroxyl gro-
ups in their composition possess complexing properties with respect
to some elements and are used in the analytical chemistry [1].However,
because of their low selectivity they haven't found large application
in the analysis.On partial or complete substitution of oxygen atoms
in the molecules of such phenols by sulphur atoms they get new proper-
ties - the spectrum of their action with metal ions is changed,they
become more selective,their complexes with metals absorb light within
a wide range of wave length [2].On interaction of such compounds with
metal ions there are scarce but high-grade data [3,4].
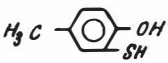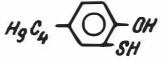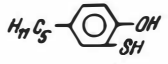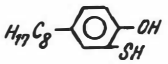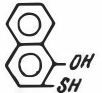
The given report is dedicated to the results of systematic study
of oxymonothiophenols (OTPh) as an extraction and extraction-photomet-
ric reagent.

It has been developed a convenient synthesis procedure - reducing
splitting of di- and polysulphides of the corresponding alkyl phenols.
Some samples of this class of compounds were synthesized by the me-
thods of element analysis,gas-liquid chromatography,spectroscopic in-
vestigation (PMR,electronic,IR),their individuality and purity were
proved.For the synthesized oxymonothiophenols the general physico-che-
mical characteristics were determined - the solubility in water (S_b),
ionization (pK) and distribution (P) constants necessary for the desc-
ription of extraction in every particular case (Table 1).Oxymonothio-
phenols are poorly soluble in water,depending on the length of the
alkyl radical $10^{-2}-10^{-5}$mole/l.The solubility decreases in the same
order with increasing of the number of benzene nuclei in their molecu-
les.They represent weak bibasic acids.With rising of the molecular
mass the numerical values of ionization constants decrease.The inter-
relation between the molecular mass and ionization constants is desc-
ribed by the equation: pK=5,72 lg M- 6,68.Distribution constants of
all the studied oxymonothiophenols increase in a series: hexane-CCl_4-
benzene.

With the help of a special research it was established a relative
stability of OTPh with respect to acids.The hydrochloric,perchloric,
phosphoric,boric,acetic acids in all the concentrations,nitric acid to
o,5n and sulphuric acid to 8n are inert towards oxymonothiophenols;
on a long contact with them OTPh undergo no changes.In a dark bottle

OTPh solutions during 10 days after their preparation independent on nature of a reagent itself and a solvent are resistant towards direct light.The relative stability of oxymonothiophenols decreases with rising of the alkyl radical in their molecule,it being dependent on the solvent nature.

Table 1.Physico-chemical characteristics of oxymonothiophenols

Name	Structural formula	S_b mole/1×10^3	pK_a	$\lg P_{CCl_4}$
2-oxy-5-methyl-thiophenol	H_3C —⟨O⟩— OH, SH	30,60	5,62	1,78
2-oxy-5-tert-butylthiophenol	H_9C_4 —⟨O⟩— OH, SH	2,73	6,07	2,75
2-oxy-5-tert-amylthiophenol	$H_{11}C_5$ —⟨O⟩— OH, SH	0,88	6,28	3,00
2-oxy-5-tert-octylthiophenol	$H_{17}C_8$ —⟨O⟩— OH, SH	0,11	6,93	3,40
2-oxythio-naphthol	⟨O O⟩— OH, SH	0,07	6,15	3,30

The presence in the molecule of oxymonothiophenols of hydroxyl and sulphhydrile groups in a position favourable for complexing,out of which proton is easily substituted by metal ions,promotes within the wide range of acidity the formation of medium of compounds being extracted with elements,for which a stable bond with sulphur is characteristic.In Table 2 extraction conditions of a number of elements out of different media by solution of 2-oxy-5-tertbutylthiophenol to CCl_4 are presented.

The extraction range for the most of metals depends both on the composition of aqueous solution and on the nature of an organic solvent.In case of application of polynuclear oxymonothiophenols under the similar conditions the range of maximum extraction is considerably narrowed and it is characteristic of all the systems studied.The extraction of separate elements is markedly affected by the length of the alkyl radical in the reagent molecule.A reagent:metal relation in the compounds being extracted generally corresponds to the oxidation

Table 2. Extraction of metals 0,005 by the solution of 2-oxy-5-tert-butylthiophenol to CCl_4

Element	pH range of maximum extraction out of	
	hydrochloric acid solution	sulphuric acid solution
Mo(VI)	pH 1,0–4,0 n.HCl	pH 1,0–3,0 n.H_2SO_4
W(VI)	pH 2,0–1,0 n.HCl	pH 2,0–1,0
Bi^{3+}	pH 4,5–0,4 n.HCl	pH 4,5–4,0 n.H_2SO_4
Co^{2+}	pH 7,5–8,2	pH 7,5–8,2
Te(IV)	pH 5,5–10,0 n.HCl	pH 5,5–11,0 n.H_2SO_4
Hg^{2+}	pH 5,0–3,5 n.HCl	pH 5,0–6,0 n.H_2SO_4
Ag^+	pH 1,0–4,0	pH 4,0–3,0 n.H_2SO_4
Se(IV)	pH 8,0–11,0 n.HCl	pH 1,0–6,0 n.H_2SO_4
Ni^{2+}	pH 6,8–7,5	pH 8,0–10,0

degree of the particular element under the extraction conditions. With bismuth as an example it has been studied crystalline structure of the compound being extracted, in which a metal atom forms a strong covalent bond with three sulphur atoms and is coordinated by one hydroxyl group. The electronic spectrum of metal oxymonothiophenolates, obtained in different extraction systems is within the range λ_{max} = 360 – 600 nm with molar absorption coefficient n·10^4. The colour of extracts is stable.

The characteristics above were the basis for the development of extraction-photometric procedures of determination of elements in concrete objects, in most cases without separation process.

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In the last years some new organophosphorous compounds have been
commercialized, among them, a lot of work has been devoted to
bis-(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272) (1) and its
ability to separate cobalt (II) from nickel (II) (2,3), however only
a few studies have been undertaken in order to describe the behaviour
of CYANEX 272 in other systems (4,5).
   In this work the extraction of zinc (II), cadmium (II), copper
(II) and iron (III) from aqueous nitrate   solution   by CYANEX 272
dissolved in Isopar-H has been studied at 25ºC.
   Distribution data have been analyzed both graphycally and
numerically using the program LETAGROP DISTR.
   The composition of the extracted species was determined and the
formation constants of the different species are given.

REAGENTS AND EXPERIMENTAL PROCEDURE

   Cyanex 272 (Bis-(2,4,4-trimethylpentyl)phosphinic acid):Supplied
By Cyanamid, it has been purified before use (6).
   Isopar-H (ESSO): has been washed twice with distilled water
before use.
   Sodium nitrate: used as ionic media, it has been prepared as
described in reference (7).
   Metal nitrate solutions have been prepared directly from metal
nitrates (Merck p.a.).
   The distribubion equilibria studies were carried out at 25ºC
shaking equal volumes (15 ml) of the organic and aqueous phases until
the equilibrium is reached.
   The organic phase composition was c mol.dm^{-3} of Cyanex 272
dissolved in Isopar-H, c was varied from 0.010 to 0.100.
   The aqueous phase composition consisted of 0.1 mol.dm^{-3} (Na$^+$,H$^+$,
M^{n+}) NO$_3^-$ where M^{n+} were Zn^{2+}, Cd^{2+}, Cu^{2+} and Fe^{3+}.
   Metal content in both phases was determined by Atomic Absoption
Spectrometry (using a 2380 Perkin Elmer Absorption Spectrometer).
Determination of metal content in the organic phase was made after
stripping with hydrochloric acid.

RESULTS

   The metal distribution between the organic and aqueous phases,
was obtained directly as the ratio of the total metal concentration
in both phases.

$$D = \frac{M^{n+}_{org}}{M^{n+}_{aq}} \cdot$$

   Distribution coefficients were measured as a function of pH and
extractant concentration at constant metal concentration of 10^{-4}
mol.dm^{-3} for Zn(II), Cd(II) and Cu(II) and 10^{-3} mol.dm^{-3} for Fe(III).
Extraction percentages against pH for the different metals at two
Cyanex 272 concentrations, are given in figure.
   The distribution equilibria of M^{n+} with cationic extractants can
be written as follows

TABLE I

Equilibrium constants for the extraction of Cu(II), Zn(II), Cd(II) and Fe(III) by Cyanex 272 dissolved in Isopar-H at 25ºC

Metal	$\log K_{20}$	$\log K_{21}$	$\log K_{22}$	$\log K_{23}$
Zn(II)		-2.12 -2.15±0.09	-1.69 -1.76(max-1.51)	
Cu(II)	-7.50 -6.67±0.17		-4.40 -4.43±0.10	
Cd(II)	-7.57 -7.34±0.25			-4.83 -4..69±0.19
	$\log K_{30}$	$\log K_{32}$		
Fe(III)	-0.86 -0.71±0.18	0.47 0.71(max1.16)		
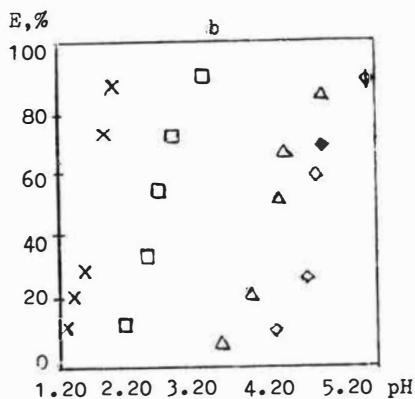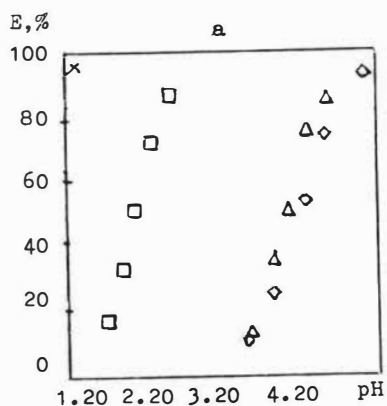
Extraction percentages as a function of pH at constant metal concentration: Cd(II), Cu(II) and Zn(II) 10^{-4} mol.dm^{-3}, Fe(III) 10^{-3} mol.dm^{-3}.

    a - Cyanex 272 concentration: 0.100 mol.dm^{-3}
    b   Cyanex 272 concentration: 0.010 mol.dm^{-3}

    □ Zn(II); Δ Cu(II); ◊ Cd(II); x Fe(III)

$$M^{n+} + (m+n)/2 \ (HA)_{2 \ org} = MA_n(HA)_{m \ org} + n \ H^+,$$
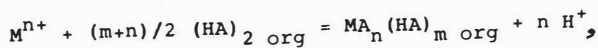
where HA refers to Cyanex 272. K_{mn} is the extraction constant defined as

$$K_{mn} = \frac{MA_n(HA)_{m \ org} \ H^{+ \ n}}{M^{n+} \ (HA)_{2 \ org}^{(m+n)/2}} \ .$$

A preliminar graphic treatment obtained by plotting logD against log $(HA)_{2\ org}$ at constant pH showed that two species, $MA_n(HA)_m$ and $MA_n(HA)_s$ were formed in organic phase for each metal.

Assuming that this two species are formed and taking into account the distribution coefficient, the following function can be obtained.

$$D\ H^{+\ n} = K_{mn}\ (HA)_{2\ org}^{(m+n)/2} + K_{sn}\ (HA)_{2\ org}^{(s+n)/2} .$$

In order to determine m, s and the extraction constant values, the experimental data, plotted as logD-npH against log $(HA)_{2\ org}$ were composed with the theoretical model function $logY = log(u^{(m+n)/2} + Lu^{(s+n)/2})$. Where

$$log\ u = 2/(m+n)logK_{mn} + log\ (HA)_{2\ org}$$

and

$$L = \frac{K_{sn}}{K_{mn}^{(s+n)/2}} .$$

By superposing the experimental curves for each metal with the theoretical model logY vs log u, values of m, s, K_{mn} and K_{sn} can be calculated. Results are shown in table I.

A refinement of the model obtained was performed by using a version of the general minimizing program LETAGROP, specially adapted to the treatment of distribution data, LETAGROP-DISTR (8). In this program, the computer searches for the best set of formation constants that minimize the error squares sum defined by:

$$U = \Sigma\ (log\ D_{exp} - log\ D_{calc})^2 ,$$

where D_{exp} represents the metal distribution ratio determined experimentally and D_{calc} represents the calculated distribution ratio value obtained by solving the mass balance equations for HA, metals and ionic media, using a set of complexes and their equilibrium constants. The program also calculates the standard deviation $\sigma(logD)$ defined by:

$$\sigma(logD) = \Sigma\ (logD_{exp} - logD_{calc})^{2/N_p\ 1/2} .$$

Results are given in Table I.

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TRIALS ON THE MOLECULAR DESIGN OF ORGANIC EXTRACTANTS

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Solvent extraction is now developed as one of the most important me-thods in isolation and purification of various ions including actinides, lanthanides, transition and precious metals. Extraction process also shows great potentiality bath in the manufacture of organic acids and in the treatment of industrial effluents contaiminated with radioactive and toxic heavy metal ions as well as organic pollutants. Metal extraction which is based on the formation of complexes by organic ligands with metal ions or corresponding ionic species, may be regarded as a multi-componental coordination process between heterogenous phases. The radical property of extraction separation is, however, dependent chiefly on the stability of metal complexes, which are closely related both to the structure of ligands and to nature of metal ions. The appearance of a new potential extractant can have very dramatic influence on the process of hydrometallurgy. However, development of such new extractants, up to now, is usually worked out by the screening method, which requires large amount of investment and labour. Quantitative examination of the contribution of structural effects on the extraction performance of ligand will provide an experimental basis for the molecular design of extractants [1]. Unfortunately, this feild still remains at the quanli-tative or semi-quantitative stage up to now.

According to Laskorin [2], the polar effect of the substituent is the predominat factor for the reactivity of the extractant. Therefore, the relationship between the extraction equilibrium constant (K_{ex}) and substituent polar parameter $\widetilde{6_{qp}}$ suggested by Kabachnik is as

$$\lg K_{ex} = a + b\widetilde{6_{qp}}. \tag{1}$$

Since the results were not satisfactory when using Eq. 1 in most cases, so they supposed that the steric and entropy effect should lso be taken in consideration. Therefore, an additional term, li, was intro-duced to represent the steric and entropy influence

$$\lg K_{ex} = a + b\widetilde{6_{qp}} + c \ li. \tag{2}$$

Unfotunately, Eq. 2 is still unable to demostrate the structural influ-ence of ligands on their behavious in metal extraction in some systems. Meanwhile, Rozen [3] proposed that the extractability of the acidic ligand should be determined by its dissociation constant pKa

$$\lg K_{ex} = a + b \ pKa. \tag{3}$$

Actually, there is no radical difference between Eqs. 1 and 3 because the pKa value of an organic acid is linearized to its of the substi-tuent of compounds.

As illustrated by our early investigation, the reactivity of coordi-nating atom or group, the steric effect and the solubility of ligands are the basic structural factors determining the extraction behaviour

of ligands in metal extraction [4]

$$lg\ K_{ex} = lg\ K_{exo} + \rho\sigma' + \delta\Sigma\ E_s + k\Sigma C, \qquad (4)$$

where Kexo is the extraction equilibrium constant of reference compound, σ', E_s and C are parameters for polar, steric and solubility effect, and ρ, δ and k are the relative coefficient respectively.

Since the polar constants of long chain alkyl and alkoxyl groups, which are specific and characteristic for organic extractant, are still insufficient in the literature [2], the QSAR studies of organic extractants was thus inhibited. As an extension of Kabachnik constant, a series of σ'^{ρ} of long chain alkyl and alkoxyl groups was proposed by us [5]. The acceptance of σ'^{ρ} as a measurement for substituent polarity was evidenced by the excellent linear relationship between this constant and other physico-chemical parameters including group connectivity[6], characteristic frequency in IR spectra, ^{31}P NMR chemical shift and rate constant of alkaline hydrolysis of alkylphosphonates [7].

It was well-established by us in our previous studies that steric effect of the substituents plays an important role in metal extraction. It is, therefore, necessary to select or establish substituent steric parameters. Unfortunately, the wider use of the classic Taft Es was restricted by its coliniearity with polar constant. The possibility of application of Charton's ν, which is evaluated based on the van der Waals radius, was examined. The results of correlation analyses were in Table 1.

Table 1. Statistic Data on Correlation Analyses in Cobalt, Nickel Extraction

$$lg\ K_{ex} = \rho\Sigma\sigma^{P} + \delta\Sigma E_{PA} + C$$

Ser.	Correlation		ρ	δ	C	r	s	ψ	n	$t\ or\ F$	C.L.(%)
1	$lg\ K_{ex}-\Sigma\sigma^{P}$	(Co)	0.86	—	-4.16	0.6938	0.34	0.76	22	4.31	99.9
2	$lg\ K_{ex}-\Sigma\nu$	(Co)	—	-1.01	-4.07	0.5145	0.39	0.95	11	1.80	98.0
3	$lg\ K_{ex}-\Sigma E_{PA}$	(Co)	—	1.01	-4.65	0.5935	0.38	0.84	22	3.30	99.0
4	$lg\ K_{ex}-\Sigma\sigma^{P}, \Sigma\nu$	(Co)	0.78	-0.81	-3.10	0.8221	0.27	0.67	11	8.34	97.5
5	$lg\ K_{ex}-\Sigma\nu, \Sigma E_{PA}$	(Co)	-0.97	0.05	-4.08	0.5150	0.41	1.00	11	1.44	—
6	$lg K_{ex}-\Sigma\sigma^{P}, \Sigma E_{PA}$	(Co)	0.86	1.00	-3.17	0.9107	0.20	0.44	22	46.20	99.5
7	$lg\ K_{ex}-\Sigma\sigma^{P}$	(Ni)	3.03	—	-2.10	0.8754	0.63	0.51	20	7.68	99.9
8	$lg\ K_{ex}-\Sigma\nu$	(Ni)	—	-3.81	-1.33	0.7156	0.91	0.79	9	2.71	95.0
9	$lg\ K_{ex}-\Sigma E_{PA}$	(Ni)	0.99	—	0.61	0.4169	1.18	0.96	20	1.95	90.0
10	$lg\ K_{ex}-\Sigma\sigma^{P}, \Sigma\nu$	(Ni)	2.56	-1.64	-0.44	0.9646	0.33	0.32	9	40.13	99.5
11	$lg\ K_{ex}-\Sigma\nu, \Sigma E_{PA}$	(Ni)	-4.47	-0.61	-4.69	0.7384	0.82	0.80	9	4.06	—
12	$lg\ K_{ex}-\Sigma\sigma^{P}, \Sigma E_{PA}$	(Ni)	3.03	1.00	5.86	0.9697	0.33	0.26	20	133.97	99.5

The data indicate that multiple regression involving σ^P and $\Sigma\nu$ provides satisfactory result only for nickel extraction (series 10) but not for cobalt (series 4). This difference is probably arised from the various steric requirments for cobalt and nickel complexes which forms tetrahedron and octahedron configration respectively. An individual substituent steric parameters for Co and Ni in extraction with acidic phosphorus esters were introduced by us [8]. By statistical treatment, an empirical equation representing quantitative relationship between structure and property of acidic phosphorus esters in cobalt and nickel extraction was proposed

$$\lg K_{ex}Co = 0.86\,\Sigma\sigma^P + 1.00\,\Sigma E,CoPA - 3.17, \qquad (5)$$

$$\lg K_{ex}Ni = 3.03\,\Sigma\sigma^P + 1.00\,\Sigma E,NiPA + 5.86. \qquad (6)$$

Establishment of equation 5 and 6 provide a theoretical basis for the design of organic extractant with expected properties towarding cobalt and nickel extraction.

As demostrated by correlation analyses (series 6 and 12 in Table 1) relating $\lg K_{ex}$ to $\Sigma\sigma^P$ and $\Sigma E,Co(Ni)PA$, the statistic parameters meet requirments excellently. It forms a contrast to single term regression with $\Sigma E,Co(Ni)PA$ (series 3 and 9). As expected, multiple regression involving $\Sigma\nu$ and $\Sigma E,Co(Ni)PA$ with $\lg Kex$ (series 5 and 11) gave also poor results.

The fact that the influence of substituent polar constant on nickel extraction is significantly greater than that for cobalt extraction can be reasonalized by different configuration of the extracted species. Since the octahedron configuration of the nickel complex, in which two positions were occupied by water molecules, may thus be treated as square planner coordination compound which is highly sensitive to the steric effect of organic extractants.

It was also found by us that there is a quantitative relationship between the separation factor and the steric parameter.

Upon comparison of equation 5 and 6, it is resonable to predict that the structure of an effective extractant for cobalt and nickel separation should be with smaller $\Sigma\sigma^P$ and larger $\Delta E,Co(Ni)PA$. By applying this principle, di(1-methylheptyl)phosphinic acid would be excellent in cobalt and nickel separation. This theoretical predication is well supported by experimental data [9,10]. It is, therefore, expected to use E,CoPA or E,NiPA in extraction those metal ions which possess similar configuration of coordination compounds in extraction process as cobalt or nickel.

Analogously, a set of substituent steric parameters for rare earth extraction by mono-basic phosphorus ligand was derived [11]. Because of the similarity of the outer-sphere electronic structure and the chemical

reactivity of lanthanide, it is reasonable to conclude that $\Sigma E,NdPA$ and $\Sigma E,SmPA$ are nearly the same. Their average deviation is less than 0.08. Averaging these two parameters, we can get the steric constant $\Sigma E,REPA$ for this series of compounds. Excellent correlation coefficients has been obtained when using steric constant $\Sigma E,REPA$, polar constant $\Sigma \sigma^f$ to correlate with K_{ex} in lanthanide extraction.

$$lg\ K_{ex}Nd = -2.69\Sigma\sigma^f + 2.89\ \Sigma E,REPA- 2.62 \qquad (7)$$
$$r = 0.999,\ S1= 0.167,\ S2= 0.058,\ S3= 0.199$$
$$T1= 16.08,\ T2= 49.58,\ T3= 13.15,\ CL=99.99,\ n=13$$

$$lg\ K_{ex}Sm = -3.31\Sigma\sigma^f + 3.12\ \Sigma E,REPA- 2.21 \qquad (8)$$
$$r = 0.999,\ S1= 0.154,\ S2= 0.054,\ S3=0.184$$
$$T1=21.51,\ T2= 58.28,\ T3= 12.03,\ CL=99.99,\ n=13.$$

The separation factor between a pair of rare earths in extraction with acidic phosphorus-based ligand can be estimation by substracting Eqs. 7 from 8

$$lg\ \beta\ Sm/Nd = -0.62\ \Sigma\sigma^f + 0.23\ \Sigma E,REPA + 0.41. \qquad (9)$$

The experimental results of separation are in good agreement with the calculated value from Eq. 9.

By the similar treatment the satisfying structural requirments for Y and Yb separation can be represented as

$$lg\ \beta\ Yb/Y = -0.65\Sigma\sigma^f + 0.30\ \Sigma E,REPA + 0.38. \qquad (10)$$

Based on above equations, it is reasonable to explain the superiority of mono-(2-ethylhexyl) ester of 2-ethylhexyl phosphonic acid ($lg\ \beta$ for Sm/Nd 1.02, for Yb/Y 0.81) over D2EHPA ($lg\ \beta$ for Sm/Nd 0.86, for Yb/Y 0.56) which has been widely used in rare earth separation in industrial scale, and it is also expected that both octyl cycohexylphosphonate and β-substituted alkyl ester of isopropyl phosphonate[12] will show better properties in lanthanide separation.

Table 2. Multiple Regression Data in Metal Extraction by Eq. 11

M	ρ	δ	r	C	RMS	R	t_ρ	t_δ	t_γ	n
Co2+	-0.368	-0.956	-0.151	-4.476	0.103	0.920	3.788	5.187	4.362	19
Ni2+	-2.006	-2.693	-0.259	-2.562	0.479	0.919	3.914	2.427	1.610	19
Nd3+	-1.764	-3.314	-1.403	9.132	0.695	0.894	3.383	1.256	2.425	8
Sm3+	-1.742	-3.699	-1.582	10.731	0.784	0.887	2.962	1.242	2.425	8
Y3+	-1.726	-4.788	-1.535	12.819	0.791	0.872	2.906	1.593	2.330	8
Yb3+	-1.600	-4.294	-1.556	13.082	0.726	0.881	2.938	1.558	2.576	8

A new approach for the evaluation of steric effect of substituents in extraction of metals (Ni, Co, RE) with acidic phosphorus ester by molecular mechanics calculations was suggested by us [13].Dialkyl tert-

butylphosphate or phosphinate was chosen as a model structure for the similation of the steric environment of complexes. The optimun geometry of these two model esters were determined by molecular mechanics program (Allinger's MM2). It was found that the difference of the local steric energy of hydroxyl oxygen in the model phosphorus ester is closely correlated with the degree of the size of substituents and can thus be used as a measurement of the steric effect of the substituent ($E_{s,ex}$). A series of $E_{s,ex}$ of alkyl and alkoxyl groups were estimated. In the meantime, since the solubility of ligand is a element which can not be neglected in the extraction process, a new term $\lg P_R$ representing the contribution of substituents on extraction, based on Hanson's $\lg P$ value was introduced

$$\lg K_{ex} = \rho \Sigma \sigma' + \delta E_{s,ex} + \gamma \lg P_R + C. \qquad (11)$$

The statistic data was shown in Table 2.

As demostrated by data on Table 2, further study on the selection of better simulation model structure is necessary in establishing substituent steric parameters by molecular mechanics studies.

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REGULARITIES OF THE EXTRACTION OF RARE EARTH ELEMENTS WITH TRIISOAMYLPHOSPHATE

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Tributylphosphate (TBP) is one of the phosphororganic compounds most frequently employed for the separation of rare earth elements (REE). At the same time it has a number of drawbacks: high solubility in water (0.39 g/l), the possibility to form the third phase upon saturation of TBP, diluted with saturated hydrocarbons, with REE nitrates and others. The present work is concerned with the study of the properties of triisoamylphosphate (TiAP), extractant devoid of the above drawbacks, its properties are compared to those of TBP.

Triisoamylphosphate containing more than 98% of the basic component (d= 0.952 g/cm^3, n_D^{20} = 1.4275, t_{boil} = 143-146°C (3-4 mmHg), content of acid impurities 0.002%) was used as an extractant.

The data on the REE extraction with TiAP are scanty and refer, mainly, to the extraction of microquantities of REE [1,2]. Primary attention in this work is paid to the study of those regularities of REE extraction with TiAP, which are of important for its practical application (isotherms of lanthanide extraction, the influence of REE concentration and concentration of salting out agents in the aqueous phase on the values of REE distribution and separation coefficients, effect of HNO$_3$ concentration and others.)

General regularities of the REE extraction with TiAP and other NPOC are analogous. For example, the shape of the dependence of the REE distribution coefficients on the HNO$_3$ concentration in the aqueous phase is typical of NPOC. It is related to the REE extraction by two mechanisms with the formation of Ln(NO$_3$)$_3$. 3S compounds over the range of moderate HNO$_3$ concentrations and HxLn(NO$_3$)$_{3+x}$) HNO$_3$ concentrations higher than 10 M. A decrease in the values of REE distribution coefficients over the acidity range 4-9 M is due to the HNO$_3$ extraction (Fig.1). By analogy with TBP TiAP extracts well HNO$_3$ (Fig. 2), the formation of the solvates HNO$_3$. S and (HNO$_3$)$_2$. S being possible. A considerable increase in the volume of the organic phase (up to 30%) is observed during extraction. The extraction isotherms (Fig. 3) happen to be the main characteristics during the REE extraction with NPOC. The shape of the isotherms is typical of all the NPOC, Sm having the highest distribution coeffiecient among them. A shift of the Y position in the REE extractability row upon the change of their concentrati-
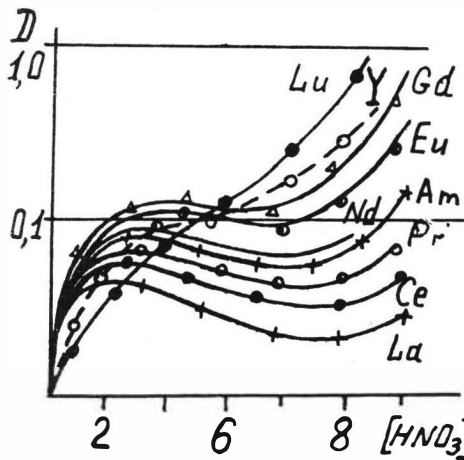
Fig. 1. Dependence of REE distribution coefficients on the HNO_3 concentration
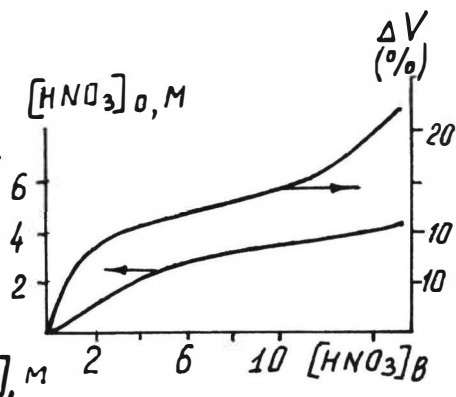
Fig. 2. Isotherm of the HNO_3 extraction and the increase in the volume of the organic phase

on in the aqueous phase is observed. The volume of the organic phase increases up to 7% in the range of the maximum saturation, when it is saturated with lanthanide nitrates. Molar ratios TiAP: REE= 3:1. Similar data were obtained by the delution method, which supports the formation of trisolvate $Ln(NO_3)_3.3S$.

The use of the diluted TiAP (up to 25%), in contrast to TBP, did not result in the formation of the third phase (Fig.4). The REE distribution coefficients regularly decline with increasing the diluent polarity (Table 1).

At the $Li(NO_3)$ concentrations equal to or exceeding 2 M the extraction order is dodecane TCB TCE toluene.

The existence of salting out agents in the aqueous phase increases the distribution coefficients of lanthanides (Fid. 5), the separation coefficients also go up, which is due to the great difference in the values of activity coefficients of lanthanides in aqueous and organic phases.

The extraction ability of TiAP is close to that of TBP (Table 2), but TiAP has a higher selectivity during the extraction of cerium REE as distribution coefficients on their ordinal number is typical of NPOC, the maximum of the distribution coefficients falls on samarium (Fig. 6-7), in any case the yttrium position shifts to the lanthane side during the extraction from more diluted solutions.

The obtained data lead us to conclude:

- TiAP is a typical representitive of NPOC, its extraction properties are close to those of TBP, but it has certain advantages over the latter.

327
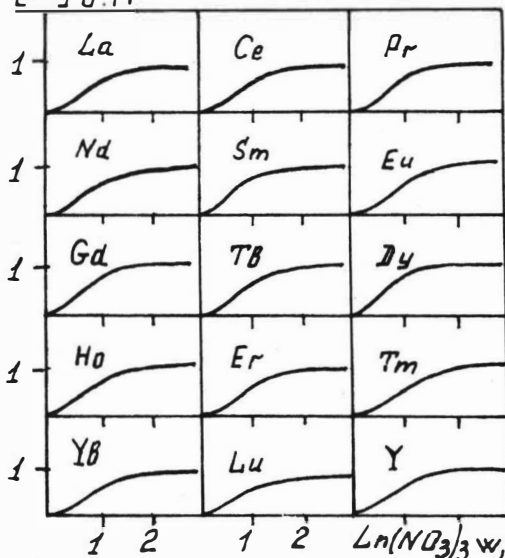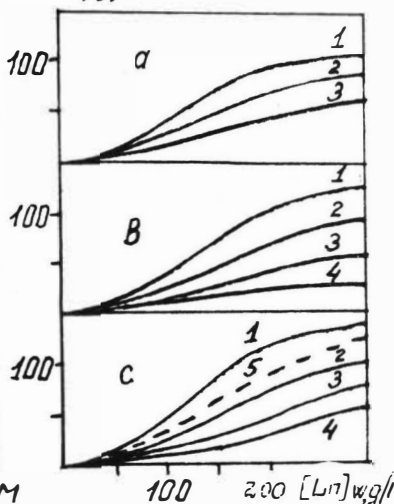
Fig. 3. Isotherms of REE with triisoamylphosphate up to 7% in the range of maximum separation

Fig. 4. Isotherms of La and Ce, Nd extraction with TiAP solutions (%) in: a) dodecane 1-100%, 2-66%, 3-50%;

b) CCl   1-100%, 2-66%; 3 50% 4)25%; c-dodecane 1-100% (25°C), 5 - 100% (80°C);2 - 66%; 3 - 50%; 4 - 25%
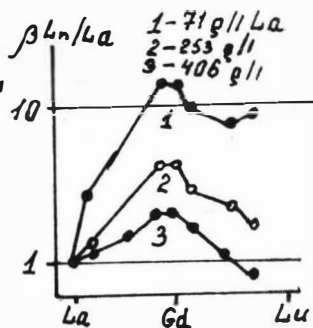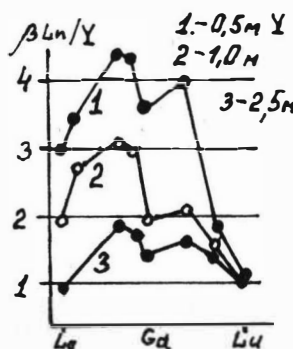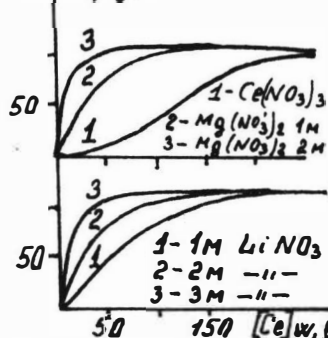
Fig.5. Isotherms of Ce extraction in the presence of salting out agents

Fig.6. Values of distribution coefficients of REE as related to Y

Fig.7. Values of distribution coefficients of REE as related to lanthane

328

Table 1. Influence of Diluents on the Values of Eu Distribution Coefficients in the System: Aqueous Phase $LiNO_3$ + 5 g/l $Eu(NO_3)_3$. Organic phase: 0.5 M TiAP Solutions in Diluents

Diluent		$LiNO_3$, M					
		1.0	1.5	2.0	3.0	4.0	5.0
Dodecane	2.014	0.039	0.11	0.34	0.96	7.25	37.1
TCB	-	0.051	0.079	0.16	0.66	2.8	11.0
TCE	2.3	0.02	0.027	0.099	0.54	2.26	9.82
Toluene	2.379	0.036	0.036	0.07	0.35	0.84	1.76

Table 2. Values of Distribution Coefficients of Eu Microquantities during the extraction with 0.5 M NPOC Solutions in Toluene in the Aqueous Phase Containing $LiNO_3$

Extractant	$LiNO_3$, M					
	1.0	1.5	2.0	3.0	4.0	5.0
TBP	0.019	0.038	0.1	0.4	1.1	2.9
TiAP	0.024	0.036	0.07	0.35	0.84	1.75
DiOMP	0.15	0.35	0.81	5.17	-	-
TOPO	51.2	161.0	269.0	919.0	-	-
T1MHPO	26.2	36.9	87.0	145.0	-	-

- The third phase during the saturation of TiAP of any concentration in saturated hydrocarbons with REE nitrates is absent.

Table 3. Separation Coefficients of Binary Lanthanide Mixtures. Concentration Ln_I + Ln_{II}= 350-450 g/l in Terms of REE Oxide

Extractant	Ce - La	Nd / Pr	Sm / Nd
TiAP	2-2.3	1.3-1.8	1.8-2.3
TBP	1.9-2.0	1.3-1.6	1.8-2.0

- Higher selectivity of TiAP during the separation of lanthanides of the cerium group is not observed.
- The TiAP losses are lower than those of TBP due to lower TiAP solubility in water.

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At present organophosphoric acids (OPA) are widely used for separa-
tion of rare earth elements (REE). The main industrial representative
of OPA is D2EHP. In saturated hydrocarbonates D2EHP is dimerized and
when extracting REE it forms compositions of a chelate type which are
characterized by the highest selectivity. At the same time high dimeri-
zation constants of D2EHP under certain conditions lead to formation
of undesired polymeric sediments. Less selective solvatic mechanism of
extraction does not practically manifest itself in chloride media in
contrast to nitrate and perchlorate media (Fig. 1). This is the reason
why the greatest attention was paid to chloride media.as the most se-
lective though less technological.

This paper presents the results of investigation of extraction of
the REE macroquantity out of nitrate solutions by the OPA examples
synthesized on the basis of the ramificated alcohol 2- isopropyl 5-
methylhexanol D-2 isopropyl 5 methylhexylphosphoric acid (D2iP5MHPA)
and 2 isopropyl 5 methylhexylphosphonic acid (2iP5MHMPA).The dimeriza-
tion constants of these acids are significantly lower thanD2 EHP and
show less tendency to form sediments $\underline{/1/}$. D2iP5MHPA has 10-12 times
less extraction capability and thus re-extraction of heavy REE is of
no difficulty (Fig. 2).
As it is known the extraction of REE by organophosphoric acids is
defined by the following four processes: extraction accordingly to ca-
tion-exchange mechanism, extraction by neutral solvates, extraction by
acid solvates, concurrence extraction of a mineral acid. The tree lat-
ter processes are most characteristic for neutral organophosphoric com-
pounds (NPC) and define the form the dependence curves between distribu-
tion coefficient value and the composition of the aqueous phase. For
OPA all the four processes must operate but the first process will be
a defining one since the REE extraction accordingly the solvating me-
chanism is less distinct at OPA than at NPC. At the extraction of HNO_3
by 1 M solution of D2EHP and TiOP (Fig. 3) the isotherms for the neut-
ral extractant are typical and their form is defined by the formation
of two solvates, i.e. 1:1 and 1:2. In case of D2EHP a noticeable the
extraction of HNO_3 is observed only at HNO_3 concentration of 3-4 M.

It is defined by the fact that the extracted solvate is formed by a
dimerized molecule of OPA, moreover the extractant remains in the

dimerization form up to the concentration of HNO_3 equaled to 10-12M. At Sm extraction by D2EHP and TiOP in dodecane the solvating mechanism for D2EHP starts to manifest itself only when the concentration of samarium nitrate is more than 1 M or NO_3^- 4M (it is correlated with the extraction of HNO_3). It is indirectly confirmed by the fact that the extraction isotherms of individual REE are described rather exactly by a simple equation within the limits of 0.1-1.0 M concentration. This equation corresponds to the ionexchange mechanism of the formation of the extracted compounds with the help of the concentration

constants:
$$Y = \frac{k \cdot x \, [H_2R_2]^3}{[H^+]^2}$$
(Fig.5).

$[HNO_3]$	K
0.43	14.02 ± 0.25
0.63	9.26 ± 0.34
0.86	6.93 ± 0.69

The form of the curves of dependences of the change between the distribution coefficients of REE and HNO_3 concentration at their extraction by the 1M solutions of D2EHP and TiOP, as well as the location and the width of the minimum change with the increase of the atomic number of the lanthanide; moreover the range of HNO_3 concentration in aqueous phase, where the supression of the cation-exchange mechanism occurs, is shifted towards the larger side and it becomes narrower with the growth of the atomic number of the lanthanide. It is quite natural since the growth of the number of the lanthanide causes the increase of the value of the extraction constant accordingly the cation-exchange mechanism (Fig. 6). At the same time the sensitivity for the concurrent extraction of HNO_3 itself becomes lower. The region of HNO_3 concentration where the change of the extraction mechanism for NPC and OPA takes place is the same and is situated within the range of formation of acid solvates(Fig.7). The depth of the minimum in the curves of NPC grows with the decrease of the atomic number and the concentration of the extractant. D_{Ln} becomes lower to the third power and D_{NHO3} - to the first power (Fig.8).

When investigating the selectivity of REE extraction in nitrate media the following system was adopted as the basic one: the extractant is 1M solution of D2EHP in dodecane (the limited loading accordingly 1:6 stechiometry is 0.15 M REE or 20-30 g/l; the aqueous phase is REE nitrates - HNO_3. REE concentration does not exceed 0.5-0.6M or 100 g/l by the oxides of REE, i.e. the condition when the solvating mechanism of extraction does not manifest itself. The lower concentration of HNO_3 is defined by the absence of polymeric sediments in the chosen system (Nd-0.3 M, Sm-0.4 M, Eu-0.5 M, Gd-0.6, Tb-1.2 M, Dy -1.5M t=20°C). The growth of the acidity of aqueous phase decreases the selectivity and loading of OPA (Fig. 9). The selectivity is usually higher at the background of macroquantity of a poorly

331

extracted component (Fig. 10) but sometimes a reverse case happens. This phenomenon can be caused by the changes of the value of the activity coefficients of cations on the system, by the fall of the coordination number with the growth of Z, by structural changes of extracted forms (it is often observed at the edges of Sm-Nd and Gd-Tb tetrades), by decrease of hydration degree by deformation of the crystalline structure of REE nitrates etc. The substitution of the diluent for a more polar one which monomerizes OPA (the worst case is when the diluent itself extracts REE after the solvating mechanism under reverse procedure of the change of D_{Ln} from Z respective to OPA) leads to the loss of selectivity (Fig. 11, 12 and Table 1). But in small quantities (0.2-0.5 M) polar diluents (modificators) ensures stability of the system for formation of sediments. A number of modificators (ethers, ketones, alcohols, carbolicacids) changes the selectivity within the accepted limits. Such modificators monomerize OPA but do not extract REE themselves.

Table 1. Effects of the modificators on loading and separation coefficients

Modificator 0.5M	$[Eu]$ g/l	$[Gd]$ g/l	β Gd - Eu
Dodecane	20.0	20.0	1.8-1.7
MiBK	19.0	21.0	1.5-1.6
Naphthenic acid	17.0	18.0	1.5-1.6
isodecanol	13.5	14.5	1.5-1.4
alkylphenol	11.5	12.5	1.6-1.5
TBP	30.0	36.0	1.3-1.25
TAA	24.0	27.0	1.2-1.1

The application of TBP is an exception . The decrease of selectivity for a number of REE (Sm-Nd,Tb-Gd) is compensated by the increase of loading and, respectively, the growth of productivity. The optimal sphere of D2EHP application is separation of the group of the middle lanthanides from Nd to Y. The analogues of D2EHP on the basis of ramificated alcohol C_{10}, with selectivity comparable with D2EHP, has certain advantages. Both samples of OPA provide extraction process under lower concentration of HNO_3 without risk of sediments formation of extracted compounds in the organic phase.

Table 2. Separation coefficients of REE of the middle group and D2EHP loading (g/l)

Ln	$[HNO_3]$ M	Modificator 0.33 M							
		Dodecane		Isodecanol		TBP		Versatic	
		β	$[Ln]_0$	β	$[Ln]$	β	$[Ln]$	β	$[Ln]_0$
Nd	0.4	-	20.0	3 -	15	-	27	-	-
Sm	0.4	5.2-5.0	22	3.0-3.5	16	2.7-2.3	35	-	-
Eu	0.6	2.0-2.2	24	1.8-1.6	18	1.3-1.2	35	1.6-1.7	20
Gd	0.8	1.8-1.7	20.5	1.5-1.4	17	1.4-1.3	35	1.6-1.7	19
Tb	1.2	4.6-4.1	25	3.9-3.5	20	3.1-2.4	38	-	-
Dy	1.5	2.8-2.6	30	2.6-2.3	25	2.3-1.8	40	-	-

The phosphone acid in dodecane is less selective but may be succ-
sefully used for separation of a number of lanthanide pairs (Fig.13,
Table 3). The analogue of D2EHP has considerable advantage at separa-
tion of yttrium REE. The selecti-
vity is rather high at 0.8M, se-
diments of extracted compounds are
absent and loading is two times
higher than for D2EHP (Fig.15,
Table 4).

Table 3. Separation coeffi-
cients and 1M 2iP5MHPAloading
in dodecane, g/l

Ln_I-Ln_{II}	$[HNO_3]$, M	β	$[Ln_I]^0$	$[Ln_{II}]^0$
Ce-La	0.2	3.0-2.4	30.0	24.0
Sm-Nd	0.2	3.3-2.5	50.0	30.0
Tb-Gd	0.8	4.5-2.1	55.0	30.0

<u>Table 4</u>

Separation coefficients and 1M 2iP5MHPA loading in dodecane, g/l

Ln	$[HNO_3]$, M	$\beta_{Ln_{\bar{i}}/Ln_I}$	$[Ln]^0$	Ln	$[HNO_3]$, M	$\beta_{Ln_{\bar{ii}}/Ln_I}$	$[Ln]^0$
La	0.2	1.0	8.5	Gd	0.8	1.0	11.0
Ce	-	3.3-3.1	13.8	Tb	-	4.3-4.7	21.6
Pr	-	1.6-1.4	15.5	Dy	-	2.7-2.65	27.0
Nd	-	1.5-1.4	28.5	Ho	-	1.9-1.5	29.0
Sm	-	4.0-4.7	28.5	Er	-	2.8-3.45	33.0
Sm	0.4	1.0	17.0	Tm	-	2.6-1.8	43.0
Eu	-	1.7-1.5	21.0	Yb	-	2.3-2.0	46.0
Gd	-	1.5-1.6	21.5	Lu	0.8	1.4-1.35	47.0
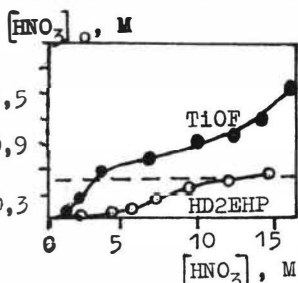
Fig.1. 0.5 M HD2EHP

Fig.2. 1 - 1 M HD2EHP
       2 - 1 M HD2iP5MHMP

Fig.3. 1 M in dodecane
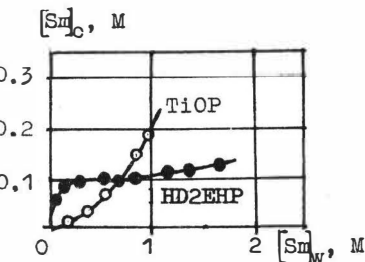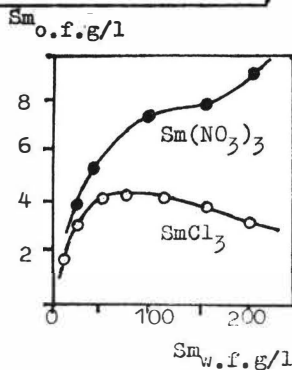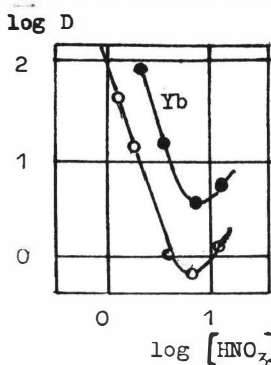
Fig.4. 1M in dodecane
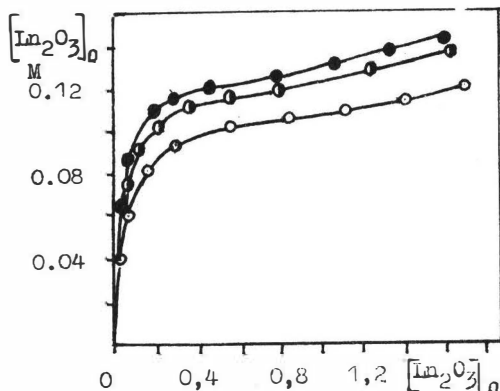
Fig.5. 1M HD2EHP in dodecane
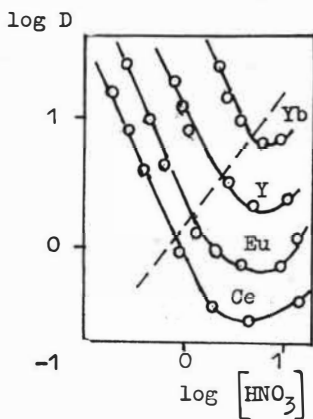
Fig.6. 1M HD2iP5MHMP
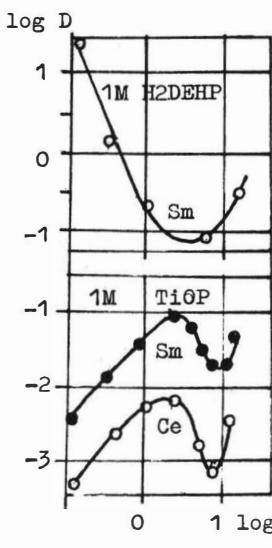
Fig.7
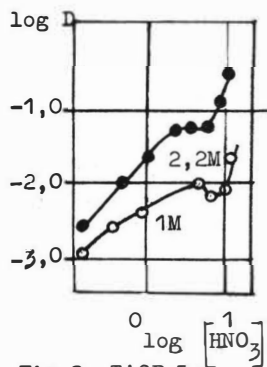
Fig.8. TiOP-Lu
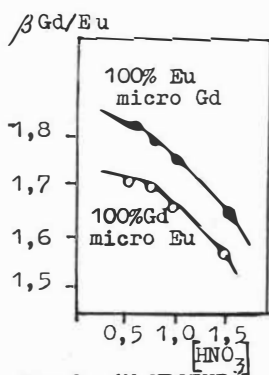
Fig.9. 1M HD2EHP
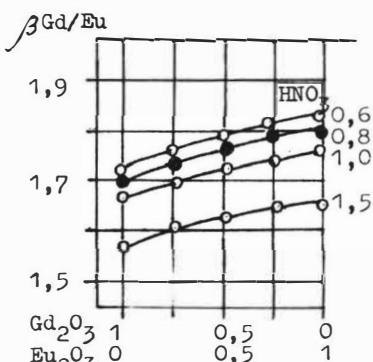
Fig.10. 1M HD2EHP
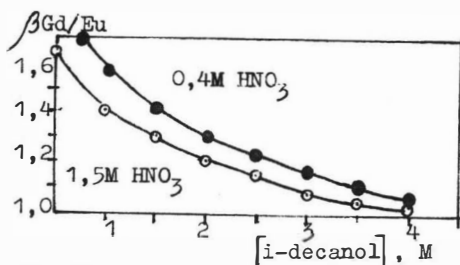
Fig.11. 1M HD2EHP+dodecane+
+ i-decanol
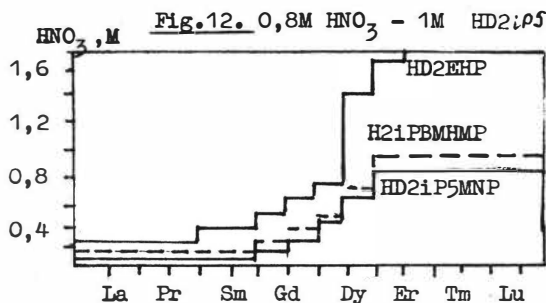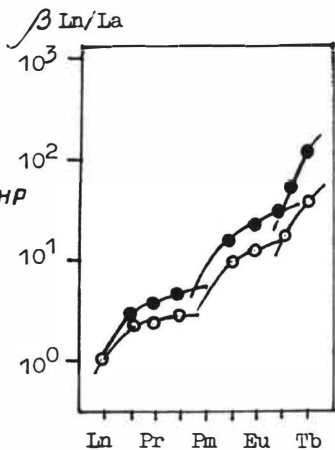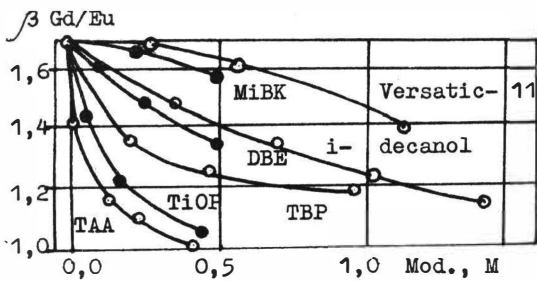
Fig.12. 0,8M HNO$_3$ - 1M HD2iP5MHP

Fig.13. 1M Phosphororg.acids in dodec

Fig.14. 1M H2iP5MHMP
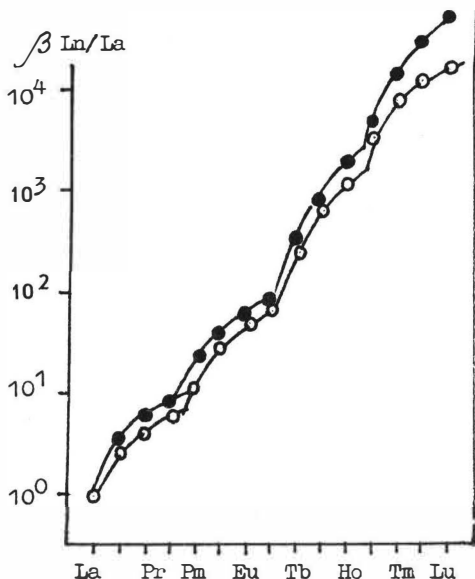
Fig.15. 1 M HD2iP5MHP

Fig.1-15. Main regularities of REE extraction by organophosphorus
acids

Reference.

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1984. V.58, N 12.

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The following compounds: $((RO)_2PO)_2NH$ with $R = Ph$ (__1a__), Hex (__1b__) or Oc (__1c__), $(PhO)_2P(S)-NH-P(O)(OPh)_2$ (__2__), $(PhO)_2P(S)-NH-P(S)(OPh)_2$ (__3__) and $((PhO)_2PO)_2CH_2$ (__4__) have been used for extraction of metal ions. These compounds are Brönsted acids, HA, and are supposed to be able to form neutral chelates MA_n. The acidity of HA decreases in the sequence $1{\sim}2 \gg 4$.

The most powerfull extraction agent for trivalent ions of rare earth and actinide elements is __1a__. The extraction is described by the equations

$$M^{3+}_{(w)} + 1.5\ (HA)_{2\ (org)} \rightleftharpoons MA_{3\ (org)} + 3\ H^+_{(w)} \qquad \text{and}$$

$$M^{3+}_{(w)} + 3\ HA_{(org)} \rightleftharpoons MA_{3\ (org)} + 3\ H^+_{(w)}$$
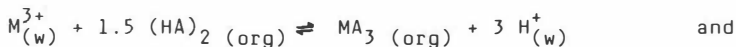
at high and low concentrations of HA in benzene and low concentrations of mineral acids, respectively [1].

At higher concentrations of e.g. $HClO_4$ a solvatation mechanism ocurred (Fig.1).
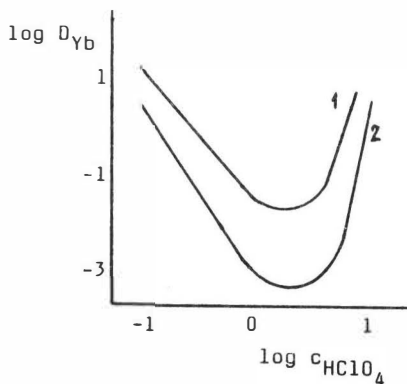
Fig.1.
Dependence of distribution of ytterbium between aqueous soln. of $HClO_4$ and soln. of HA in benzene
1 - 5.10^{-3} mol.l^{-1} __1c__,
2 - 5.10^{-4} mol.l^{-1} __1a__

The metal ions are coordinated to the extractant through the phosphoryl oxygen atoms in the ligand. If phenyl groups in 1a are substituted by octyl or hexyl groups (compounds 1b, 1c) the distribution ratios D drop by about two orders of magnitude. Whereas the hard cations Sc^{3+}, Ln^{3+} and Hf^{4+} are extracted excellently by 1a the softer ions Ag^+, Hg^{2+} and Au^{3+} are not extracted. The opposite behavior was observed for the sulfur containing extractants 2 and 3. Here the first group of elements is not extracted while the extractability of the second group is very good. The best extraction of Ag^+, Hg^{2+} and Au^{3+} was observed with 2. For extraction of Ag^+ from 0,1 M HNO_3 even with 10^{-5} M 2 in benzene D values of about 10 were obtained $/2/$. The about by two orders of magnitude higher D values of Ag^+, Hg^{2+} and Au^{3+} with 2 in comparison with 3 can be explained by the higher acidity of 2. The composition and stability of the complexes extracted, AgA(HA) and HgA_2, were derived from the dependences of the distribution ratios of the respective metals on the acidity of the aqueous phase and analytical concentration of reagent.

Interesting is so that the metal ion e.g. Yb^{3+} in the YbA_3 (HA = 1a) is coordinated through the two oxygen atoms of the phosphoryl groups, forming a 6 membered ring $/3/$, the Pd^{2+} in the complex PdA_2 (HA= 2) is coordinated with a sulfur and the nitrogen atoms of the extractant, forming a 4 membered ring $/4/$.

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SOME INVESTIGATIONS ON THE SOLVENT EXTRACTION OF
CHROMIUM (VI) BY BIS - (2,4,4, - TRIMETHYLPENTYL)-
PHOSPHINIC ACID (CYNEX - 272)

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Although the extration of hexavalent chromium by neutral organophosphorus copounds is reported by some workers (1-7), not much is known about the liquid-liquid extraction of chromium (VI) into acdic organophosphorus extractants. The present communication describes our studies on the extraction of chromium (VI) from hydrochloric, hydrobromic, sulphuric, nitric and perchloric acid solutions by bis (2,4,4 - trimethylpentyl) phosphinic acid (CYNEX - 272) in benzene. These studies mainly deal with our investigations on :

(1) The effect of various parameters such as the effect of the acid, concentration of the metal ion, concentration of the extractant on the extraction and stripping of chromium (VI) from the organic phase.

(2) Determination of the nature of the extracted chromium (VI) species using radiotracer techniques and the data on the absoption spectra of the organic phase.

It has been observed that a single extraction is sufficient for removal of 99% of acqueous phase chromium (VI) with all the acid systems. Further it is observed that the distribution coefficient increases with increasing acidity. At low acid region (< 0.5M) the distribution of chromium (VI) is rather similar in all the acid systems. However at higher acidities (> 0.5M) the increase in the distribution coefficient with increasing acidity is more gradual, the slope of the curves being approximately 1.0 at 1.5-2.0 M acidity. Addition of sodium salts of the corresponding acid solutions resulted in a decrease in the extraction, the decrease being in the order $HCl > HBr > H_2SO_4 > HClO_4 \simeq HNO_3$.

Stripping of Chromium (VI) . Hydrochloric acid, nitric acid, sodium chloride and sodium nitrate and distalled water are used to strip the extracted chromium (VI) from 0.32 M Cynex - 272 in benzene. It is noticed that hydrochloric acid, nitric acid, sodium chloride and sodium nitrate are extremely poor stripping agents for chromium (VI). On the otherhand distilled water alone is a comparatively good stripping agent. The stripping time of five minutes would be optimal to recover 90% of chromuim (VI) by making contact three times with equal volume (15 ml) of distilled water.

Nature of the extracted species . The increase in the distribution coefficient with decrease in pH in the range 1-10 and with increasing acidity clearly indicates the involvement of acidic metallic species in the extraction mechanism. Further the log-log plots

of the equilibrium chromium (VI) concentration in the aqueous phase vs. organic phase gave straight lines of unit slope with all the acid systems, indicating the extracted chromium (VI) species is monomeric in nature (the concentration range of chromium (VI) being 10^{-3} - 10^{-2} g/l and the concentration of the extractant in benzene being 0.028 M). The log-log plots of k_d vs. Cynex - 272 from 2.0 M perchloric acid solutions (0.1-2.0 M) gave slope values of unity indicating the formation of monosolvates in the organic phase. On the otherhand the slope analysis of the distribution data in hydrochloric, hydrobromic and sulphuric acid systems indicate that the solvation number depends on the concentration of the acid. At low acid concentrations (< 0.1 M) the log-log plots show that the solvation number is close to unity with these acid systems (Fig -1). As the concentration of the acid is increased the stoichiometric ratio of the components in the organic phase increases gradually indicating the different extraction mechanisms are operating probably due to the formation of a mixture of species in the organic phase. The extraction of mixture of compounds of chromium (VI) from hydrochloric acid medium is further confirmed by carrying out the distribution studies at various aqueous phase chromium (VI) concentrations using ^{36}Cl as radiotracer. (Fig.2) The results of these studies show that a certain amount of chloride is retained in the organic phase in the $(Cr(VI))_{aq}$ concentration range 0.78 - 1.56 g/l at 2.0 M acid. These results confirmed that the species of chromium (VI) extracted into the organic phase are of mixed type predomi-
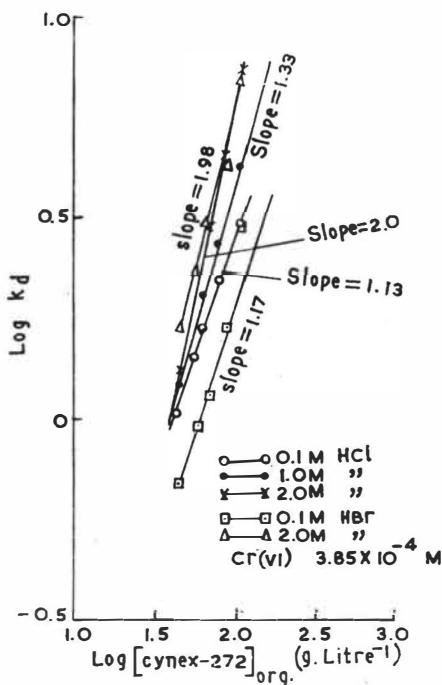
Fig.1. Composition of the extracted
species

339
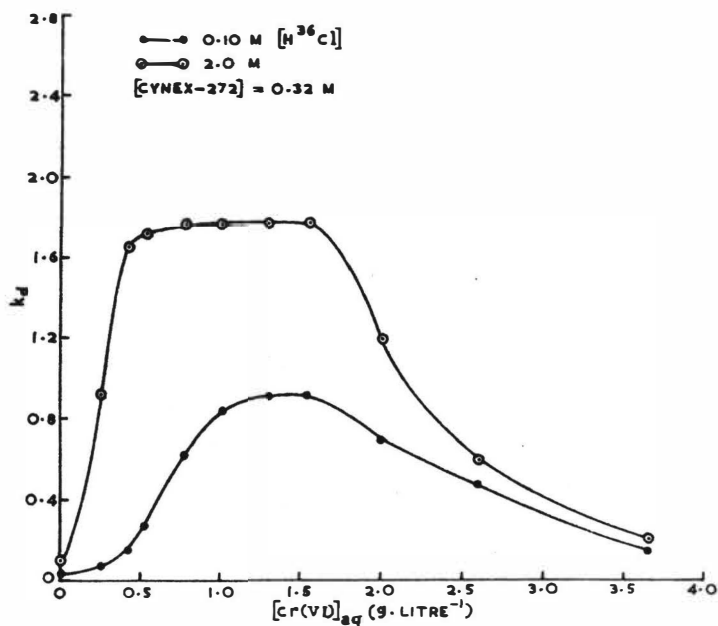
Fig.2. Distribution of chloride as a function of [Cr(VI)]

nantly associated with chromium (VI) and chloride ion. Similar studies have been made using appropriate radiotracers to characterize the extracted species. Further supporting evidence for the nature of extracted species is obtained by ultraviolet and visible spectral data.

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A survey of the literature clearly shows that compounds of general formula:

$$HO - \overset{\overset{O}{\|}}{\underset{\underset{ZO}{/}}{P}} - A - \overset{\overset{O}{\|}}{\underset{\underset{OZ}{\backslash}}{P}} - OH$$ in which A and/or Z represent hydrophobic groups, are

powerful extractants for metals, even from acidic and complexing solutions. These
extractants operate by a cation exchange mechanism and could form very stable six-
membered chelates. They are particularly effective for high charges cations and
have thus often been investigated and proposed for the recovery of U^{4+} from phos-
phoric acid.

So dioctylpyrophosphoric acid (A=O and $Z=C_8H_{17}$) has been used on an industrial
scale (1,2). However the principal disadvantages of the process were solvent de-
composition and impurity of the product.

Diphosphonic esters for which the P-O-P linkage is replaced by C-P bonds,
A= CH_2 (3-5), CH_2-CH_2 (6,7), $CH_2-CH(CH_3)$, $CH=CH-CH_2$, $CH_2-C(=CH_2)$ (7), and Z= C_4H_9
(6,7), C_8H_{17} (3-7), $C_{12}H_{35}$ (7) are quite stable compounds but their synthesis
is rather difficult.

Lately a new class of extractants, the hydroxydiphosphonic acids (A= C(OH)(R)
and Z = H),has been proposed (8). This paper reports the synthesis of these extrac-
tants and the extractive properties of a member of the series: $C_{17}H_{35}C(OH)(PO_3H_2)_2$
named OHDP. A serious drawback is the poor solubility of this extractant and of
the extracted species in the organic diluents. A strategy to design a performing
molecule will be proposed.

SYNTHESIS . For instance OHDP synthesis is relatively easy. It is obtained
by the sequence :

sulfolane, 9 hours at 90°C

12 RCOOH + 8 PCl$_3$ + 10 PO$_3$H$_3$ $\xrightarrow{\hspace{3cm}}$ Mixture of products

Then the mixture undergoes the following reactions :

H$_2$O + HCl conc, 9 hours at 135°C
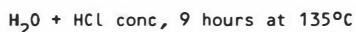
Mixture of products $\xrightarrow{\hspace{3cm}}$ PURIFICATION

This procedure has been also applied to a lot of different carboxylic acids with R as different as: CH_3-, $C_6H_5CH_2-$, $C_6H_5-C_6H_4-CH_2-$, $CH_3(CH_2)_3CH(C_2H_5)-$, $CH_3(CH_2)_{16}-$ etc. To control the purification, the analysis were performed in water-isopropanol mixtures by potentiometry using an automatic titration system (10) ; the diphosphonic acid, phosphorous acid and carboxylic acid contents are obtained by processing of the data.

<u>EXTRACTION PROPERTIES</u> . The extraction of uranium(IV) and some lanthanides (dysprosium(III), europium(III)) by an extractant of this type (OHDP) was studied, the aqueous medium being perchloric acid.

Unfortunately OHDP as well as the extracted species is poorly soluble in all the common diluents (solubility $<$ 10^{-3} mol l^{-1}), so that the presence of a modifier is required. For example the following values were obtained at 25°C (diluent, modifier v/v: solubility in mol l^{-1}) kerosene, octanol 10% : 0.017 ; kerosene, octanol 20% : 0.054 ; kerosene, TBP 10% : 0.04. It should be pointed out that the solubility slowly decreases with time and to avoid any precipitation, the studies were carried out at 50°C and for a diluent composed of dodecane 70% and octanol 30%.

The extraction of each metal was studied versus different parameters : acidity of the aqueous phase (1 to 6 mol l^{-1}), concentration of the metallic cation (2.10^{-4} to 10^{-2} mol l^{-1}), concentration of the extractant (5.10^{-3} to 2.10^{-2} mol l^{-1}).

1) <u>Extraction of uranium(IV)</u> . Whatever was the acidity of the aqueous phase, U^{4+} is quantitatively extracted, provided that the extractant is sufficiently concentrated. To determine this limit, we studied the influence of the metal concentration on its extraction. An example of the distribution curves is presented on the figure 1 for a HClO$_4$ concentration of 4 mol l^{-1}.

The horizontal part of each curve corresponds to the complete saturation of the extractant. In all the cases the ratio OHDP/U is close to 2.
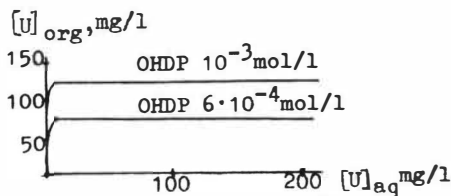
Figure 1. Extraction of U^{4+}

2) <u>Extraction of lanthanides</u> . The distribution curves of Eu^{3+} and Dy^{3+} were drawn for different acidities of the aqueous phase and for different extractant concentrations (figure 2). Eu and Dy behaviour in the same manner. The

342

extraction is depending on the acidity : it is lowered when the acidity is increased. To determine the stoechiometry of the extracted species, we studied the variations of the distribution ratio $\mathcal{D}$ with the concentration of the "free" extractant, i.e. not bound to the metallic cation. For acidities from 2 to 4 mol l^{-1} the slope of the straight line $\log \mathcal{D} = f(\log [ODHP]_{free})$ is close to 3. For 6 mol l^{-1} in $HClO_4$ the slope is equal to 2.5, which suggests another stoechiometry containing ClO_4.
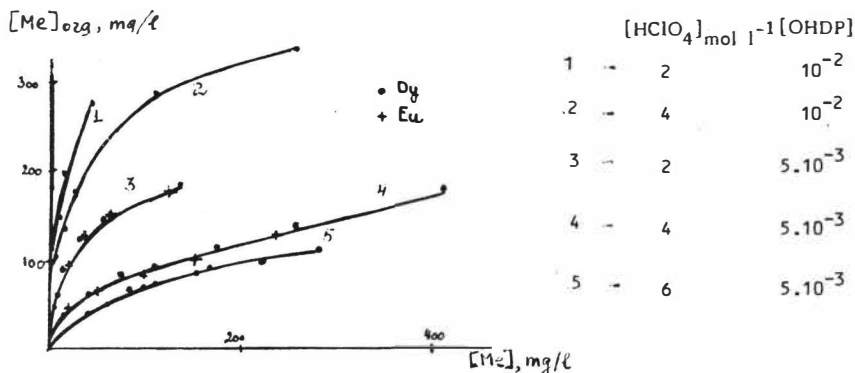
Figure 2 . Extraction of lanthanides

	$[HClO_4]_{mol\ l^{-1}}$	[OHDP]
1 -	2	10^{-2}
.2 -	4	10^{-2}
3 -	2	5.10^{-3}
4 -	4	5.10^{-3}
5 -	6	5.10^{-3}

3) Comparison of the studied cations .   There are some major differences in the extraction of U^{4+} and lanthanides :

. the negative influence of the acidity is not observed for U^{4+} unlike lanthanides

. the reaction is quantitative for U^{4+}, when it is equilibrated for the lanthanides

. the reactions can be written as follows :

$$2\ H_2B\ +\ U^{4+} \longrightarrow UB_2\ +\ 4\ H^+$$

$$3\ H_2B\ +\ Me^{3+} \rightleftarrows Me(HB)_3\ +\ 3\ H^+,$$
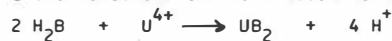
where H_2B is OHDP and Me, Eu or Dy.

In the case of U^{4+}, OHDP is able to exchange two protons per molecule, on the contrary for Me^{3+}, each molecule exchanges only one proton.

In conclusion the affinity of OHDP for U^{4+} is high: the extraction is quantitative even at strong acidity. The lanthanides are less extracted ; OHDP has a smaller affinity for these trivalent cations.

DESIGN OF AN IMPROVED MOLECULE . From these experiments it appears that the hydroxydiphosphonic group exhibits remarkable complex-forming properties but that the introduced $-C_{17}H_{35}$ chain is unable to compensate for its hydrophilic character, leading to a poor solubility in the organic diluents.

343

In order to select an appropriate hydrocarbonated chain R, a systematic study of the partition coefficients and of the solubilities was undertaken, the diluent being a mixture of kerosene and octanol 10%. The requirements to meet are a solubility of 0.5 mol l^{-1} and a partition coefficient greater than 10^3. The partition coefficients P of the synthesised compounds follow the linear relationship of Rekker (11) : log P = constant $+ \Sigma f_n$,

where f_n represents the hydrophobic fragmental constant, the lipophilicity contribution of a fragment (CH_3, CH_2...) of the chain R to the total lipophilicity, the f_n values being tabulated. It is thus easy to select the chain(s) giving P > 10^3.

The changes in the solubility with R cannot be readily rationalized but give information upon the favourable structures for R.

On the basis of these determinations a new R has been chosen and the related molecule synthetized. The results are very promising since the previous requirements are attained and a patent should be taken out. Yet additional work is needed because the starting carboxylic acid, commercialy available, was impure.

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A novel method for extraction from aqueous solution which avoids the
normal mixing energy input is that which uses the consolute point system.
Various compounds such as PEG derivatives have been used in such two-phase
aqueous systems in the past [1] but these immiscible systems still require
a mixing stage.

In order to explore the new system a great variety of solvents exhibiting
consolute behaviour have been reviewed. Here, we report on some glycol
ethers which are cheap and readily available compounds in the chemical
industry.

The typical behaviour of such ethers is shown in Figure 1. An upper and
lower consolute point is seen, it is the
lower point (LCPT) which is presently most
useful especially where the value is near
to ambient.

A variety of solutes have been studied with
one particular glycolether namely n-
butoxyethanol. In Figure 2 we give examples
for the distribution of simple acids and in
Figure 3 simple base type solutes are
explored.
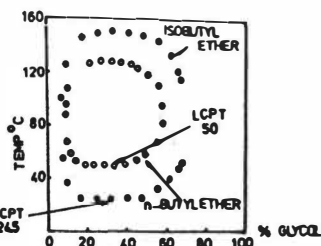
Fig. 1. Phase diagrams for two glycols studied
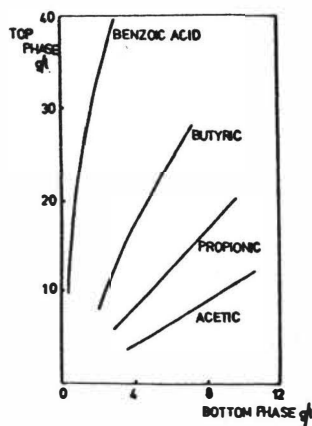
Fig. 2. The 'extraction' of acids by n-butoxyethanol
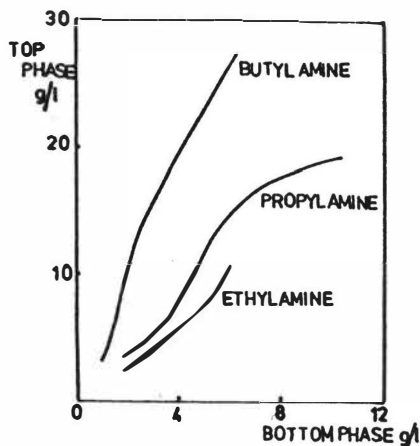
Fig. 3. The 'extraction' of amines by n-butoxyethanol

345

In these last experiments a homogeneous phase is first found at 25°C when thirty mls of aqueous phase (containing the solute) are mixed with twenty mls of the glycol. The homogeneous mixture is then raised to 70°C when two phases form, one is rich in glycol and the other is depleted in glycol. In the particular case of n-butoxyethanol we find the top phase contains about 45% water and the bottom phase is 85% water.

In other experiments we have explored the distribution of metal thiocyanates. Typical distribution plots are given in Figures 4 and 5.
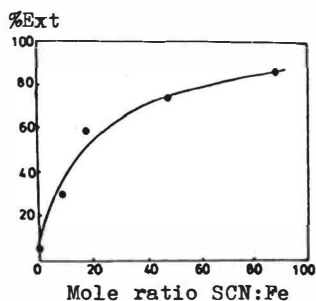
Fig. 4. Effect of varying SCN content on iron III extraction; temperature 70°C, pH 1.7, feed Fe = 0.15 g ℓ^{-1}
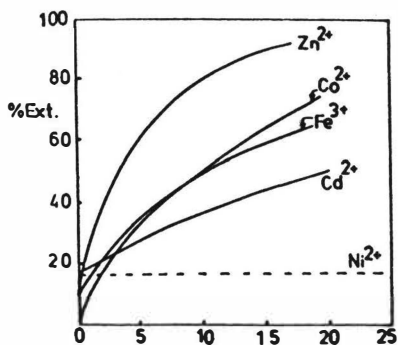
Fig. 5. Comparison of the extraction of various metal thiocyanate complexes; temperature 70°C, pH 1.7, feed metal = 2 g ℓ^{-1}

The species which are distributed are of the neutral thiocyanate complex type i.e. in the case of iron the main species would be H $Fe(SCN)_4$ or $\left[Fe_2(SCN)_3 \right]$. This is confirmed for iron where all the species in equilibria have been analysed in a computer study. The modelling of equilibria was based upon that originally proposed by Rice [2] ; the species distribution is sensitive to pH as is the extraction, see Figures 6 and 7.
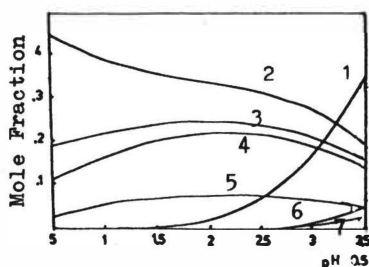
1 - $Fe(OH)^{2+}$; 2 - $Fe(SCN)^{2+}$;
3 - $Fe(SCN)_2^+$; 4 - $Fe(SCN)_3$;
5 - $Fe(SCN)_4^-$; 6 - $Fe(OH)_2^+$;
7 - $Fe(OH)_3$

Fig. 6. Distribution of species according to computer program calculations

346
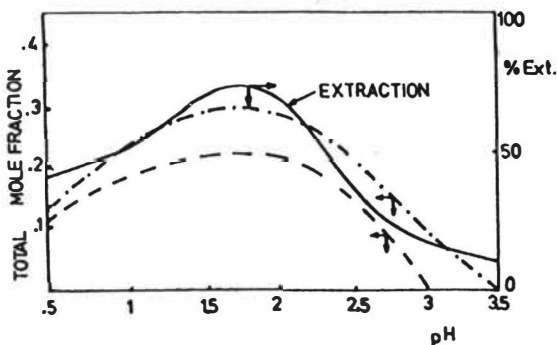
Fig. 7. % extraction of iron III varying with pH, and sum of
neutral species and iron pairs.

$$-\cdot- \left\{ \left[\mathrm{Fe\,(SCN)}_3 \right] - \left[\mathrm{Fe\ OH} \right]^{2-} - \left[\mathrm{Fe\,(OH)}_2 \right]^- - \left[\mathrm{Fe\,(OH)}_3 \right] \right\}$$

$$--- \left\{ \left[\mathrm{Fe\,(SCN)}_3 \right] + \left[\mathrm{Fe\ SCN} \right]_4^- - \left[\mathrm{Fe\ OH} \right]^{2-} - \left[\mathrm{Fe\,(OH)}_2 \right]^- - \left[\mathrm{Fe\,(OH)}_3 \right] \right\} .$$
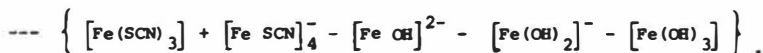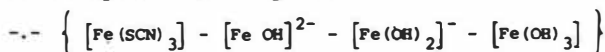
Of course, distribution is reduced as the hydroxide complexes begin to
form at the higher pH values.

This idea has been hardly touched upon by previous workers. In the past
propylene carbonate has received some attention, this is also a relatively
cheap chemical [3,4,5]. Any commercial development of this idea does
require the recovery of the glycol from the aqueous raffinate. However, the
principle of the separation is now being being followed up further in our
laboratories [6].

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Polymers can swell and form gels when they are immersed into an adequate solvent. According to this property, and by choosing solvents commonly used in solvent extraction processes, metal extracting gels can be prepared.

The examples presented here relate to the liquid-gel extraction of precious metals from diluted solutions.

Extraction of gold and silver from alkaline cyanide solutions. The gels were prepared by soaking sheets of cross-linked polybutadiene (0, 1% dicumylperoxide) in a solution of 10^{-2} M dicyclohexyl-18-crown-6 (DC 18C6) crown-ether in $CHCl_3$. The maximum swelling of the polymer (10 ml/g) was reached after a few hours, but a three days time of contact with the DC 18C6 solution was necessary to get an homogeneous distribution of the extractant between the gel and the solution.

The gels thus prepared were then contacted with solutions of 5.10^{-4} M $Au(CN)_2^-$ or $Ag(CN)_2^-$ (100mg/l in Au, 54mg/l in Ag) in 0, 1 M KOH.

The results show that both metals are extracted according to the reaction that takes place in the conventionnal liquid-liquid process, and which is known as :

$$K^+ + \overline{DC\ 18C6} + M(CN)_2^- \rightleftharpoons \overline{(KDC\ 18C6)^+\ M(CN)_2^-} \ .$$
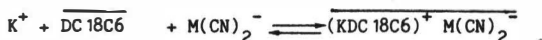
The extraction constants found in the liquid-gel process are similar to those found by liquid-liquid extraction (log K_{Au} = 4,2 and log K_{Ag} = 3,2). The extraction being reversible, the stripping can be achieved by contacting the loaded gels with water.

If the presence of the polymer has no effect on the thermodynamics of the reactions, it nevertheless causes an alteration in their kinetics : a few hours are necessary to reach the equilibria, whereas liquid-liquid extractions take only a few minutes. This phenomenon can be explained by the limitation of the contact surface between the two phases, and by the fact that the solvent is immobilized in the gel, thus increasing the diffusion distance of the extracted species.

Moreover, experiments allowing the determination of the apparent diffusivities of the extracted species have shown that these diffusivities are lower in the gel than in the pure $CHCl_3$ (about four times).

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Extraction of gold from chloride medium. The gels were prepared by soaking pieces of polyvinyl chloride (PVC) tubes in pure tributyl phosphate (TBP) for about 5 hours. The swelling of the PVC then reached $0,8$ ml/g. The gels were then contacted with solutions of $AuCl_4^-$ in $0,5$ M HCl.

Figure 1 shows an example of kinetics measurements of gold extraction, at 25°C.
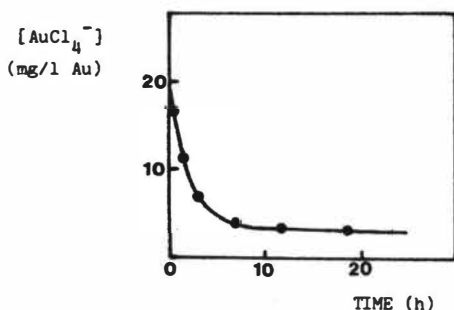
Fig. 1 . Kinetics of extraction of $AuCl_4^-$, by a TBP-PVC gel
(aqueous/gel volume ratio = 960)

The high distribution coefficient of gold in these gels (D_{Au} = 9000) allows extraction at high aqueous/gel volume ratios ($V/\overline{V}_{gel}$), with high yields (84 % at $V/\overline{V}_{gel}$ = 960, for an initial gold concentration of 20 mg/l), and high concentration factors (until 10 % of the gel weight).

It also allows total recovery of the metal from a diluted solution, with a few gels immersed one after another, as shown in Figure 2.
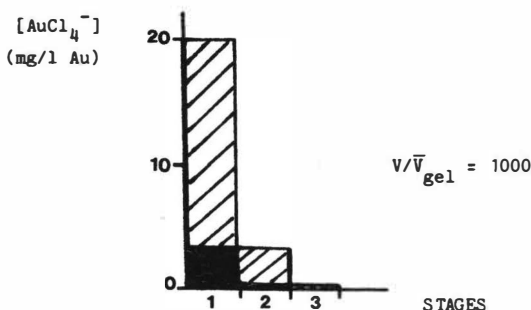
Fig. 2 . Total gold recovery from Cl^- medium, with
3 PVC-TBP gels, immersed one after another

After extraction, the part of the TBP dissolved in the aqueous phase can be recovered by contacting pieces of PVC with the aqueous phase.

349

Extraction of platinum from chloride medium. Attempts have been made in order to prepare a gel containing trioctylamine (TOA). The first trials consisted in soaking a cross-linked butadiene-styrene copolymer in a 0,2 M TOA-toluene solution. The extraction of $PtCl_6^{2-}$ from 0,5 M HCl with this gel was limited by the poor penetration of   TOA in the gel during the swelling of the polymer, and by the loss of solvent at the aqueous phase contact.

Replacing the toluene by chloroform stabilized   TOA in the gel, thanks to the better solvatation of the ammonium salt, but could not avoid the loss of the extracted species.

It seems at the present time that an interesting alternative could consist in inserting an extracting TOA-TBP solution [3] in PVC (work in progress).

Conclusion. Metal extracting gels can be prepared by soaking cheap current polymers (e.g. PVC) in extraction solvents. These gels can extract metals from large volumes of diluted solutions, with large aqueous/gel volume ratios (leading to large concentration effects), and with no problem of phase separation.

Taking into account their simplicity of preparation, their low prices, and their simplicity of use (sheets, beads, in cartridges or columns), these gels could constitue serious rivals for the ion exchange resins, and could find interesting developments as supported liquid membranes.

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CONTENTS