

Acidic Dissociation of Diprotonated Piperazine in Methanol-Water Solvents From 10 to 40 °C

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The first dissociation constant of piperazinium ion has been determined by the emf method in five methanol-water solvents (10 to 70 wt % MeOH) at 25 °C and in three solvents (10, 20, and 50 wt % MeOH) from 10 to 40 °C. From the variation of the dissociation constant with temperature, the changes of enthalpy, entropy, and heat capacity were derived and compared with similar data for piperazinium ion in water. The variation of pK , ΔS° , and ΔC_p° have been used to interpret the effect of the double positive charge on the solute-solvent interactions as compared to the effect exhibited by a single positive or a negative charge.

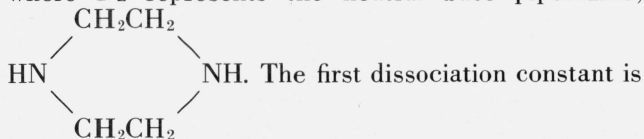
Key words: Dissociation constant; ionization constant; methanol; mixed solvents; piperazine; pK ; thermodynamics.

1. Introduction

The piperazinium ion dissociates in two stages:



where Pz represents the neutral base piperazine,

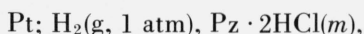


about 25,000 times as large as the second, so the two equilibria can conveniently be studied separately.

In elucidating the role of ionic charge in ion-solvent interactions, the influence of changing solvent composition on an equilibrium such as the first stage in the dissociation of diprotonated piperazinium ion is of unusual interest. Although considerable attention has been devoted to the nature of solvent effects on the dissociation and related thermodynamic behavior of neutral and singly charged acids, it appears that no similar investigation of the dissociation of a doubly charged cation acid has been made. It is the purpose of this paper to report the results of a study of the first dissociation of piperazinium ion in five methanol-water solvents containing 10, 20, 33.4, 50, and 70 wt percent methanol.

2. Method

The $p_s K_1$ of piperazinium ion in methanol-water mixtures was determined by measuring the emf of the cell



where m is molality and X is 10, 20, 33.4, 50, or 70 wt percent. The measurements in 33.4 and 70 wt percent methanol were made at 25 °C and those in 10, 20, and 50 wt percent methanol from 10 to 40 °C.

The $p_s K_1$ was calculated by the equation

$$p_s K_1 = \frac{(E - {}_s E^\circ)F}{RT \ln 10} + \log m_{\text{Cl}^-} + \log \frac{m_{\text{PzH}_2^{2+}}}{m_{\text{PzH}^+}} + \log \left(\frac{\gamma_{\text{PzH}_2^{2+}} \gamma_{\text{Cl}^-}}{\gamma_{\text{PzH}^+}} \right) \quad (1)$$

where ${}_s E^\circ$ is the standard potential of the silver-silver chloride electrode in methanol-water mixtures [1–4].¹

The activity coefficients of each ionic species i was estimated with the aid of the Debye-Hückel equation

$$-\log {}_s \gamma_i = \frac{A \sqrt{I} \sqrt{d_0}}{1 + B a^\circ \sqrt{I} \sqrt{d_0}} \quad (2)$$

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¹ Figures in brackets indicate the literature references at the end of this paper.

where A and B are the constants of the Debye-Hückel theory, dependent only on the temperature and dielectric constant of the solvent, d_0 is the density of the solvent, I is the total ionic strength, and \hat{a} is the ion-size parameter. The values of $A\sqrt{d_0}$ and $B\sqrt{d_0}$ for the solvent mixtures have been given elsewhere [3, 5, 6].

A small correction for the ionization of the PzH_2^{++} ion was made by estimating the molality of hydrogen ion formed with the aid of the approximation

$$-\log m_{\text{H}} = p_s(a_{\text{H}}\gamma_{\text{Cl}}) + \log s(\gamma_{\text{H}}\gamma_{\text{Cl}}) = p_s(a_{\text{H}}\gamma_{\text{Cl}})$$

$$-\frac{2A\sqrt{I}\sqrt{d_0}}{1+B\hat{a}\sqrt{I}\sqrt{d_0}} \quad (3)$$

The acidity function $p_s(a_{\text{H}}\gamma_{\text{Cl}})$ was derived from the experimental data by the equation

$$p_s(a_{\text{H}}\gamma_{\text{Cl}}) = \frac{(E - {}_sE^\circ)F}{RT \ln 10} + \log m_{\text{Cl}^-} \quad (4)$$

TABLE 1. *Electromotive force of the cell: Pt; H₂(g, 1 atm), Piperazine · 2HCl (m), Piperazine · HCl (m), AgCl; Ag in water-methanol mixtures from 10 to 40 °C (in volts)*

m	10°	15°	20°	25°	30°	35°	40°
10 Wt % Methanol							
0.002689	0.66092	0.66031	0.65949	0.65844	0.65713	0.65564	0.65397
.005166	.64872	.64792	.64689	.64563	.64417	.64248	.64058
.007367	.64245	.64155	.64043	.63908	.63751	.63573	.63375
.009903	.63747	.63652	.63532	.63389	.63226	.63041	.62835
.01218	.63415	.63314	.63189	.63041	.62873	.62683	.62473
.01471	.63112	.63006	.62877	.62725	.62553	.62360	.62145
.01746	.62851	.62741	.62608	.62451	.62277	.62078	.61862
.01981	.62653	.62532	.62401	.62244	.62062	.61853	.61644
.02226	.62482	.62366	.62227	.62067	.61885	.61682	.61461
.02463	.62332	.62215	.62073	.61910	.61728	.61524	.61299
.03761	.61742	.61615	.61465	.61293	.61101	.60889	.60658
.04970	.61364	.61230	.61073	.60897	.60700	.60484	.60247
20 Wt % Methanol							
0.003242	0.64453	0.64354	0.64234	0.64090	0.63928	0.63741	0.63545
.006150	.63318	.63203	.63066	.62906	.62727	.62528	.62305
.008753	.62734	.62610	.62465	.62295	.62110	.61904	.61675
.01204	.62226	.62094	.61941	.61766	.61573	.61358	.61122
.01513	.61884	.61748	.61591	.61410	.61211	.60993	.60752
.01781	.61651	.61511	.61350	.61167	.60967	.60745	.60502
.02146	.61382	.61238	.61073	.60886	.60682	.60457	.60210
.02382	.61242	.61096	.60930	.60741	.60536	.60309	.60061
.02714	.61062	.60914	.60745	.60553	.60345	.60117	.59867
.03270	.60812	.60658	.60486	.60292	.60082	.59849	.59597
.04548	.60395	.60237	.60057	.59855	.59641	.59405	.59148
.04863	.60308	.60147	.59967	.59767	.59550	.59312	.59055
50 Wt % Methanol							
0.002483	0.61288	0.61033	0.60773	0.60490	0.60189	0.59882	0.59559
.005169	.60115	.59846	.59568	.59271	.58953	.58618	.58280
.007478	.59609	.59336	.59051	.58747	.58425	.58090	.57746
.009872	.59211	.58933	.58647	.58339	.58015	.57673	.57326
.01198	.58983	.58699	.58407	.58100	.57780	.57439	.57088
.01501	.58688	.58407	.58115	.57803	.57469	.57133	.56784
.01728	.58540	.58258	.57966	.57653	.57325	.56982	.56630
.01996	.58360	.58076	.57781	.57469	.57142	.56795	.56445
.02213	.58262	.57980	.57685	.57371	.57041	.56698	.56344
.02501	.58113	.57826	.57532	.57216	.56888	.56542	.56190
.04988	.57446	.57156	.56857	.56541	.56210	.55864	.55511

The "approximate" dissociation constant $p_sK'_1$ was then defined as follows:

$$p_sK'_1 = \frac{(E - {}_sE^\circ)F}{RT \ln 10} + \log m_{\text{Cl}^-} + \log \frac{m - m_{\text{H}^+}}{m + m_{\text{H}^+}} - \frac{4A\sqrt{I}\sqrt{d_0}}{1+B\hat{a}\sqrt{I}\sqrt{d_0}} = p_sK_1 - \beta I \quad (5)$$

where β is the slope parameter. The $p_sK'_1$ varies linearly with I when the proper value of \hat{a} is chosen; its value at infinite dilution is p_sK_1 . The method of least squares with the OMNITAB computer program was used to calculate the values of p_sK_1 , β , and \hat{a} . The "true" values of p_sK_1 , β , and \hat{a} were assumed to be those which gave the smallest standard deviation of regression.

3. Experimental Procedure

The general experimental procedures closely followed those used previously in methanol-water

system [3] and applied to a determination of the dissociation constants of piperazinium ion in water [7]. The cells used were of the improved type described elsewhere [8].

A stock solution containing equal moles of piperazine mono- and dihydrochloride was prepared by dissolving the required weight of free piperazine in standard aqueous hydrochloric acid. Weight dilutions with additional water and methanol were made to achieve the desired molality and solvent composition.

Methanol (spectro grade) was used as obtained commercially without further purification. Hydrochloric acid for the preparation of solutions was distilled twice and standardized by gravimetric determination of chloride. The piperazine was a portion of the same material used for the study in water [7].

4. Results

The emf data, corrected to 1 atm hydrogen pressure, are summarized in tables 1 and 2. The values of p_sK_1 and a derived from the experimental data are listed in table 3. The estimated uncertainties in p_sK_1 are given in the last column of table 3. They represent two standard deviation limits.

The experimental p_sK_1 values were fitted to the Harned-Robinson equation [9], where T is the thermodynamic temperature,

$$pK = A/T + B + CT \quad (6)$$

by the method of least squares using the OMNITAB computer program. The constants A , B , and C are given in table 4. The residual standard deviation of the fit to the Harned-Robinson equation was less than 0.001 in all three methanol-water mixtures.

5. Thermodynamic Functions

The standard thermodynamic quantities for the acidic dissociation of piperazinium ion in three methanol-water mixtures were calculated by the usual thermodynamic formulas from the constants of eq (6) given in table 4. The values for 10, 25, and 40 °C are listed in table 5. The estimated uncertainties in these values at 25 °C are given in parentheses. They again represent two standard deviation limits as obtained by variance analysis.

6. Discussion

The effect of changing solvent composition on the acidic dissociation constant of diprotonated piperazinium ion and the associated thermodynamic constants for the dissociation process are summarized in table 6. As is the case for singly charged cation acids, enrichment of the solvent with methanol increases the degree of dissociation. Unlike most of the singly charged cation acids, however, the pK of diprotonated piperazinium ion appears not to have reached a minimum at a solvent composition of 70 wt percent methanol.

With the decrease in pK there is a small regular increase in the enthalpy of dissociation. Much more striking, however, are the changes in the entropy and heat capacity of dissociation when the percentage of methanol in the solvent is increased. The entropy change becomes rapidly more positive, while the

TABLE 2. *Electromotive force of the cell: Pt; H₂(g, 1 atm), Piperazine · 2HCl (m), Piperazine · HCl (m), AgCl; Ag in water-methanol mixtures at 25 °C (in volts)*

Wt % Methanol			
33.4		70	
<i>m</i>	<i>E</i>	<i>m</i>	<i>E</i>
0.002375	0.62944	0.002457	0.57070
.004876	.61584	.005206	.56024
.007578	.60842	.009058	.55410
.009933	.60416	.01009	.55289
.01261	.60060	.01241	.55097
.01495	.59817	.01456	.54940
.01762	.59588	.01844	.54744
.02032	.59396	.01976	.54682
.02253	.59255	.02388	.54534
.02516	.59114	.02458	.54508
.03744	.58620	.03653	.54222
.05018	.58279		

TABLE 3. *The first dissociation constant of piperazinium ion in five water-methanol solvent mixtures from 10 to 40 °C*

Wt % Methanol	<i>t</i>	p_sK_1	<i>a</i>	Estimated uncertainty
	°C		(\AA)	
10	10	5.496	3.1	0.001
	15	5.390	3.1	.001
	20	5.288	3.1	.001
	25	5.190	3.2	.001
	30	5.095	3.2	.001
	35	5.002	3.3	.001
	40	4.911	3.3	.001
20	10	5.372	2.8	.001
	15	5.260	2.9	.001
	20	5.152	2.9	.001
	25	5.048	2.9	.001
	30	4.949	3.0	.001
	35	4.851	3.0	.001
	40	4.756	3.1	.001
33.4	25	4.854	3.0	.001
50	10	4.916	2.1	.003
	15	4.798	2.0	.003
	20	4.690	2.1	.003
	25	4.583	2.1	.003
	30	4.481	2.1	.003
	35	4.384	2.1	.003
	40	4.291	2.1	.003
70	25	4.293	0	.005

TABLE 4. Values of the constants for the temperature variation of the dissociation constant

Wt % Methanol	A	B	C
10	1534.587	0.6891	-0.00216628
20	1890.389	-1.5377	.000824178
50	2353.773	-5.0240	.00574370

change in heat capacity, which has a large positive value in the aqueous solvent, decreases sharply, reaching a value of $-66 \text{ J K}^{-1} \text{ mol}^{-1}$ when half of the mass of the water solvent has been replaced by methanol.

The contrary variation of ΔS° and ΔC_p° as the molecular structure of the acid is modified progressively by substitution or as the composition of the solvent is progressively altered has long been observed but is not completely understood. Electrostatic interactions between simple ions and dipolar solvent molecules would be expected to alter the entropy and heat capacity of the system in the same direction. Indeed, orientation of solvent molecules in the neighborhood of the ions should lead to a decrease in both quantities. The fact that methanol is less polar than water is therefore consistent with the observation that ΔS° for the dissociation of diprotonated piperazinium ion increases as methanol is added to the solvent.

Everett and his coworkers [10-12] have suggested that the variation of heat capacity effects in the opposite sense to entropy effects may be caused by "hydrophobic interactions" between neutral molecules and the solvent structure. Although the locus of charge on the monoprotonated piperazinium ion presumably is surrounded by a hydration shell, there remains a considerable length of hydrocarbon chain beyond the influence of the charge. This portion of the structure can interact with the solvent in the same way as a neutral molecule [11]. In the diprotonated ion, however, the two charges at opposite ends of the ring assure, through their cooperative influence, that hydrophobic interactions with the solvent are of little importance.

Solvent effects on the pK of weak acids in methanol-water solvents are strongly dependent on the charge type of the dissociation process [6]. In figure 1, the change in pK , namely $p(sK) - p(wK)$, as methanol is added to the aqueous solvent is plotted for acids of four charge types. These acids are dihydrogen phosphate ion [13, 14], acetic acid [15], ammonium ion [5], and the doubly charged piperazinium cation, PzH_2^{++} . Although some individual variations are to be expected, the strong interactions between bivalent ions and the solvent molecules are reflected in the sign and magnitude of the solvent effect.

TABLE 5. Standard thermodynamic quantities for the acidic dissociation of PzH_2^{++} ion in water-methanol solvent mixtures

Wt % Methanol	t	ΔH°	ΔS°	ΔC_p°
	$^\circ\text{C}$	$\text{J mol}^{-1}{}^\alpha$	$\text{J K}^{-1} \text{ mol}^{-1}{}^\alpha$	$\text{J K}^{-1} \text{ mol}^{-1}{}^\alpha$
10	10	32,706	10.3	23
	25	33,068 (69)	11.5 (0.2)	25 (16)
	40	33,448	12.8	26
20	10	34,928	20.5	-9
	25	34,790 (118)	20.0 (0.4)	-9 (27)
	40	34,645	19.6	-10
50	10	36,248	33.9	-62
	25	35,289 (97)	30.6 (0.3)	-66 (22)
	40	34,281	27.3	-69

${}^\alpha 4.184 \text{ J} = 1 \text{ cal.}$

TABLE 6. Solvent effect on the thermodynamic quantities for the acidic dissociation of PzH_2^{++} ion in water-methanol solvents at 25°C

Wt % Methanol	pK	ΔH°	ΔS°	ΔC_p°
		J mol^{-1}	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{J K}^{-1} \text{ mol}^{-1}$
${}^\alpha 0$	5.333	31,080	2.2	86
10	5.190	33,068	11.5	25
20	5.048	34,790	20.0	-9
33.4	4.854
50	4.583	35,289	30.6	-66
70	4.293

${}^\alpha$ Reference [7].

7. References

- [1] Harned, H. S., and Thomas, H. C., *J. Am. Chem. Soc.* **57**, 1666 (1935); **58**, 761 (1936). The sE° values of Harned and Thomas at 25 °C have been recalculated (see ref. [4]). The sE° values at other temperatures have been corrected in the same ratio.
- [2] Bates, R. G., and Rosenthal, D., *J. Phys. Chem.* **67**, 1088 (1963).
- [3] Paabo, M., Robinson, R. A., and Bates, R. G., *J. Chem. Eng. Data* **9**, 374 (1964).
- [4] Paabo, M., Bates, R. G., and Robinson, R. A., *Anal. Chem.* **37**, 462 (1965).
- [5] Paabo, M., Bates, R. G., and Robinson, R. A., *J. Phys. Chem.* **70**, 247 (1966).
- [6] Bates, R. G., and Robinson, R. A., Acid-base behavior in methanol-water solutions, in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, eds. (John Wiley & Sons, Inc., New York, N.Y., 1966).
- [7] Hetzer, H. B., Robinson, R. A., and Bates, R. G., *J. Phys. Chem.* **72**, 2081 (1968).
- [8] Gary, R., Bates, R. G., and Robinson, R. A., *J. Phys. Chem.* **68**, 1186 (1964).
- [9] Harned, H. S., and Robinson, R. A., *Trans. Faraday Soc.* **36**, 973 (1940).
- [10] Everett, D. H., Landsman, D. A., and Pinsent, B. R. W., *Proc. Roy. Soc. A* **215**, 403 (1952).
- [11] Cox, M. C., Everett, D. H., Landsman, D. A., and Munn, R. J., *J. Chem. Soc. (B)*, 1373 (1968).
- [12] Timimi, B. A., and Everett, D. H., *ibid.*, 1380 (1968).
- [13] Ender, F., Teltschik, W., and Schafer, K., *Z. Elektrochem.* **61**, 775 (1957).
- [14] Paabo, M., Robinson, R. A., and Bates, R. G., *J. Am. Chem. Soc.* **87**, 415 (1965).
- [15] Shedlovsky, T., and Kay, R. L., *J. Phys. Chem.* **60**, 151 (1956).

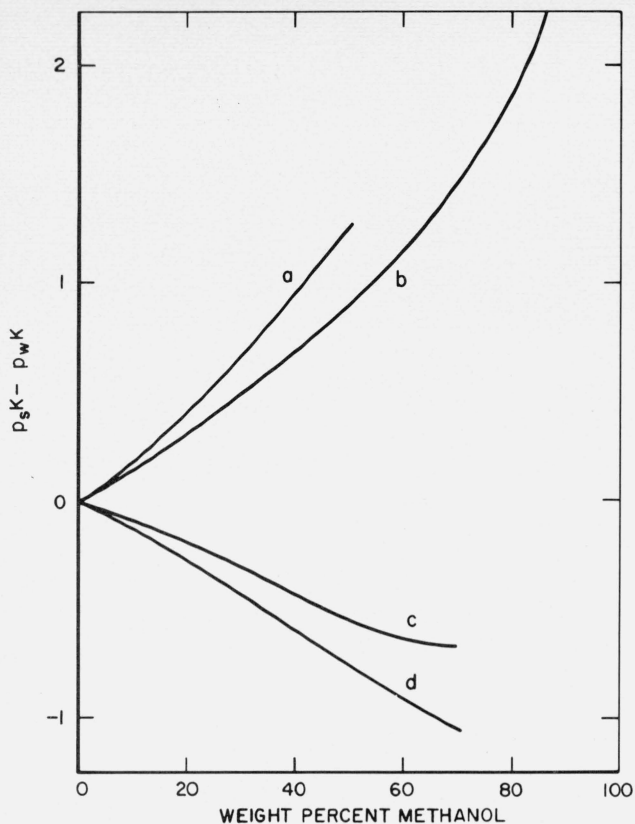


FIGURE 1. Change of pK with solvent composition for weak acids of four different charge types: (a) dihydrogen phosphate ion; (b) acetic acid; (c) ammonium ion; (d) diprotonated piperazinium ion.

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