Concentration of Dairy Flavours using Pervaporation

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Food Technology

at Massey University, Auckland, New Zealand

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2008

Abstract

The food industry could potentially benefit from using pervaporation, a membrane process, to concentrate flavours. This research aimed to investigate its application for concentrating flavours in dairy process streams. Pervaporation experiments were carried out at a range of operating conditions, using hydrophobic membranes. The feed mixtures were either aqueous model solutions of dairy flavour compounds (acids, esters and ketones), complex model mixtures containing flavour compounds plus non-volatile dairy components, or real dairy products.

Flavour compound enrichment factors ranged from below one to above 30, with esters and ketones being concentrated more effectively than acids. Thus, the flavours could be partially fractionated based on their chemical structure. The permeation of acids was reduced by approximately 50% when the feed pH was increased to near their pK_a values.

For flavour compounds with lower molecular weights than approximately 120 g mol^{-1}, permeation was controlled mainly by sorption in the membrane; for larger compounds it was controlled mainly by diffusion through the membrane. The mass transfer of each flavour compound increased with temperature, following an Arrhenius-like relationship. The activation energy was a function of each compound's heat of sorption, its molecular weight, and the elastic modulus of the membrane. The activation energy was also related to the Arrhenius pre-exponential factor. Thus, fluxes could be estimated through empirical correlations.

The non-volatile feed composition was an important factor influencing the pervaporation performance. Milk protein isolate (4% w/v) or lactose (6% or 12% w/v) bound with the flavour compounds in the feed, thus lowering the enrichment of sorption-controlled compounds. Milk fat (up to 38% w/v, in the form of cream) reduced the enrichment of all the flavour compounds tested. Esters and ketones became unavailable for pervaporation as they partitioned into the fat phase; acids remained mainly in the aqueous phase, but their permeation was reduced because the added cream increased the feed pH.

Experiments with real dairy products showed that pervaporation could be used to concentrate diacetyl in starter distillate, and to selectively recover short-chain esters from ester cream. Of these two products, starter distillate is the more promising for use as a pervaporation feed stream.

Acknowledgements

I would like to thank my supervisor, Dr Marie Wong, and co-supervisors Dr John Harrison and Dr Lílian Ferreira, for all their help and encouragement during my PhD. Each of them provided valuable support, and helped me to become a better researcher. I would recommend any of them to future students as examples of excellent supervisors.

Thanks also to the other Fonterra staff who provided useful suggestions and discussion: Dr Vaughan Crow, Dr Ross Holland and Dr Paul Andrewes. I would also like to thank the laboratory staff at Massey and Fonterra, Helen Matthews and Andrew Broome, for helping my laboratory work to go smoothly.

Many long hours were spent in the chemistry laboratory at Massey University, and I thank the various staff, postgraduate students and fourth year students who provided company during that time. I am also grateful for the friendship of other PhD students who understood the ups and downs of the PhD process, particularly Christine Flynn, with whom I shared an office throughout most of my PhD.

Finally I must thank my parents for putting up with me living at home much longer than I should have.

This work was funded by Fonterra Co-operative Group Ltd and the Foundation for Research, Science and Technology (Technology Industry Fellowship programme; contract number FCGL0403). Pervaporation membranes were kindly supplied by GKSS-Forschungszentrum Geesthacht GmbH.

List of publications and presentations

Peer-reviewed publications

Overington, A., Wong, M., Harrison, J., & Ferreira, L. (2008). Concentration of dairy flavour compounds using pervaporation. *International Dairy Journal, 18*(8), 835–848.

Overington, A.R., Wong, M., Harrison, J.A. & Ferreira, L.B. (2009). Estimation of mass transfer rates through hydrophobic pervaporation membranes. *Separation Science and Technology, 44*(4), 787–816.

Conference presentations

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Concentration of dairy flavour compounds using pervaporation*. 5th NIZO Dairy Conference: Prospects for flavour formation and perception. Papendal, The Netherlands, 13–15 June 2007. (Poster and oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Modelling of pervaporation for concentration of flavour compounds*. IMSTEC 07: The 6th International Membrane Science and Technology Conference. Sydney, Australia, 5–9 November 2007. (Oral presentation).

Overington, A.. *Flavour concentration by pervaporation: Effect of feed solution characteristics*. Fonterra Science and Technology Seminar Series. Palmerston North, New Zealand, 12 June 2008. (Oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of feed solution characteristics on flavour concentration by pervaporation*. NZIFST Conference 2008: Food Sustainability. Rotorua, New Zealand, 24–26 June 2008. (Oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of dairy fat on pervaporative flavour compound concentration*. NZIFST Conference 2008: Food Sustainability. Rotorua, New Zealand, 24–26 June 2008. (Poster presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of feed solution characteristics on flavour concentration by pervaporation*. ICOM 2008: International Congress on Membranes and Membrane Processes. Honolulu, Hawaii, USA, 12–18 July 2008. (Oral presentation).

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List of symbols and abbreviations

a	Activity (dimensionless)
a,b,c,d	Empirical constants (Equations (2-22) and (B-10))
A	Membrane area (m^2)
B	Plasticising coefficient
c	Concentration (mol m^{-3})
C	Flux correction factor (dimensionless)
C_i	Coupling factor (dimensionless)
D	Diffusion coefficient (m^2 s^{-1})
df	Driving force (dimensionless)
d_h	Hydraulic diameter (m)
E_a	Activation energy (kJ mol^{-1})
E_D	Activation energy of diffusion (kJ mol^{-1})
f	Frictional force (N)
ΔH	Enthalpy change (kJ mol^{-1})
ΔH_S	Heat of sorption (kJ mol^{-1})
J	Flux (mg m^{-2} s^{-1} or mol m^{-2} s^{-1})
k	Mass transfer coefficient (mol m^{-2} s^{-1})
k'	Mass transfer coefficient (mol m^{-2} s^{-1} Pa^{-1})
k_0	Pre-exponential factor (mol m^{-2} s^{-1})
k_D	Darcy's law coefficient (mol m^{-1} s^{-1} Pa^{-1})
l	Membrane thickness (m)
L	Phenomenological coefficient
L_c	Length of membrane cell (m)
m	Mass (kg)
M	Molecular weight (g mol^{-1})
M_0	Elastic modulus extrapolated to a reference temperature (Pa)
n	Number of runs with one membrane piece
N	Number of carbon atoms
p	Partial pressure (Pa)
P	Permeability (mol m^{-1} s^{-1} Pa^{-1})
Pe	Peclet number (dimensionless)
PI	Production index (mol m^{-2} s^{-1})
PSI	Pervaporation separation index (mol m^{-2} s^{-1})
q	Surface parameter (dimensionless)
r	Volume parameter (dimensionless)
R	Gas constant (8.314 J mol^{-1} K^{-1})
Re	Reynolds number (dimensionless)
S	Sorption coefficient (dimensionless)
S_0	Pre-exponential factor for sorption (dimensionless)
ΔS	Entropy change (kJ mol^{-1} K^{-1})
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
Sl	Slope of J_i versus n (mg m^{-2} s^{-1})
t	Time (s)
T	Temperature (K)

u	Velocity (m s^{-1})
V	Molar volume (m^3 mol^{-1})
w	Mass fraction (dimensionless)
x	Mole fraction (dimensionless)
y	Number of molecules
$y_{intercept}$	y-Intercept of Figure 9-5
z	UNIQUAC coordination number (= 10)

Greek letters

α	Separation factor (dimensionless)
α_{dist}	Relative volatility (dimensionless)
β	Enrichment factor (dimensionless)
γ	Activity coefficient (dimensionless)
δ	Boundary layer thickness (m)
ε	Strain (dimensionless)
ϵ	Empirical constant
η	Viscosity (Pa s)
θ	Empirical constant
Θ	Surface fraction (dimensionless)
λ	Empirical constant
μ	Chemical potential (J mol^{-1})
ρ	Density (kg m^{-3})
σ	Shape factor
ζ	Empirical constant
τ (with subscript)	Binary interaction parameter
τ (no subscript)	Defined by Equation (B-11) (dimensionless)
φ	Volume fraction of particles (dimensionless)
Φ	Volume fraction of mixture component (dimensionless)
χ	Flory-Huggins interaction parameter (dimensionless)
ω	Empirical constant

Superscripts

*	Modified (e.g. to account for hydrogen bonds)
/	In membrane
∞	At infinite dilution
0	At reference conditions

Subscripts

0	Initial or pre-exponential
av	Average for membrane pieces of the same type
avail	Available
between	Between separate membrane pieces of the same type

bl	In feed boundary layer
c	Critical
f	On feed side of membrane
i	Component *i* or membrane piece *i*
int	Intrinsic
j	Component *j*
k	Component *k*
l	Liquid phase
m	In membrane, or referring to membrane polymer
max	Maximum
ov	Overall
p	On permeate side of membrane
s	Solvent
tot	Total
uncorrected	Without applying flux correction factors
v	Vapour phase
w	Water
within	Within one membrane piece

Abbreviations

EPDM	Ethylene-propylene-diene terpolymer
GC	Gas chromatography
GCMS	Gas chromatography-mass spectrometry
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PEBA	Polyether-block-amide
POMS	Polyoctylmethylsiloxane
PTMSP	Poly(1-trimethylsilyl-1-propyne)
SPE	Solid phase extraction
SPME	Solid phase micro-extraction
UNIQUAC	Universal quasi-chemical

Chapter 1

Introduction

Consumers are increasingly moving away from artificially-flavoured foods, preferring to select naturally-flavoured products. As flavour compounds are typically found at low levels in foods, it is not usually feasible to use a complete food as a flavouring ingredient. Instead, flavours are recovered from natural foods, and concentrated for use as flavouring ingredients.

Traditionally, the dairy industry has created flavouring ingredients by using enzymes or fermentation techniques to intensify the flavours naturally present in many dairy products. A well-known example is enzyme-modified cheese, which provides a cheese flavour when used as a food ingredient (Kilcawley et al., 1998). In New Zealand, Fonterra Co-operative Group Ltd produces fermented dairy flavour ingredients for use in other Fonterra products, including enzyme-modified cheese and a fermented enzyme-modified cheese flavour concentrate (Crow et al., 2003). Tatua Co-operative Dairy Company produces lipolysed cream and lipolysed butter oil, which are sold as pastes or powders (Tatua Co-operative Dairy Company, 2004).

Sometimes it is advantageous to separate the flavours from the food matrix. Some methods that the flavour industry currently uses to recover or concentrate flavours include techniques based on extraction, distillation, partial condensation and gas stripping (Karlsson & Trägårdh, 1997; Quirin & Gerard, 1998; Ziegler & Ziegler, 1998a; Ziegler & Ziegler, 1998b). Recently, attention has turned to pervaporation, a membrane separation process, as an alternative concentration method. In hydrophobic pervaporation, volatile hydrophobic compounds, such as flavours, pass through the polymeric membrane more readily than water, and are thereby concentrated in the permeate (Lipnizki et al., 1999). Pervaporation has several advantages over other flavour recovery techniques: no additives are necessary, energy usage is comparatively low, the product remains natural, and low to moderate operating temperatures mean that thermal degradation either does not

occur or is minimised (Karlsson & Trägårdh, 1997; Lipnizki et al., 1999; Willemsen et al., 2004).

Pervaporation has been used in the chemical industry since the 1980s, to remove water from solvents (Néel, 1991; Jonquières et al., 2002). Its potential for flavour recovery has been identified by a large number of researchers (reviewed by Karlsson & Trägårdh, 1993, 1996; Baudot & Marin, 1997; Pereira et al., 2006), but the food industry has only just begun to use pervaporation for flavour recovery on a commercial basis (Willemsen, 2005). One reason for the slow uptake by food and flavour manufacturers is that it is difficult to predict pervaporation performance. Published results of pervaporation research vary widely because of differences in the membranes, the operating conditions, the pervaporation unit and the feed solution.

When the feed solution contains more than one flavour compound, it is possible for the various compounds to interact during pervaporation (Kedem, 1989; Karlsson & Trägårdh, 1993). The situation potentially becomes more complex if the feed mixture contains other components apart from flavour compounds and water. For example, most dairy products contain fat, protein and lactose; these non-volatile components do not pass through pervaporation membranes, but they could nevertheless interact with flavour compounds and affect their pervaporation behaviour.

Simple model feed solutions therefore provide the best method to study the pervaporation process without any complicating factors, but results with real feed mixtures do not always match those with model feeds (Souchon et al., 2002; Kanani et al., 2003). Real feed mixtures are best to evaluate pervaporation for a particular application, but the results obtained apply only to the feed mixture tested and cannot be extrapolated to other applications. In order to link these two extremes and reduce the need to test each feed mixture individually, there is a need for more research to understand how, or if, the characteristics of the feed mixture affect the pervaporation of flavours.

The aim of this study was to investigate pervaporation as a means of concentrating flavour compounds in selected dairy process streams. Experiments were designed to understand the effect of each operating parameter, and each

aspect of the feed mixture, on the pervaporation of flavour compounds. The majority of the study focussed on model dairy flavour compounds: organic acids, esters and ketones. Compounds from these three functional groups contribute to the flavour of cheese and other dairy products (Urbach, 1997a; Keen, 1998). Pervaporation of the model flavour compounds was investigated using various feed mixtures of relevance to dairy processing.

The specific objectives of this study were as follows:

- To compare the pervaporation behaviour of a range of dairy flavour compounds in a model feed solution, in order to determine the influence of functional group and molecular weight on flux and selectivity.
- To determine how the operating conditions affected the pervaporation of each flavour compound, in an aqueous feed solution and with the addition of dairy fat.
- To determine how the pervaporation of each flavour compound was influenced by the feed mixture, including the feed pH, the presence of other volatile compounds, and the presence of non-volatile dairy components.
- To use pervaporation to concentrate or fractionate flavours in real dairy process streams.
- To develop an empirical model to predict the pervaporation fluxes of dairy flavour compounds.

Chapter 2

Literature review

Dairy flavours are generally complex mixtures of flavour compounds. Despite several decades of study, the flavours of many dairy products have not been completely characterised (Nursten, 1997; McSweeney & Sousa, 2000). For this reason, dairy flavours are difficult to reproduce artificially; this fact has led researchers to focus instead on recovery and concentration of natural dairy flavours (Sibeijn et al., 2004). Traditional methods for achieving this goal include distillation, evaporation, gas stripping and solvent extraction (Karlsson & Trägårdh, 1997). A potential new method is pervaporation, a membrane separation process. This literature review provides an overview of dairy flavour chemistry, including methods for flavour recovery and concentration, followed by a summary of the current knowledge of pervaporation as applied to flavour concentration.

2.1 Chemistry of dairy flavours

Flavour is defined as the entire sensory experience when a food is eaten, including taste, aroma, sight, feeling and sound. Within this grouping, flavour chemistry is usually restricted to those compounds that contribute to either the taste or aroma of a food (Hansen & Booker, 1996; Lindsay, 1996; Nursten, 1997). Aroma compounds are usually volatile, and only very small amounts are needed to have an impact (Hansen & Booker, 1996). For example, some of the sulphur compounds found in cheese can be detected by humans at less than 10 parts per billion (Molimard & Spinnler, 1996). The overall flavour of a food is made up of a mixture of many flavour compounds; some have a greater influence than others, and in some cases one characteristic flavour compound dominates all others (Hansen & Booker, 1996). It is generally accepted that flavours of many dairy products depend on a mixture of flavour compounds being present in the right proportions (the component balance theory), rather than having one characteristic flavour compound (Badings & Neeter, 1980; McSweeney & Sousa, 2000;

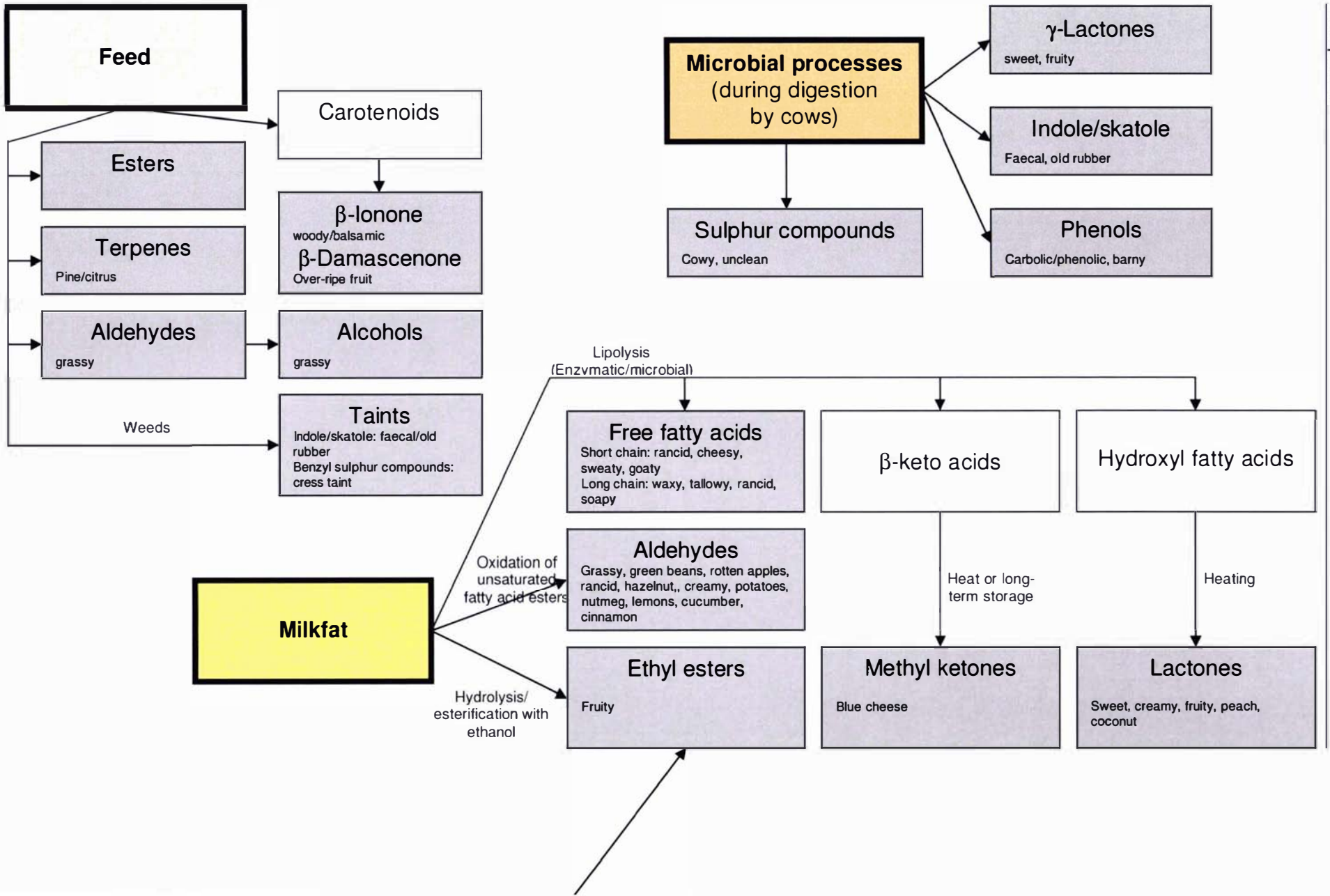
Zehentbauer & Reineccius, 2002). However, some researchers suggest that characteristic flavour compounds may exist for these products, but current techniques do not allow them to be isolated or identified yet (Lindsay, 1996; Urbach, 1997b).

Figure 2-1 presents an overview of the formation of the main flavour compounds found in dairy products. These compounds originate either in the raw milk or from degradation of the main constituents of milk (fat, protein and lactose). The particular flavour of each product depends on which of the degradation pathways in Figure 2-1 is dominant. Several reviews discuss the reactions in Figure 2-1 in more detail (Fox & Wallace, 1997; Keen, 1998; McSweeney & Sousa, 2000).

Unfermented dairy products, such as milk and cream, have a bland flavour. Aroma compounds in fresh milk originate from the cows' feed and from microbial processes during digestion (Nursten, 1997; Keen, 1998), but they are mostly present below threshold levels (Badings & Neeter, 1980). The perceived flavour of milk is therefore mostly due to basic tastes (a sweet taste from lactose and a salty taste from salts) and mouthfeel (Badings & Neeter, 1980; Heath, 1983; Nursten, 1997). Mouthfeel has relatively more impact on flavour in bland products such as milk (Goulden, 1970).

The main difference between milk, cream and butter is their fat levels. Flavour contributions from the fat globule membrane and in the fat itself therefore become more important for higher-fat products. Compounds in the aqueous phase still contribute to the flavour of cream, but butter flavour is mainly due to fat-soluble compounds (Badings & Neeter, 1980; Mallia et al., 2008).

Cultured milks and yoghurt have a stronger flavour than fresh milk, because lactose is fermented during the production process, creating lactic acid, diacetyl and acetaldehyde (Nursten, 1997). Diacetyl and acetaldehyde are also responsible for the flavour of unripened cheese, due to fermentation of lactose by the starter bacteria (Urbach, 1997a). The stronger, more complex flavours of ripened dairy products, such as most cheeses, are caused by the activity of enzymes and secondary microflora, as well as the starter culture (Urbach, 1997a). These microorganisms and enzymes break down milk fat, lactose and protein, to produce a wide variety of flavour compounds. Compounds derived from the degradation of


Feed
Carotenoids
Esters
β-Ionone
woody/balsamic
β-Damascenone
Over-ripe fruit
Terpenes
Pine/citrus
Aldehydes
grassy
Alcohols
grassy
Weeds
Taints
Indole/skatole: faecal/old rubber
Benzyl sulphur compounds: cress taint
Microbial processes (during digestion by cows)
γ-Lactones
sweet, fruity
Indole/skatole
Faecal, old rubber
Sulphur compounds
Cowy, unclean
Phenols
Carbolic/phenolic, barny
Lipolysis (Enzymatic/microbial)
Free fatty acids
Short chain: rancid, cheesy, sweaty, goaty
Long chain: waxy, tallowy, rancid, soapy
β-keto acids
Hydroxyl fatty acids
Milkfat
Oxidation of unsaturated fatty acid esters
Aldehydes
Grassy, green beans, rotten apples, rancid, hazelnut,, creamy, potatoes, nutmeg, lemons, cucumber, cinnamon
Heat or long-term storage
Heating
Hydrolysis/ esterification with ethanol
Ethyl esters
Fruity
Methyl ketones
Blue cheese
Lactones
Sweet, creamy, fruity, peach, coconut

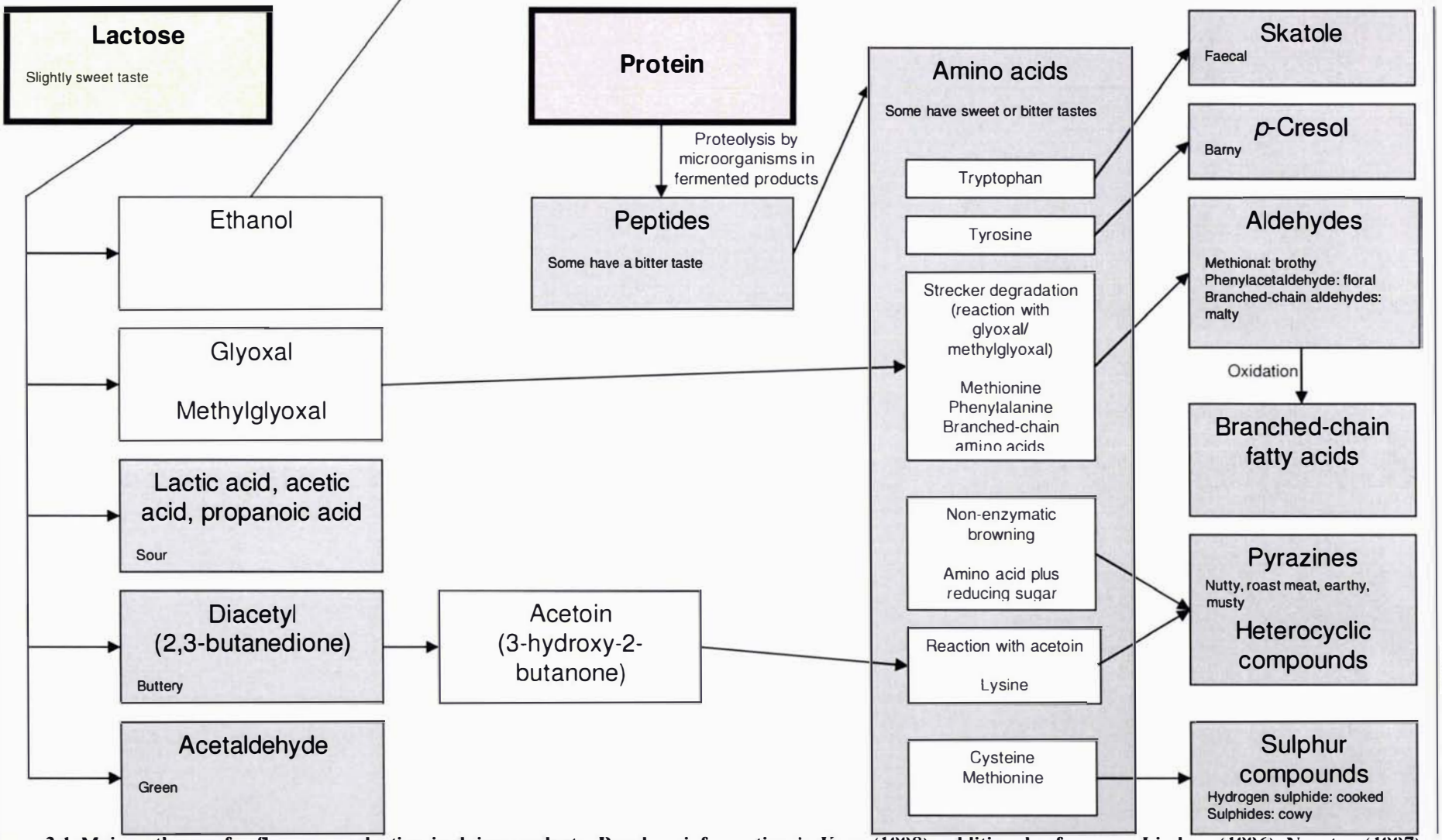


Figure 2-1: Main pathways for flavour production in dairy products. Based on information in Keen (1998); additional references: Lindsay (1996), Nursten (1997), McSweeney & Sousa (2000).

casein (the main protein in cheese) are the main contributors to the flavour of most cheeses, but fat-derived compounds are important in creating the flavour of mould-ripened cheeses (Schormüller, 1968; Smit et al., 2002).

Apart from the desired flavour, dairy products are also susceptible to off-flavours. These can originate from taints in the cows' feed, uncontrolled hydrolysis of fat to produce free fatty acids, or uncontrolled oxidation of fatty acids (Keen, 1998; Mallia et al., 2008). Consumers can easily detect off-flavours because milk is so bland (Goulden, 1970; Nursten, 1997). Raw cream is therefore usually treated to remove any strong flavours resulting from the cows' feed. In New Zealand, this is usually achieved with a Flavourtech spinning cone column, which will be described in Section 2.2.2 (FT Technologies, 2006).

2.2 Recovery and concentration of dairy flavours

Because such a wide variety of flavours can be produced by fermenting dairy substrates, many flavouring ingredients are dairy-derived. For example, snacks, sauces, dressings, baked goods and confectionary may all use dairy-derived flavours (Sibeijn et al., 2004). However, it is uncommon to add dairy products straight into a food for the purpose of flavouring, because a large amount would need to be added to achieve a strong enough flavour. This can alter the balance of fat, protein and lactose in the final product, as well as being expensive (Kilcawley et al., 1998). It is therefore preferable to use a highly concentrated flavouring ingredient at low dosage rates. These ingredients may be created via several methods: blending chemicals to produce an artificial flavour (Reineccius, 2006), creating stronger flavours by modifying the dairy substrate (Eaton, 1994; Kilcawley et al., 1998; Reineccius, 2006), or using separation processes to recover and concentrate the flavours already present in the dairy substrate (Sibeijn et al., 2004).

The flavour of artificial blends can be precisely controlled (Reineccius, 2006), but this method has some drawbacks when used for dairy flavours. As mentioned in the previous section, dairy flavours tend to be very complex, which makes it difficult and expensive to artificially create an authentic dairy flavour (Eaton, 1994; Kilcawley et al., 1998; Sibeijn et al., 2004). Consumers also tend to avoid

artificially-flavoured products (Eaton, 1994; Reineccius, 2006). Hence, it is preferable to create natural flavours from dairy ingredients.

To obtain a natural flavouring ingredient, intense flavours can be created in a dairy substrate by accelerating the flavour-forming reactions in Figure 2-1. Enzyme-modified cheese is one flavouring ingredient that uses this technology. This product is manufactured by incubating cheese with enzymes and/or microorganisms, which break down protein and fat to create flavour compounds (Kilcawley et al., 1998). When enzyme-modified cheese is used as a flavouring ingredient, the normal usage rate is a few percent or less, as the flavour is usually between five and 25 times as intense as in regular cheese (Moskowitz & Noelck, 1987).

Alternatively, a concentrated flavouring ingredient can be produced by concentrating the flavours already present in a dairy substrate. Flavours can be concentrated either by removing water (thus concentrating both the flavours and the other components of the food) or by using separation techniques to remove the flavour compounds from the food. Separation techniques split a mixture into two phases, using either temperature-based separation (some components are removed as solids or vapour, while others remain liquid), extraction (some components move from one solvent phase to another) or membrane separation (some components pass through a semi-permeable membrane, while others cannot permeate). The following subsections describe some methods for flavour recovery and concentration.

2.2.1 Flavour concentration by removing water

The concentration processes described in this section rely on removing water to create a concentrated flavour in the original matrix. As these processes are not strictly flavour recovery methods, they will be described here only briefly.

2.2.1.1 Freeze concentration

Freeze concentration has mainly been studied as a means of concentrating fruit juices. The process involves removing the water in a solution as ice crystals, so that the remaining components are concentrated. Like other processes that operate at low temperatures, freeze concentration requires little energy and does not

thermally damage the product (Mannheim & Passy, 1975; Ramteke et al., 1993). However, its major disadvantage is the limit to the concentrations that can be achieved. As the mixture becomes more concentrated, the freezing point is depressed and viscosity increases, making it more difficult to remove ice crystals and freeze further (Husain & Lai, 1987; Ramteke et al., 1993). Freeze concentration can concentrate juices to about 40–55% dry matter (Ramteke et al., 1993); starting with a typical juice with 10% solids (Thijssen, 1970), this represents only a four- to five-fold concentration.

Thijssen (1970) noted that any insoluble materials present in fruit juice would be removed along with the ice. The same restriction would be true for fat-containing products — both fat and water would crystallise out during freeze concentration. Many flavour compounds associate with the fat phase in a fat/water mixture (de Roos, 1997), so may also be removed during freeze concentration.

2.2.1.2 Reverse osmosis

Reverse osmosis is a pressure-driven membrane process, in which water and some low molecular weight solutes permeate through the membrane, but most solutes remain in the retentate (Pozderović & Moslavac, 1999; Walstra et al., 2006). Reverse osmosis is already used in the dairy industry, although its purpose is usually to concentrate whey or other products prior to spray drying, rather than to concentrate flavours (Walstra et al., 2006).

Pozderović & Moslavac (1999) used reverse osmosis to concentrate apple juice aroma from evaporator condensate. When 70% of the water was removed, 67–78% of the aroma remained in the retentate; hence the aroma was concentrated by a factor of 2.3–2.6. Their results reflect earlier work by Matsuura et al. (1975), who concentrated apple juice aroma by a factor of 1.65–2.22 using reverse osmosis. Similarly, Kane et al. (1995) concentrated lemon aroma compounds by a factor of 1.8–2.9 using reverse osmosis. Sensory tests confirmed that there was no detectable difference between the original lemon aroma and the concentrate after reverse osmosis, when both were diluted to the same strength.

Low temperatures and high pressures are the most effective operating conditions for aroma concentration using reverse osmosis (Matsuura et al., 1975; Kane et al., 1995; Pozderović & Moslavac, 1999). However, Walstra et al. (2006) cautioned

that lactose could crystallise at low operating temperatures, meaning that reverse osmosis may be more effective for concentrating flavours in aqueous process streams than in dairy products.

2.2.2 Recovery of flavour compounds

Freeze concentration and reverse osmosis tend not to achieve particularly high concentration factors, as noted in the previous section. To achieve a greater concentration factor, the volatile flavour compounds can be separated from the food matrix using one of the techniques described below.

All of the following methods are selective to some degree; that is, some flavour compounds are concentrated more effectively than others. Depending on the separation method, selectivity may be based on differences in the volatility of each flavour compound, or on differences in the affinity of each flavour compound for a solvent, adsorbent or membrane.

2.2.2.1 Distillation-based methods

Distillation is a common flavour recovery method in the food industry (Karlsson & Trägårdh, 1997; Ziegler & Ziegler, 1998a). It involves boiling a liquid mixture and condensing the vapour in different fractions, depending on the boiling points of the components of each fraction (Ziegler & Ziegler, 1998a). Feed components are thus separated based on their relative volatilities. If one component is much more volatile than the others (that is, if the vapour composition is very different from the liquid composition), then the volatile component will be easily separated using distillation (Treybal, 1980). In other words, good candidates for flavour recovery by distillation are food products in which all the important flavour compounds are more volatile than water, and have similar volatilities to each other. Various flavour compounds have relative volatilities ranging from less than one to more than 500 compared with water (Thijssen, 1970), meaning that a flavour mix concentrated by distillation is unlikely to have exactly the same composition as the unconcentrated flavour mix.

The relative volatility of two components, α_{dist}, is given by the following equation (Treybal, 1980):

$$\alpha_{\text{dist}} = \frac{x_{i,v}/(1-x_{i,v})}{x_{i,l}/(1-x_{i,l})} = \frac{x_{i,v}(1-x_{i,l})}{x_{i,l}(1-x_{i,v})} \quad \textbf{(2-1)}$$

where $x_{i,l}$ is the mole fraction of the more volatile compound in the liquid phase, and $x_{i,v}$ is the equilibrium mole fraction of the more volatile compound in the vapour phase. Equation (2-1) shows that the relative volatility is given by the relative amounts of two components in the vapour, divided by their relative amounts in the liquid. The relative volatility can also be seen in a phase diagram (Figure 2-2), in which the relative volatility refers to the distance between the bubble point (temperature versus liquid composition) and dew point (temperature versus vapour composition) curves (Treybal, 1980). From Figure 2-2, it can be seen that at a given temperature, the mole fraction of the more volatile component in the vapour will be greater than its mole fraction in the liquid. Hence, the two components can be separated by distillation.

Compounds with a relative volatility close to one (compared with water) cannot be recovered using distillation (Thijssen, 1970). This means that some low-volatility flavour compounds may not be recovered. For example, acetic acid has a relative volatility of 0.73 compared with water (Thijssen, 1970). Distillation also

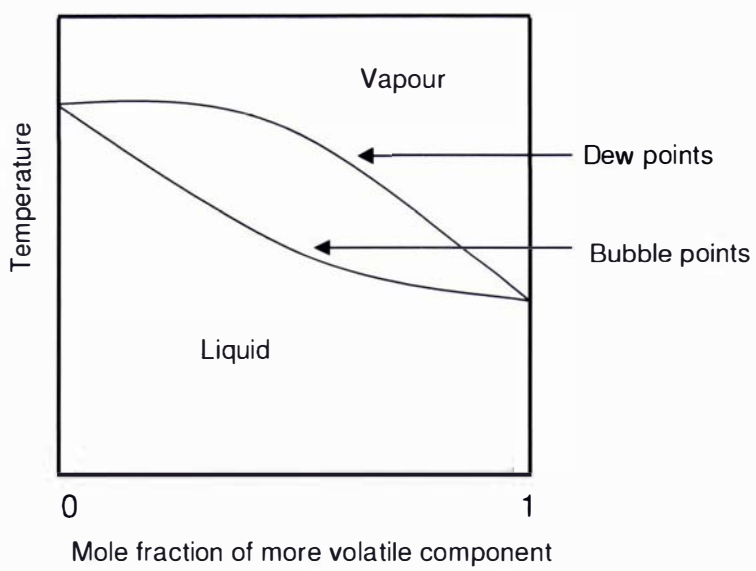


Figure 2-2: Constant-pressure phase diagram for a two-component system (adapted from Treybal, 1980; Karlsson & Trägårdh, 1997).

cannot achieve a complete separation in situations where an azeotropic mixture is formed, for example in the separation of ethanol and water (Treybal, 1980). To break the azeotrope, distillation can be combined with another separation technique.

In the food industry, high temperatures may damage flavours during distillation. This thermal damage can be avoided by carrying out distillation at a reduced pressure, which enables the mixture to boil at a lower temperature (Karlsson & Trägårdh, 1997; Ziegler & Ziegler, 1998a). However, lowering the pressure can result in flavour compounds being lost with the vent gases (Ribeiro et al., 2004).

Distillation has the advantage of being a well-established, well-understood technique. Its major limitations are thermal damage and its high energy use, as energy must be supplied to overcome the latent heat of evaporation (Ziegler & Ziegler, 1998a).

A related technique is the single-stage process of flash vaporisation. The liquid feed is partially vaporised by heating it and reducing the pressure, then the vapour and liquid phases are separated after reaching equilibrium (Treybal, 1980). As long as the relative volatility (Equation (2-1)) is not equal to one, the vapour and liquid phases will have different compositions. Similarly, the flash vaporisation process may be reversed, with a vapour instead of liquid feed, to produce partial condensation (Treybal, 1980).

In partial condensation, a mixed vapour is condensed into several fractions by two or more condensers in series, working at different temperatures (Karlsson & Trägårdh, 1997). Most of the water vapour is retained in the initial condenser, while the majority of aroma compounds pass this stage and are collected in a later condenser. Baudot & Marin (1999) combined pervaporation with partial condensation, for concentrating ethyl acetate. They condensed the pervaporation permeate vapour in two stages: the first condenser, set between 10 and −10°C, condensed most of the water in the permeate, and the second condenser, at −70°C, collected the majority of the ethyl acetate. In this way, they were able to achieve a concentration up to four times better than pervaporation alone.

2.2.2.2 Gas stripping

Gas stripping involves contacting a flavour-containing feed liquid with steam or an inert gas, so that volatile flavour compounds are transferred from the feed to the gas, to be separated in a condenser or wet scrubber (Karlsson & Trägårdh, 1997). A good contact between the liquid and the gas is needed, so the process may be carried out in a distillation column, packed tower, sparged aerator or bubble column (Karlsson & Trägårdh, 1997; Ribeiro et al., 2004). An alternative design is a spinning cone column. Inside a spinning cone column there is a series of inverted cones, half of which are fixed and half of which are rotating. The feed is passed into the top of the column onto the first spinning cone, and is spun out in a thin film over the edge of the spinning cone onto a fixed cone below, as shown in Figure 2-3 (Flavourtech Ltd, no date). The feed slides down the fixed cone and onto the next spinning cone, thus working its way down the column. Simultaneously, steam or an inert gas enters the bottom of the column and works its way up, so that volatiles are transferred from the feed to the stripping gas (Pyle, 1994; Anon., 2004).

Spinning cone columns are used in the dairy industry to deodorise cream (FT Technologies, 2006). They are therefore useful in principle for separating flavour compounds from dairy products.

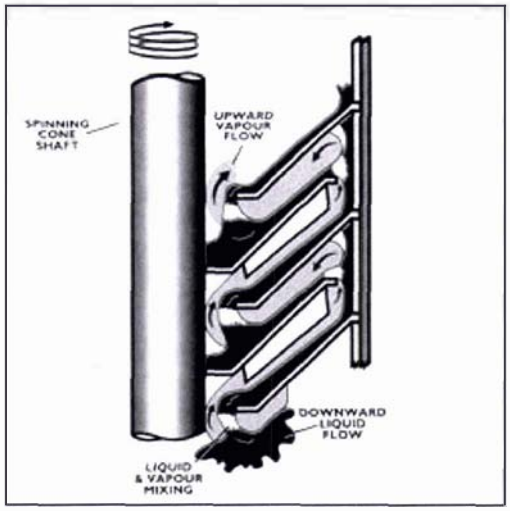


Figure 2-3: Diagram of Flavourtech spinning cone column (Flavourtech Ltd, no date).

2.2.2.3 Solvent extraction

Flavours may be extracted from either a solid or liquid substrate, into a solvent which readily dissolves the flavour compounds but not other components of the mixture (Karlsson & Trägårdh, 1997; Ziegler & Ziegler, 1998b). Solvent extraction is better than distillation in situations where a water-free aroma extract is needed (Schultz & Randall, 1970). However, this flavour recovery technique has several drawbacks. Many solvents are able to extract flavours, but these often have boiling points close to those of the aroma compounds, so that it is difficult to separate the solvent from the aroma concentrate (Schultz & Randall, 1970). Solvent extraction is also not very selective compared to some other separation processes, which can cause the extract to have an unsatisfactory flavour (Pierre et al., 2001; Kattenberg & Willemsen, 2002). As many solvents are unsuitable for food grade use, liquid solvent extraction is uncommon in food processing (Karlsson & Trägårdh, 1997).

To overcome this disadvantage, a supercritical fluid may be used instead of a liquid solvent. Dissolved compounds are easily recovered by lowering the density of the supercritical fluid (which reduces its solvent capacity); this can be achieved by lowering the pressure or increasing the temperature (Palmer & Ting, 1995). Carbon dioxide is almost always used as the supercritical fluid, as it is a good solvent, as well as being inexpensive, with no major safety issues (Palmer & Ting, 1995; Quirin & Gerard, 1998). However, supercritical fluid extraction is costly, and has the disadvantage that fat is also extracted along with the aromas (Kattenberg & Willemsen, 2002).

Schultz and Randall (1970) used liquid, rather than supercritical, carbon dioxide to extract flavour compounds from pear, apple and orange juices, ground coffee and orange pieces. They found similar volatile profiles in both the raw material and the aroma extract, although compounds with longer gas chromatography retention times (greater than 10 minutes) were extracted more efficiently. Carbon dioxide is selective towards lipophilic compounds (Quirin & Gerard, 1998), which would often have longer retention times.

An alternative to supercritical fluid extraction, which also has some advantages over traditional liquid extraction, is solvent extraction using a membrane

contactor as an interface between the feed and the solvent. This technique has the advantage that the two phases do not mix, so no agitation is necessary, emulsification does not occur and both liquids can have the same density (Pierre et al., 2001). Pierre et al. (2001) used membrane-based solvent extraction to recover the aroma compounds dimethyl disulphide, dimethyl trisulphide and methylthiobutanoate from aqueous solutions. Membrane-based solvent extraction achieved a higher flux than pervaporation for the three compounds tested, but was less selective.

2.2.2.4 Adsorption

Flavour recovery by adsorption involves passing the feed liquid through a column filled with adsorbent material. Flavour volatiles adsorb to the material and the remainder of the feed passes through. Volatiles can then be removed from the sorbent by washing with a liquid or gas, or altering the pressure or temperature so that the sorption capacity is reduced (Karlsson & Trägårdh, 1997).

Parliment (1981) used an adsorbent (C18 reverse-phase Hi-Flosil, consisting of octadecyl groups bonded to a silica gel backbone) to recover flavour compounds from various systems. Flavour compounds were desorbed using a solvent which was gradually changed from water to acetone. In this way, flavours were fractionated; compounds with a low molecular weight and high polarity eluted first (while the solvent was mostly water) and compounds with a high molecular weight or low polarity eluted last (while the solvent was mostly organic).

Krings et al. (1993) tested 31 different adsorbents for removing 12 aroma compounds from a model solution. Activated carbon was the best adsorbent, but using this material it is difficult to desorb compounds using organic solvents (Krings et al., 1993). Styrene-divinylbenzene resins and zeolite showed good adsorption as well as desorption. Most materials had non-specific adsorption, but an exception was β-cyclodextrin which adsorbed only some of the compounds in the model solution (Krings et al., 1993).

More recently, Edris et al. (2003) used activated carbon adsorption to recover aroma compounds from an aqueous waste stream produced during essential oil manufacture. Between 40% and 90% of each compound was recovered from the waste stream onto the carbon.

Adsorption is not commonly used in the food industry, mainly because of difficulties desorbing flavour compounds from the adsorbent in a way that is acceptable in food processing (Karlsson & Trägårdh, 1997).

2.2.2.5 Pervaporation

Pervaporation is a membrane process in which components of the liquid feed are selectively transported through a non-porous membrane into a vapour phase on the permeate side of the membrane (Néel, 1991; Börjesson et al., 1996; She & Hwang, 2004).

The first industrial-scale pervaporation plants were built in Europe in 1982 (Mulder, 1996). Their purpose was to dehydrate organic solvents, which remains the main industrial application of pervaporation today (Jonquières et al., 2002; Schäfer & Crespo, 2003). In recent years, pervaporation has attracted interest as a potential technique for flavour recovery and concentration. A juice processing plant in The Netherlands recently began using pervaporation to recover flavours lost during processing (Willemsen, 2005).

Despite a large volume of literature on pervaporation for aroma recovery, only one food processing company is publicly known to have an industrial-scale pervaporation plant in operation for this purpose. Food companies are slow to adopt pervaporation because it is a new technique with relatively little industrial information; for example, the membrane performance over time under process conditions is unknown, the sensory profile of the permeate has not been studied for many applications, there are few pilot-scale facilities worldwide, and commercial membranes are expensive and difficult to source (Kanani et al., 2003; Willemsen, 2005).

Pervaporation has the advantage that it can be operated at ambient temperature, which means that flavour compounds will not be damaged by heat. During pervaporation, only a small fraction of the feed evaporates (the fraction that passes through the membrane). This means that the phase change in pervaporation requires less energy than in distillation-type processes, which rely on evaporating a large portion of the feed. No additives are necessary; thus the recovered flavour can be regarded as natural (Karlsson & Trägårdh, 1996, 1997; Lipnizki et al., 1999; Willemsen et al., 2004).

The remaining sections in this literature review will cover the current knowledge of pervaporation, with a particular focus on literature relevant to flavour concentration.

2.3 Fundamental aspects of pervaporation

In membrane separation processes, a permselective membrane forms a barrier between a feed phase and a permeate phase (Mulder, 1996). The feed can be separated because some components pass through the membrane into the permeate phase more easily than others (Huang & Rhim, 1991; Ho & Sirkar, 1992; Wijmans et al., 1994; Mulder, 1996). Membrane processes differ as to which feed components permeate through the membrane and which are retained; separation is based on permeant size in some membrane processes, whereas for other processes it is based on the chemical affinity between the permeants and the membrane (Mulder, 1996). Pervaporation falls in the latter category. Pervaporation membranes are non-porous, which means that they do not sieve particles based on their size. Instead, separation occurs on a molecular scale: permeant molecules dissolve in the membrane then diffuse through to the downstream side (Mulder, 1996).

In pervaporation, the driving force for transport is a chemical potential gradient across the membrane, due to a difference in activity (and partial pressure) of each permeant compound between the feed and permeate sides (Rautenbach & Albrecht, 1989; Bengtsson et al., 1992; Fleming & Slater, 1992a; Karlsson & Trägårdh, 1993; Lipnizki et al., 1999; Trifunovic & Trägårdh, 2002; Peng et al., 2003). This is almost always achieved by using a vacuum pump to reduce the total pressure on the permeate side, but may also be achieved by heating the feed stream or cooling the permeate stream to condense it, or by sweeping an inert gas over the permeate side to dilute the permeant (Böddeker, 1990; Wijmans et al., 1994; Lipnizki et al., 1999). However, the latter method is only preferred if the permeate does not need to be recovered (Wijmans et al., 1994), which means that it is of little use for flavour concentration, in which the permeate is the valuable fraction.

The low downstream pressure causes the permeate to evaporate, which makes pervaporation unique among membrane processes, in that the feed is a liquid and the permeate is a vapour (Mulder, 1996).

Pervaporation performance is measured by the parameters of flux and selectivity. The flux is defined as the amount flowing through the membrane per unit area and time (Karlsson & Trägårdh, 1996; Mulder, 1996). The flux of each permeant compound depends on its driving force as well as the ease with which it passes through the membrane (Mulder, 1996).

Selectivity is determined by the relative permeation rates of different components (Huang & Rhim, 1991; Urtiaga et al., 2002). Selectivity can be defined in two ways: the separation factor (α) and the enrichment factor (β).

The separation factor is the ratio of two components in the permeate divided by their ratio in the feed:

$$\alpha = \frac{x_{i,p} / x_{j,p}}{x_{i,f} / x_{j,f}} \qquad \textbf{(2-2)}$$

where $x_{i,p}$ and $x_{j,p}$ are the concentrations of components i and j in the permeate, and $x_{i,f}$ and $x_{j,f}$ are their concentrations in the feed (Wijmans et al., 1994; Karlsson & Trägårdh, 1996; Baudot & Marin, 1997; Lipnizki et al., 1999; Peng & Liu, 2003). As this formula only allows for two components, the separation factor can strictly be defined only for binary mixtures. To avoid this difficulty it is possible to define, for example, j to be water and i to be all other components of the mixture (Sampranpiboon et al., 2000b).

Wijmans et al. (1994) modified the expression for the separation factor by modelling pervaporation as two steps: evaporation of the feed liquid and permeation through the membrane. This is not what happens in reality, but is thermodynamically equivalent to the real situation (Wijmans et al., 1994). Each step had its own separation factor, and the two were multiplied to give the total separation factor. The selectivity of the evaporation step depended on the vapour-liquid equilibrium (analogous to distillation, Equation (2-1)), and was thus regarded separately from the intrinsic membrane selectivity (Wijmans et al., 1994). Baudot & Marin (1997) applied this theory to the selectivities reported in

the flavour pervaporation literature, showing how pervaporation was more selective than distillation for some compounds, but less selective for other compounds.

The other common measure of selectivity, the enrichment factor, is the ratio between a particular component's concentration in the permeate and its concentration in the feed (Karlsson & Trägårdh, 1996; Baudot & Marin, 1997; Lipnizki et al., 1999):

$$\beta = \frac{x_{i,p}}{x_{i,f}} \qquad \textbf{(2-3)}$$

If the concentrations of both the feed and the permeate are low, the separation factor and the enrichment factor are similar, because the solvent concentration ($x_{j,f}$ and $x_{j,p}$) is close to a mole fraction of one (Beaumelle et al., 1992; Karlsson & Trägårdh, 1993, 1996; Baudot & Marin, 1997; Peng et al., 2003). Therefore, for pervaporation of dilute mixtures of flavour compounds, most researchers measure the selectivity in terms of the enrichment factor.

Flux and selectivity are both important parameters to consider when evaluating pervaporation performance; the flux will determine the throughput of a particular pervaporation system and therefore help to determine its economic viability, and the selectivity will determine the degree to which the required separation will be achieved (Beaumelle et al., 1993; Karlsson & Trägårdh, 1996). Higher selectivities also reduce the energy cost, as less water needs to be evaporated and condensed (Beaumelle et al., 1993). There is often, but not always, a trade-off between flux and selectivity (Huang & Rhim, 1991; Sampranpiboon et al., 2000a); for example, the flux may need to be very low in order to achieve the desired selectivity. Figure 2-4 illustrates this trade-off, with data from Sampranpiboon et al. (2000b), showing how the operating conditions that achieved the highest flux resulted in the lowest separation factor. Therefore, pervaporation system designers must decide how much importance to place on each of these two parameters.

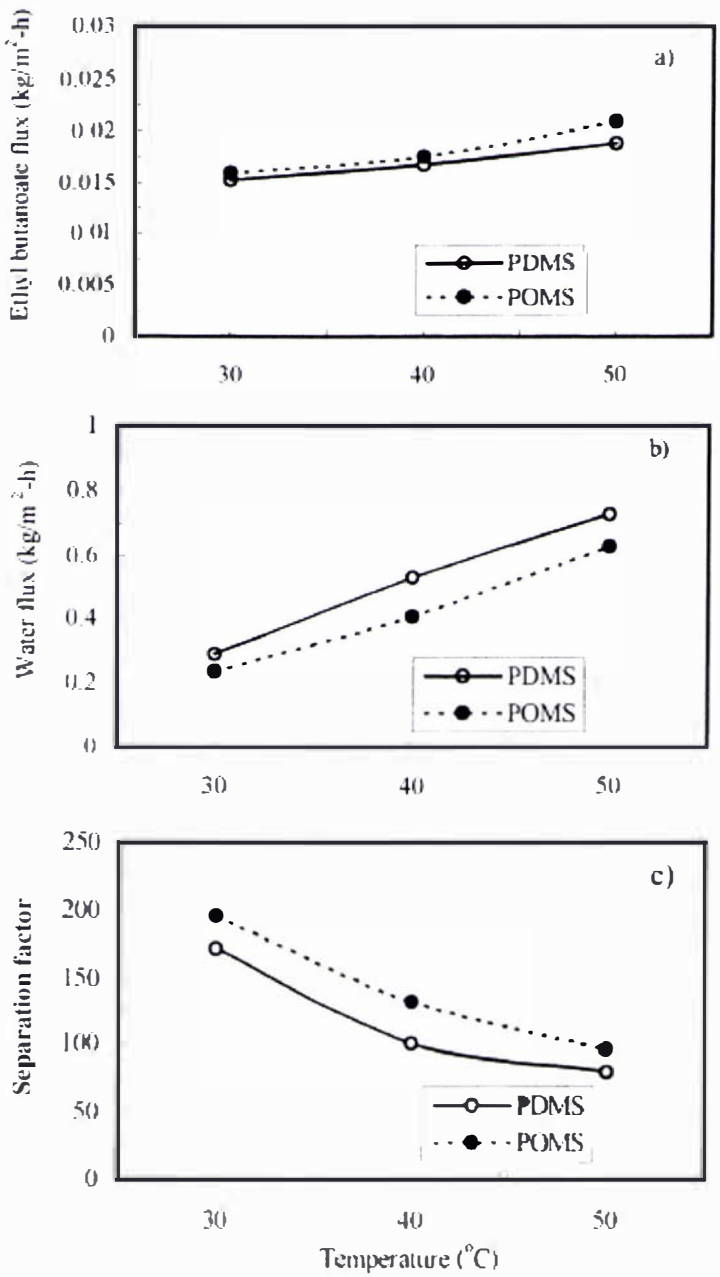


Figure 2-4: Graphs reproduced from Sampranpiboon et al. (2000b) showing how ethyl butanoate and water fluxes increased, but the separation factor decreased, as the temperature was raised. Likewise, the PDMS (polydimethylsiloxane) membrane allowed a higher total flux (water plus ethyl butanoate) but a lower separation factor than the POMS (polyoctylmethylsiloxane) membrane.

To reflect both the flux and the selectivity in a single term, thereby indicating the overall efficiency of pervaporation, Huang & Rhim (1991) defined the pervaporation separation index (*PSI*) as:

$$PSI = J_{tot}\alpha \qquad \textbf{(2-4)}$$

where J_{tot} is the total flux. Jiraratananon et al. (2002b) modified the definition slightly:

$$PSI = J_{tot}(\alpha - 1) \quad \textbf{(2-5)}$$

This means that when *PSI* is zero, there is either no flux or no separation, as separation will not occur if α is equal to one (Sampranpiboon et al., 2000a). A similar parameter, the production index (*PI*), was defined by Liu et al. (1996) as:

$$PI = J_i(\beta - 1) \quad \textbf{(2-6)}$$

The flux term in the *PSI* equations refers to the total flux, whereas in the *PI* equation it refers to the flux of only the component of interest. *PI* is therefore a better measure of efficiency when pervaporation is used for flavour concentration, because there is little point in aiming for a high total flux if the fluxes of flavour compounds are not significantly increased.

The usefulness of the pervaporation separation index was shown by Jiraratananon et al. (2002b), who tested several different membranes for the pervaporation of an ethyl butanoate solution, using *PSI* as defined in Equation (2-5). They found that a polyether-block-amide/polysulphone membrane had the greatest *PSI* over the range of feed concentrations tested, although it did not produce either the highest separation factor or highest flux. However, *PSI* and *PI* are only useful in situations where flux and selectivity have equal importance. In reality, the separation objective of each application should be considered carefully when deciding whether to place more importance on flux or selectivity. For example, aroma recovery applications often require the permeate to have a similar aroma profile to the feed; this means that all compounds that contribute to the aroma must have similar enrichment factors. Pervaporation must achieve this prerequisite in order to be feasible, even if a high flux would lead to a high *PSI*. This need for an individualised approach is probably why *PSI* and *PI* are rarely reported in hydrophobic pervaporation literature; even researchers who do report them also give fluxes and selectivities separately (Liu et al., 1996; Sampranpiboon et al., 2000a; Jiraratananon et al., 2002b).

2.4 Factors that determine pervaporation performance

Figure 2-5 shows the range of factors that can affect each step in pervaporation. Some of these factors are known to influence results in a particular way. For example, an increased feed temperature always leads to a higher flux. However, differences between different permeant compounds, and interactions of permeants with one another and with non-permeating feed components, are less clear.

As so many factors influence pervaporation performance, results from different studies cannot be directly compared unless they were obtained using the same pervaporation system at the same operating conditions. To enable easier comparisons between studies, Wijmans (2003) encouraged researchers to report permeabilities (fluxes normalised for the partial pressure difference across the membrane) instead of simply fluxes. However, this approach only removes one confounding factor, permeate pressure, out of the many factors that can influence results. The following subsections describe each of the factors shown in Figure 2-5.

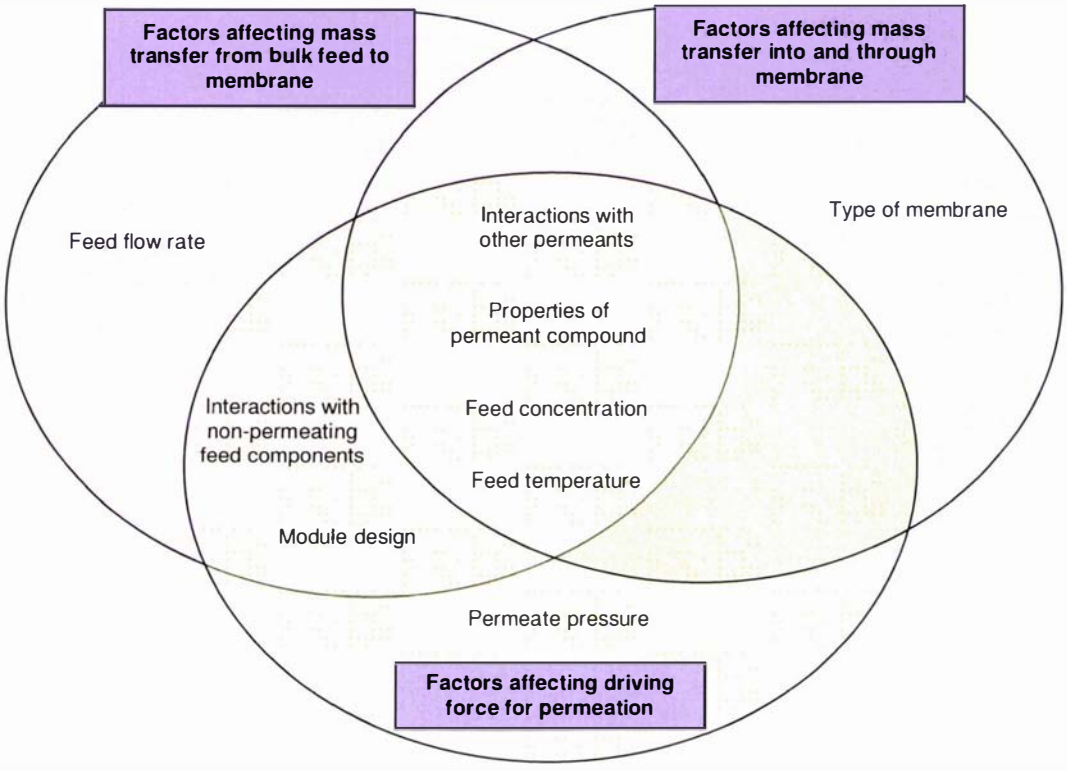


Figure 2-5: Operating conditions and feed solution aspects that may affect pervaporation. In many cases each factor is not independent.

2.4.1 Influence of membrane type

The type of membrane governs which mixture components will permeate preferentially. Pervaporation uses non-porous, polymeric membranes, which may be either hydrophilic or hydrophobic (organophilic). Water permeates preferentially through hydrophilic membranes, whereas hydrophobic membranes allow hydrophobic organic compounds to permeate more easily.

Hydrophilic pervaporation is more advanced commercially than hydrophobic pervaporation. By the mid-1990s, 62 pervaporation plants had been installed worldwide for solvent dehydration (hydrophilic pervaporation), but there was only one industrial plant for recovering volatile compounds from water (hydrophobic pervaporation) (Jonquières et al., 2002). Since then, at least one other hydrophobic pervaporation plant has been installed (Willemsen, 2005), but hydrophilic pervaporation is still more common.

Pervaporation is most efficient if the preferentially permeating compound is the minor feed component (Feng & Huang, 1997; Peng et al., 2003); hence the main use of hydrophilic membranes is for solvent dehydration (Jonquières et al., 2002). Hydrophilic membranes are of no use in concentrating flavour compounds, because water is the major component of dilute flavour mixes. Hydrophilic pervaporation is reviewed by Semenova et al. (1997) and Chapman et al. (2008), and will not be considered further here.

Hydrophobic membrane materials that can be used for pervaporation include polydimethylsiloxane (PDMS), PDMS filled with silicalite, polyoctylmethylsiloxane (POMS), polyether-block-polyamide (PEBA), polytetrafluoroethylene, polybutadiene, and polypropylene (Lipnizki et al., 1999; Jonquières et al., 2002). Apart from these polymers, inorganic zeolite membranes may also be used for pervaporation; their use was reviewed by Bowen et al. (2004).

PDMS is the main type of hydrophobic membrane available commercially (Jonquières et al., 2002), and the vast majority of literature on hydrophobic pervaporation uses PDMS membranes. The more common materials for hydrophobic membranes will be discussed below. However, results from different researchers cannot be directly compared because pervaporation performance is

affected not only by the membrane type, but also by all the other factors in Figure 2-5.

2.4.1.1 Polydimethylsiloxane (PDMS)

PDMS is the membrane material most frequently used for hydrophobic pervaporation experiments. It is a polymer consisting of the monomer units shown in Figure 2-6 (Börjesson et al., 1996; Mulder, 1996). The lack of double bonds allows rotation around each bond (Mulder, 1996), making PDMS a flexible polymer.

The free volume theory states that molecules can diffuse through the membrane by moving through molecular-sized holes, or free volume, between the polymer chains (Yeom et al., 1999; Peng et al., 2003). As PDMS is flexible, it allows molecules to diffuse through it easily and hence permits higher fluxes than most other membranes (Karlsson & Trägårdh, 1993). PDMS separates permeants based on their chemistry rather than their molecular size (Yeom et al., 1999), so that most hydrophobic flavour compounds will permeate preferentially over water, even though they are usually much larger.

Recently, Verhoef et al. (2008) showed that a PDMS membrane designed for nanofiltration could also be used for separating an ethanol/water mixture using pervaporation. The nanofiltration membrane, with a larger free volume than traditional pervaporation membranes, allowed a higher flux and a comparable or better selectivity than two PDMS pervaporation membranes. This finding helps to overcome one of the barriers to adopting pervaporation technology, the lack of inexpensive commercial membranes. In Verhoef et al.'s (2008) study, the feed contained up to 50% ethanol, which was able to swell the nanofiltration

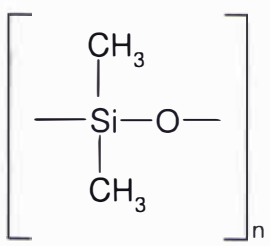


Figure 2-6:Structure of a PDMS monomer unit.

membrane and make it more dense (in other words, more like a pervaporation membrane). Therefore, their results may not be directly applicable to pervaporation of flavour compounds, which are typically present at concentrations too low to significantly swell the membrane.

Although PDMS exhibits good pervaporation performance in terms of high fluxes, it lacks mechanical strength (Uragami et al., 2001; Liu & Xiao, 2004) and its selectivity is poor (Dotremont et al., 1995). To overcome the lack of selectivity, a zeolite filler, such as silicalite, is often incorporated in the membrane. Silicalite, which has the structure shown in Figure 2-7, is a hydrophobic zeolite with pores of about 5 Å diameter (Mulder, 1996). The pores allow silicalite to act as a 'molecular sieve' to reduce the diffusion of large molecules (Dotremont et al., 1995). Silicalite's hydrophobicity causes it to improve the sorption of most compounds in the membrane (Kumar et al., 1997). As silicalite increases sorption but decreases diffusion, its effect on pervaporation performance depends on the type of compounds being separated.

The addition of silicalite to a membrane improves the selectivity, not by increasing the transport of organic molecules, but by lowering the transport of water; hydrophobic molecules preferentially sorb into silicalite, which means that water cannot penetrate through the membrane as easily (Baudot & Marin, 1996; Vankelecom et al., 1997; Baudot et al., 1999). However, a less hydrophobic zeolite, zeolite Y, reduced the enrichment factor of aroma compounds (compared with a pure PDMS membrane), as it allowed a higher water flux (Vankelecom et al., 1997).

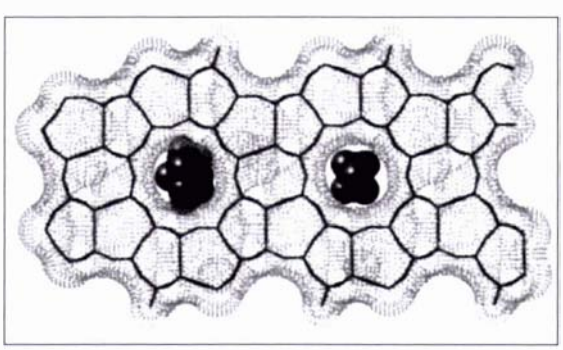


Figure 2-7: Silicalite pores viewed from above, showing two molecules adsorbed inside (reproduced from Jobic, no date).

Vankelecom et al. (1997) took advantage of the molecular sieve effect in experiments to remove ethanol from a model solution without removing flavour compounds, using PDMS membranes with and without added silicalite. They found that, of the membranes tested, PDMS with 40% silicalite was best because it allowed ethanol (a small molecule) to pass through, but larger aroma compounds did not permeate as easily. The hydrophobic silicalite caused the membrane to exclude water (Vankelecom et al., 1997). Likewise, Baudot et al. (1999) observed that ethyl acetate sorbed in the silicalite portion of a filled PDMS membrane, thus lowering water transport and increasing the selectivity. The same result was observed by Baudot and Marin (1996) for methylthiobutanoate, but diacetyl, a more hydrophilic molecule, did not lower the water transport in this way.

Zeolite-filled membranes have the advantage of high selectivities, but the molecular sieve effect means that they often cannot reach the high fluxes of unfilled PDMS membranes, especially for large, high-boiling organic molecules (Baudot et al., 1999). Vankelecom et al. (1997) achieved organic fluxes of 5.52–5.80 g m^{-2} h^{-1} with membranes incorporating various zeolites, compared with 7.34 g m^{-2} h^{-1} for an unfilled PDMS membrane. Souchon et al. (2002) found that unfilled PDMS membranes achieved a higher methylthiobutanoate flux than silicalite-filled PDMS. However, both membrane types had a similar selectivity for this compound. Silicalite fillers decreased the flux of isopropanol and acetic, propanoic and butanoic acids, compared with an unfilled PDMS membrane (Kumar et al., 1997).

However, adding zeolites to a membrane does not always decrease the flux. Some polar compounds such as methanol, ethanol and diacetyl sorb weakly in PDMS, which may lead to the sorption capacity of the filler being greater than that of the PDMS (Kumar et al., 1997; Vankelecom et al., 1997). This greater sorption can cause filled membranes to allow higher fluxes than unfilled membranes, in some circumstances. For example, Dotremont et al. (1995) found that higher levels of silicalite in a PDMS membrane improved the sorption of trichloroethylene in the membrane, provided that the feed vapour pressure was not too high. However, the permeability of tetrachloromethane was reduced, due to the molecular sieve effect (Dotremont et al., 1995).

Apart from zeolites, several researchers have made other modifications to PDMS membranes. Some examples are given below. These mainly involve altering the hydrophobicity of PDMS, rather than altering both sorption and diffusion as zeolites do. It is difficult to evaluate the effect of each modification because none has been extensively studied under a range of conditions.

Mishima & Nakagawa (2000) experimented with PDMS membranes grafted with 1H,1H,9H-hexadecafluorononyl methacrylate, a hydrophobic polymer. The grafted membrane had a lower total flux (20–40 g m^{-2} h^{-1}) than unfilled PDMS (30–150 g m^{-2} h^{-1}). The grafted membrane was more selective, due to the hydrophobicity of the filler. This allowed high sorption of trichloroethylene, and the presence of both trichloroethylene and hydrophobic 1H,1H,9H-hexadecafluorononyl methacrylate reduced the diffusion of water and benzene (Mishima & Nakagawa, 2000).

Uragami et al. (2001) made graft copolymer membranes of polymethyl methacrylate, polyethyl methacrylate or poly-*n*-butyl methacrylate grafted to PDMS. In general, higher PDMS contents caused higher permeation rates. The permselectivity increased when the copolymer contained greater than 40% PDMS (for membranes containing polymethyl methacrylate) or greater than 70% PDMS (for membranes containing polyethyl methacrylate), as the PDMS became the continuous phase. The membrane containing poly-*n*-butyl methacrylate did not show microphase separation (Uragami et al., 2001).

Miyata et al. (1997) modified the surface of PDMS membranes by adding either hydrophilic (PDMS-polydiethylacrylamide) or hydrophobic (PDMS-nonafluorohexyl methacrylate) block copolymers to a PDMS base. These surface modifiers altered the membrane selectivity, making it either water-selective or ethanol-selective, without affecting diffusion (Miyata et al., 1997). This is a potential improvement over adding silicalites to a membrane, as permeability is not lowered.

Liang & Ruckenstein (1996) tested PDMS-polystyrene interpenetrating polymer network membranes for separating ethanol from water. Membranes with more polystyrene were stronger, but had a lower permeation rate than those with less polystyrene. As polystyrene is more hydrophobic than PDMS, the separation

factor increased with increasing polystyrene content (Liang & Ruckenstein, 1996).

2.4.1.2 Polyoctylmethylsiloxane (POMS)

POMS has a similar structure to PDMS, except that one methyl side group is replaced by an octyl group (Figure 2-8) (Börjesson et al., 1996; Trifunović & Trägårdh, 2006). The larger side group causes the polymer chains to be further apart, and reduces their rotational capacity (Mulder, 1996), making POMS less flexible than PDMS. POMS therefore does not achieve such high fluxes as PDMS, but its selectivity is better (Sampranpiboon et al., 2000b; Olsson, 2001).

Sampranpiboon et al. (2000b) found that POMS gave better separation factors than PDMS, for concentrating aqueous solutions of ethyl butanoate and ethyl hexanoate. At temperatures below 40°C, both membranes gave similar aroma compound fluxes, but PDMS allowed more water to permeate. The PDMS membrane presented such a small resistance to mass transfer, that transport in the feed boundary layer was the rate-limiting step (Sampranpiboon et al., 2000b).

Olsson (2001) evaluated several types of PDMS, POMS and PEBA membranes for recovery of aroma compounds from model apple juice. Good performances (100- to 1000-fold enrichments) were achieved with two POMS membranes and one PDMS membrane. Of these, the PDMS membrane gave higher mass transfer coefficients but lower selectivities than the POMS membranes (Olsson, 2001).

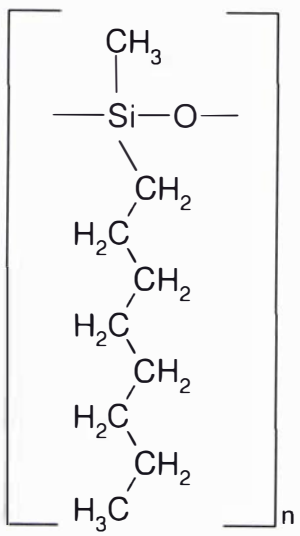


Figure 2-8: Structure of a POMS monomer unit (Trifunović & Trägårdh, 2006).

2.4.1.3 Polyether-block-amide (PEBA)

PEBA consists of amorphous polyether blocks and crystalline polyamide blocks, with transport mainly occurring in the more flexible polyether part of the membrane (Djebbar et al., 1998). PEBA membranes have good permselectivity, and are stable to heat, chemicals and mechanical force (Sampranpiboon et al., 2000a). A PEBA membrane was able to concentrate methyl anthranilate by a factor of 15.3, compared to 9.3 with a membrane made of a PDMS-polycarbonate block copolymer (Rajagopalan & Cheryan, 1995). Baudot & Marin (1996) tested PEBA and silicalite-grafted PDMS membranes for the recovery of diacetyl and methylthiobutanoate by pervaporation. The enrichment factor of diacetyl was similar whichever membrane was used, but the enrichment factor of methylthiobutanoate was much higher with a PEBA membrane than with silicalite-filled PDMS. This was because the partial flux of methylthiobutanoate was 2- to 4-fold greater through PEBA compared to PDMS, but the water flux was lower. Of the three membrane materials tested by Souchon et al. (2002) (PEBA, filled PDMS and unfilled PDMS), only PEBA achieved a higher methylthiobutanoate selectivity than would be expected from its vapour-liquid equilibrium. In other words, pervaporation with both PDMS membranes was less efficient than distillation.

PEBA often does not allow such high fluxes as unfilled PDMS, as its polymer chains are less flexible (Djebbar et al., 1998). However, its fluxes are still competitive with other membranes. Souchon et al. (2002) found that PEBA membranes achieved methylthiobutanoate fluxes of 0.23 or 0.30 $g\ m^{-2}\ h^{-1}$, compared to 0.67 $g\ m^{-2}\ h^{-1}$ with a pure PDMS membrane. With a silicalite-filled PDMS membrane, the flux was only 0.17 $g\ m^{-2}\ h^{-1}$. However, Souchon et al. (2002) did not list the thicknesses of the two PDMS membranes, which is necessary for a reliable comparison. Djebbar et al. (1998) compared five PEBA membranes, of differing composition, with a PDMS membrane. Ester fluxes with the best-performing PEBA membrane were 19–84% lower than those obtained with the PDMS membrane. Rajagopalan & Cheryan (1995) observed that a PEBA membrane could achieve a flux almost double that of a PDMS-polycarbonate block copolymer, during pervaporation of an aqueous solution of methyl anthranilate.

Within PEBA, the branched polyether units are more hydrophobic than the polyamide units, which means that organic compounds interact with the polyether portion and water interacts with the polyamide portion (Jiraratananon et al., 2002b). Hence, Djebbar et al. (1998) found that PEBA membranes with a greater polyether content permitted greater ester fluxes, and Böddeker et al. (1997) found that a PEBA membrane with 80% polyether sorbed vanillin better than one containing 50% polyether. Fluxes, separation factors and pervaporation separation indices, for separating ethyl butanoate from water, were all higher with a PEBA membrane that had 62 polyether units per polyamide as opposed to 53, as the former membrane had more free volume as well as a higher affinity for ethyl butanoate (Jiraratananon et al., 2002b).

2.4.1.4 Poly(1-trimethylsilyl-1-propyne) (PTMSP)

PTMSP is becoming more popular, as it can achieve high fluxes without compromising selectivity (Fadeev et al., 2000; Gonzalez-Velasco et al., 2002). PTMSP has the advantage that it can be used to make thinner membranes than PDMS (Gonzalez-Velasco et al., 2002). However, the separation factor and permeation rate achieved with this membrane do not stay constant over time. This variable performance could be caused by membrane swelling, membrane compaction, chemical degradation of the polymer, or contamination (fouling) of the membrane (Fadeev et al., 2000; Gonzalez-Velasco et al., 2002; Fadeev et al., 2003).

In addition to the membrane types mentioned above, new pervaporation membranes are always being developed. Approximately one-third of the pervaporation-related European patents granted between 1980 and 1999 were for membrane development (Jonquières et al., 2002). Most published research uses PDMS, POMS or PEBA membranes; other types of hydrophobic membrane have only been studied briefly, so are not reviewed here.

2.4.1.5 Influence of membrane structure

Pervaporation membranes have either a single thick layer, or a composite structure consisting of a thin active layer cast onto a porous support layer, which is sometimes cast onto backing material (Figure 2-9) (Koops & Smolders, 1991; Baudot & Marin, 1997; Kujawski, 2000; Trifunović & Trägårdh, 2005). The latter

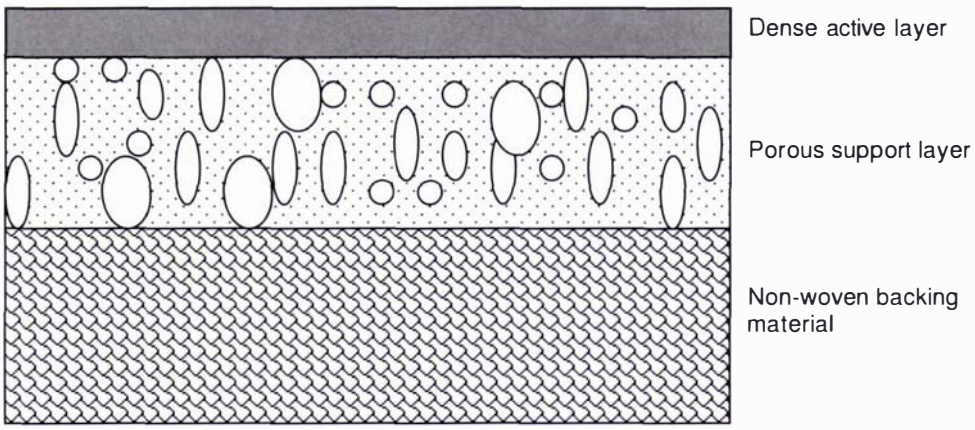


Figure 2-9: Cross-sectional schematic view of a composite membrane (Koops & Smolders, 1991).

form allows the membrane to be self-supporting with a thinner active layer, which permits higher fluxes. Pervaporation fluxes are normally inversely proportional to the active layer thickness, because thicker membranes present a greater resistance to mass transfer (Spitzen et al., 1988; Baker et al., 1997; Pereira et al., 1998). An exception to this rule occurs with very thin membranes, if the membrane resistance becomes so low that it is no longer the rate-limiting factor. For example, Baker et al. (1997) found that the relationship between toluene flux and inverse membrane thickness plateaued at thicknesses of 10–20 μm, depending on the membrane type. However, for the water flux, the relationship remained linear at all thicknesses tested.

There is also evidence that thin membranes have lower selectivities (Baudot & Marin, 1997). For example, Diban et al. (2008) found that (*E*)-2-hexen-1-ol had an enrichment factor of 160 with a PDMS membrane 1480 μm thick, compared to just 20 with a membrane 14.8 μm thick. Spitzen et al. (1988) explained the effect on selectivity in terms of the membrane manufacturing process: thin membranes require less time for the solvent to evaporate when they are cast, causing them to have a less dense structure, which is not as selective. Alternatively, Baudot & Marin (1997) suggested that thick membranes have high selectivities because they can strongly sorb organic compounds.

The porous support layers of composite membranes are largely ignored in pervaporation studies. However, several researchers have shown that the support layer can significantly affect results. Jiraratananon et al. (2002b) investigated the effect of the type of porous support on the pervaporation of ethyl butanoate aqueous solutions through PEBA membranes. Polysulphone supports achieved a better pervaporation separation index than the more hydrophilic polyacrylonitrile. Trifunović & Trägårdh (2005) compared polyetherimide and polyacrylonitrile support layers, with a POMS active layer, for pervaporation of aqueous ester and alcohol solutions. Both types of support layer reduced the permeability, with the effect being more apparent for larger permeant compounds. With a polyetherimide support, the intrinsic permeability of the active layer was up to five times higher than the overall permeability of the composite membrane, whereas the polyacrylonitrile support only caused a 30% difference. Both support layers also reduced the selectivity and the driving force.

Commercial hydrophobic membranes are available from limited suppliers; hence almost all researchers either obtain prototype membranes from a research institution (commonly GKSS-Forschungszentrum Geesthacht GmbH) or make their own. Thus, membranes used for different studies often differ considerably, even if they are made of the same polymer type. For example, pervaporation membrane active layers are usually between about 10 and 150 μm thick (Baudot & Marin, 1997), but membranes as thin as 0.1 μm (Kujawski, 2000) and as thick as 1480 μm (Diban et al., 2008) have been reported. In addition, support layers of different types (or no support layer at all) have been used with PDMS active layers. This makes it difficult to compare findings from different studies. Despite this caveat, the above discussion on different membranes suggests that PDMS is the best choice in situations where a high selectivity is not required, because its flux is generally higher than the other commonly available membranes. There are more published results available for PDMS than any other hydrophobic membrane, which is an advantage if pervaporation system designers need to choose a membrane without doing extensive trials. In spite of these advantages, more selective membranes would be a better choice in certain situations, such as when a high enrichment factor is required and flux is not so important.

2.4.2 Influence of feed solution

2.4.2.1 Feed concentration

The feed concentration of each permeant directly affects its driving force, so that in dilute solutions, individual compound fluxes usually increase proportionally with the feed concentration, and the concentration does not greatly affect the water flux (Karlsson & Trägårdh, 1994; Lamer et al., 1996; Mishima & Nakagawa, 2000; Jiraratananon et al., 2002b; Peng et al., 2003; Isci et al., 2006; Pereira et al., 2006). Therefore, theoretically, the feed concentration should not influence the selectivity in this case. This is the most common situation in pervaporation of flavour compounds, as feed solutions tend to be dilute.

When the feed concentration is greater than a few hundred parts per million, the effect of concentration becomes more complex, and the relationship between concentration and flux may no longer be linear (Karlsson & Trägårdh, 1994). At high feed concentrations, the permeant may plasticise (swell) the membrane. Plasticising compounds increase the flexibility of the membrane polymer by lowering its glass transition temperature (Alger, 1989), thereby increasing the membrane free volume and facilitating diffusion. The increase in diffusivity causes higher organic and/or water fluxes than would be expected from the raised driving force (Mulder, 1996; Feng & Huang, 1997; Peng et al., 2003). This may lead to the selectivity either increasing or decreasing at higher concentrations, depending on how much the organic and water fluxes change.

Sampranpiboon et al. (2000a) found that the total flux of an isopropanol–water mixture increased more than four-fold when the isopropanol concentration was raised from 10% to 40% (w/w). This was caused by increases in both the isopropanol and water fluxes. In pervaporation of flavours, it is rare for plasticisation to occur, because the feed concentration is usually too low. However, an example of plasticisation was reported by Rajagopalan et al. (1994), who studied pervaporation of aqueous diacetyl solutions. The total flux remained fairly constant with a feed concentration between 20 mg L^{-1} and 2000 mg L^{-1}, but when the concentration was increased to 20,000 mg L^{-1}, a much higher total flux was obtained. The authors explained that the PDMS membrane may have been plasticised by diacetyl at this level, causing the water flux to increase. The diacetyl flux was linearly dependent on the feed concentration.

Also, the activity (which determines the driving force) is only linearly dependent on the concentration in very dilute solutions. Sampranpiboon et al. (2000b) found that ethyl butanoate fluxes increased less than proportionally to the feed concentration, which was between 300 and 700 ppm. They attributed this to a decrease in the activity coefficient at higher concentrations; in other words, as the concentration increased, the driving force increased less than proportionally. This led to the separation factor decreasing as the feed concentration was raised.

The effect of feed concentration depends on the permeant and on the membrane. With a PEBA membrane, the separation factor of an ethyl butanoate–water solution increased with increasing feed concentration (Sampranpiboon et al., 2000a), but the opposite was true with PDMS and POMS membranes (Sampranpiboon et al., 2000b). Similarly, Mishima & Nakagawa (2000) found that the total flux through a PDMS membrane increased with increasing benzene concentration (0.005–0.035% w/w), but the benzene concentration had a much smaller effect on the total flux through a fluoroalkyl methacrylate-grafted PDMS membrane. The concentrations of other compounds tested (trichloroethylene, tetrachloroethylene, toluene, ethyl butanoate and ethyl benzoate) did not affect the total flux, either with grafted or non-grafted PDMS (Mishima & Nakagawa, 2000). The feed concentration did not affect the selectivity of a POMS membrane for small alcohols and esters, but had more effect on larger compounds within these functional groups (Trifunović & Trägårdh, 2006).

Lu et al. (2000) found that the separation factor and flux both increased with concentration for pervaporation of acetic acid/water mixtures through pure PDMS membranes at 25°C. However, for silicalite-filled PDMS the results were slightly different. With a silicalite loading of 17.8% (w/w) the separation factor began to decrease at a concentration above 30% acetic acid (w/w), although the flux still increased with concentration. With a silicalite loading of 49.9% (w/w), the separation factor reached a maximum at a concentration of 20% acetic acid (w/w), and the flux reached a minimum at just below this level. These results were explained by the PDMS component of the membrane competing with the silicalite component (Lu et al., 2000).

2.4.2.2 Type of permeant

In pervaporation, separation is determined by the interactions between the permeant and the membrane on a molecular scale (Pereira et al., 2006). Therefore, the molecular properties of each permeant compound, together with the membrane properties, govern how easily each permeant will pass through the membrane. The size and shape of permeants, and their solubility in the membrane, determine their permeability (Binning et al., 1961).

Pervaporation studies reporting on more than one compound may be grouped into two categories: those that select compounds for study based on what is found in a certain product (for example apple juice (Börjesson et al., 1996) or blueberry aroma (Peng & Liu, 2003)), and those with a more systematic approach, either comparing compounds from within a homologous series, or comparing similar-sized compounds from different functional groups. While the former approach is ideal for studying a particular application, the latter is much more useful for understanding why certain compounds permeate through pervaporation membranes more easily than others. The following paragraphs give some examples of these studies.

In general, less polar compounds are more soluble in hydrophobic membranes, so that the membrane will be more selective for these compounds (Baudot & Marin, 1997). However, larger compounds do not diffuse through the membrane as easily (Lamer et al., 1994). This means that the flux and selectivity may either increase or decrease with increasing molecular size within a functional group, depending on whether sorption or diffusion is the controlling factor.

The most common way to determine whether sorption or diffusion is dominant is to experimentally measure the solubility of a compound in the membrane polymer, and to measure the pervaporation flux or permeability. If the fluxes and permeabilities of each compound follow the same order as their solubilities, then sorption is dominant; if they follow the opposite order, then diffusion is dominant. In this way, Lamer et al. (1994) found that fluxes of esters and an alcohol were determined mainly by their sorption in the silicone rubber membrane, not by their diffusivity. In contrast, Vankelecom et al. (1997) found that less polar compounds sorbed better in PDMS, but the chain length was more important than polarity to

determine the enrichment factor. Trifunović & Trägårdh (2003, 2006) examined sorption and pervaporation of homologous series of esters and alcohols in POMS membranes. Within each homologous series, the sorption coefficient increased exponentially with increasing molecular size. Esters were more soluble than alcohols in POMS; ester fluxes were consequently one or two orders of magnitude higher than alcohol fluxes. However, within each homologous series, fluxes increased with increasing molecular size up to a point, then decreased. Trifunović & Trägårdh (2006) explained that the decreasing region was due to the larger compounds having lower diffusivities.

Bengtsson et al. (1992) concentrated natural apple aroma condensate using a PDMS membrane. The enrichment factors followed the order of polarity; esters in the apple condensate had enrichment factors of 26–133, aldehydes 16–67 and alcohols 2–22. Vankelecom et al. (1997) also observed that esters had higher enrichment factors than alcohols, with aldehydes and ketones showing intermediate behaviour.

In other studies, polarity was less important than molecular size. Binning et al. (1961) found that the permeation rate decreased as chain length increased, for a homologous series of hydrocarbons. Peng & Liu (2003) used pervaporation to concentrate binary aqueous solutions of linalool, d-limonene, 1-heptanol, 1-hexanol, *trans*-2-hexenal and ethyl acetate. They showed that ethyl acetate, which had the lowest molecular weight and was also less polar then most other compounds tested, had the highest mass transfer coefficient through a PDMS membrane. d-Limonene had the lowest mass transfer coefficient because of its bulky structure (Peng & Liu, 2003). Molecular size becomes more important with silicalite-filled membranes, as larger molecules cannot easily pass through the silicalite pores (Dotremont et al., 1995; Baudot et al., 1999).

Molecular shape can also influence pervaporation. Dotremont et al. (1995) found that *t*-C_4H_9Cl sorbed less in PDMS than *n*-C_4H_9Cl or *i*-C_4H_9Cl. Binning et al. (1961) discovered that branched compounds permeated more slowly than straight-chain compounds, and the presence of a double bond increased the permeation rate. Double bonds cause molecules to have a plane geometry, which is conducive to permeation (Dotremont et al., 1995).

As pervaporation performance depends on chemical interactions between the permeants and the membrane, the effect of compound type on pervaporation is linked with the membrane type. As was discussed in Section 2.4.1.5, membranes used in independent studies are rarely identical. Therefore, even limiting to PDMS (the most commonly-studied hydrophobic membrane) only, the current literature comparing different compound types contains widely-varying results. For example, Baudot & Marin (1997) listed nine studies of ethyl butanoate pervaporation through PDMS membranes, in which the selectivities (separation factors and enrichment factors) ranged from 56 to 1944. This makes it difficult to analyse data across different studies, meaning that there is no quantitative model of the differences between pervaporation performance with different compounds, only the general rule of thumb that smaller and/or less polar compounds tend to permeate more easily.

2.4.2.3 Interactions with other permeants

In a mixed feed, permeants may interact with each other, so that the flux and enrichment factor of a certain compound may differ depending on whether the feed is a pure liquid, a binary solution or a mixture (Karlsson & Trägårdh, 1993). Permeant interactions fall into two categories: flow coupling (that is, how components enhance or hinder the permeation of other components through the membrane) and alteration of the driving force by changing the partial pressure of other compounds in the feed (Kedem, 1989; Karlsson & Trägårdh, 1993; Baudot & Marin, 1996, 1997; Berendsen et al., 2006). Flavours are usually mixtures of many compounds, so it is useful to understand how interactions between flavour compounds affect pervaporation.

Interactions between permeants may have either a positive or negative effect on pervaporation performance. In some studies, ester fluxes were reduced when other esters were added to the feed solution (Sampranpiboon et al., 2000b; Isci et al., 2006). In contrast, Peng & Liu (2003) found that the flux of 1-heptanol more than doubled when other flavour compounds were present in the feed. Kanani et al. (2003) observed that alcohols tended to have higher permeabilities in a multicomponent feed mixture than in binary solutions, whereas most aldehydes had lower fluxes in the multicomponent feed.

On the other hand, permeants do not always interact with each other at the low concentrations typical of flavour systems. As a result, some studies have not found any evidence of this phenomenon (Karlsson & Trägårdh, 1993; She & Hwang, 2006a). There is some evidence that the operating conditions affect how strongly the permeant interactions will influence pervaporation (Sampranpiboon et al., 2000b; Peng & Liu, 2003), which could be why permeant interactions affect pervaporation differently in different studies.

Although flavour compounds are normally present in low concentrations, some flavour systems also contain significant amounts of ethanol. As both ethanol and flavour compounds will permeate through the membrane, high ethanol concentrations may affect pervaporation of flavours.

With increasing ethanol concentration, the permeabilities of ethyl acetate, *i*-butanol, *n*-butanol and *i*-amyl alcohol decreased (Tan et al., 2005) and the flux of linalool decreased (Karlsson & Trägårdh, 1994). In both studies, the authors explained that a feed solution containing both ethanol and water is less hydrophilic than a solution without any ethanol, and is therefore a more favourable environment for hydrophobic compounds, so that they have less incentive to pass into the membrane. Ethanol had no effect on 2-methylpropanal, 1-penten-3-ol, *trans*-2-hexenal, methanol or propanol (Karlsson & Trägårdh, 1994; Tan et al., 2005). Similarly, Ferreira (1998) did not find evidence that the fluxes of *n*-propanol, *n*-butanol, *i*-butanol or ethyl acetate (at levels lower than 0.2% (w/w)) were influenced by the flux of ethanol, in pervaporation experiments where the ethanol level ranged from 0% to 20% (w/w). In contrast, the flux of *i*-amyl alcohol was correlated to the ethanol flux, which Ferreira (1998) hypothesised was due to its higher feed concentration than the other minor components (1% w/w). However, it was not possible to conclude whether the flux of *i*-amyl alcohol was in fact coupled to the ethanol flux or to the total flux (Ferreira, 1998).

In other cases, ethanol has a positive effect on flavour compound fluxes. Beaumelle et al. (1992) found that 10% ethanol increased the fluxes of propanol, ethyl acetate and ethyl butanoate, although it decreased their separation factors because the total flux was higher in the presence of ethanol. Karlsson & Trägårdh

(1994) observed that the flux of 2-methyl-butanal increased with increasing ethanol concentration up to 3–6% ethanol, then plateaued.

Flavour compounds can also alter the pervaporation behaviour of ethanol. Beaumelle et al. (1992) found that the separation factor of a 10% ethanol-water mixture was reduced when 500 mg kg^{-1} each of propanol, ethyl acetate and ethyl butanoate were added to the feed solution. Similarly, Tan et al. (2005) noticed that the membrane became slightly less permeable to ethanol when flavour compounds were added to the feed mixture, although the flavour concentrations were too low for the effect to be significant. They explained that the ethanol permeability was reduced because aroma compounds preferentially sorbed in the membrane. Karlsson & Trägårdh (1994) observed that a mixture of three aldehydes and two alcohols had no effect on the flux of ethanol. However, their total flavour compound concentration was only 96 ppm, so it is possible that higher concentrations would affect the ethanol flux.

There are few in-depth studies of interactions between permeants in dilute aqueous solutions (such as flavours) during pervaporation. Generally, researchers simply compare the flux of each component in a mixed feed with its flux in a single-component feed solution. This gives useful information if the degree of coupling is compared for several different compounds. However, it is of little value if only one or two compounds are tested. The above studies have shown that permeant interactions depend on the concentration and nature of each compound in the feed, as well as on the operating conditions; therefore interactions between compounds cannot reliably be compared unless they can be tested under the same experimental conditions. There is a need for more research into which compounds positively or negatively affect the fluxes of other compounds.

2.4.2.4 Interactions with non-permeating feed components

Dairy systems present a technological challenge for pervaporation, because as well as containing many flavour compounds, they also contain carbohydrates, proteins and fats. These food components are expected to influence pervaporation, as they are known to interact with flavour compounds (Mills & Solms, 1984; Hansen & Booker, 1996; Hatchwell, 1996; de Roos, 1997; Godshall, 1997; Leland, 1997; Guichard & Langourieux, 2000; Kühn et al., 2007).

The most common foods studied for flavour recovery by pervaporation are aqueous solutions such as juices (Bengtsson et al., 1992; Rajagopalan & Cheryan, 1995; Börjesson et al., 1996; Pereira et al., 2006), which do not contain significant amounts of fat. As a result, there is currently no literature on how fat affects flavour pervaporation, and very little on proteins or carbohydrates. Baudot & Marin (1996, 1997) provided a good discussion on some potential issues with pervaporation of dairy systems, describing how non-volatile compounds should not enter the membrane, but could change the feed side activities of flavour compounds, thus altering their driving forces. However, most of their discussion has not yet been experimentally verified. To date, research on the effect of non-permeating feed components has mainly tended to focus on fermentation broths (reviewed by Vane, 2005), but there have been a few studies focussing on foods.

Aroujalian et al. (2003) examined the effect of protein on pervaporation of ethanol from a dilute aqueous solution. Soy protein, at 10 g L^{-1}, did not have a significant effect on the total flux or the ethanol selectivity. The interaction of protein presence with permeate pressure was not statistically significant either, but the interaction of protein with feed temperature did have a significant effect on selectivity (though not on the total flux). The authors attributed this to the fact that protein becomes less soluble at higher temperatures.

Glucose, xylose and lactose have all been found to reduce the total flux of an ethanol-water solution (Ikegami et al., 1999; Aroujalian et al., 2006). The effect on selectivity was less clear; in some cases the sugars had a greater effect on the water flux than on the ethanol flux, causing the selectivity to increase, but in other cases the sugars caused decreases in ethanol selectivity (Ikegami et al., 1999; Aroujalian et al., 2006). However, lactose did not significantly affect the flux or selectivity of methylthiobutanoate (Baudot et al., 1996) or diacetyl (Rajagopalan et al., 1994).

Membrane fouling, caused by non-permeating feed components, can be a problem in some membrane processes (Mulder, 1996). It is often assumed that as pervaporation membranes are non-porous, fouling does not occur (Mulder, 1996; Baudot et al., 1999; Schäfer & Crespo, 2003). No fouling of a PDMS membrane by protein was observed (Aroujalian et al., 2003). However, Fadeev et al. (2003) found that a nanoporous PTMSP membrane was fouled by a fermentation broth.

This fouling was not caused by fermentation media or yeast cells, but rather by low-volatility compounds in the fermentation broth sorbing in the membrane, thus blocking the pathway for other compounds to permeate (Fadeev et al., 2003).

In addition, non-volatile compounds generally increase the viscosity of a solution, which could influence the mass transfer of permeants on the feed side of the membrane. For most liquid milk products, the Krieger-Dougherty equation can be used to estimate the viscosity (Walstra et al., 2006):

$$\eta = \eta_s \left(1 - \frac{\varphi}{\varphi_{max}}\right)^{-2.5\varphi_{max}} \quad \textbf{(2-7)}$$

where η is the viscosity of the solution, η_s is the viscosity of the solvent (water in this case), φ is the volume fraction of particles (fat globules, casein micelles or serum proteins), and φ_{max} is the maximum volume fraction of particles (approximately 0.8 for liquid milk products) (Walstra et al., 2006). Therefore, the viscosity increases as more non-volatile feed components are added.

Viscosity differences cause the diffusivities of flavour compounds in oil or protein solutions to be approximately an order of magnitude lower than their diffusivities in water (Voilley & Souchon, 2006). The lower diffusivity causes an increase in the resistance to mass transfer on the feed side of the membrane, thereby decreasing the overall mass transfer coefficient. A high viscosity should affect diffusivities of all compounds to a similar degree; de Roos (1997) noted that when thickening agents are added to a flavour mixture, the flavour is weaker due to a lower rate of release, but has a similar character to a non-thickened mixture if flavours do not interact with the thickening agent. In contrast, Godshall (1997) argued that, as flavour molecules of different sizes have different diffusivities, the flavour profile could change in mixtures with different thickeners. In pervaporation, diffusivities in the membrane are much lower than in the feed solution, so even though a high feed viscosity would reduce fluxes overall, it is assumed that the feed viscosity would affect the relative fluxes of each flavour compound only slightly.

2.4.3 Influence of operating conditions

2.4.3.1 Feed temperature

It is generally agreed that, as the feed temperature increases, the flux will increase. Vapour pressures of each compound in the feed increase as the temperature is raised, which leads to a higher driving force (Lipnizki et al., 1999). Also, all of the mass transfer steps in pervaporation — diffusion through the feed boundary layer, sorption in and diffusion through the membrane, and evaporation on the permeate side — are potentially affected by the temperature (Sampranpiboon et al., 2000b; Peng et al., 2003; Liu et al., 2005; Isci et al., 2006). The effect of temperature on flavour compound fluxes seems to be determined mainly by the permeability increase, whereas for water fluxes it is determined mainly be the driving force increase (Olsson & Trägårdh, 1999). Baudot & Marin (1996) found that the permeability of water through PDMS or PEBA membranes was not affected by the temperature at all; the increase in water flux with increasing temperature was solely due to the driving force.

As permeation through membranes is a rate process, fluxes usually change within the normal range of operating temperatures according to an Arrhenius-type relationship (Feng & Huang, 1996; Peng et al., 2003); such a relationship is illustrated in Figure 2-10. The activation energy, which indicates how strongly the flux is affected by temperature, is normally of the order of 20–60 kJ mol^{-1} (Feng & Huang, 1996). With an activation energy of this magnitude, it can be calculated from the Arrhenius relationship that a temperature increase from 20°C to 30°C will lead to the flux increasing by a factor of 1.3–2.3. The pre-exponential factor in the Arrhenius relationship (that is, the logarithm of the hypothetical flux at infinite temperature) is rarely reported in the pervaporation literature.

There have been some attempts to compare activation energies for different compounds and membranes. Mohammadi et al. (2005) determined that methanol had a higher activation energy than ethanol, with a PDMS membrane. They postulated that the activation energy increases as the difference in solubility parameter between the membrane and the permeant becomes larger, but this is difficult to prove based on results from only two permeant molecules. In contrast, the activation energy for pervaporation of esters was found to increase with the

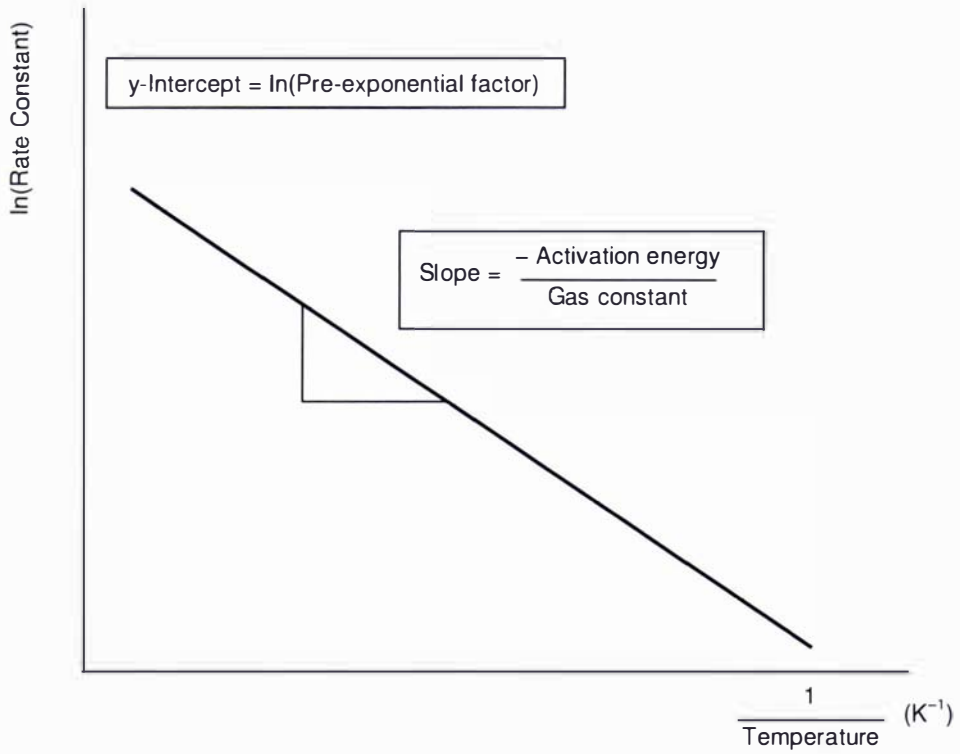


Figure 2-10: Arrhenius plot showing how the logarithm of the rate constant (usually defined as the flux rate in pervaporation literature) is linearly related to the inverse temperature (general form of Arrhenius plot adapted from Silberberg (2006)).

carbon chain length (Song & Lee, 2005). Kabra et al. (1995) found that the activation energy of butanoic acid was slightly greater than isobutanoic acid, and 1.5–3 times greater than propanoic acid, for pervaporation through both plain and silicalite-filled PDMS membranes. The silicalite-filled membrane, for which fluxes were lower, needed greater activation energies than the unfilled membrane. Liang & Ruckenstein (1996) also found that membranes for which the flux was lower had a higher activation energy, for pervaporation of ethanol–water mixtures. However, Djebbar et al. (1998) could not find a relationship between the activation energy and the membrane type or the permeant properties.

Because the feed temperature affects the driving force as well as the mass transfer through the membrane, the activation energy is a combined parameter showing the effect of temperature on both these factors (Feng & Huang, 1996). To understand how the effect of temperature changes with different compounds and membranes, it would be more useful to consider the driving force separately from the mass transfer. Therefore, Feng & Huang (1996) recommended calculating the

activation energy from the relationship between temperature and permeability, rather than temperature and flux. They further explained that the activation energy of permeation, calculated in this way, is itself a combination of the energy needed for sorption and the energy needed for diffusion. These observations provide a basis for analysing the effect of temperature more carefully, showing its separate effects on sorption, diffusion and driving force, and thus should make it easier to explain the different activation energies reported for different membrane/permeant combinations.

However, although Feng & Huang's paper was published in 1996, since then few researchers have followed their recommendations, with most continuing to report activation energy based on flux only. One exception is Olsson & Trägårdh (1999), whose results suggest that activation energies could be predicted for each permeant compound, as a function of the infinite dilution activity coefficient, the liquid molar volume and the functional group. Karlsson et al. (1995) also calculated activation energies in a similar way, although they determined the permeability by normalising the flux for the feed concentration rather than the true driving force. For most of the compounds they tested, the activation energies roughly followed the same order as the boiling points.

More activation energies of permeation must be reported for a variety of situations, before general conclusions can be made regarding the activation energy for different permeants and membranes.

The influence of temperature on pervaporation selectivity depends on the relative activation energies of the compounds to be separated. Compounds with a high activation energy have their flux influenced to a greater extent by temperature changes (Peng et al., 2003; Isci et al., 2006). Therefore, if an aroma compound in an aqueous solution has a higher activation energy than water, a higher feed temperature will give better aroma recovery (Lipnizki et al., 2002). Usually in the pervaporation of volatile compounds from aqueous solutions, the selectivity decreases with temperature, as was found for model solutions of blueberry aroma compounds (Peng & Liu, 2003); ethyl butanoate and ethyl hexanoate (Sampranpiboon et al., 2000b); ethyl butanoate, ethyl acetate and ethyl propanoate (Djebbar et al., 1998); and dichloroethane (Yeom et al., 1999). Djebbar et al. (1998) suggested that the activation energy for water permeation was higher than

for ester permeation because water penetrated through the hydrophobic PEBA membrane in clusters rather than as individual molecules. Yeom et al. (1999) found that the water flux actually decreased at higher temperatures during pervaporation of di-, tri- or tetrachloromethane in water. They also used water clustering to explain this phenomenon. As more chloromethane dissolved in the PDMS membrane at higher temperatures, the membrane became more hydrophobic, so that water clustering occurred to a greater extent (Yeom et al., 1999).

However, selectivity may also increase with temperature, as was found by Rajagopalan & Cheryan (1995) for an aqueous methyl anthranilate solution, and Liang & Ruckenstein (1996) for an ethanol/water mixture. Liang & Ruckenstein (1996) attributed this to a lower amount of hydrogen bonding occurring between ethanol and water at a higher temperature. Baudot & Marin (1996) reported that for a water-diacetyl binary mixture, the selectivity of a PDMS 1070 membrane was slightly better at 50°C than 30°C, whereas the selectivity of a PEBA 40 membrane was not affected by temperature. Rajagopalan et al. (1994) also observed that the selectivity of a diacetyl–water solution increased with temperature.

Isci et al. (2006) studied the recovery of methyl butanoate from an aqueous solution using pervaporation. As methyl butanoate had a higher activation energy than water, the selectivity increased with increasing temperature between 30°C and 40°C. However, the selectivity decreased with increasing temperature between 40°C and 50°C. Their explanation was that there was more free volume in the membrane at higher temperatures, so that water clusters could permeate more readily.

2.4.3.2 Permeate pressure

The permeate pressure determines the activity of each compound on the permeate side of the membrane, thereby controlling the driving force (Böddeker, 1990; Ten & Field, 2000; Lipnizki et al., 2002). Its effect on pervaporation flux has been well characterised: a higher permeate pressure reduces the driving force, resulting in a lower flux (Rajagopalan et al., 1994; Baudot & Marin, 1996; Lamer et al., 1996; Sampranpiboon et al., 2000b). Sampranpiboon et al. (2000b) increased the

downstream pressure from 0.4 to 2 kPa, and found that aroma fluxes of ethyl butanoate and ethyl hexanoate decreased by 28.5% and 33.3% respectively using a PDMS membrane, and 27.9% and 45.8% respectively using a POMS membrane. Rajagopalan et al. (1994) found that the diacetyl flux, from a feed of 200 mg L^{-1} diacetyl in water, decreased from approximately 0.4 to 0.15 g m^{-2} h^{-1} when the permeate partial pressure of diacetyl was increased from 1.33 to 5.33 Pa. The total permeate flux of an aqueous methylthiobutanoate solution decreased by about 45% and 50% for a PDMS membrane and a PEBA membrane respectively, when the permeate pressure was increased from 0.5 to 2.5 kPa (Baudot & Marin, 1996). Lamer et al. (1996) found that with a downstream pressure increase from 35 to 700 Pa, the flux of benzaldehyde in an aqueous solution decreased from 1.7 to 0.3 g m^{-2} h^{-1}.

When the driving force is approximated by the partial pressure difference across the membrane, the flux may be described by the following equation (Ji et al., 1994):

$$J_i = \frac{P_i}{l}\left(p_i^0 \gamma_{i,f}^{\infty} x_{i,f} - p_{i,p}\right) \qquad \textbf{(2-8)}$$

where J_i is the flux of component i, P_i is the membrane permeability to component i, l is the membrane thickness, p_i^0 is the saturated vapour pressure of component i, $\gamma_{i,f}^{\infty}$ is the activity coefficient of component i in the feed, $x_{i,f}$ is the mole fraction of component i in the feed, and $p_{i,p}$ is the partial pressure of component i on the permeate side.

When the difference in partial pressure across the membrane (the term inside the brackets) is small, the driving force approaches zero. Therefore, the permeate pressure has a greater impact on the driving force of compounds that have a low feed side partial pressure. As most volatile organic compounds have high saturated vapour pressures and activity constants compared with water, the permeate pressure normally has a larger effect on the water flux than on organic compound fluxes (Peng et al., 2003). The permeate pressure can therefore influence the selectivity.

As an example, She & Hwang (2004) found that water, benzaldehyde and *trans*-2-hexenal fluxes decreased with increasing permeate pressure, but the flux of ethyl butanoate remained relatively constant. Because ethyl butanoate has a high saturated vapour pressure and activity coefficient, its driving force was only negligibly altered over the small pressure range investigated (0.1 to 0.6 Pa). As a result, the enrichment factor of ethyl butanoate was strongly dependent on the permeate pressure, with this compound being more highly enriched at higher permeate pressures (She & Hwang, 2004). Baker et al. (1997) obtained similar results for trichloroethylene; the water flux was affected to a greater extent than the organic flux when the permeate pressure was increased from 5.3 to 10.7 kPa, which meant that the separation factor also increased.

However, the permeate pressure does not always control the selectivity in this way. Baudot et al. (1999) systematically investigated four flavour compounds with different characteristics. Pervaporation selectivities for low-boiling compounds (diacetyl and ethyl acetate), which had high saturated vapour pressures, were not affected by the permeate pressure. Conversely, the flux of γ-decalactone, which has a very high boiling point, decreased hyperbolically rather than linearly with increasing permeate pressure, which caused its separation factor to decrease also. Methylthiobutanoate, with a moderately high boiling point, displayed an intermediate behaviour: the permeate pressure had either a positive or negative effect on its separation factor, depending on the membrane used.

In industrial processes, the permeate pressure may range from several hundred to several thousand Pascals, which is a much weaker vacuum than can be achieved on a laboratory scale (Baudot et al., 1999; Pereira et al., 2006). The membrane module and permeate side of the pervaporation system should be designed carefully to enable good control over the permeate pressure, for example by using short, large-diameter permeate tubing (Peng et al., 2003; Willemsen et al., 2004).

2.4.3.3 Feed flow rate

In membrane processes, the feed flow rate determines how easily permeants can get to the membrane. When the feed liquid flows through the membrane module, friction between the membrane and liquid causes a gradient in velocity next to the

membrane (Wijmans et al., 1996). For convenience, these flow conditions are approximated by assuming that instead of a gradient, there are just two distinct velocity regions: the bulk flow region and a stagnant boundary layer next to the membrane (Wijmans et al., 1996). The thickness of this boundary layer depends on the feed flow conditions: the more turbulent the flow, the thinner the boundary layer (She & Hwang, 2004).

The driving force causes the feed liquid to flow from the well-mixed bulk through the stagnant boundary layer towards the membrane. Because one component permeates preferentially, this results in a build-up of the other component close to the membrane (Karlsson & Trägårdh, 1993; Wijmans et al., 1996; Lipnizki et al., 1999). In flavour pervaporation, this translates as a layer close to the membrane which is depleted in aroma compounds and enriched in water. This phenomenon is termed concentration polarisation.

The concentration polarisation-induced boundary layer presents an extra resistance to mass transfer, in addition to the membrane resistance. If the boundary layer is thick and the membrane is highly permeable, mass transfer through the boundary layer may become the rate-limiting step in pervaporation, rather than mass transfer through the membrane (resistance to mass transfer on the permeate side is usually considered negligible) (Huang & Rhim, 1991; Jiang et al., 1997; Meuleman et al., 1999; Lipnizki & Trägårdh, 2001; Peng et al., 2003).

To prevent the boundary layer from limiting the flux, its thickness should be minimised by using a turbulent feed flow. The degree of turbulence can be measured by the Reynolds number (Mulder, 1996):

$$Re = \frac{\rho u d_h}{\eta} \qquad \textbf{(2-9)}$$

where Re is the Reynolds number, ρ is the fluid density, u is the flow velocity, d_h is the hydraulic diameter and η is the fluid viscosity. A Reynolds number greater than about 2000 indicates turbulent flow (Mulder, 1996), and Equation (2-9) shows that one way to achieve this is with a high flow velocity. To ensure turbulent flow, the membrane module must also be well designed; this will be discussed in Section 2.4.4.

Concentration polarisation may still occur even when the Reynolds number is as high as can practically be achieved (Baker et al., 1997; Schäfer & Crespo, 2007). Therefore, a greater flux is achieved at higher flow rates. Bengtsson et al. (1993), working with a very laminar flow regime (Reynolds numbers between 1.4 and 51), discovered that the flux of butyl butanoate depended on the flow turbulence, with the logarithm of the flux linearly related to the logarithm of the Reynolds number. Sampranpiboon et al. (2000b) also used a laminar feed flow, with Reynolds numbers ranging from 143 to 190. They observed slight increases in the fluxes of ethyl butanoate and ethyl hexanoate, as the flow rate was increased. With Reynolds numbers between 26 and 126, She & Hwang (2004) found that the fluxes of ethyl butanoate, benzaldehyde and *trans*-2-hexenal increased almost linearly with increasing feed flow rate.

In flavour pervaporation, the water flux remains relatively constant with increasing flow rate, because concentration polarisation of water occurs to a very low extent in dilute solutions (Bengtsson et al., 1993; She & Hwang, 2004). Contrary to these findings, Sampranpiboon et al. (2000b) observed a slight increase in the water flux as the feed flow rate was raised from 29.4 to 39 L h^{-1}. They suggested that temperature polarisation may have occurred as well as concentration polarisation.

As the flow rate usually has a greater effect on flavour compound fluxes than on the water flux, increasing the feed flow rate will lead to a higher selectivity. Bengtsson et al. (1993) showed that the enrichment factor of butyl butanoate was linearly dependent on the Reynolds number. Similarly, Sampranpiboon et al. (2000b) found that the separation factors of ethyl butanoate or ethyl hexanoate in water increased by 3–14% when the Reynolds number increased from 143 to 190.

Shepherd et al. (2002) studied the effect of flow rate on pervaporation of an orange juice by-product consisting of water, ethanol and many aroma compounds. With increasing flow rate between 20 and 100 L h^{-1}, the ethanol and total aroma enrichment factors remained fairly constant, but when the flow rate was changed to 300 L h^{-1} the total aroma enrichment factor increased, whereas the ethanol enrichment factor did not change markedly. Although Shepherd et al. (2002) did not state the Reynolds numbers corresponding to these flow rates, it is possible that the change in enrichment factor was caused by the feed flow changing from

laminar to turbulent. This would agree with the jump in selectivity between laminar and turbulent flow regimes in a simulation by Trifunović et al. (2006).

She & Hwang (2004) calculated the boundary layer thickness under different flow conditions; a higher flow rate caused a thinner boundary layer. The boundary layer thickness was inversely proportional to the enrichment factors of benzaldehyde, ethyl butanoate and *trans*-2-hexenal.

2.4.4 Influence of module design

The module designs most suitable for pervaporation are hollow fibre, spiral wound and plate-and-frame configurations (including a plate-and-frame-like pocket module, available from GKSS-Forschungszentrum), as these can be used with a large pressure difference across the membrane (Rautenbach & Albrecht, 1989; Lipnizki et al., 1999; Peng et al., 2003). Of these, Strathmann & Gudernatsch (1991) recommended a hollow fibre module, with the feed inside the fibres, as the best configuration. They based their decision on the ease of mass transport on the permeate side, the ability to add intermediate heating stages and the cost per unit area. However, hollow fibres are not easy to clean (Mulder, 1996), which makes them less suitable for pervaporation of most dairy products. Industrial pervaporation processes usually use plate-and-frame modules (Shao & Huang, 2007), although most industrial plants are in the chemical industry rather than the dairy industry. Some novel configurations, such as vibrating modules and monolithic modules with open flow channels, have been developed to avoid fouling (Vane, 2005). Figure 2-11 illustrates some of the available module designs.

The choice of module determines the hydrodynamics of feed and permeate flow (Lipnizki et al., 1999). Concentration polarisation is lowest when the flow is turbulent, so a module that allows a high Reynolds number is beneficial. This can be achieved by designing the feed side of the module to have a large flow path hydraulic diameter, according to Equation (2-9). A vibrating membrane module has also been investigated as an alternative way of increasing turbulence (Vane & Alvarez, 2005). Some other ways to minimise the boundary layer resistance are to use turbulence promoters, to use a pulsating flow, or to use corrugated membranes to break the boundary layer (Mulder, 1996).

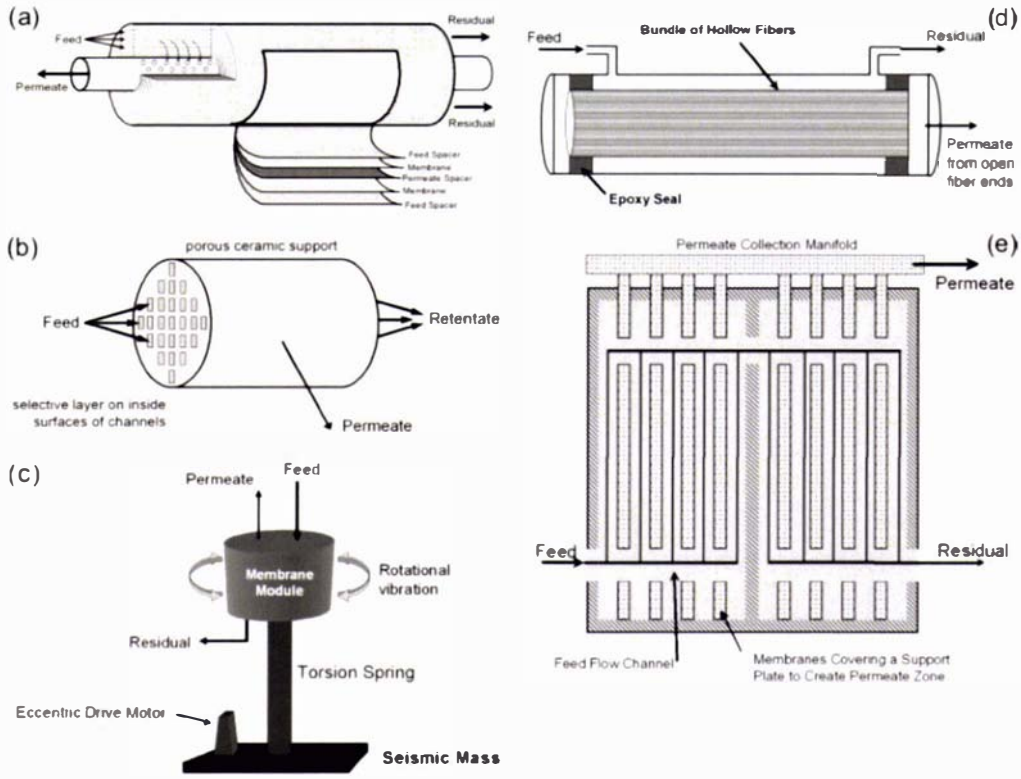


Figure 2-11: Illustrations of various membrane module configurations: (a) spiral wound, (b) monolithic ceramic, (c) vibrating disc stack, (d) hollow fibre, (e) plate and frame. Reproduced from Vane (2005).

A few studies have shown how mass transfer on the feed side contributes to the performance of different module designs. Shepherd et al. (2002) obtained better mass transfer with a well-spaced hollow fibre module than with modules without spacers. Schäfer & Crespo (2007) compared two pervaporation modules, both of which used a flat membrane, for pervaporation of alcohols and esters. The radial module operated under laminar flow conditions, and the single-channel module allowed turbulent flow. The alcohols and ethyl acetate had similar fluxes in both modules, but the larger esters were influenced by the module type, with higher fluxes being achieved with the single-channel module. Therefore, the permeate composition depended on the module chosen. Trifunović et al. (2006), however, performed simulations to show that the feed flow rate had a greater effect on mass transfer than the hydraulic diameter of the module.

Apart from the feed flow characteristics, the module also influences the driving force, by determining the lowest achievable permeate pressure. Without varying the membrane area, Trifunović et al's (2006) simulations showed that increasing

the module width and reducing its length caused the feed Reynolds number to decrease, but minimised the pressure drop on the permeate side. The net effect was an increase in flux when the width-to-length ratio was increased. Similarly, increasing the height of the permeate channel reduced the pressure drop, thereby increasing the flux. However, a larger permeate channel meant that less membrane area could fit into a given module volume, resulting in a lower productivity (flux per unit module volume) (Trifunović et al., 2006).

In a hollow fibre module, the permeate pressure builds up inside the thin fibres due to friction, which reduces the driving force for mass transfer (Rautenbach & Albrecht, 1989; Rautenbach et al., 1991; Feng & Huang, 1997). There can also be a temperature drop along the hollow fibre (Fleming & Slater, 1992b), although this is more important in hydrophilic pervaporation, in which elevated temperatures are often used, than in pervaporation for aroma recovery, in which the temperature must be kept reasonably low to avoid damaging the aroma compounds.

Economic considerations are also important when deciding which module to use. The initial capital cost, maintenance costs and space required per unit membrane area should all be taken into account (Mulder, 1996; Smitha et al., 2004). Mulder (1996) listed the common module designs for membrane processes in order according to their advantages and disadvantages:

1. Tubular
2. Plate-and-frame
3. Spiral-wound
4. Capillary
5. Hollow fibre

Those designs at the beginning of the list are easier to clean and less likely to foul, but are more expensive and require more space for the same membrane area, than those at the bottom of the list (Mulder, 1996). The best module design depends on which of these attributes are most important in each application. With a dairy-based feed, it must be possible to hygienically clean the membrane (Krack, 1995). In the past, tubular and plate-and-frame modules were the most common configurations used for membrane processes in dairy applications (Mulder, 1996), but spiral-wound membranes are now more popular (Walstra et al., 2006).

2.5 Models to describe pervaporation

Various models exist that describe the mass transfer during pervaporation. These include overall models describing the whole process, as well as more specific models describing each step. The different model types are outlined in the following sections; several reviews provide a more detailed discussion (Karlsson & Trägårdh, 1993; Wijmans & Baker, 1995; Lipnizki & Trägårdh, 2001).

2.5.1 Resistance-in-series model

The resistance-in-series model is an overall model for the pervaporation process, covering mass transfer on the feed side, through the membrane and on the permeate side. This model is based on the film theory, which assumes that there is a stagnant film (the boundary layer), which molecules cross by diffusion, adjacent to every interface (Cussler, 1997).

There are six steps involved in mass transfer during pervaporation (Beaumelle et al., 1993; Beaumelle & Marin, 1994; Meuleman et al., 1999; Jiraratananon et al., 2002a; Peng et al., 2003):

- Diffusion from the liquid bulk to the membrane through the boundary layer
- Sorption into the membrane
- Diffusion through the membrane
- Desorption on the downstream side of the membrane
- Diffusion of the vapour through the membrane porous support
- Diffusion of the vapour to the condenser.

Each step presents a resistance to mass transfer, but the membrane and feed side resistances are the most important; resistances from the other steps are usually neglected (Jiang et al., 1997; Vane & Alvarez, 2005), on the assumption that the vapour phase presents relatively little resistance to mass transfer. Hence, the most common form of the resistance-in-series model is as follows (Jiang et al., 1997; Sampranpiboon et al., 2000b; Peng et al., 2003; She & Hwang, 2004):

$$\frac{1}{k_{ov}} = \frac{1}{k_{bl}} + \frac{1}{k_m} \qquad \textbf{(2-10)}$$

where k_{ov} is the overall mass transfer coefficient, k_{bl} is the boundary layer mass transfer coefficient, and k_m is the membrane mass transfer coefficient. The membrane mass transfer coefficient is a function of the permeability P (including sorption into and diffusion through the membrane) and the active layer thickness l (Baudot et al., 1999):

$$k_m = \frac{P}{l} \tag{2-11}$$

The relative importance of each mass transfer resistance depends on the system in question. Usually only the boundary layer and membrane active layer resistances are considered, but the resistance in the porous support layer can also be significant (Trifunović & Trägårdh, 2005).

The mass transfer coefficient for each step is the proportionality constant between the flux and the driving force for that step. The following set of equations shows each mass transfer step, if the driving force is defined as the difference in permeant volume fraction across each region (Meuleman et al., 1999):

Feed side: $$J_i = k_{i,bl}(\Phi_{i,f} - \Phi_{i,fm}) \tag{2-12}$$

Interface between feed and membrane: $$S_{i,fm} = \frac{\Phi'_{i,fm}}{\Phi_{i,fm}} \tag{2-13}$$

Membrane: $$J_i = k_{i,m}(\Phi'_{i,fm} - \Phi'_{i,pm}) \tag{2-14}$$

Interface between membrane and permeate: $$S_{i,pm} = \frac{\Phi'_{i,pm}}{\Phi_{i,pm}} \tag{2-15}$$

Permeate side: $$J_i = k_{i,p}(\Phi_{i,pm} - \Phi_{i,p}) \tag{2-16}$$

where J_i is the flux of compound i, $k_{i,bl}$ is the mass transfer coefficient across the boundary layer, $\Phi_{i,f}$ is the volume fraction of i in the feed, $\Phi_{i,fm}$ is the volume fraction of i at the feed-membrane interface (in the feed) $S_{i,fm}$ is the partition coefficient of i between the feed and the membrane, $\Phi'_{i,fm}$ is the volume fraction of i at the feed-membrane interface (in the membrane), $k_{i,m}$ is the mass transfer coefficient in the membrane, $\Phi'_{i,pm}$ is the volume fraction of i at the permeate–

membrane interface (in the membrane), $S_{i,pm}$ is the partition coefficient of i between the membrane and the permeate, $\Phi_{i,pm}$ is the volume fraction of i at the permeate-membrane interface (in the permeate), $k_{i,p}$ is the mass transfer coefficient across the downstream boundary layer, and $\Phi_{i,p}$ is the volume fraction of i in the permeate.

Combining and simplifying the above equations leads to:

$$J_i = k_{i,ov}(\Phi_{i,f} - \Phi_{i,p}) \quad \textbf{(2-17)}$$

(Shepherd et al., 2002; Peng et al., 2003), or simply:

$$J_i = k_{i,ov}\Phi_{i,f} \quad \textbf{(2-18)}$$

if the permeate pressure is low enough that $k_{i,p}$ and $\Phi_{i,p}$ can be considered negligible (Meuleman et al., 1999; Sampranpiboon et al., 2000b).

The same principle can be used with different units for the driving force, such as partial pressure (Equation (2-19)) or activity (Equation (2-20)) (Baudot et al., 1999; Jiraratananon et al., 2002b; Trifunović & Trägårdh, 2006):

$$J_i = k'_{i,ov}(p_{i,f} - p_{i,p}) \quad \textbf{(2-19)}$$

$$J_i = k_{i,ov}(a_{i,f} - a_{i,p}) \quad \textbf{(2-20)}$$

The magnitude and units of the mass transfer coefficient depend on the units chosen for the driving force, so that $k_{i,ov}$ and $k'_{i,ov}$ have a slightly different meaning between Equations (2-17), (2-19) and (2-20).

Ji et al. (1994) used the resistance-in-series model to describe multicomponent pervaporation, and found that this model provided a good description of the pervaporation process. An advantage of the resistance-in-series model is that the membrane and boundary layer resistances can be evaluated separately, enabling the permeability of different membranes to be compared regardless of feed conditions (Ji et al., 1994). Models to describe transport through the feed side boundary layer and through the membrane will be outlined in the following sections.

2.5.2 Mass transfer on the feed side

Resistance to mass transfer on the feed side (the first step of the resistance-in-series model) results from the stagnant boundary layer described in Section 2.4.3.3. The boundary layer mass transfer coefficient (k_{bl}) can be estimated using empirical correlations; the mass transfer coefficient is a function of the Sherwood dimensionless number, which is itself a function of the Reynolds and Schmidt numbers (Beaumelle et al., 1993). Different empirical correlations have been proposed for different situations, but for cross-flow pervaporation these are generally of the form in Equations (2-21) to (2-23) (Beaumelle et al., 1993; Karlsson & Trägårdh, 1993; Mulder, 1996; Jiang et al., 1997; Lipnizki et al., 1999; Lipnizki et al., 2002):

$$Sh = \frac{k_{bl} d_h}{D_i} \tag{2-21}$$

where:

$$Sh = aRe^b Sc^c \left(\frac{d_h}{L_c} \right)^d \tag{2-22}$$

$$Sc = \frac{\eta}{\rho D_i} \tag{2-23}$$

in which Sh is the Sherwood number, d_h is the hydraulic diameter of the membrane cell, D_i is the diffusivity in the boundary layer, Re is the Reynolds number (defined in Equation (2-9)), Sc is the Schmidt number, L_c is the length of the membrane cell, η is the viscosity of the feed liquid, and ρ is the density of the feed liquid. a, b, c and d are empirical constants which depend on the flow regime (whether laminar or turbulent) and on the geometry of the membrane module (Karlsson & Trägårdh, 1993; Mulder, 1996). The diffusivity in the boundary layer can be estimated with the Wilke-Chang equation (Peng et al., 2003):

$$D_i = 7.4 \times 10^{-8} \frac{(2.6 M_w)^{0.5} T}{\eta V_i^{0.6}} \tag{2-24}$$

where M_w is the molecular weight of water, T is the absolute temperature, η is the viscosity of the feed solution, and V_i is the molar volume of the permeating

species. The constant 2.6 only applies when water is the solvent (Peng et al., 2003).

The above model assumes that transport through the boundary layer is solely caused by diffusion rather than convection (Wijmans et al., 1996). Although diffusion is the main transport mechanism (Karlsson & Trägårdh, 1993; Baker et al., 1997), some models do not neglect convection. The Peclet number is the ratio of convective to diffusive transport in the boundary layer (Karlsson & Trägårdh, 1993; Wijmans et al., 1996; Baker et al., 1997):

$$Pe = \frac{J\delta}{D} = \frac{u_i}{k_{bl}} \tag{2-25}$$

where δ is the boundary layer thickness and u_i is the permeant velocity. If convective as well as diffusive flow is considered, the concentration polarisation equation is used instead (Matsuura, 1994; Tyagi et al., 1995):

$$\frac{x_{i,fm} - x_{i,p}}{x_{i,f} - x_{i,p}} = \exp\left(\frac{u_i}{k_{bl}}\right) \tag{2-26}$$

which is equivalent to the following (Wijmans et al., 1996):

$$\frac{\frac{1}{\beta_{\text{int}}} - 1}{\frac{1}{\beta} - 1} = \exp\left(\frac{u_i}{k_{bl}}\right) \tag{2-27}$$

where β_{int} is the intrinsic enrichment factor in the absence of a boundary layer (equal to $x_{i,p}/x_{i,fm}$). Because $J_i = u_i\rho$ multiplied by the extent of concentration polarisation, the flux equation becomes after rearranging (Wijmans et al., 1996; Jiraratananon et al., 2002a):

$$J_i = \frac{u_i\rho\left(x_{i,f} - x_{i,fm}\right)}{\left(1 - \frac{1}{\beta_i}\right)\left(\exp\left(\frac{u_i}{k_{bl}}\right) - 1\right)} \tag{2-28}$$

Some authors have found the effect of concentration polarisation to be negligible (Jiraratananon et al., 2002a), but others argue that it has a large effect and may be

the dominant resistance to mass transfer in pervaporation (Bengtsson et al., 1993; Wijmans et al., 1996; Baker et al., 1997; Jiang et al., 1997). Lipnizki et al. (1999) stated that concentration polarisation is important when the separation factor is large, or if there is little or no flow turbulence in conjunction with a high flux. According to Beaumelle & Marin (1994), mass transfer resistance on the feed side of the membrane becomes important at feed concentrations of less than 1%.

2.5.3 Mass transfer in the membrane

Mass transfer inside the membrane may be described either by a structure-related model such as the solution-diffusion model or pore flow model, or a non-structure-related ('black box') model such as the thermodynamics of irreversible processes (Mulder, 1996). Both approaches will be described below.

2.5.3.1 Solution-diffusion model

The model most frequently used to describe the pervaporation process is the solution-diffusion model. As well as for pervaporation, the solution-diffusion model is generally accepted for describing transport in other membrane processes that use non-porous membranes, such as reverse osmosis, gas separation, dialysis and vapour permeation (Rautenbach & Albrecht, 1985; Bhattacharyya & Williams, 1992; Kessler & Klein, 1992; Zolandz & Fleming, 1992; Wijmans & Baker, 1995; Ghoreyshi et al., 2004; Wijmans, 2004).

The solution-diffusion model was first adapted for pervaporation by Binning et al. (1961), who described the process as a series of three steps:

- Sorption into the membrane
- Diffusion through the membrane
- Desorption and vaporisation on the permeate side of the membrane.

Sorption and desorption are based on thermodynamics, whereas diffusion is based on kinetics (Shieh & Huang, 1998b). A number of models exist that describe each of the first two steps, which will be discussed in the following sections. Usually the last step is considered to present a negligible resistance to mass transfer, if the permeate pressure is reasonably low (Huang & Rhim, 1991; Meuleman et al., 1999; Lipnizki & Trägårdh, 2001). Therefore, the membrane permeability for

each compound (P_i) is a function of the sorption coefficient (S_i) and the diffusion coefficient (D_i) (Enneking et al., 1996):

$$P_i = S_i D_i \tag{2-29}$$

The permeability is related to the membrane mass transfer coefficient through Equation (2-11).

The flux at any point in the membrane is a function of the concentration at that point (c_i), the diffusion coefficient (D_i) and the chemical potential driving force $\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}l}\right)$ (Baudot et al., 1999; Lipnizki et al., 1999):

$$J_i = \frac{-c_i(l)D_i(l)}{RT}\frac{\mathrm{d}\mu_i}{\mathrm{d}l} \tag{2-30}$$

The advantage of using a chemical potential driving force is that separate modelling of sorption is unnecessary, because thermodynamic equilibrium can be assumed at the membrane interface (Lipnizki et al., 1999). All driving forces can be reduced to a gradient in chemical potential, using the following relationship (Wijmans & Baker, 1995):

$$\mathrm{d}\mu_i = RT\,\mathrm{d}\ln(\gamma_i c_i) + V_i\,\mathrm{d}p \tag{2-31}$$

where μ_i is the chemical potential, γ_i is the activity coefficient, c_i is the molar concentration and v_i is the molar volume. The solution-diffusion model assumes that the gradient in chemical potential is expressed solely as an activity gradient, $\mathrm{d}\ln(\gamma_i c_i)$, so that the second term on the right hand side of the equation is eliminated (Wijmans & Baker, 1995).

Combining Equation (2-30) with $\mu_i = \mu_i^0 + RT\ln a_i$ gives the following equations (Baudot et al., 1999; Lipnizki et al., 1999):

$$J_i = c_i D_i \frac{\mathrm{d}(\ln a_i)}{\mathrm{d}l} \tag{2-32}$$

$$J_i = \frac{c_i D_i}{a_i}\frac{\mathrm{d}a_i}{\mathrm{d}l} \tag{2-33}$$

As the sorption coefficient is the ratio of the concentration in the membrane (c_i) and the activity (a_i) (Baudot et al., 1999):

$$S_i = \frac{c_i}{a_i}, \tag{2-34}$$

Equation (2-33) can be rewritten as the following (Baudot et al., 1999; Lipnizki et al., 1999):

$$J_i = D_i S_i \frac{\mathrm{d}\, a_i}{\mathrm{d}\, l} \tag{2-35}$$

$$J_i = \frac{P_i}{l}(a_{i,f} - a_{i,p}) \tag{2-36}$$

where $a_{i,f}$ is the activity of component i on the feed side and $a_{i,p}$ is its activity on the permeate side. Activity can be described as an effective concentration, accounting for non-ideality, and is given by the product of each component's mole fraction and activity coefficient (Lee, 1999).

The two contributors to permeability, the sorption coefficient and the diffusion coefficient, are not independent (Huang & Rhim, 1991). A high solubility causes a high degree of membrane swelling, thus enabling easier rotation about the polymer axis and greater free volume, so that diffusivity is enhanced (Huang & Rhim, 1991). Also, molecules diffuse more readily through a membrane containing a large proportion of liquid, rather than through a solid membrane (Huang & Rhim, 1991). However, other researchers found that compounds with higher diffusion coefficients seemed to have lower sorption coefficients (Lamer et al., 1994; Souchon et al., 1996, 2002). These findings are backed up by Hall (1989), who suggested that organic vapours with high solubilities in a polymer may diffuse slowly because they tend to be large molecules and also may interact with the polymer, which is what caused them to be highly soluble. Huang & Rhim's (1991) theory probably only applies if the permeant concentration inside the membrane is high, causing significant swelling, as opposed to pervaporation of dilute flavour compounds.

As an alternative to combining the sorption coefficient and the diffusion coefficient into a single permeability term, the two can be modelled separately as follows.

Models for sorption

Sorption models aim to calculate the concentration or activity of a permeant just inside the membrane on the feed side, based on its concentration or activity in the feed solution. In other words, the aim is to model the curve in Figure 2-12. If the activity coefficient is close to one throughout the entire concentration range (that is, if the activity of each component is similar to its mole fraction), the solution will behave similarly to an ideal solution which obeys Raoult's law (Böddeker, 1990). Raoult's law states that for ideal solutions, the vapour pressure of a particular component in solution is equal to the vapour pressure of that component as a pure liquid, multiplied by its mole fraction in the solution (Lee, 1999). For systems that obey Raoult's law, the concentration of each permeant in the membrane (at the feed side) is directly proportional to its concentration in the feed (Figure 2-12). However, pervaporation membranes frequently deviate from this behaviour (Huang & Rhim, 1991; Heintz & Stephan, 1994).

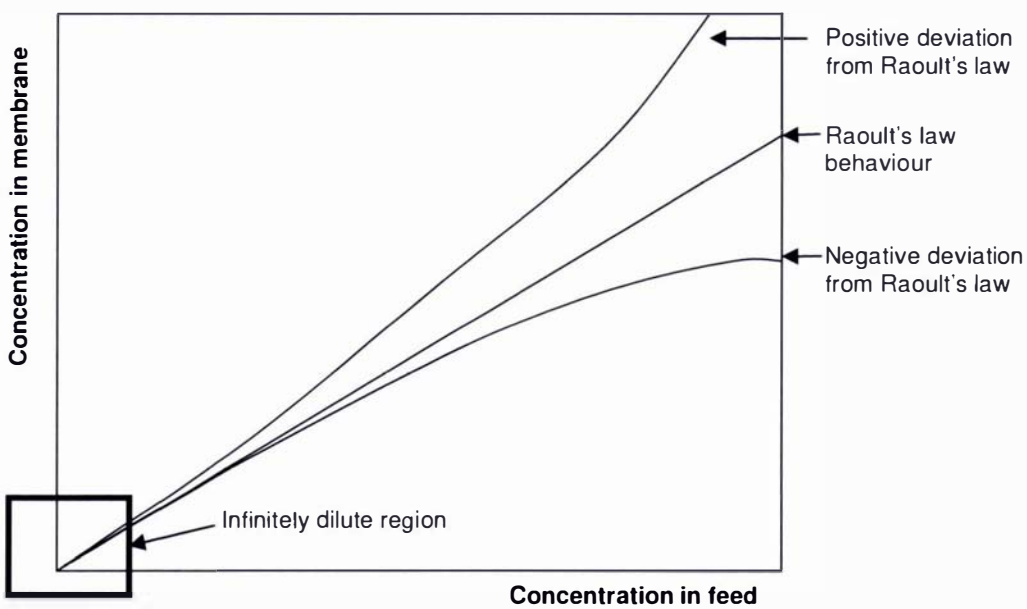


Figure 2-12: Types of sorption isotherm encountered in pervaporation (adapted from Böddeker, 1990).

As a result, some complex models have been proposed to describe the sorption of permeants into membrane polymers. The two sorption models commonly cited are the Flory-Huggins model and the universal quasi-chemical (UNIQUAC) model. Derivations of these models are given by Flory (1953) and Abrams & Prausnitz (1975) respectively. Both models give the activity of each component as a function of the mixture composition (volume fractions and/or weight fractions), where the membrane polymer is viewed as being mixed with the permeants.

The following equation is the Flory-Huggins model in the form used by Favre et al. (1993):

$$\ln a_s = \ln \Phi_s + (1-\Phi_s) - \left(\frac{V_s}{V_w}\right)\Phi_w - \left(\frac{V_s}{V_m}\right)\Phi_m + [(\chi_{sw}\Phi_w + \chi_{sm}\Phi_m)(\Phi_w + \Phi_m)] - \chi_{wm}\left(\frac{V_s}{V_w}\right)\Phi_w\Phi_m \quad \textbf{(2-37)}$$

where a is activity, Φ is volume fraction, V is molar volume, χ is the Flory-Huggins interaction parameter, and the subscripts s, m and w stand for solvent, membrane polymer and water respectively.

Heintz & Stephan (1994) used the UNIQUAC equations in the form below to predict the solubility coefficient of mixture component i in a membrane:

$$a_i = a_i' \quad \textbf{(2-38)}$$

$$\ln a_i(w_1,\ldots w_i,\ldots w_n) = \ln \Phi_i + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \sum_{j=1}^{n} \Phi_j \frac{r_i}{r_j} l_j - q_i^* \ln \sum_{j=1}^{n} \Theta_j^* \tau_{ji} + q_i^* - q_i^* \sum_{j=1}^{n} \frac{\Theta_j^* \tau_{ij}}{\sum_{k=1}^{n} \Theta_k^* \tau_{kj}} \quad \textbf{(2-39)}$$

$$\ln a_i'(w_1',\ldots w_i',\ldots w_n', w_M') = \ln \Phi_i + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \sum_{j\neq m}^{n} \Phi_j \frac{r_i}{r_j} l_j - r_i \Phi_m \left(\frac{z}{2}\left(1 - \frac{q_m}{r_m}\right) - 1\right)$$

$$+ q_i^* - q_i^* \ln \sum_{j=1}^{m} \Theta_j \tau_{ij} - q_i^* \sum_{j=1}^{m} \frac{\Theta_j^* \tau_{ij}}{\sum_{k=1}^{m} \Theta_k^* \tau_{kj}} \quad \textbf{(2-40)}$$

where:

$$\Phi_i = \frac{w_i / \rho_i}{\sum_{j=1}^{n} w_j / \rho_j} \quad \textbf{(2-41)}$$

$$\Theta_i = \frac{\Phi_i (q_i / r_i)}{\sum_{j=1}^{n} \Phi_j (q_j / r_j)} \quad \textbf{(2-42)}$$

$$\Phi_i^* = \frac{\Phi_i (q_i^* / r_i)}{\sum_{j=1}^{n} \Phi_j (q_j^* / r_j)} \quad \textbf{(2-43)}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad \textbf{(2-44)}$$

In the above set of equations, a is the activity in the feed, a' is the activity in the membrane, w is the weight fraction, Φ is the volume fraction, z is the UNIQUAC coordination number (assumed equal to 10), q is a dimensionless surface parameter, q^* is a modified surface parameter for molecules that form hydrogen bonds, Θ_i is the surface fraction of component i in the mixture, r is a dimensionless volume parameter, and τ is a binary interaction parameter. Subscripts i, j and k refer to feed components, and m refers to the membrane material.

The large number of unknown parameters in the Flory-Huggins and UNIQUAC models makes them difficult to use practically. These models can be fitted to experimental results, but the interaction parameters must be determined experimentally (Favre et al., 1993; Heintz & Stephan, 1994).

Fortunately, in the pervaporation of flavour compounds, the situation is much less complex because these compounds are typically present at low concentrations in the feed stream. The sorption isotherm can therefore be approximated by a straight line, as shown by the boxed region in Figure 2-12 (page 62). Several studies have confirmed the validity of this approximation for esters and alcohols, at concentrations up to 120 ppm (Trifunović & Trägårdh, 2003), 900 ppm (Jiraratananon et al., 2002b), and 1.2 kg m^{-3} (Lamer et al., 1994). When this approximation is valid, the activity in the membrane is directly proportional to the feed concentration.

Models for diffusion

Fick's law is commonly used to model diffusion through the membrane. In this model, the flux is proportional to the concentration gradient in the membrane (Börjesson et al., 1996; Mulder, 1996):

$$J_i = -D_i \frac{\mathrm{d}c_i}{\mathrm{d}l} \tag{2-45}$$

where J_i is the flux, D_i is the diffusion coefficient, c_i is the concentration in the membrane and l is the position in the membrane. The diffusion coefficient depends on both concentration and temperature (Karlsson & Trägårdh, 1993). Since there is both a temperature gradient and a concentration gradient across the membrane (Feng & Huang, 1997), the diffusion coefficient may not remain constant across the membrane. Its dependence on the concentration has been modelled in different ways by different authors (Fleming & Slater, 1992a; Lipnizki & Trägårdh, 2001), but is usually expressed by:

$$D_i = D_i^{\infty} \exp(Bc_i) \tag{2-46}$$

where D_i^{∞} is the diffusion coefficient at infinite dilution, and B is a plasticising coefficient (Mulder, 1991; Karlsson & Trägårdh, 1993; Mulder, 1996). However, Rautenbach & Albrecht (1985) found that the diffusion coefficient was adequately described using:

$$D_i = D_i^{\infty} w_{i,m} \tag{2-47}$$

where $w_{i,m}$ is the mass fraction of component i in the membrane.

In some cases, calculations can be simplified by assuming that the diffusion coefficient does not change with the concentration. Meuleman et al. (1999) found less than 1% difference between concentration-dependent and concentration-independent diffusion coefficients.

An Arrhenius relationship is used to describe the influence of temperature on diffusivity (Karlsson & Trägårdh, 1993):

$$D_i^{\infty} = D_{i,0}^{\infty} \exp\left(-\frac{E_a}{RT}\right) \tag{2-48}$$

where $D_{i.0}^{\infty}$ is a pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.

Fick's law does not usually account for flow coupling, but it can be altered to include coupling by either modifying the diffusion coefficient or by modifying the whole flux equation, so that the flux is equal to [flux excluding coupling] plus [flux due to coupling] (Karlsson & Trägårdh, 1993; Meuleman et al., 1999).

Another diffusion model sometimes used is the Maxwell-Stefan equation (Bitter, 1991; Karlsson & Trägårdh, 1993; Lipnizki & Trägårdh, 2001; Ghoreyshi et al., 2004). This model is based on the assumption that during steady-state flow, the driving force exerted on a species (in terms of a gradient in chemical potential) is balanced by frictional forces exerted on that species by other components present in the mixture. If f_{ij} is the force exerted on a molecule i by a molecule j, then:

$$f_{ij} = \frac{RT}{D_{ij}}\left(u_i - u_j\right) \tag{2-49}$$

where u_i and u_j are the velocities of each species (Bitter, 1991). Then the average force exerted on molecule i by all other components in a mixture with s components, each comprising y molecules, is given by the total force on all molecules divided by the total number of molecules (Bitter, 1991):

$$f_{i.av} = \frac{\sum_{k=1}^{n_j} \frac{RT}{D_{ij(k)}}\left(u_i - u_j\right)_k}{\sum_{j=1}^{s} y_j} \tag{2-50}$$

which simplifies to the following (Bitter, 1991):

$$f_{i.av} = -\operatorname{grad}\mu_i = \sum_{j=1}^{s} \frac{RT}{D_{ij}} x_j \left(u_{i.av} - u_{j.av}\right) \tag{2-51}$$

and rearranges to:

$$\frac{\operatorname{grad}\mu_i}{RT} c_i = \sum_{\substack{j=1 \\ j \neq i}}^{s} \frac{x_i J_j - x_j J_i}{D_{ij}} \tag{2-52}$$

where D_{ij} is the binary Maxwell-Stefan diffusivity (not the same as the Fick diffusivity), J_i is the molar mass transfer of component i, and x_i is the mole fraction of component i (Bitter, 1991).

This model assumes that the interaction between molecules i and j is independent of the presence of other molecules, which is not valid for liquids (Bitter, 1991). Therefore, Bitter (1991) modified the equation by introducing a friction coefficient based on the shape factor σ_i and viscosity η_m:

$$^{*}\sigma_i \eta_m = \frac{RT}{^{*}D_{im}} \tag{2-53}$$

where $^{*}D_{im}$ is the coefficient of self-diffusion of i in the mixture. The modified Maxwell-Stefan equation is then written as follows (Bitter, 1991):

$$^{*}D_{im} \frac{\text{grad}\,\mu_i}{RT} c_i = \sum_{\substack{j=1 \\ j \neq i}}^{s} (x_i J_j - x_j J_i) \tag{2-54}$$

This reduces to the thermodynamic model given by Equation (2-30) (Bitter, 1991).

Using Fick's law or thermodynamic diffusion equations, binary diffusivity or binary phenomenological coefficients cannot easily be related to the same parameters in a multicomponent mixture (Ghoreyshi et al., 2004), which makes multicomponent modelling difficult. In contrast, Maxwell-Stefan diffusivities obtained using binary data can be used to model multicomponent systems (Ghoreyshi et al., 2004). Also, Maxwell-Stefan diffusivities have a physical meaning (related to frictional forces between molecules), unlike Fick diffusivities or phenomenological coefficients which relate the flux to the driving force (Ghoreyshi et al., 2004). However, Matsuura (1994) stated that phenomenological coefficients (L_{ii}) do have a physical meaning:

$$L_{ii} = \frac{c_{i,m}}{f_{i,m}} \tag{2-55}$$

where $c_{i,m}$ is the concentration of component i in the membrane, and $f_{i,m}$ is the friction between the permeant and the membrane.

2.5.3.2 Pore flow model

The pore flow model for membrane processes is based on the assumption that separation is achieved due to filtration through pores in the membrane (Wijmans & Baker, 1995). The model assumes that the following three steps take place during pervaporation (Okada & Matsuura, 1991; Feng & Huang, 1997):

- Liquid is transported from the pore inlet to the vapour-liquid phase boundary
- Evaporation takes place at the phase boundary
- Vapour is transported from the phase boundary to the pore outlet.

Okada & Matsuura (1991) assumed that the separation would take place in the vapour phase within the pore.

In contrast to the solution-diffusion model, the pore flow model assumes that concentration is constant across the membrane and a pressure gradient exists instead. In Equation (2-31), the first term on the right hand side is now eliminated instead of the second term. Therefore, Darcy's law (Equation (2-56)) is used instead of Fick's law (Wijmans & Baker, 1995):

$$J = \frac{k_D}{l}(p_{fm} - p_{pm}) \qquad \textbf{(2-56)}$$

where k_D is the Darcy's law coefficient, l is the membrane thickness, p_{fm} is the pressure at the feed-membrane interface, and p_{pm} is the pressure at the permeate-membrane interface.

The membrane is not necessarily porous in the sense that an ultrafiltration membrane is, for example, but the pores represent void spaces which may not be much larger than the permeating molecules (Okada & Matsuura, 1992; Shieh & Huang, 1998a). For the model to work, the pores must be so small that most of the vapour molecules flowing through adsorb to the pore wall (Okada & Matsuura, 1991, 1992). Pervaporation membranes generally have angstrom sized pores (Feng & Huang, 1997).

Because of the assumption that the pressure is not constant across the membrane, the pore flow model predicts that inside the membrane there are two layers: a swollen upstream layer in which the permeants are liquid, and a downstream layer

in which the permeate is in the vapour phase (Okada & Matsuura, 1991; Tyagi et al., 1995; Feng & Huang, 1997; Vallieres et al., 2001). This assumption of two layers was also used by Binning et al. (1961) for the solution-diffusion model. Tyagi et al. (1995) presented a theoretical method of calculating the position of the phase boundary within the membrane. Darcy's law applies to liquid flow through the upstream layer of the membrane, and a surface-flow mechanism is used to describe vapour flow through the downstream membrane layer (Vallieres et al., 2001). This means that increasing the downstream pressure causes the flux to level off, rather than reaching zero when the downstream pressure is equal to the saturated vapour pressure of the permeate (Vallieres et al., 2001). Therefore, a decision on whether the pore flow model or the solution-diffusion model is more correct could be based on flux behaviour observed with increasing downstream pressure (Vallieres et al., 2001). However, Vallieres et al. (2001) showed that the pore flow flux pattern could equally be achieved with the solution-diffusion model, once air leaks in the system are taken into account.

The pore flow model is not widely used in pervaporation studies. Wijmans & Baker (1995) showed that the solution-diffusion model, in which free volume appears and disappears rather than having fixed pores, gives a better description of pervaporation than the pore flow model (which is better suited to processes such as ultrafiltration).

2.5.3.3 Thermodynamics of irreversible processes

Unlike the solution-diffusion model, models based on the thermodynamics of irreversible processes do not require any knowledge of what happens inside the membrane (Bitter, 1991; Mulder, 1996; Molina et al., 1997). The membrane is considered to be a 'black box', and the flux through this black box is proportional to the driving force from one side of the box to the other. The proportionality constant between the flux and the driving force is not given any physical meaning, but is regarded simply as a phenomenological coefficient that quantifies the mass transfer.

The major advantage of this approach is the ability to describe coupling interactions between permeants. Molina et al. (1997) described the flux as being

regulated by the self-driving force of permeants as well as by the coupling effects between separate permeants and between permeants and the membrane:

$$J_i = \frac{L_{ii}}{T}\,\mathrm{grad}(-\mu_i') + \frac{L_{im}}{T}\,\mathrm{grad}(-\mu_m') + \sum_{j \neq i} \frac{L_{ji}}{T}\,\mathrm{grad}(-\mu_j') \qquad \textbf{(2-57)}$$

where L is a local phenomenological coefficient, i and j are the permeants, and m refers to the membrane material (Molina et al., 1997).

2.6 Literature review conclusions

Pervaporation is a useful technique for aroma recovery, because it can be carried out at low temperatures so that aroma compounds are not thermally damaged. It is also more selective than some other techniques, and produces a highly concentrated extract because only volatile compounds can pass through the membrane. Therefore, pervaporation may be a good method for concentrating and fractionating flavour compounds from dairy streams.

Many models have been proposed to explain pervaporation, but there is not yet complete understanding of the processes occurring in the membrane. Models in the current literature are mainly descriptive rather than predictive: none of the current models can predict pervaporation results without needing experimental data on the system in question. The two main models used to describe pervaporation are the solution-diffusion model and the pore flow model; of these, the solution-diffusion model is more widely accepted.

PDMS is the membrane type most often used for organophilic pervaporation. This membrane allows high fluxes, but is not as selective as some other membrane types. Therefore, for a feed stream containing many different flavour compounds, PDMS is a good choice for concentrating the total volatile fraction without altering the flavour too much, but more selective membranes would potentially be useful for fractionating the feed into two or more streams with different flavours.

The influence of operating conditions (feed temperature, permeate pressure and feed flow rate) on pervaporation fluxes is fairly well defined. In general, the highest fluxes can be achieved with a high feed temperature, a low permeate pressure, and a high feed flow rate. However, different compounds are affected by

operating conditions in different ways, making it impossible to quantitatively predict the flux or enrichment of a particular compound without the need for experiments. This means that, before any new work can take place, the effect of operating conditions on the permeants in question, using the pervaporation system in question, must be determined.

More research is required on how volatile and non-volatile components of the feed mixture affect pervaporation. This is an important consideration in moving from simple model feed solutions to complex dairy products. The current study aims to clarify how dairy components affect pervaporation of flavour compounds.

Chapter 3

General methods

3.1 Feed solutions

Feed solutions for each pervaporation experiment were made by dissolving the appropriate flavour compounds in distilled water. A fresh 5 L batch of model feed solution was used for each pervaporation experiment. Each batch of feed solution was checked by analysing a retentate sample taken at the beginning of each pervaporation experiment.

3.1.1 Standard multicomponent feed

An aqueous model solution, containing nine flavour compounds at the concentrations listed in Table 3-1, was used for experiments to compare various operating conditions, and as a basis for comparison with different feed solutions. The standard multicomponent feed was based on the volatile composition of two dairy process streams (ester cream and a confidential process stream), which were initially identified by Fonterra as candidates for pervaporation. Flavour compounds were added on a volumetric basis, and their densities were used to calculate the mass concentrations in Table 3-1. Sigma-Aldrich, Aldrich, Sigma

Table 3-1: Composition of the standard multicomponent feed solution.

Compound	Molecular weight (g mol^{-1})	Feed concentration (mg L^{-1})	Brand
Acids:			
Acetic acid	60	105	Sigma-Aldrich
Butanoic acid	88	107	Aldrich
Hexanoic acid	116	111	Fluka
Octanoic acid	144	105	Sigma
Esters:			
Ethyl butanoate	116	101	Fluka
Ethyl hexanoate	144	100	Aldrich
Ethyl octanoate	172	10.4	Aldrich
Ketones:			
2-Heptanone	114	9.8	Fluka
2-Nonanone	142	9.8	Fluka

and Fluka brand chemicals were all supplied by Sigma-Aldrich Co. (St Louis, MO, USA). All chemicals had purities greater than 98%.

3.1.2 Model feed solutions with additional flavour compounds

For experiments that included extra volatile components, feed solutions had the same composition as the standard multicomponent feed (Table 3-1), plus one of the following additions:

- 114 mg L^{-1} propanoic acid (Sigma-Aldrich), 108 mg L^{-1} pentanoic acid (SigmaUltra) and 106 mg L^{-1} heptanoic acid (Sigma)
- 10.3 mg L^{-1} ethyl decanoate (Aldrich)

These chemicals were obtained from Sigma-Aldrich Co. (St Louis, MO, USA), and had purities greater than 97%.

3.1.3 Model feed solutions with different volatile compositions

For experiments to evaluate the effect of ethanol, the feed solution had the same composition as the standard multicomponent feed (Table 3-1), except that ethanol (Anchor Ethanol Ltd, Reporoa, New Zealand; 99.88% pure) was added to give 5% (v/v) ethanol in the final solution.

For experiments to evaluate coupling effects between different compounds, feed solutions contained between one and nine of the compounds in Table 3-1. The standard multicomponent feed was used as a control. The following feed solutions were made with each compound at the same concentration as in Table 3-1 unless otherwise indicated:

- 2-Heptanone only
- 2-Nonanone only
- Ethyl butanoate only
- Ethyl hexanoate only
- Ethyl octanoate only
- Acetic acid only
- Butanoic acid only
- Hexanoic acid only
- Octanoic acid only

- Ethyl butanoate and 2-nonanone
- Ethyl butanoate and 10.5 mg L^{-1} acetic acid
- Ethyl butanoate and 105 mg L^{-1} acetic acid
- Ethyl butanoate and 210 mg L^{-1} acetic acid
- Ethyl butanoate and ethyl octanoate
- 2-Heptanone and 2-nonanone
- Ketones and acids: 2-heptanone, 2-nonanone, acetic acid, butanoic acid, hexanoic acid, octanoic acid
- Ketones and esters: 2-heptanone, 2-nonanone, ethyl butanoate, ethyl hexanoate, ethyl octanoate
- Multicomponent except ethyl butanoate: 2-heptanone, 2-nonanone, ethyl hexanoate, ethyl octanoate, acetic acid, butanoic acid, hexanoic acid, octanoic acid

In addition, the standard multicomponent feed, and the first nine feed solutions listed above, were also tested with each compound at 50% of the concentration shown in Table 3-1.

3.1.4 Model feed mixtures containing non-volatile dairy ingredients

Experiments were carried out with non-volatile dairy ingredients added to the feed solution, including cream (Anchor brand, Fonterra Co-operative Group Ltd, Auckland), milk protein isolate (specification 0664901009740, Fonterra, New Zealand) and lactose (edible grade from Fonterra, New Zealand; extra pure grade from Scharlau, Barcelona, Spain). Table 3-2 gives the composition of each dairy ingredient. Feed mixtures contained the same flavour compounds as in the standard multicomponent feed, at the concentrations given in Table 3-1, plus additional dairy ingredients as follows:

- Cream. Various ratios of cream to water were used to create mixtures containing 0.5%, 1%, 5%, 10%, 20% and 38% fat (w/v). The highest fat mixture corresponded to 100% cream. Mixtures were stirred only, not homogenised. A creamy layer rose to the top of solutions with 0.5% and 1% fat, but feed solutions with higher fat levels remained homogeneous. Cream was chosen as a convenient fat source because it contains the right mix of fats, at the right fat globule size, to be directly applicable to dairy systems.

Table 3-2: Proximate composition of cream, milk protein isolate and edible grade lactose.

Component	Concentration (% w/w)		
	Cream[a]	Milk protein isolate[b]	Edible grade lactose[c]
Water	54.9	5.93	0.06
Protein	2.0	84.4	0.3
Fat	40.0	1.4	0
Carbohydrates (lactose)	2.8	1.72	99.3
Ash	0.38	6.8	0.34

[a]From New Zealand food composition tables (Visser et al., 1991; Athar et al., 2003); confirmed by a company representative to be similar to the brand of cream used in experiments (Attanayake, 2008, personal communication).

[b]From Fonterra laboratory tests on the batch used for pervaporation experiments (Ferreira, 2008, personal communication).

[c]From product bulletin (Anon., no date).

- 4% (w/v) milk protein isolate, equivalent to 3.4% total protein in the feed solution. Milk protein isolate contains a blend of casein and whey proteins. This protein level was chosen because it is almost double the protein level in cream, while being comparable to the amount of protein in milk (Swaisgood, 1996).
- Cream diluted to 20% fat, plus extra milk protein isolate to make the total protein up to 3.5% (w/v), in order to discover any interactions between protein and fat.
- 6% or 12% (w/v) edible grade lactose. The lower level of lactose was chosen because it is double the amount of lactose in cream, while being similar to the lactose level in milk (Swaisgood, 1996). The higher level was chosen to test the effect of lactose concentration.
- 6% (w/v) extra pure lactose, in order to discover whether impurities in the edible grade lactose had any effect on results.
- Cream diluted to 20% fat (w/v), plus extra edible grade lactose to make the total lactose up to 6% (w/v), in order to discover any interactions between lactose and fat.

3.1.5 Real dairy products

For experiments using real dairy products as the feed, either ester cream or starter distillate was used without adding any further flavour compounds to each product.

Ester cream was prepared in batches of 2.5 L or 4 L, by fermenting a mixture of diluted cream and ethanol (the exact process is confidential to Fonterra Co-operative Group Ltd). A separate batch was used for each run. Anchol natural starter distillate (30 ×) was obtained from Anchor Ethanol Ltd (Tirau, New Zealand).

3.2 Pervaporation apparatus

Figure 3-1 shows the pervaporation unit. The feed was continuously recirculated past the membrane and back into the jacketed feed tank at approximately 1 L min^{-1} (corresponding to a Reynolds number of approximately 500), using a diaphragm pump (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). The retentate was returned to the middle of the feed tank, in order to ensure adequate mixing. The feed temperature was controlled by recirculating water from a temperature-controlled water bath (Grant Instruments Ltd, Cambridgeshire, UK) through the jacket of the stainless steel feed tank. If necessary, a water bath cooling unit (Julabo Labortechnik, Seelbach, Germany) was used to cool the water to below room temperature. The module temperature was measured with a thermocouple inserted into the top of the membrane module. The permeate

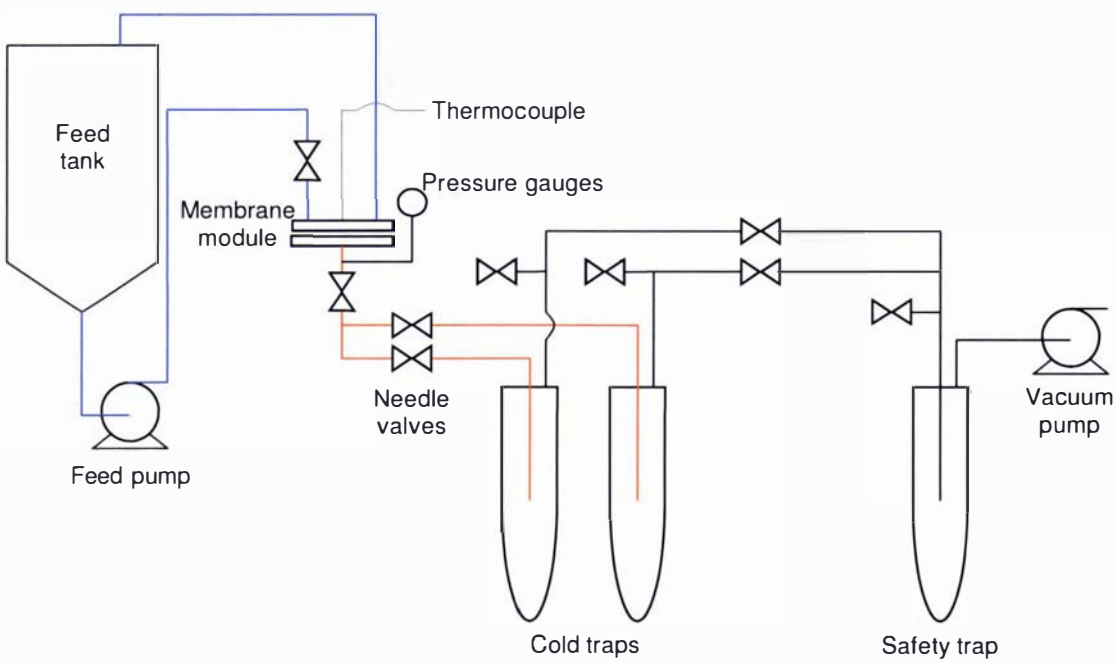


Figure 3-1:Schematic diagram of the pervaporation unit. Tubing in blue shows the feed/retentate flow and tubing in orange shows the permeate flow.

pressure was measured just downstream of the membrane, using Baratron pressure gauges (model 622A11TDE for pressures up to 1.3 kPa, or model 315BA-00100 for higher pressures; both from MKS Instruments Ltd, Burlington, MA, USA), and was controlled by adjusting the needle valves upstream of the cold traps. A Squirrel 2020 data logger (Grant Instruments Ltd, Cambridgeshire, UK) recorded outputs from both pressure gauges and from the thermocouple, at one-minute intervals.

Figure 3-2 shows the stainless steel membrane module, which housed a rectangular membrane of effective area 0.012 m^2. Three types of composite flat-sheet hydrophobic membranes were supplied by GKSS-Forschungszentrum Geesthacht GmbH (Geesthacht, Germany); their properties are given in Table 3-3. The membrane rested on a sintered stainless steel support, and was sealed inside the module with an ethylene-propylene-diene terpolymer (EPDM) gasket.

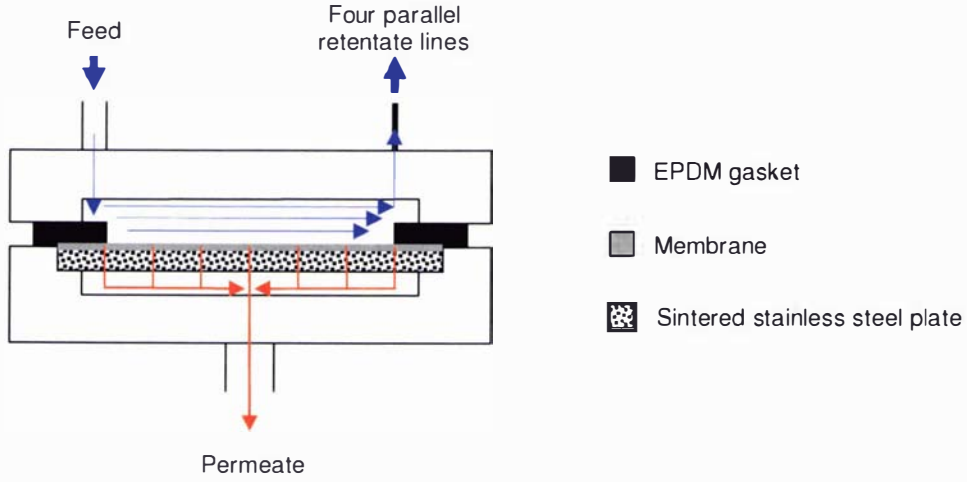


Figure 3-2: Cutaway diagram of membrane module. Blue arrows show the feed/retentate flow and orange arrows show the permeate flow.

Table 3-3: Properties of pervaporation membranes used in this study (all supplied by GKSS-Forschungszentrum).

Membrane	Active layer material	Active layer thickness (μm)	Support layer material
PDMS Type 1	Polydimethylsiloxane	0.5	Polyacrylonitrile
PDMS Type 2	Polydimethylsiloxane	1.5	Polyacrylonitrile
POMS	Polyoctylmethylsiloxane	5–6	Polyetherimide

The vacuum on the permeate side of the system was maintained with a vacuum pump (model RV5, BOC Edwards, West Sussex, UK), which operated continuously during experiments.

The permeate was collected in glass cold traps, which were cooled with liquid nitrogen. Only one of the two parallel cold traps was used at a time, and the active cold trap was changed every hour to enable permeate samples to be removed during each pervaporation run.

3.3 Pervaporation experiments

New membranes were conditioned before use in pervaporation experiments, by recirculating approximately 500 mL of distilled water at 30°C through the pervaporation apparatus for 12 h, with the membrane installed and the permeate side under maximum vacuum (between 0.2 and 1.2 kPa, depending on the membrane). It was assumed that 12 h was sufficient to pre-swell the membrane to allow steady state operation.

One or two pervaporation runs were completed each day. Before each run, if the feed solution did not contain all of the volatile compounds that were in the feed from the previous run, potentially cross-contaminating volatiles were removed by recirculating 500 mL of distilled water for 30 minutes, with the permeate side under maximum vacuum. Still under vacuum, the membrane was then conditioned for one hour with 500 mL of feed solution, prior to each pervaporation run. After conditioning, the feed tank was drained and refilled with fresh feed solution, which had been warmed to the required temperature in a water bath. When both runs for one day used feed solutions of the same composition, the conditioning step was carried out only at the start of the day, because the first run acted as the conditioning step for the second run.

Each pervaporation run was carried out over four hours. Samples of retentate were taken at time zero, and after two and four hours. Permeate samples were taken every hour, after thawing and weighing of the entire permeate collected during that hour. Retentate and permeate samples were kept at –18°C prior to analysis.

The feed temperature, permeate pressure, membrane type and feed solution varied according to the experiment to be carried out, and are described in the relevant chapters. Not all pressure/temperature combinations could be used with each membrane, as the lowest achievable permeate pressure depended on the flux through the membrane. At operating conditions that allowed high fluxes, the permeate could not be pumped away fast enough to maintain very low permeate pressures. Experiments were completed in triplicate unless otherwise stated.

The module temperature and permeate pressure were recorded every minute during pervaporation runs. Generally, the average temperature and pressure recorded during a run were within 0.3°C or 0.03 kPa of the target conditions.

Following runs with aqueous feed solutions, the feed side of the pervaporation unit (including the membrane) was rinsed with water, then distilled water was recirculated through the feed side overnight, with the permeate side open to the atmosphere. When the feed solution contained fat or protein, the membrane module was bypassed, and the feed tank and feed lines were cleaned with a 1% solution of Reflux B620 alkaline detergent (Orica Chemnet, New Zealand). As this cleaning solution (pH 11.9) was beyond the membrane's stated pH limit of 10–11 (Ohlrogge, 2005, personal communication), the membrane module was cleaned separately by soaking in absolute ethanol. The feed side and module were then rinsed with distilled water overnight, as with aqueous feed solutions.

3.4 Calculation of fluxes and enrichment factors

3.4.1 Enrichment factors and uncorrected fluxes

Enrichment factors were defined as the ratio between the permeate concentration and the feed concentration of each compound.

The total flux was calculated according to Equation (3-1):

$$J_{uncorrected} = \frac{m}{A \times t} \qquad \textbf{(3-1)}$$

where $J_{uncorrected}$ is the total flux, m is the mass of permeate collected, A is the membrane area and t is the time taken for permeate collection. Individual fluxes

of each compound were calculated by multiplying their mass fraction in the permeate by the total flux. Total and individual fluxes were measured after one, two, three and four hours of pervaporation, and the mean of the four measurements was recorded as the flux for each run. Fluxes remained relatively constant within each run, showing that steady state was achieved quickly.

The following section describes how fluxes were corrected to account for changing membrane performance.

3.4.2 Monitoring of membrane performance

Membrane performance was monitored by regularly carrying out a pervaporation run under standard operating conditions (30°C/1.5 kPa for PDMS Type 1, 20°C/0.5 kPa for PDMS Type 2 and 30°C/0.3 kPa for POMS) with the standard multicomponent feed solution. This monitoring revealed that the flux declined over time. Membranes were replaced when the total flux, measured under these standard conditions, had decreased by 25–35% (after approximately 30–50 pervaporation runs).

So that runs carried out on different dates could be compared, correction factors were applied to account for the decrease in flux with time (Equation (3-2)) and for differences between different membrane pieces of the same type (Equation (3-3)), determined using data from all the runs under standard conditions for each membrane.

$$C_{within} = \frac{J_{0,i}}{J_{0,i} + n \times Sl} \tag{3-2}$$

$$C_{between} = \frac{J_{0,av}}{J_{0,i}} \tag{3-3}$$

In Equations (3-2) and (3-3), C_{within} is the within-membrane correction factor; $J_{0,i}$ is the flux recorded, under standard conditions, for the first four-hour run with a particular membrane piece; n is the number of pervaporation runs carried out with a particular membrane piece; Sl is the slope of a graph of flux, under standard conditions, versus run number for each membrane piece (for runs with non-

volatile feed components, two slopes were used because the flux decline was not linear); $C_{between}$ is the between-membrane correction factor; and $J_{0,av}$ is the average of all $J_{0,i}$ values for membrane pieces of that type. The corrected flux J was then given by Equation (3-4):

$$J = J_{uncorrected} \times C_{within} \times C_{between} \quad \textbf{(3-4)}$$

3.5 Analysis of retentate and permeate samples

3.5.1 Extraction of aqueous samples

All permeate samples, as well as retentate samples that did not contain non-volatile dairy components, were extracted with diethyl ether (Scharlau, Barcelona, Spain) prior to analysis by gas chromatography (GC). Internal standard (propyl butanoate, Fluka, 50 µL of a 873 mg L^{-1} solution) and formic acid (Scharlau, 50 µL of a 10% (v/v) aqueous solution) were added to 0.5 g of each sample. Each sample was extracted with three 0.5 mL aliquots of diethyl ether, by mixing at 35 Hz on a vortex mixer for one minute before drawing off the aqueous layer with a syringe. The three ether extracts were combined.

3.5.2 Extraction of samples containing non-volatile components

Retentate samples that contained fat, protein or lactose underwent solid phase extraction (SPE) prior to GC analysis. The SPE procedure was based on a method used at Fonterra. Samples (2.0 g) were mixed well with 6 g sodium sulphate, 100 µL internal standard (an aqueous mixture of 873 mg L^{-1} propyl butanoate and 918 mg L^{-1} heptanoic acid, both from Sigma-Aldrich), 0.3 mL of 5 M sulphuric acid, 5 mL of heptane and 5 mL of diethyl ether (all from Scharlau). A 3 mL portion of the extract (top layer) was passed through a GracePure aminopropyl SPE cartridge (conditioned with heptane); the eluate was known as 'extract 1' and analysed for esters and ketones, using propyl butanoate as the internal standard peak. A 2:1 (v/v) mixture of chloroform and isopropanol (3 mL; both from Scharlau) was passed through the SPE cartridge, and the eluate was discarded. The acids were then eluted off the SPE cartridge with a solution of 6% formic acid in 2:1 (v/v) heptane/diethyl ether; this eluate was known as 'extract 2' and analysed for acids, using heptanoic acid as the internal standard peak.

3.5.3 Gas chromatography

One microlitre of either the combined extract from Section 3.5.1, or extract 1 or extract 2 from Section 3.5.2, was injected into a Shimadzu GC-17A (Shimadzu Corporation, Kyoto, Japan) with an Alltech EC-1000 column (30 m long, 0.25 mm diameter, 0.25 μm film thickness) (Grace Davison, Deerfield, IL, USA). The injector was at 180°C, the flame ionisation detector was at 250°C and the oven temperature programme was increased from 35 to 210°C at 12°C min^{-1}. Injection was in split mode. The carrier gas (nitrogen) flow rate was 1.8 mL min^{-1}, with a split ratio of 5:1. Each extract was injected in duplicate.

Compounds were quantified by the internal standard method, comparing peak areas with that of an internal standard of known concentration. The calculated concentrations in the ether extract were multiplied by the extraction efficiency for each compound (determined by extracting samples of known composition) to obtain the concentrations in each sample. Extraction efficiencies are given in Appendix A.

3.5.4 Analysis of real dairy products

3.5.4.1 Ester cream

Ester cream permeate and retentate samples were extracted following the methods in Sections 3.5.1 and 3.5.2 respectively. Extracts were analysed using a similar GC method to that described in Section 3.5.3, except that the oven temperature was programmed from 35°C to 230°C (12°C min^{-1}) and held for one minute, to allow time for all peaks to elute.

GC peaks corresponding to some esters (present in ester cream but not in model solutions) overlapped with acid peaks, so ester cream samples were also analysed with a different column, using gas chromatography-mass spectrometry (GCMS) rather than GC. The GCMS method was as follows: 1 μL of extract was injected into a QP2010 GCMS (Shimadzu, Japan) with a Restek Rxi-5ms column (30 m long; 0.25 mm diameter; 0.25 μm film thickness). Injection was in the split mode (split ratio 5) and the injector temperature was 250°C. The carrier gas (helium) column flow rate was 1.12 mL min^{-1}. The mass spectrometer ion source temperature was 200°C and the interface temperature was 250°C. The oven

temperature was held at 35°C for 5.5 minutes, then increased to 230°C at 20°C min^{-1} and held for 5 minutes. Each extract was injected in duplicate.

With the Restek Rxi-5ms column, acid peaks were normally too small to quantify, and were separated from ester peaks. Acetic acid and butanoic acid concentrations were then deduced from the difference between the chromatograms with the two different columns. This method did not give accurate concentrations of hexanoic and octanoic acids, so they were excluded from the ester cream results.

3.5.4.2 Starter distillate

Starter distillate retentate and permeate samples were extracted using the method in Section 3.5.1. The concentration of diacetyl was determined using the same GC (not GCMS) method as for ester cream (Section 3.5.4.1), with an external standard (Fluka brand, ≥ 99.4% purity, Sigma Aldrich).

GC analysis of starter distillate revealed many unknown peaks. Samples were re-analysed using GCMS, to identify some of the unknown compounds. Headspace solid phase micro-extraction (SPME) was used with untreated samples, rather than ether extracts, to avoid obscuring peaks behind the solvent peak. One millilitre of sample was placed in a 20 mL headspace vial, and the headspace was exposed to a PDMS-divinylbenzene SPME fibre (65 µm film thickness; Supelco, Bellefonte, PA) for 30 minutes at 35°C, with agitation. Volatiles were desorbed from the SPME fibre into a GCMS-QP5000 (Shimadzu, Japan) with a sampling time of 0.5 minutes. Injection was in the splitless mode. The column was an Alltech EC-1000 (30 m long, 0.25 mm diameter, 0.25 µm film thickness) (Grace Davison, Deerfield, IL, USA). The carrier gas (helium) column flow rate was 1.8 mL min^{-1}. The injection port and interface temperatures were both 250°C, and the oven temperature was programmed from 35°C to 230°C at 5°C min^{-1}, then held for 21 minutes. SPME and GCMS were carried out in duplicate for each sample, but the second replicate of each sample had smaller peak areas than the first replicate because volatile compounds evaporated after the vial septum had been pierced. Therefore, only one replicate of each sample was used in calculations.

Compounds in starter distillate (other than diacetyl) were tentatively identified from their mass spectra (by comparison with the NIST62 library) and from their

order of elution, and were not confirmed using standards. Tentatively identified compounds were not quantified, but their enrichment factors were estimated from the ratio between peak areas in permeate and retentate samples.

3.6 Error reporting

Whenever experimental errors are indicated throughout this thesis, these refer to standard errors unless otherwise indicated (i.e., $x \pm y$ means that x is the mean and y is the standard error). Means and standard errors were calculated from three replicates unless otherwise noted.

Chapter 4

Flux variation over time

Membrane performance monitoring (described in Section 3.4.2) showed that fluxes did not remain constant over time as expected. The purpose of this chapter is to discuss possible reasons for the flux variation, and to validate flux correction factors so that results from different runs could be compared.

4.1 Flux decline with volatile feed components

When membranes had only been in contact with feed solutions containing volatile compounds and water, total fluxes (measured under standard operating conditions defined in Section 3.4.2) decreased over the lifetime of each membrane, as shown by Figure 4-1.

Usually, flux decline in membrane processes is caused by fouling of the membrane surface and pores, by substances such as protein (Mulder, 1996). However, as pervaporation membranes are non-porous, fouling does not normally occur to a great degree (Mulder, 1996; Baudot et al., 1999; Schäfer & Crespo, 2003). The aqueous model solutions used for the majority of experiments consisted of only volatile compounds and water, and did not contain any components that would reasonably be expected to foul the membrane. Experiments with non-volatile feed components were only carried out after all other experiments were complete; these are not included in Figure 4-1, and will be discussed in Section 4.2.

Few researchers have reported flux decline during pervaporation, yet it occurred to a similar extent with all three membranes tested in this study. This suggests that it may have been caused by certain feed compounds used in this study but rarely mentioned in pervaporation literature, for example hexanoic acid and octanoic acid. These compounds are not very volatile; at 30°C their saturated vapour pressures are 9.1 Pa and 0.9 Pa respectively, compared with 45–2750 Pa for the

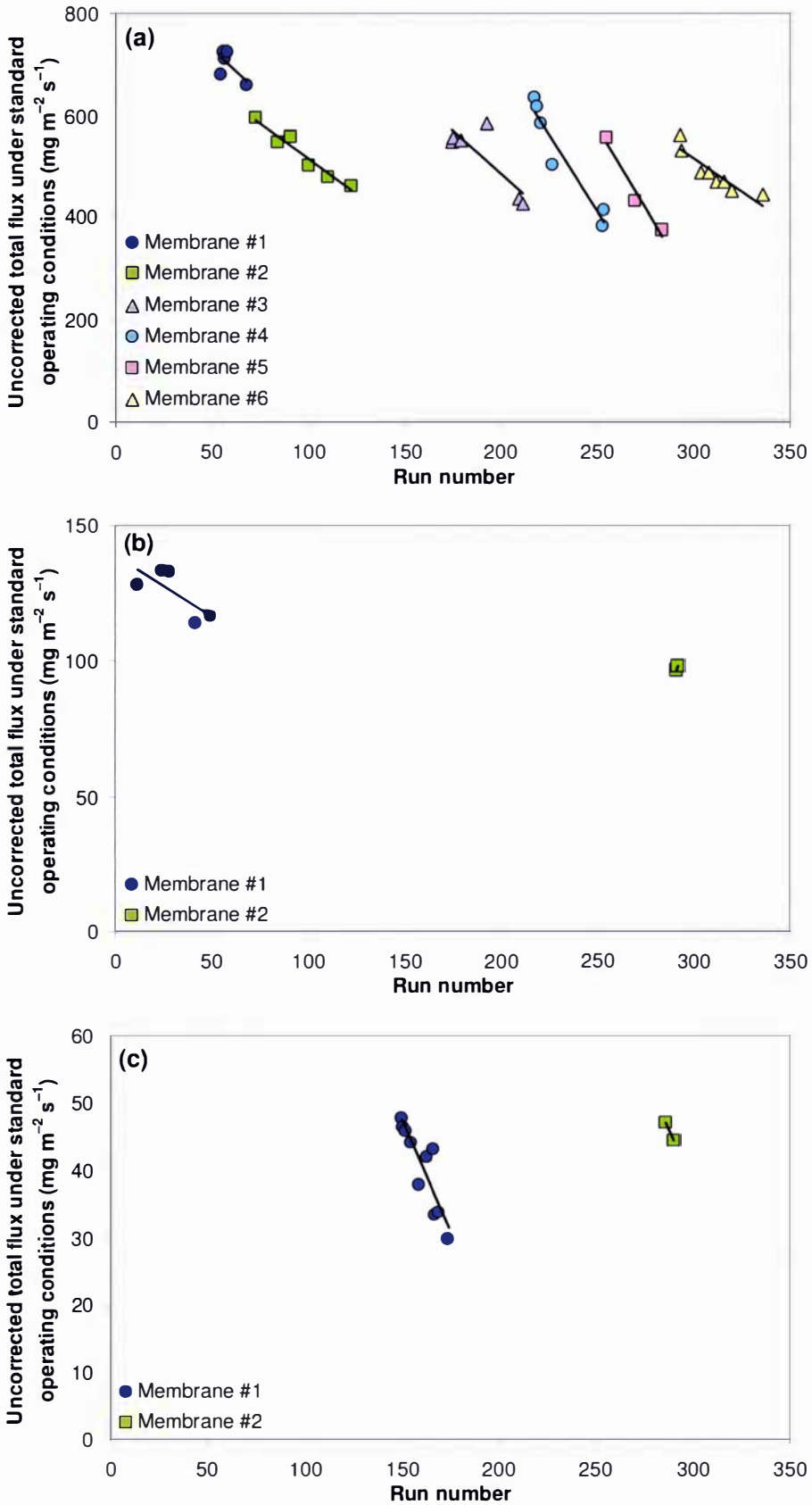


Figure 4-1: Decrease in uncorrected total fluxes between runs, for (a) PDMS Type 1 membrane (30°C feed temperature; 1.5 kPa permeate pressure), (b) PDMS Type 2 membrane (20°C feed temperature; 0.5 kPa permeate pressure) and (c) POMS membrane (30°C feed temperature; 0.3 kPa permeate pressure). Standard multicomponent feed solution used for all runs shown.

other flavour compounds in this study (Poling et al., 2001; Speight, 2003; Lide, 2005). This lack of volatility could prevent these compounds from being completely evaporated and transported away from the downstream side of the membrane. Octanoic acid in particular was found to carry over between pervaporation runs, and could still be detected in the permeate after several hours of pervaporation with pure water as the feed.

Octanoic acid has also been found to cause flux decline during ultrafiltration with a hydrophobic polysulphone membrane, due to adsorption on the pore walls, thus decreasing the pore size (Lindau et al., 1995). In a subsequent study (Brinck et al., 2000), the same research group showed that the flux decline could be eliminated by increasing the feed pH to above 10, so that the majority of the octanoic acid was in the dissociated form, which is more soluble in water than the undissociated acid. Hence, it may also be possible to prevent flux decline in pervaporation by adjusting the feed pH, provided that the acidic compounds were the only contributors to flux decline. In contrast to ultrafiltration, increasing the pH would also reduce the permeation of acids through pervaporation membranes, as the dissociated form is less volatile.

Fadeev et al. (2003) also observed flux decline during pervaporation of yeast fermentation broth with a nanoporous poly(1-trimethylsilyl-1-propyne) membrane (without a porous support layer). They concluded that compounds with low volatility, which were absorbed into the membrane but did not permeate, caused the flux decline by occupying the free volume in the membrane. In the present study, even the least volatile flavour compounds tested still permeated to some degree, so presumably they condensed in the porous support layer as well as, or instead of, the active layer of the membrane.

As a result of a discussion with researchers from GKSS-Forschungszentrum, the research institution that supplied the membranes, it is believed that the flux decline in the current study was due to permeants being adsorbed in the porous support layer of the membranes. The pervaporation unit used for the experiments had relatively long permeate tubing with a small diameter, which was not ideal as it could have caused a pressure gradient between the downstream side of the membrane and the vacuum pump. This pressure drop could lead to less-volatile compounds condensing in the porous layer of the membrane, especially given the

high fluxes through the thin membranes used. The porous support layer has a very large surface area, as it contains many small pores. Therefore, it is likely that these condensed compounds adsorbed on this surface (Wind, Bengtson, & Brinkmann, 2007, personal communication).

To confirm this hypothesis, it would be necessary to carry out 10–20 pervaporation runs with pure water and with single-component feed solutions of each flavour compound, starting with a new membrane for each feed solution. Due to time constraints, this set of experiments was not included in this study. If the flux declined over time with one or more of the single-component feed solutions but not with pure water, it could be concluded that the flux decline was caused by flavour compounds either blocking the free volume in the membrane active layer, or adsorbing in the support layer. To determine which of these places was being blocked, the experiment could be repeated with a homogeneous membrane that had no support layer.

4.2 Flux decline with non-volatile feed components

After using the membrane for experiments with non-volatile feed components in the feed solution, the flux decline was no longer linear as in Figure 4-1; instead the flux decreased rapidly for the first few runs and then stabilised at approximately 45% of the initial flux (Figure 4-2). This pattern of flux decline matches that normally observed with dairy liquids in pressure-driven membrane processes (Marshall & Daufin, 1995), suggesting that the non-volatile feed components fouled the membrane.

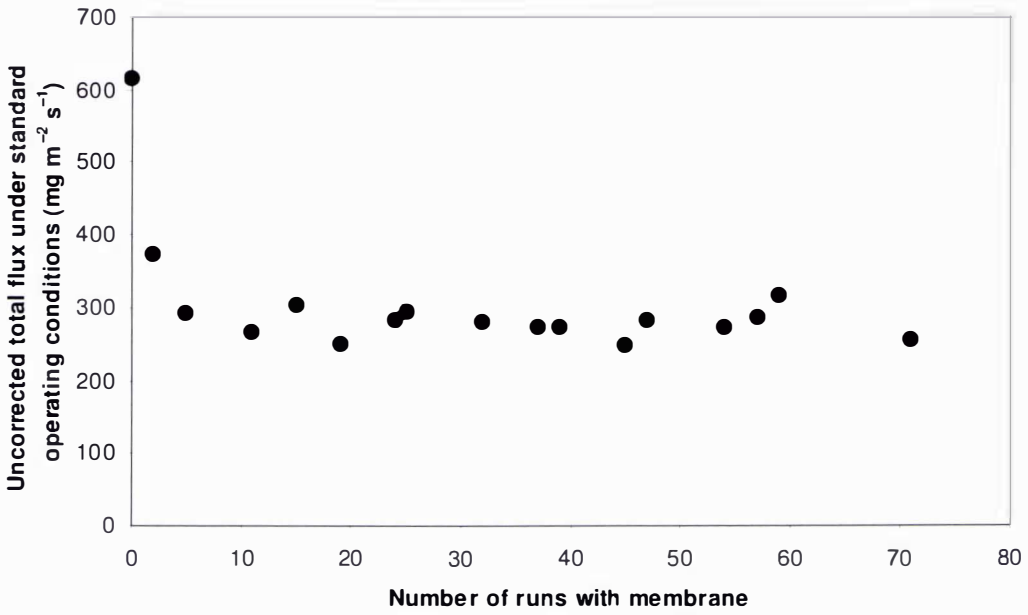


Figure 4-2: Decrease in uncorrected total fluxes between runs, when the membrane had been used with feed solutions containing non-volatile compounds (standard multicomponent feed; standard operating conditions: PDMS Type 1 membrane, 30°C feed temperature, 1.5 kPa permeate pressure).

4.3 Flux variation between membrane pieces

Figure 4-1 shows slight differences between the initial flux of different membrane pieces of the same type. Scanning electron microscopy showed that the active layer thickness varied over each membrane (Figure 4-3), which is the most likely reason for flux variation between membrane pieces. Microscopy was undertaken by the Institute of Molecular Biosciences at Massey University (Palmerston North, New Zealand).

Isci et al. (2006) also found differences in flux between different pieces of the same membrane type, reporting that fluxes deviated from the mean by up to 7.2%.

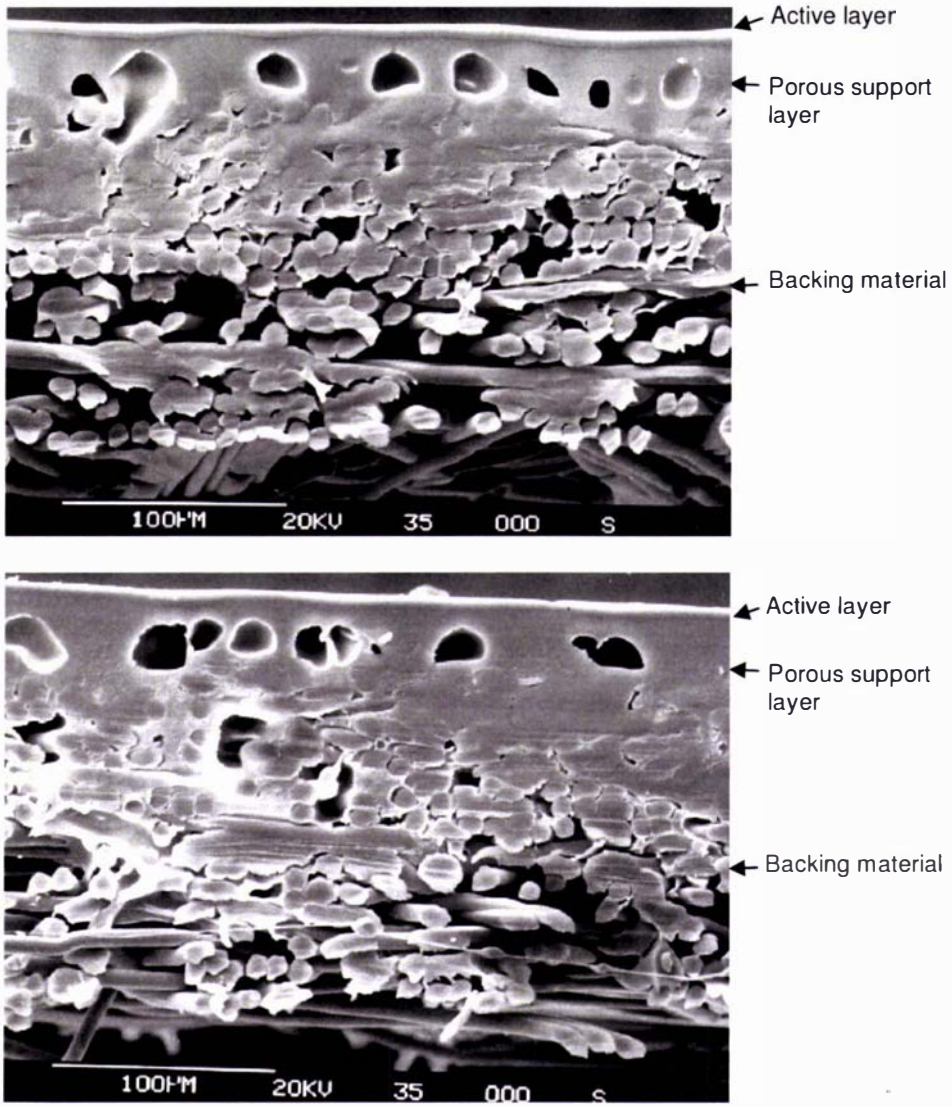


Figure 4-3:Scanning electron microscope images (320 × magnification of cross-sectional slice) of two samples of the PDMS Type 2 membrane, showing how the active layer thickness varied between membrane pieces.

4.4 Validation of flux correction factors

Figure 4-4 shows the fluxes for all runs carried out at standard operating conditions, after applying the correction factors in Section 3.4.2. Corrected fluxes varied only slightly over 417 pervaporation runs, which were carried out over a period of almost two years. Standard deviations of the data in Figure 4-4 were 33.9 mg m^{-2} s^{-1}, 5.3 mg m^{-2} s^{-1} and 6.5 mg m^{-2} s^{-1} for PDMS Type 1, PDMS Type 2 and POMS respectively. Experiments with non-volatile feed components took place between run numbers 346--417, during which time corrected fluxes at standard conditions varied slightly more than when the feed solutions contained only volatile compounds. The consistency between runs shows that it was valid to

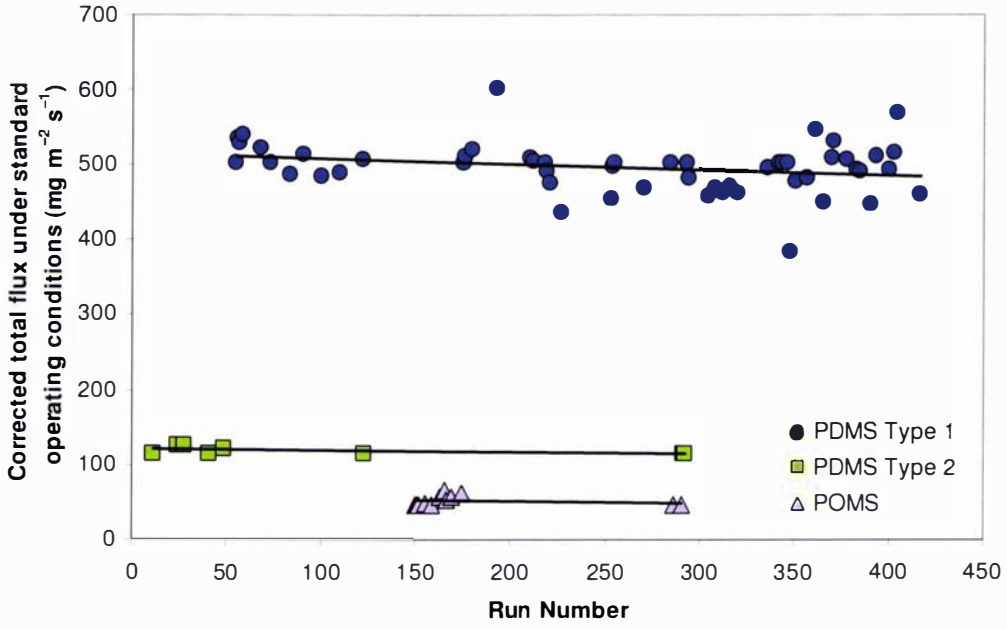


Figure 4-4: Total fluxes at standard operating conditions (PDMS Type 1 membrane: 30°C feed temperature, 1.5 kPa permeate pressure; PDMS Type 2 membrane: 20°C feed temperature, 0.5 kPa permeate pressure; POMS membrane: 30°C feed temperature, 0.3 kPa permeate pressure), after applying correction factors (Equation (3-4) in Chapter 3).

apply correction factors, to take into account the flux decline between experiments. Therefore, all fluxes reported in this thesis are corrected fluxes, and the results are assumed not to be affected by flux decline.

However, if pervaporation were to be used in an industrial setting, the flux decline itself would need to be prevented as much as possible, to reduce the cost of continually replacing membranes. The pervaporation unit should be designed so that the permeate could be efficiently pumped away from the membrane (by using short, wide-bore permeate tubing and a high-capacity vacuum pump), to prevent flavour compounds from condensing in the support layer. A more open structure for the support layer would also allow a stronger vacuum close to the membrane, thus reducing condensation.

Chapter 5

Effect of operating conditions and compound type on pervaporation

5.1 Introduction

In order to investigate pervaporation for concentrating dairy flavours, it was first necessary to characterise the behaviour of the flavour compounds of interest during pervaporation, without any complicating factors such as alterations to the feed solution. Many researchers have studied pervaporation of flavour compounds (reviewed by Karlsson & Trägårdh, 1993; Baudot & Marin, 1997). However, it is not possible to directly compare results unless they have been obtained with the same operating conditions and the same feed solution, on the same pervaporation apparatus.

The objective of this study was to compare pervaporation of nine flavour compounds in a model feed solution, under a range of operating conditions (membrane type, feed temperature and permeate pressure). From a review of the literature (Chapter 2; Section 2.4.3), it was expected that fluxes would increase as the temperature was increased or as the permeate pressure was decreased. Flavour compounds were selected from three homologous series (acids, esters and ketones), enabling comparisons between different types of permeating molecules. It was assumed that the degree of sorption of flavour compounds in the membrane would depend on their hydrophobicity, and that the diffusion of flavour compounds through the membrane would depend on their molecular size.

Much of the discussion in this chapter is based on a published paper (Overington et al., 2008).

5.2 Experimental

Pervaporation experiments were carried out following the procedure in Chapter 3, using the standard multicomponent feed solution described in Section 3.1.1.

Experiments were completed in triplicate with different membranes (PDMS Type 1, PDMS Type 2, POMS), module temperatures (20–40°C) and permeate pressures (0.3–3.3 kPa absolute).

Some additional pervaporation experiments were carried out with a feed solution that contained the standard nine flavour compounds as well as either ethyl decanoate or three extra acids with odd-numbered carbon chain lengths (Section 3.1.2). These experiments used the PDMS Type 1 membrane, feed temperatures of 20°C, 30°C or 40°C, and a permeate pressure of 2 kPa.

The standard multicomponent feed solution had a pH of 3.5. To test the effect of feed pH on pervaporation, pervaporation runs were carried out with the pH of the multicomponent feed solution adjusted to 2.5 with hydrochloric acid (1 mol L^{-1}), or to 4.8 or 7.0 with potassium hydroxide (1 mol L^{-1}). For a 5 L batch of feed solution, approximately 10 mL of hydrochloric acid solution was added to reach pH 2.5, and 15 mL or 25 mL of potassium hydroxide solution was added to reach pH 4.8 or 7.0 respectively. pH effects were tested at one set of operating conditions only (PDMS Type 1 membrane, feed temperature 30°C, permeate pressure 1.5 kPa).

5.3 Results and discussion

5.3.1 Effect of operating conditions on flux

Figure 5-1 shows the total flux achieved at each combination of operating conditions. The total flux increased with increasing temperature, as is generally found during pervaporation (Karlsson et al., 1995; Lipnizki et al., 1999; Peng et al., 2003; She & Hwang, 2006a). In general, the total flux decreased linearly with increasing permeate pressure at a particular temperature. This is because the driving force for permeation is directly related to the difference in partial pressure between the feed and permeate sides of the membrane. There were some exceptions to the expected trend; the flux was lower than expected at 40°C/3.3 kPa with the PDMS Type 2 membrane, and was higher than expected at 40°C/2 kPa with the POMS membrane.

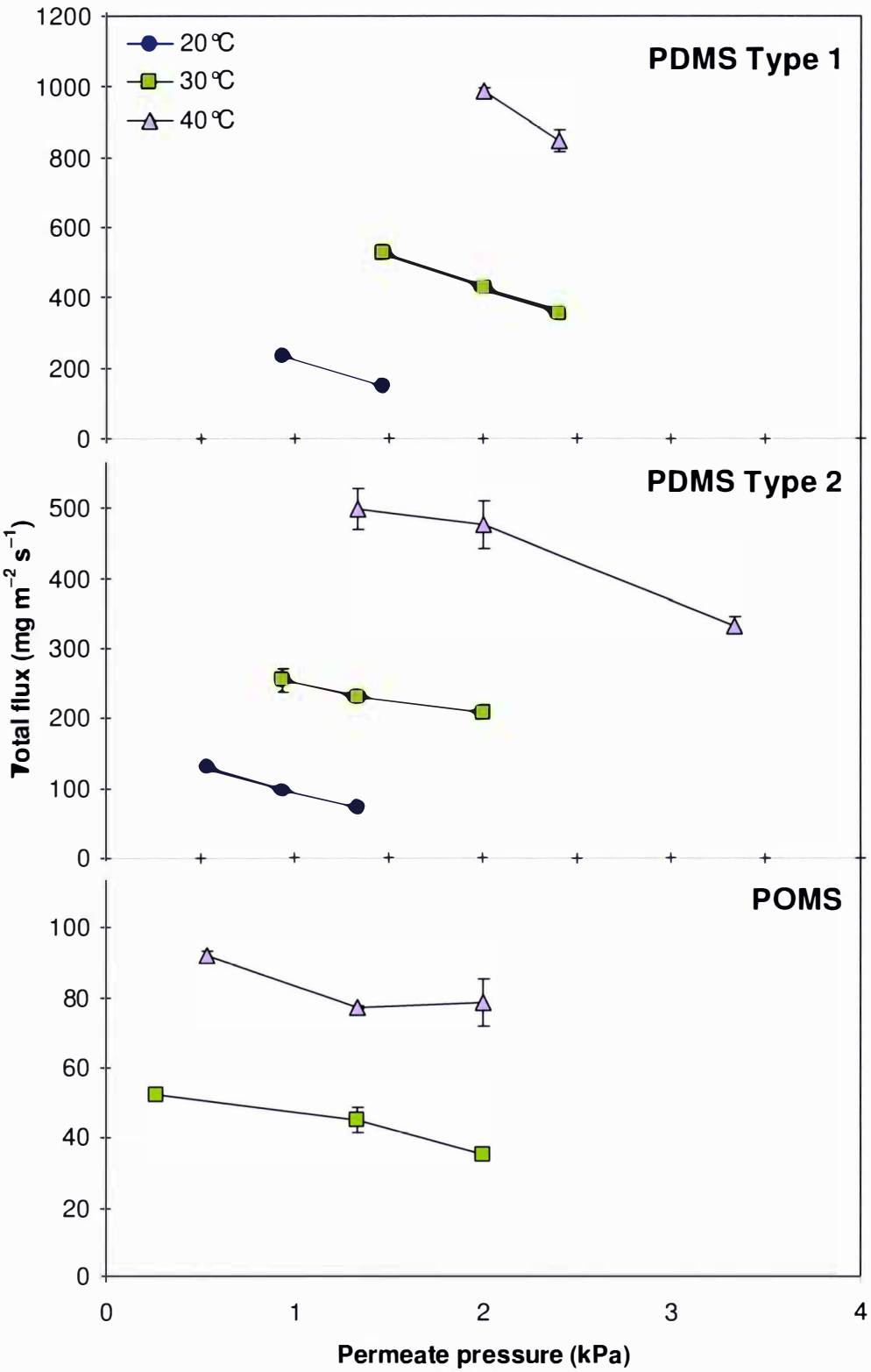


Figure 5-1: Effect of operating conditions on total flux of the model feed solution through PDMS Type 1, PDMS Type 2 and POMS membranes. Each point is the mean (± standard error) of at least three replicates.

As the permeate consisted almost entirely of water (the total flavour compound concentration was always less than 1%), the total fluxes in Figure 5-1 can be considered equal to the water flux. Fluxes of distilled water were generally not significantly different from the total flux with the model solution at the same operating conditions (95% confidence). Individual flavour compounds showed similar trends to those in Figure 5-1, but their fluxes were several orders of magnitude lower. An example of flavour compound fluxes at 2 kPa is given in Table 5-1. This table also includes feed partial pressures (calculated as described in Appendix B), which determine the driving force of each compound.

No significant losses of flavour compounds occurred during pervaporation runs at any of the operating conditions tested (mass balance shown in Appendix C).

5.3.2 Effect of membrane type on total flux and flavour compound fluxes

The PDMS Type 1 membrane gave the greatest total fluxes, followed by the PDMS Type 2 membrane and then the POMS membrane (Figure 5-1). This trend follows membrane thickness; multiplying by active layer thickness reduced the difference between the three membranes, but the fluxes with the PDMS membranes were still greater than those with the POMS membrane. For example, at 30°C/2 kPa, thickness-normalised fluxes were 214 ± 5 µm mg m^{-2} s^{-1} for PDMS Type 1, 310 ± 6 µm mg m^{-2} s^{-1} for PDMS Type 2 and 193 ± 5 µm mg m^{-2} s^{-1} for POMS. Figure 5-1 shows total fluxes that have not been normalised for membrane thickness. Although the PDMS Type 1 membrane was one third the thickness of PDMS Type 2, the total flux with PDMS Type 1 was on average only 2.2 times as high as that with PDMS Type 2 at the same operating conditions.

Membranes made of the same polymer would be expected to have similar total fluxes, after taking membrane thickness into account. The difference between the two PDMS membranes could have been due to concentration polarisation becoming more significant with a thinner membrane. Concentration polarisation is a phenomenon in which the faster-permeating component is depleted in the feed adjacent to the membrane, meaning that its driving force is reduced and its flux would therefore be lower than expected, whereas the opposite is the case for

Table 5-1: Fluxes (mean ± standard error) and feed partial pressures of flavour compounds at different temperatures (all at 2 kPa permeate pressure).

Membrane/ Compound	Feed concentration (mmol L^{-1})	Partial vapour pressure in feed (Pa)			Flavour compound flux ($\times 10^9$ mol m^{-2} s^{-1})		
		20°C	30°C	40°C	20°C	30°C	40°C
PDMS Type 1							
2-Heptanone	0.1	0.35	0.71	1.39	110 ± 4	430 ± 60	840 ± 50
2-Nonanone	0.1	2.40	4.35	7.61	10.5 ± 0.4	100 ± 4	248 ± 4
Acetic acid	1.7	0.15	0.27	0.48	51 ± 5	460 ± 40	1420 ± 9
Butanoic acid	1.2	0.06	0.14	0.29	47 ± 4	520 ± 60	1840 ± 40
Hexanoic acid	1.0	0.04	0.10	0.25	31 ± 3	630 ± 100	2560 ± 180
Octanoic acid	0.7	0.04	0.12	0.32	13 ± 3	270 ± 20	1300 ± 200
Ethyl butanoate	0.9	19.82	42.62	84.37	1350 ± 70	4600 ± 500	8600 ± 200
Ethyl hexanoate	0.7	33.46	62.36	113.9	250 ± 10	1822 ± 8	4640 ± 140
Ethyl octanoate	0.1	10.59	20.81	40.00	4.2 ± 0.4	42 ± 4	161 ± 5
PDMS Type 2							
2-Heptanone	0.1		0.71	1.39		278 ± 10	420 ± 40
2-Nonanone	0.1		4.35	7.61		57 ± 2	130 ± 30
Acetic acid	1.7		0.27	0.48		250 ± 70	410 ± 50
Butanoic acid	1.2		0.14	0.29		290 ± 50	600 ± 70
Hexanoic acid	1.0		0.10	0.25		220 ± 30	610 ± 70
Octanoic acid	0.7		0.12	0.32		47 ± 6	290 ± 30
Ethyl butanoate	0.9		42.62	84.37		1530 ± 70	2250 ± 160
Ethyl hexanoate	0.7		62.36	113.9		840 ± 60	1800 ± 300
Ethyl octanoate	0.1		20.81	40.00		28 ± 9	73 ± 14
POMS							
2-Heptanone	0.1		0.71	1.39		75 ± 2	170 ± 20
2-Nonanone	0.1		4.35	7.61		18 ± 3	25 ± 5
Acetic acid	1.7		0.27	0.48		28.9 ± 1.1	110 ± 15
Butanoic acid	1.2		0.14	0.29		38.2 ± 1.2	210 ± 30
Hexanoic acid	1.0		0.10	0.25		20 ± 2	112 ± 14
Octanoic acid	0.7		0.12	0.32		7 ± 2	18 ± 6
Ethyl butanoate	0.9		42.62	84.37		990 ± 40	2100 ± 300
Ethyl hexanoate	0.7		62.36	113.9		320 ± 50	380 ± 80
Ethyl octanoate	0.1		20.81	40.00		6 ± 2	6 ± 2

slower-permeating components (Feng & Huang, 1997; Bowen et al., 2004). Sampranpiboon et al. (2000b) found that, because there is less resistance to mass transfer through thinner membranes, mass transfer resistance on the feed side of the membrane (primarily caused by concentration polarisation) becomes relatively more important compared with mass transfer through the membrane itself.

5.3.3 Influence of membrane type on permeate composition

Figure 5-2 shows the difference between the three membranes at 40°C/2 kPa, in terms of the enrichment factors of each compound. Similar trends with compound and membrane type were obtained at the other operating conditions at which the membranes were compared. Ethyl butanoate and 2-heptanone were enriched the most; their enrichment factors ranged from 5.4–33.2 and 6.1–26.5 respectively (including all operating conditions tested, not only those shown in Figure 5-2). For these two compounds, the POMS membrane gave an enrichment factor 2–5 times that of the PDMS membranes. The membrane type had a lesser effect on the enrichment factors of the other flavour compounds, which had enrichment factors of less than 10 for most of the operating conditions tested. Therefore, the choice

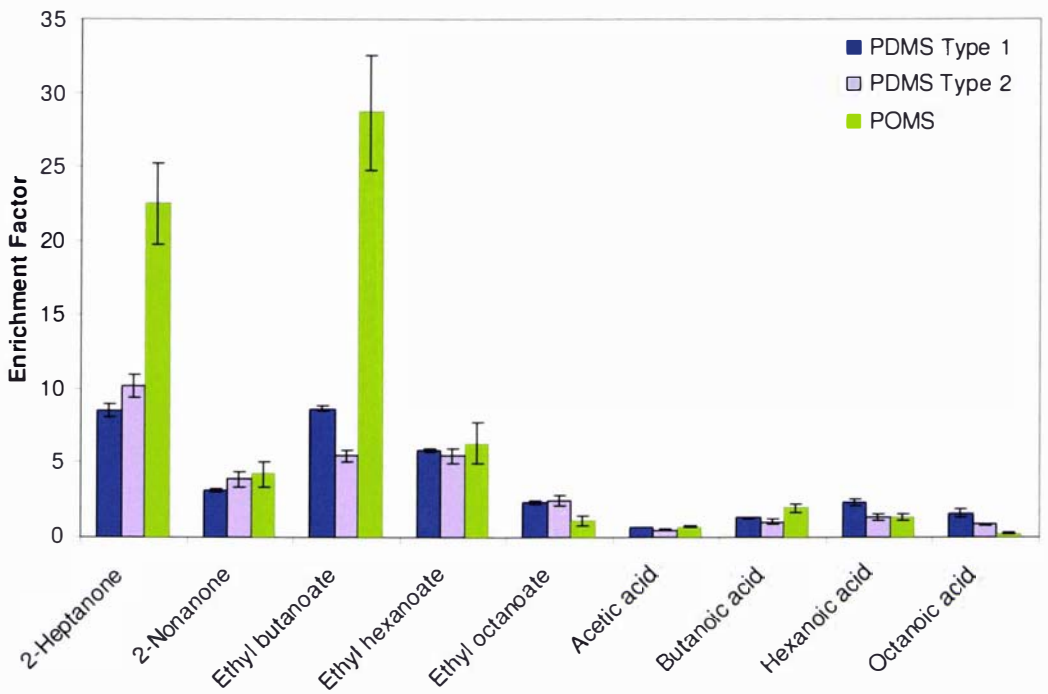


Figure 5-2: Enrichment factors (mean ± standard error) of each model solution compound at a feed temperature of 40°C and a permeate pressure of 2 kPa.

of membrane influenced the relative amounts of short-chain esters and ketones compared with the other flavour compounds.

As PDMS and POMS polymers have the same backbone structure, any differences in flux or enrichment would be due to the different size side chains of these polymers (Figure 2-6 compared with Figure 2-8; pages 25 and 29 respectively). Membrane permeability is due to the combined effects of permeant sorption in and diffusion through the membrane (Feng & Huang, 1996; Pereira et al., 1998; Isci et al., 2006):

$$P_i = S_i D_i \qquad \textbf{(2-29)}$$

where P_i, S_i and D_i are the permeability, solubility and diffusion coefficients respectively. According to Trifunović & Trägårdh (2006), permeant sorption is greater in POMS than in PDMS, but diffusion is greater in PDMS. This may help to explain the results in Figure 5-2. Similar enrichment factors were achieved with all membranes for most compounds, but, for the smallest ester and the smallest ketone tested, the enrichment factors were considerably higher with the POMS membrane than with the PDMS membranes. The higher degree of sorption in POMS would be cancelled out by the lower diffusivity, for all but the smallest molecules, which had high diffusivities regardless of the membrane type.

The results found here reflect those of She & Hwang (2006a), who found that PDMS membranes gave lower enrichment factors but a higher total flux than POMS membranes, for the pervaporation of ethyl butanoate. They explained that the bulky octyl group present in POMS may have reduced the amount of water that could permeate through the membrane. POMS is more hydrophobic than PDMS because of its larger side group (Kanani et al., 2003; Trifunović & Trägårdh, 2006).

Sampranpiboon et al. (2000b) also compared PDMS and POMS membranes for pervaporation of aqueous ethyl butanoate and ethyl hexanoate, and found that both membranes had similar ester fluxes, but that the POMS membrane had a higher separation factor because its water flux was lower. Kanani et al. (2003) obtained greater separation factors with POMS membranes than with PDMS membranes for some tea aroma compounds such as linalool and *cis*-3-hexenol.

However, PDMS membranes gave better separation factors for aldehydes and some other compounds.

The PDMS membranes used in this study had a polyacrylonitrile (PAN) support layer, whereas the support layer of the POMS membrane was polyetherimide (PEI). Trifunović & Trägårdh (2005) found some differences in performance between these two support layer materials; PEI reduced the driving force more than PAN for some esters and alcohols, and also caused the membrane to have slightly lower overall permeability, but selectivity was better with PEI than with PAN. Therefore, the fact that the PDMS membranes used here had higher fluxes and (in some cases) lower enrichment factors than the POMS membrane may have been partly due to their PAN support layers.

5.3.4 Influence of compound type and operating conditions on enrichment

As can be seen in Figure 5-2, esters and ketones had greater enrichment factors than acids. Within the esters and ketones homologous series, the enrichment factors decreased with increasing molecular weight, but acids did not show this trend. Butanoic and hexanoic acids had greater enrichment factors than acetic and octanoic acids at all operating conditions tested, although there were only small differences between the four acids during pervaporation at 40°C/2 kPa, as shown by Figure 5-2.

Table 5-2 shows the flavour compound enrichment factors at various operating conditions with the PDMS Type 1 membrane. Other membranes showed similar trends with feed temperature and permeate pressure (Appendix D). Within the esters and ketones, the enrichment of the smallest compound with each functional group was influenced by the operating conditions, but the enrichment of the larger compounds was not. Enrichment factors of ethyl butanoate and 2-heptanone, the smallest ester and the smallest ketone respectively, were greatest at the conditions that gave the lowest total flux (low temperatures and high permeate pressures) for all three membranes. However, there were no obvious trends with feed temperature or permeate pressure for ethyl hexanoate, ethyl octanoate or 2-nonanone.

Table 5-2: Enrichment factors (mean ± standard error) of flavour compounds at different operating conditions (PDMS Type 1 membrane).

	Enrichment factor								
Feed temperature	**20°C**			**30°C**			**35°C**	**40°C**	
Permeate pressure	0.9 kPa	1.5 kPa	2.0 kPa	1.5 kPa	2.0 kPa	2.4 kPa	2.0 kPa	2.0 kPa	2.4 kPa
2-Heptanone	12.4 ± 1.1	16.7 ± 0.4	19.7 ± 0.1	8.0 ± 0.5	9.8 ± 1.6	11.9 ± 0.9	8.7 ± 0.3	8.5 ± 0.4	6.1 ± 0.4
2-Nonanone	3.7 ± 0.2	3.5 ± 0.2	2.3 ± 0.1	3.0 ± 0.1	2.9 ± 0.1	3.8 ± 0.2	2.9 ± 0.2	3.12 ± 0.08	2.8 ± 0.2
Acetic acid	0.46 ± 0.05	0.46 ± 0.01	0.45 ± 0.02	0.49 ± 0.02	0.52 ± 0.04	0.53 ± 0.04	0.58 ± 0.02	0.71 ± 0.01	0.56 ± 0.02
Butanoic acid	0.70 ± 0.05	0.61 ± 0.03	0.59 ± 0.04	0.80 ± 0.04	0.9 ± 0.1	0.88 ± 0.02	1.05 ± 0.06	1.32 ± 0.05	0.93 ± 0.04
Hexanoic acid	0.88 ± 0.05	0.68 ± 0.01	0.50 ± 0.05	1.2 ± 0.1	1.3 ± 0.2	1.29 ± 0.06	1.8 ± 0.2	2.3 ± 0.2	1.5 ± 0.2
Octanoic acid	0.43 ± 0.07	0.26 ± 0.03	0.27 ± 0.06	0.81 ± 0.05	0.77 ± 0.04	0.62 ± 0.06	1.0 ± 0.1	1.6 ± 0.3	1.4 ± 0.2
Ethyl butanoate	13.0 ± 1.4	17.8 ± 0.1	24.0 ± 0.4	8.8 ± 0.5	10.5 ± 1.5	13.2 ± 0.5	9.1 ± 0.4	8.6 ± 0.2	6.1 ± 0.5
Ethyl hexanoate	6.6 ± 0.3	6.9 ± 0.4	5.6 ± 0.4	5.2 ± 0.2	5.2 ± 0.2	7.2 ± 0.4	5.4 ± 0.3	5.8 ± 0.1	4.6 ± 0.2
Ethyl octanoate	2.3 ± 0.1	1.8 ± 0.4	1.1 ± 0.1	1.6 ± 0.1	1.4 ± 0.2	2.6 ± 0.2	2.0 ± 0.4	2.31 ± 0.09	1.9 ± 0.5

The enrichment factors of acids were in many cases less than one, meaning that their concentrations were lower in the permeate than in the feed. The effect of feed temperature and permeate pressure on the enrichment of acids was opposite to the effect on the enrichment of small esters and ketones; with acids, greater enrichment factors generally occurred at high temperatures and low permeate pressures.

5.3.5 Effect of compound type and molecular weight on flux

Differences in enrichment factors between compounds were also reflected in the relative fluxes of each compound (Figures 5-3 to 5-5). In these figures, the flux of each compound has been normalised by dividing by its feed mole fraction, so that compounds at different feed concentrations could be compared. When the feed partial pressure was halved, by halving the concentration of each compound in the feed, the enrichment factors did not significantly change (95% confidence; data shown in Appendix E). All data points in Figures 5-3 to 5-5 were obtained at 2 kPa, but similar trends were observed at other permeate pressures.

Individual fluxes depend on each compound's permeability in the membrane and on its driving force for permeation. Compounds with greater partial pressures on the feed side of the membrane have higher driving forces. Of the compounds tested, esters had the greatest feed partial pressures, followed by ketones then acids (Table 5-1). This high driving force caused esters and ketones to have larger enrichment factors (Figure 5-2) and higher normalised fluxes than acids (Figures 5-3 to 5-5).

Within each functional group, however, the fluxes did not follow the trends expected from partial vapour pressures. Mole fraction-normalised ester fluxes decreased with increasing molecular weight within the homologous series of esters (Figure 5-3), although the flux of ethyl hexanoate (molecular weight of 144 g mol^{-1}) did not quite fit this trend with the PDMS Type 2 membrane at 40°C, as its flux was similar to that of ethyl butanoate (molecular weight of 116 g mol^{-1}) at these operating conditions. Ketone fluxes followed the same trend as ester fluxes, in that the smaller of the two ketones had the higher flux (Figure 5-4). In contrast, two opposing trends were observed when the mole fraction-

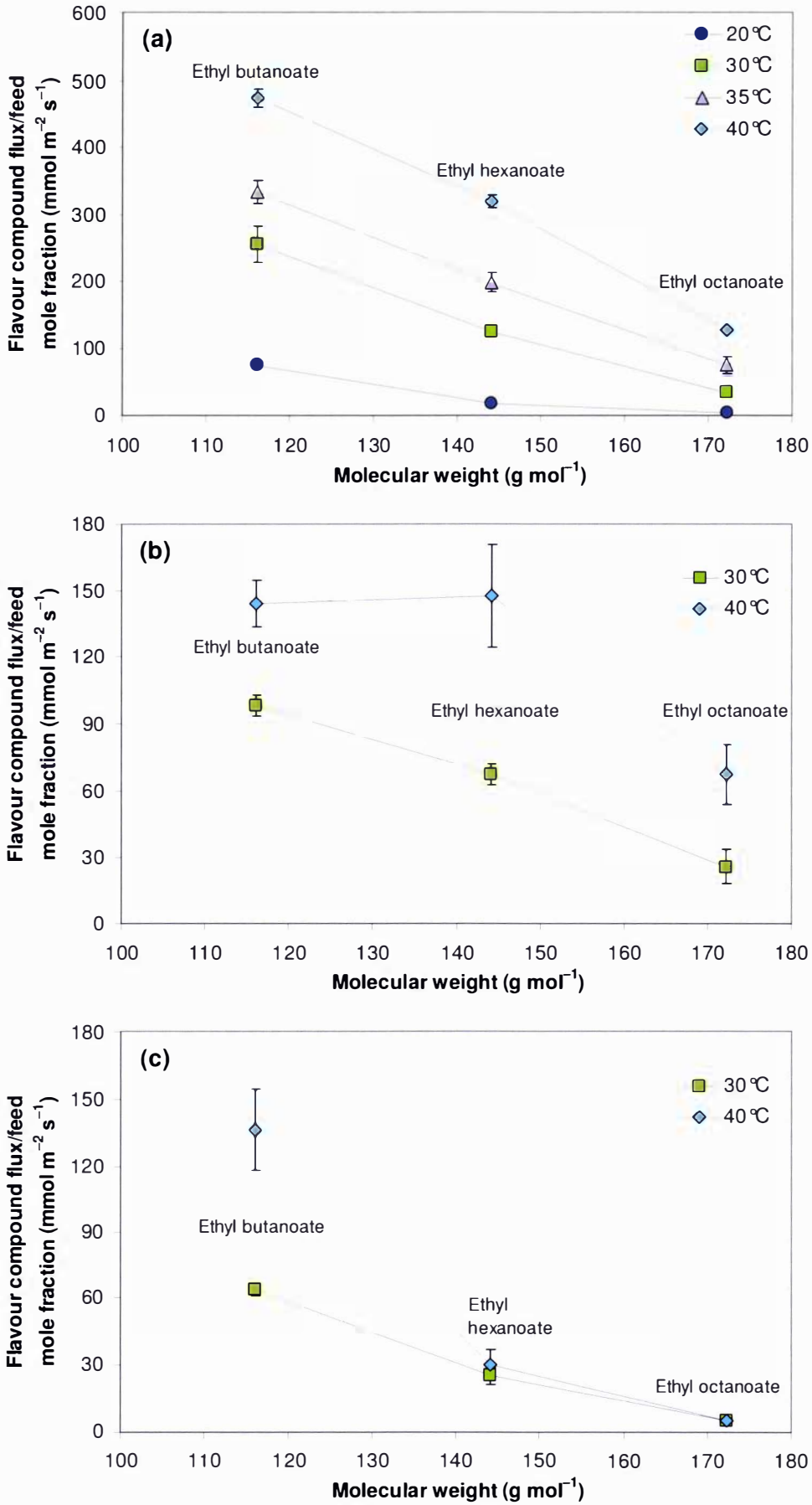


Figure 5-3:Effect of molecular weight on flux of esters (normalised for feed mole fraction) through (a) PDMS Type 1, (b) PDMS Type 2, (c) POMS. Data points are the mean (± standard error) of three replicates, all at 2 kPa permeate pressure.

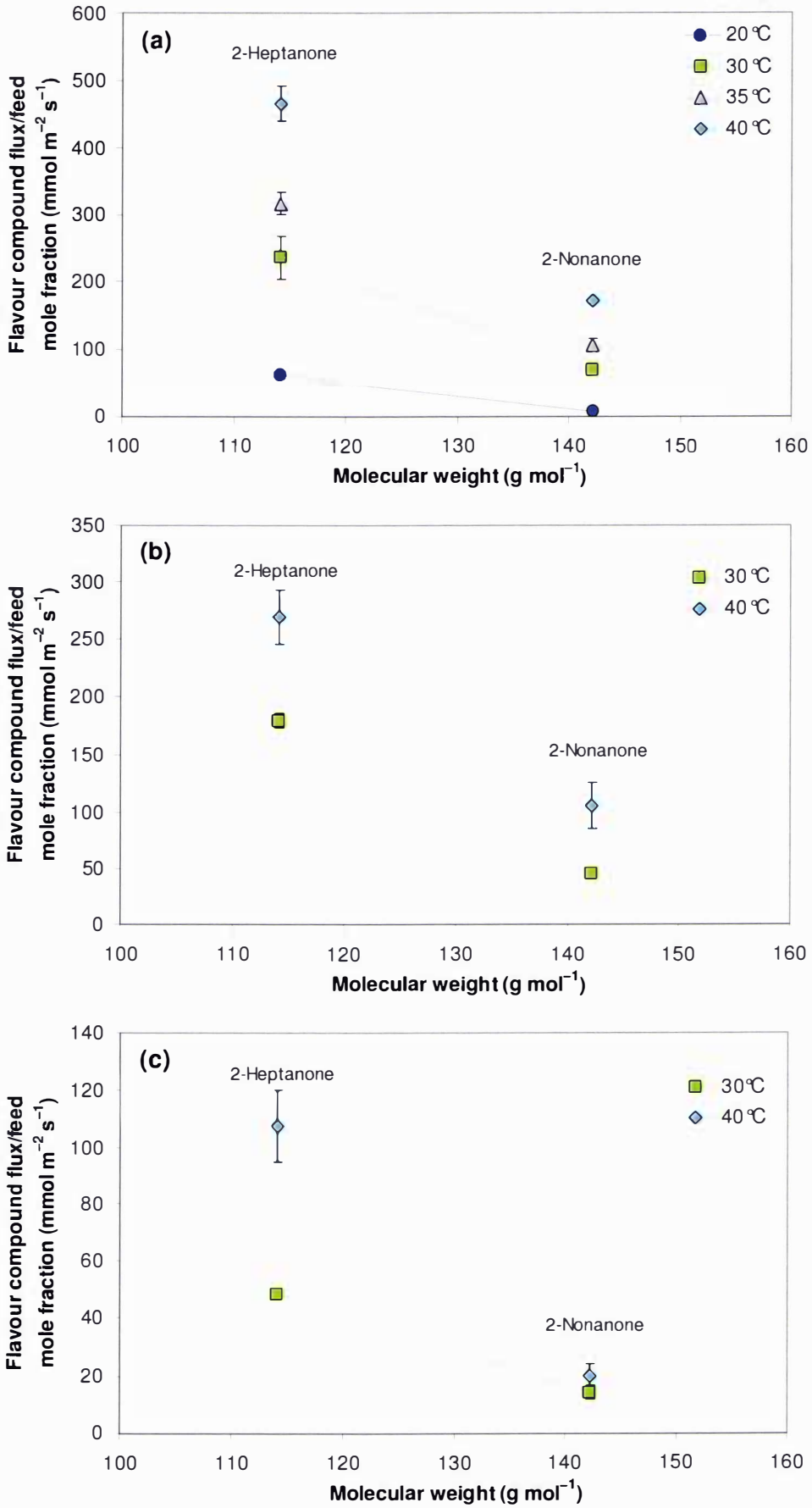


Figure 5-4: Effect of molecular weight on flux of ketones (normalised for feed mole fraction) through (a) PDMS Type 1, (b) PDMS Type 2, (c) POMS. Data points are the mean (± standard error) of three replicates, all at 2 kPa permeate pressure.

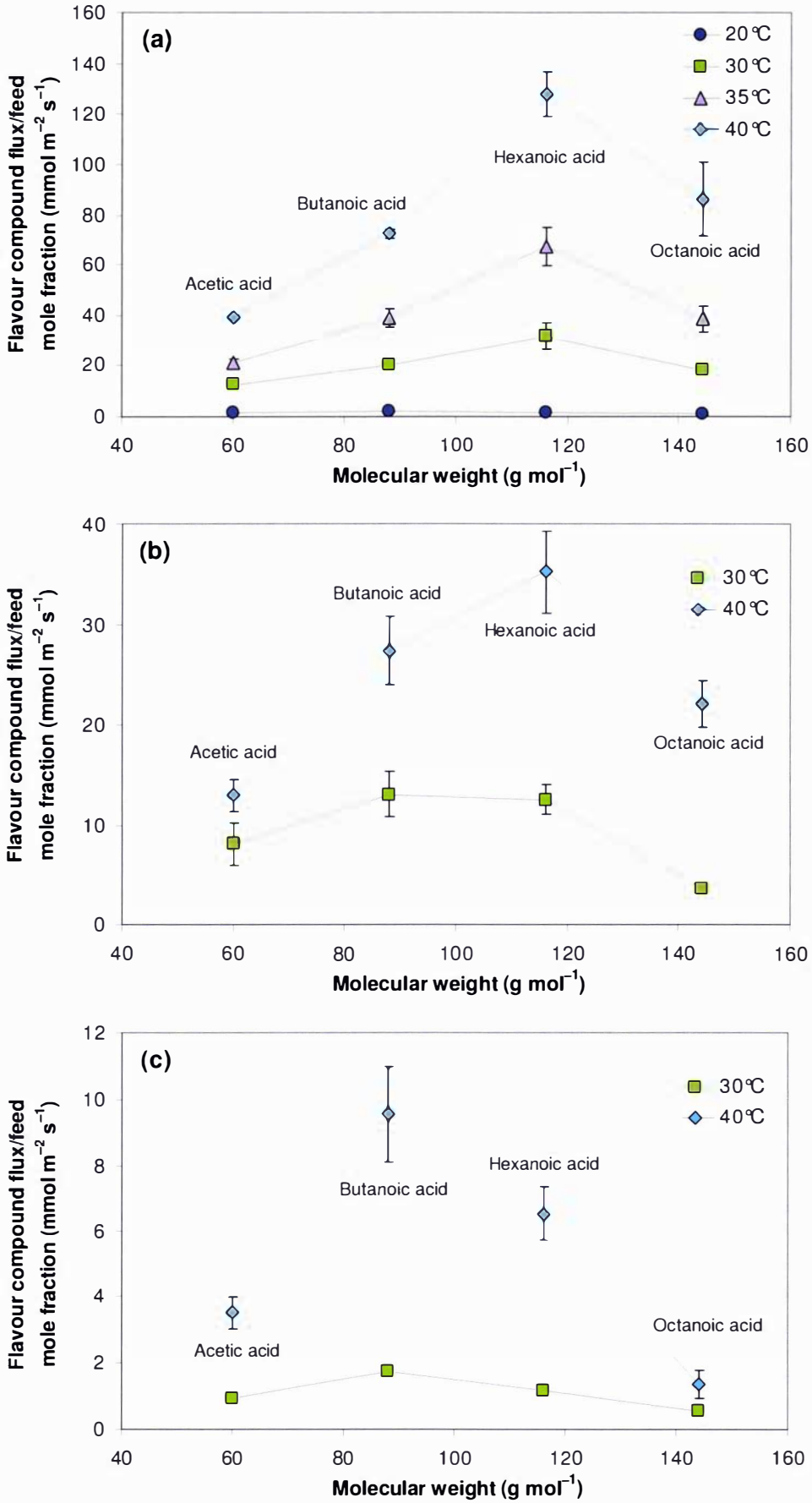


Figure 5-5:Effect of molecular weight on flux of acids (normalised for feed mole fraction) through (a) PDMS Type 1, (b) PDMS Type 2, (c) POMS. Data points are the mean (± standard error) of three replicates, all at 2 kPa permeate pressure.

normalised fluxes of acids were plotted against their molecular weight (Figure 5-5). The fluxes of smaller acids increased with increasing molecular weight; however, the fluxes of larger acids decreased with increasing molecular weight, as was seen for esters and ketones. Therefore, driving force variation was not the sole reason for the trends with molecular weight (within each functional group) shown in Figures 5-3 to 5-5: the molecular weight also influenced the permeability (sorption and diffusion) of each compound in the membrane.

For the flavour compounds in this study, hydrophobicity (as determined by log(octanol/water partition coefficient)) depends linearly on molecular weight within each compound type. Therefore, smaller molecules are more hydrophilic. This is especially true for acetic acid and butanoic acid, which have log(octanol/water partition coefficient) values of –0.17 and 0.79 respectively, compared with 1.85 to 3.81 for the other compounds in the standard multicomponent feed (Howard & Meylan, 1997). As the membranes used here were hydrophobic, the degree of sorption would have been lower for the more hydrophilic compounds.

In some pervaporation systems, sorption has been found to be more important than diffusion, as the fluxes of similar compounds increased with increasing compound hydrophobicity (Souchon et al., 1996; Sampranpiboon et al., 2000b). In other systems, fluxes increased with decreasing molecular size, showing that diffusion was more important (Kabra et al., 1995; Isci et al., 2006). The results in Figures 5-3 to 5-5 suggest that either sorption or diffusion was the controlling factor in this study, depending on the flavour compound.

The negative slopes in Figures 5-3 and 5-4 imply that diffusion was the rate-limiting factor for the fluxes of esters and ketones, as well as for high molecular weight acids (Figure 5-5). Conversely, the positive-slope region in Figure 5-5 shows that sorption was more important than diffusion for smaller acids. For esters and ketones, there was no transition from positive slope to negative slope within the range of molecular weights tested. Therefore, from these figures it is not possible to tell whether the smallest compound from each of these homologous series was sorption-limited or diffusion-limited, as there is a chance that they lay on the transition point between positive-slope and negative-slope regions.

5.3.5.1 Esters

The results reported in the literature, using several different membranes, vary as to whether fluxes increase or decrease with molecular size within a homologous series of esters. This may be due to the relative importance of sorption and diffusion in different systems. For systems in which sorption was the rate-limiting factor, it could be assumed that larger, more hydrophobic esters would have a greater solubility in the membrane and hence a higher flux. Conversely, if diffusion was the rate-limiting factor, then smaller esters would be expected to have a greater flux, as they would have higher diffusivities. In the present study, the fluxes of esters decreased with increasing molecular weight (Figure 5-3), so it appears that diffusion was the rate-limiting factor for ethyl hexanoate and ethyl octanoate, with all three membranes. Ethyl butanoate may have been diffusion-limited, or may have lain on the transition point between sorption-limited and diffusion-limited compounds. In this system, molecular size was therefore an important factor in determining how easily a particular ester would pass through the membrane.

Some researchers have found that the fluxes of esters decreased with increasing molecular size, in agreement with the results observed here. Using a zeolite-filled PDMS membrane, Isci et al. (2006) compared the fluxes of methyl butanoate, ethyl butanoate, butyl butanoate, methyl hexanoate and ethyl hexanoate. The smaller esters had greater fluxes because their diffusivities were higher. It can also be calculated from results given in She & Hwang (2006b) that, during pervaporation of orange aroma, which contained two esters, the flux of ethyl acetate was greater than that of ethyl butanoate. Trifunović & Trägårdh (2005) found that, with a POMS membrane, the permeability of esters (acetates and butanoates) decreased with molecular size.

However, in other cases, the opposite effect of molecular size on ester fluxes was seen. Song & Lee (2005) found that larger esters had greater fluxes in the pervaporation of ethyl acetate, propyl acetate and butyl acetate through a surface-modified hydrophobic membrane (alumina substrate modified with perfluoro-alkylsilane). They attributed this to the fact that the larger, more hydrophobic esters had a greater affinity to the membrane surface. Beaumelle et al. (1992) also found that ethyl butanoate had a greater flux than ethyl acetate, using a PDMS

membrane. Djebbar et al. (1998) found that ester fluxes did not change linearly with their carbon chain lengths, for a homologous series of ethyl esters using a PDMS membrane. Ethyl butanoate had the highest flux, followed by ethyl acetate and then ethyl propanoate. However, the esters studied by Djebbar et al. (1998) were all present at saturation concentrations in the feed, rather than at the same concentration. If their data are reinterpreted by dividing the ester flux by the saturation concentration, the larger esters have a greater concentration-normalised flux through PDMS membranes.

The reason for these apparently contradictory results could be that the above researchers (Beaumelle et al., 1992; Djebbar et al., 1998; Song & Lee, 2005) compared esters of the same and lower molecular weights than the smallest ester used in this study. It is possible that ester fluxes increase with molecular weight up to a point and then decrease, as was seen in the current study with acids (Figure 5-5). In fact, Trifunović & Trägårdh (2006) observed this phenomenon for esters; as the molecular size approached that of ethyl butanoate, from both above and below, ester fluxes through a POMS membrane increased.

Sampranpiboon et al. (2000b) studied pervaporation of ethyl butanoate and ethyl hexanoate from aqueous solutions. They found that ethyl hexanoate had a greater flux than ethyl butanoate through PDMS and POMS membranes, which is the opposite result to that observed in this study. This is possibly because Sampranpiboon et al. (2000b) used a higher feed concentration and lower feed flow rates than those used here, resulting in a significant concentration polarisation effect. They concluded that the mass transfer was dependent mainly on the feed-side conditions rather than on the membrane. Therefore, concentration polarisation may have caused the relative permeation rates of ethyl butanoate and ethyl hexanoate in the work of Sampranpiboon et al. (2000b) to differ from what they would have been if concentration polarisation did not occur. Djebbar et al. (1998), Beaumelle et al. (1992), and Song & Lee (2005) also used much higher feed concentrations than those used in this study (6000–84,000 ppm, 500 ppm and 1500–6000 ppm respectively; feed concentrations in the current study ranged from 10 to 111 ppm). As well as possibly contributing to concentration polarisation in the latter two cases (for which feed flow rates were low), these high concentrations would create a large driving force. If the driving force were

large enough that it (rather than the permeability) determined whether ester fluxes increased or decreased with increasing molecular weight, this could be an additional reason that their results did not agree with those in the current study.

5.3.5.2 Ketones

There have been very few studies comparing pervaporation of different ketones. Souchon et al. (1996) found the opposite effect from this study; larger ketones had greater fluxes in the pervaporation of 2-heptanone, 2-octanone and 2-nonanone through a PDMS membrane, leading them to conclude that sorption was more important than diffusion in this case. Souchon et al. (1996) tested each ketone separately, whereas, in the current study, all nine compounds were together in the model feed solution. This may explain why different results were obtained, as sometimes there are interactions or competition between components present in the feed solution, leading to enhanced or hindered pervaporation fluxes (Kedem, 1989; Karlsson & Trägårdh, 1993).

5.3.5.3 Acids

Within the acids homologous series, the transition from positive slope to negative slope depended on the membrane type and the operating conditions (Figure 5-5). At conditions where the flux was low (POMS membrane, or low temperature/high permeate pressure with PDMS Type 2 membrane), the transition point was at butanoic acid; for higher-flux conditions the transition point was at hexanoic acid. In other words, more acids were diffusion-limited at operating conditions that caused the flux to be low.

The operating conditions that caused low fluxes also made it difficult for flavour compounds to diffuse through the membrane, which is why diffusion was the rate-limiting factor for most acids under these conditions. At low temperatures, diffusivity through the membrane would be low because the polymer chains move around less and so there is less free volume in the membrane (Peng et al., 2003). The rate of diffusion is also proportional to the chemical potential gradient across the membrane; hence the diffusive flux is lower for a thicker membrane. POMS was the thickest membrane tested, followed by PDMS Type 2. Even under these conditions, acetic acid was still sorption-limited, because it has the lowest

hydrophobicity (leading to a low level of sorption) and the lowest molecular weight (leading to a high rate of diffusion) out of all the compounds tested.

For conditions at which diffusion through the membrane was rapid (PDMS Type 1 membrane, or PDMS Type 2 membrane at operating conditions that created a large driving force), diffusion presented less resistance to the permeation of flavour compounds, and sorption presented relatively more resistance. Therefore, sorption became the rate-limiting step for more acids at operating conditions that caused high fluxes.

Kabra et al. (1995) found that the fluxes of acids (acetic acid, propanoic acid and butanoic acid) through a PDMS membrane decreased with molecular size. However, the feed concentration (10% w/w) was approximately 1000 times greater than in the present study. Kabra et al. (1995) also stated that diffusivity depends not only on molecular size and shape, but also on the extent to which the permeating molecules aggregate inside the membrane. Molecular aggregation is an alternative mechanism which could possibly explain the results obtained in the present study, where acid fluxes increased and then decreased with increasing molecular weight. Small acids might have aggregated together (as they are hydrophilic and so do not associate easily with the hydrophobic membrane), and hence formed clusters that did not diffuse through the membrane easily, because their apparent size was larger than permeants that diffused through as single molecules. Trifunović & Trägårdh (2006) found that the diffusivities in POMS membranes of low molecular weight alcohols, and to a lesser extent esters, went against the trend of decreasing diffusivity with increasing molecular size. They suggested that this was caused by small molecules clustering together during diffusion, increasing their apparent size. The extent of aggregation of small molecules in the polymer depends on the degree to which these molecules form hydrogen bonds with each other (Trifunović & Trägårdh, 2006). Organic acids have a hydroxyl group, which would allow hydrogen bonding, and hence it is possible that small acids cluster together. Organic acids often form dimers in solution, especially when in a hydrophobic solution as opposed to an aqueous solution (Yamamoto & Nishi, 1990). The results from Elabd & Barbari (2001) suggest that acids also form dimers in polymers. However, this thesis assumes that

permeation is via the solution-diffusion mechanism discussed above; therefore, the molecular aggregation mechanism will not be explored further here.

5.3.5.4 Extra flavour compounds added to feed solution

The standard multicomponent feed solution contained between two and four flavour compounds from each functional group. To enable trends to be seen more easily, some extra pervaporation experiments were carried out, with additional acids or an additional ester added to the standard model solution.

The flux of ethyl decanoate was 0.0025 ± 0.0008 μmol m^{-2} s^{-1}, 0.019 ± 0.008 μmol m^{-2} s^{-1} and 0.13 ± 0.04 μmol m^{-2} s^{-1}, at feed temperatures of 20°C, 30°C and 40°C respectively (with the PDMS Type 1 membrane and a permeate pressure of 2 kPa). Figure 5-6 shows the mole fraction-normalised fluxes of the four esters (three esters from the standard multicomponent feed, plus ethyl decanoate). Ethyl butanoate, ethyl hexanoate and ethyl octanoate did not have exactly the same fluxes as in Figure 5-3a, because the feed solution was not identical; hence, coupling interactions between permeants were not equal. Nevertheless, these three esters followed the same decreasing trend with increasing molecular weight, regardless of whether ethyl decanoate was included

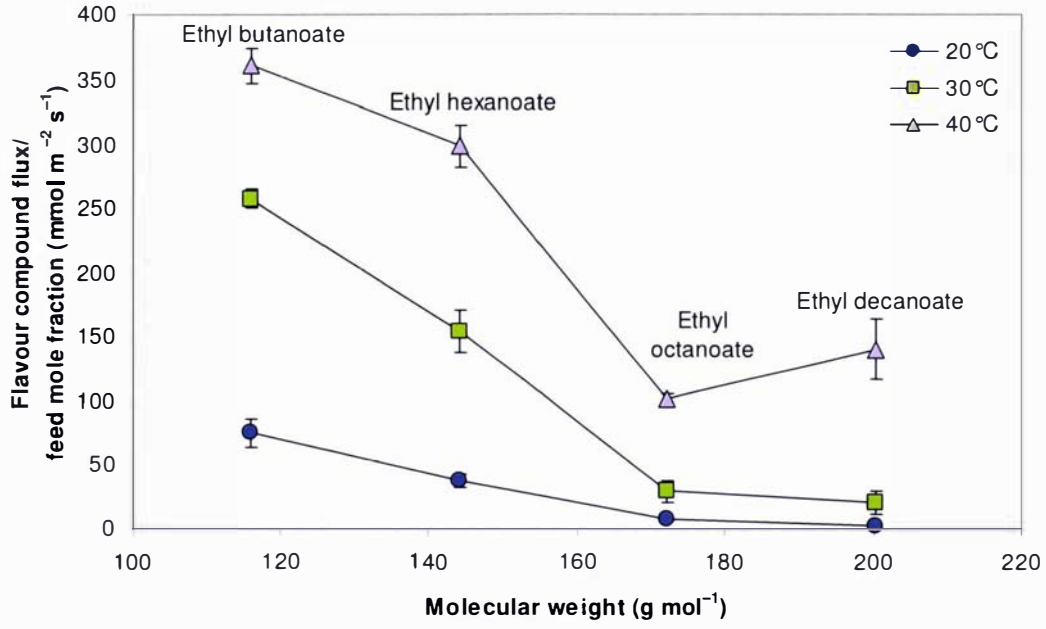


Figure 5-6: Mole fraction-normalised fluxes of esters, including ethyl decanoate (mean ± standard error of three replicates). Operating conditions: PDMS Type 1 membrane, 2 kPa permeate pressure.

in the feed. In Figure 5-6, this trend did not continue linearly, but levelled off between ethyl octanoate and ethyl decanoate. The reason for this observation is unclear. At 40°C, the mole fraction-normalised flux of ethyl decanoate was greater than that of ethyl octanoate, contrary to expectations, although this was only true in two out of three replicates. Normally, an increasing flux with increasing molecular weight would indicate that sorption was the dominant factor in the mass transfer mechanism. However, as the molecular weight increases within a homologous series, sorption should become easier (as compounds become more hydrophobic) and diffusion should become more difficult (as compounds become larger). Hence, the rate-limiting factor should change from sorption to diffusion, and not the other way around. Therefore, the anomalous result at 40°C was probably caused by experimental variation rather than a change in mechanism, especially as it did not occur in all replicates.

Figure 5-7 shows how the mole fraction-normalised fluxes of acids, including three acids additional to those in the standard multicomponent feed, depended on their molecular weight. The same general trend was observed as in Figure 5-5; the mole fraction-normalised fluxes increased with increasing molecular weight for small compounds, then decreased as the molecular weight was increased further.

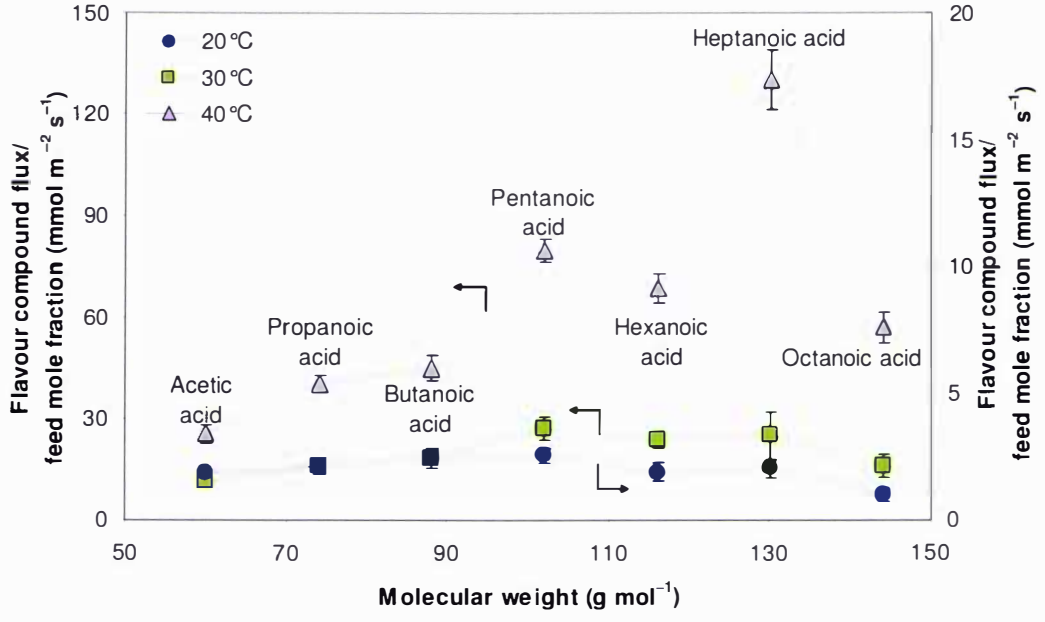


Figure 5-7: Mole fraction-normalised fluxes of acids, including three acids additional to those in the standard multicomponent feed solution (mean ± standard error of three replicates). Operating conditions: PDMS Type 1 membrane, 2 kPa permeate pressure.

The three additional acids (propanoic acid, pentanoic acid and heptanoic acid) did not fit perfectly into this overall trend; they had higher fluxes than expected, leading to the alternating pattern shown in Figure 5-7.

The three additional acids had odd-numbered carbon chain lengths, whereas the four acids in the standard multicomponent feed had even-numbered carbon chains. Odd-numbered acids have previously been reported to behave differently from even-numbered acids in several aspects. This phenomenon may be caused by odd-numbered acids having a different orientation from even-numbered acids (Lunkenheimer et al., 2003). Properties relevant to pervaporation, for which different odd-even behaviour has been reported, include the adsorption of acids at interfaces (Lunkenheimer et al., 2003) and the vapour pressures of acids (Bilde et al., 2003). Greater sorption and higher vapour pressures would both cause odd-numbered acids to have greater fluxes than even-numbered acids, as shown in Figure 5-7.

5.3.6 Effect of feed pH on pervaporation

As shown in Figure 5-8, the feed pH strongly influenced the pervaporation of

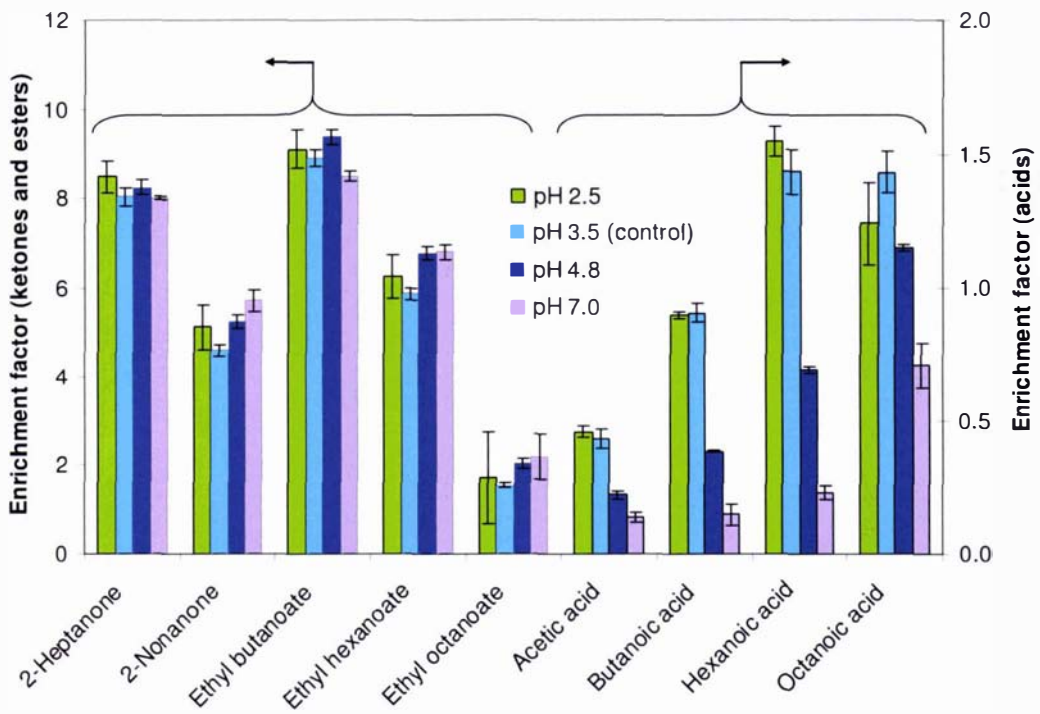


Figure 5-8: Effect of feed pH on enrichment factor (mean ± standard error) of each flavour compound. Operating conditions: PDMS Type 1 membrane; feed temperature 30°C; permeate pressure 1.5 kPa.

acids, but had little or no effect on the other flavour compounds. Acidifying the feed solution to pH 2.5 (from an initial pH of 3.5) had little effect on enrichment. However, increasing the feed pH reduced the enrichment factors of acetic, butanoic and hexanoic acids to less than half of their original values. Octanoic acid also had a lower enrichment factor at higher pH, but it was not affected to the same degree as smaller acids. Ethyl hexanoate, ethyl octanoate and 2-nonanone had slightly higher enrichment factors at pH 4.8 and 7.0 compared to pH 3.5, although enrichment factors of these compounds at pH 2.5 were not significantly different from those at higher pH levels. The total flux did not differ significantly between the highest and lowest pH feed solutions tested.

The permeation of acids depended on the feed pH, because the pH determined the proportion of each acid in its dissociated and undissociated forms. At low pH, the proportion in the undissociated form was greater, as shown in Table 5-3. The undissociated (uncharged) form is more permeable, because charged compounds should not pass through pervaporation membranes (Baudot & Marin, 1997; Lipnizki et al., 2004). Ikegami et al. (2005) confirmed that the affinity of succinic acid for a hydrophobic membrane material (silicalite) decreased with increasing pH, as the proportion in the undissociated form decreased. Therefore, in the current study, the enrichment factors of acids were reduced when the pH was increased.

The reason for the positive effect of increased pH on 2-nonanone, ethyl hexanoate and ethyl octanoate enrichment is less obvious. With lower levels of acids entering the membrane at higher pH, there would have been less competition between permeants for sites in the membrane, enabling esters and ketones to be more highly enriched. Ethyl butanoate and 2-heptanone already had high enrichment factors, so the lack of competition brought no further improvement in

Table 5-3: pK_a values of acids used in the model solution, at 25°C (James & Lord, 1992), and proportions of each acid in the undissociated form (calculated using the Henderson-Hasselbach equation).

Compound	pK_a	Proportion in undissociated form (%)			
		pH 2.5	pH 3.5	pH 4.8	pH 7.0
Acetic acid	4.75	99.4	94.7	47.1	0.6
Butanoic acid	4.83	99.5	95.5	51.7	0.7
Hexanoic acid	4.88	99.6	96.0	54.6	0.8
Octanoic acid	4.89	99.6	96.1	55.2	0.8

their enrichment. Competition between flavour compounds will be further discussed in Chapter 6.

Figure 5-9 shows how the fluxes of acids depended on how much of each acid was in the undissociated form, which was determined by the feed pH. The total feed concentration of each acid (undissociated plus dissociated forms) was 105–111 mg kg^{-1} (Table 3-1, page 72). At pH 2.5–3.5, all acids were at least 94.7% undissociated, so that the undissociated concentration in Figure 5-9 was close to the total concentration. Hence, the fluxes and enrichment factors were relatively high at these low pH levels. Between pH 2.5 and 4.8, the percentage undissociated decreased from almost 100% to approximately 50%; the fluxes likewise decreased by 24–62%. Between pH 4.8 and 7.0, the percentage undissociated decreased from approximately 50% to less than 1%; the fluxes continued to decrease, but at a lesser rate.

5.4 General discussion

It was possible to concentrate dairy flavour compounds from aqueous solutions using pervaporation, with esters and ketones (especially short chain molecules)

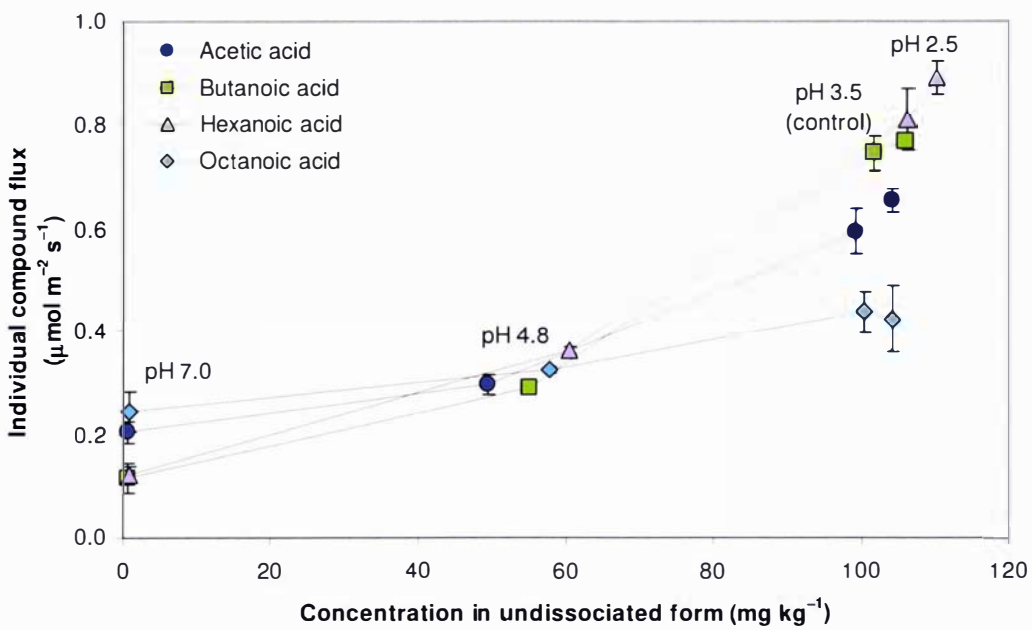


Figure 5-9: Individual fluxes (mean ± standard error) of acids in feed solutions at different pH, plotted against the concentration of each acid in its undissociated form. Operating conditions: PDMS Type 1 membrane; feed temperature 30°C; permeate pressure 1.5 kPa.

being more efficiently concentrated than acids. Therefore, the flavour profile of the permeate would differ from that of the feed.

Table 5-4 lists some odour descriptors reported for the flavour compounds in the standard multicomponent feed. These odour descriptors can be used, together with the enrichment factors, to estimate how pervaporation would alter the flavour of a mixture. Compared with the feed, the permeate had relatively more esters and ketones and lower levels of acids, meaning that the permeate flavour would be more fruity and blue cheese-like, and less pungent and goaty, than the feed flavour. Also, as the total concentration of flavour compounds in the permeate was up to 10 times higher than in the feed, the permeate flavour would be stronger overall than the feed flavour.

For the high molecular weight flavour compounds in this study (esters, ketones and high molecular weight acids), diffusion was the controlling mechanism in the membranes tested, but low molecular weight acids went against the trend seen for other compounds. The point of transition between increasing and decreasing flux with increasing acid molecular weight was dependent on the operating conditions, and is postulated to be due to the relative influences of sorption into, and diffusion through, the pervaporation membrane.

The PDMS Type 1 membrane, a high feed temperature and a low permeate pressure were the conditions leading to the greatest fluxes. The PDMS Type 1

Table 5-4: Odour descriptors of flavour compounds used in the feed solution.

Compound	Odour description
2-Heptanone	Musty, varnish, sweet[a]; blue cheese, Roquefort cheese[b]
2-Nonanone	Floral, fruity, peachy[a]; musty[b]
Ethyl butanoate	Fruity-melon, sweet[a]; pineapple[b]; pleasant, green fruit[c]
Ethyl hexanoate	Fruity, grape melon[a]; pineapple, banana[b]; young cheese[c]
Ethyl octanoate	Apricot, wine[b]
Acetic acid	Vinegar-sour, sharp[a]; pungent[d]
Butanoic acid	Rotten, sharp[a]; buttery, sweaty[d]; cheesy, rancid[e]
Hexanoic acid	Sharp, goaty[a]; pungent, blue cheese[b]; pungent, musty[d]; cheesy, acrid[e]
Octanoic acid	Wax, sheep, goat, musty, rancid, fruity[b]

[a]Frank et al. (2004)

[b]Molimard & Spinnler (1996)

[c]Arora et al. (1995)

[d]Schieberle et al. (1993)

[e]Peterson & Reineccius (2003)

membrane was therefore chosen to be used for all further experiments in the following chapters. However, the POMS membrane gave greater enrichment factors than the other membranes, for the major compounds in the permeate. The enrichment factors of some compounds also depended on the feed temperature and permeate pressure. Therefore, it is important to consider enrichment as well as flux when selecting operating conditions for pervaporation.

When the feed pH was increased, a greater proportion of each acid was in the less-permeable form. Therefore, manipulation of the feed pH appears to be a simple way of controlling the permeate composition when the feed contains acids.

The results in this chapter provide baseline data with a simple model feed solution, which will be compared with modified feed solutions in the following chapters.

Chapter 6

Coupling between model solution compounds

6.1 Introduction

Pervaporation of a particular compound is often, but not always, influenced by the presence of other permeating components (Néel, 1991); this phenomenon is known as coupling. Pervaporation results with one feed solution can only be used to predict results with different feed solutions if the extent of coupling is known. Unfortunately, the mechanism of coupling is not well understood. Hence, coupling effects cannot be reliably predicted, and must be determined on a case-by-case basis.

Coupling effects comprise two parts: thermodynamic coupling and kinetic coupling (Berendsen et al., 2006). Thermodynamic coupling alters the concentration of a permeant inside the membrane, and kinetic coupling alters how permeants interact with the membrane polymer as they are passing through the membrane (Berendsen et al., 2006). Therefore, thermodynamic coupling affects the sorption coefficient and kinetic coupling affects the diffusion coefficient.

The purpose of this chapter was to evaluate coupling effects between flavour compounds in the standard multicomponent feed. Ideally, a full coupling analysis, showing the interactions between each of the nine flavour compounds in the multicomponent feed solution and how each was affected by the concentrations of the others, would be desirable. However, a large number of experiments would be needed to obtain a complete picture of which compounds coupled to each other. Many more experiments would be required to determine the effect of feed concentration or operating conditions, or to obtain information on coupling effects between three or more compounds. Therefore, the experiments in this chapter were designed to complete only a small part of this complex puzzle. Binary aqueous solutions (one flavour compound plus water) were compared with feed solutions that contained selected mixtures of two to eight flavour compounds, and with the multicomponent feed solution that contained nine flavour compounds.

Feed solutions with one or nine flavour compounds were compared at two temperatures and two concentrations, in order to obtain as much information as possible within the time constraints for this study.

Apart from flavour compounds and water, some flavour-containing process streams, such as fermentation systems or alcoholic beverages, also contain ethanol. Percentage levels of ethanol can affect the volatilities of flavour compounds, and can also cause membrane swelling. These effects may lead to flavour compound fluxes increasing, decreasing or remaining constant, when ethanol is added to the feed solution (Beaumelle et al., 1992; Karlsson & Trägårdh, 1994; Tan et al., 2005). Therefore, the influence of ethanol on the nine flavour compounds in this study was also tested.

6.2 Experimental

Pervaporation experiments were carried out following the procedure in Chapter 3, using the PDMS Type 1 membrane. The permeate pressure was always kept at 1.5 kPa, and the feed temperature was either 20°C or 30°C. The feed solutions listed in Section 3.1.3 were compared; these contained various combinations of the flavour compounds in the standard multicomponent feed solution. In addition, 5% (v/v) ethanol was added to one feed solution (Section 3.1.3). The standard multicomponent feed solution (Section 3.1.1) was used as a control. Flavour compound concentrations were either the same as in the standard multicomponent feed (referred to from now on as 'standard concentrations') or 50% of this concentration. Most experiments were carried out in duplicate or triplicate, except that not all replicates were completed with the binary octanoic acid/water feed solution. Runs at standard conditions (described in Chapter 3) were carried out more frequently.

6.3 Results and discussion

6.3.1 Total flux with binary and multicomponent feed solutions

Figure 6-1 shows how the total fluxes differed between pure water, binary feed solutions of each flavour compound, and the standard multicomponent feed solution. The flavour compounds never represented more than 0.5% of the total

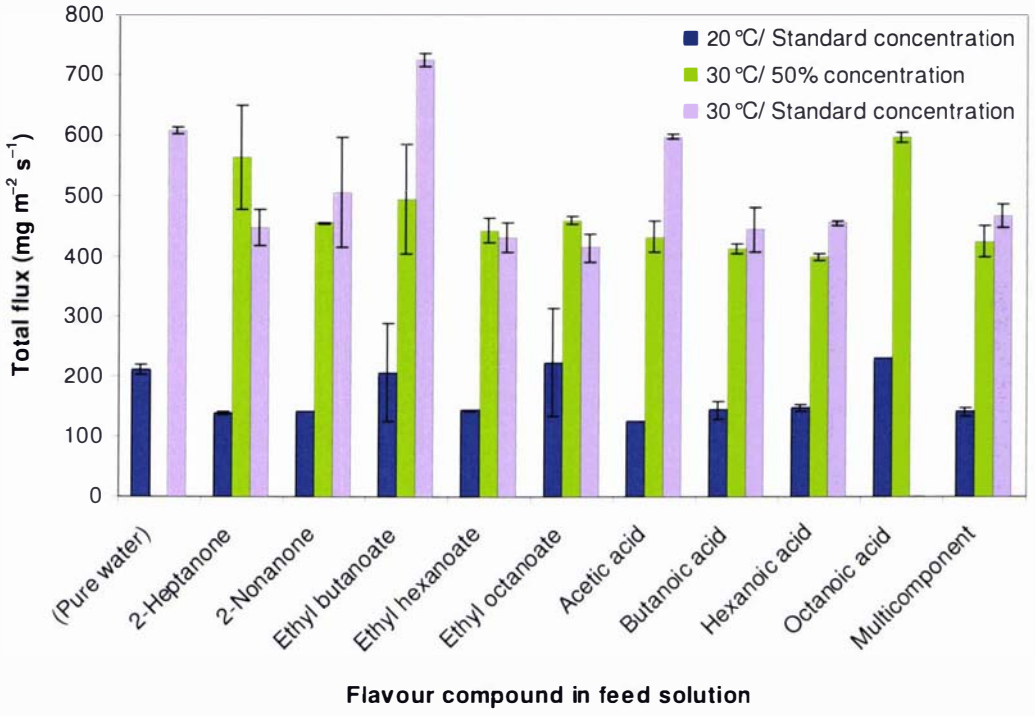


Figure 6-1: Comparison between total fluxes of pure water, binary feed solutions (one flavour compound plus water) and multicomponent feed solutions (nine flavour compounds plus water). Operating conditions: PDMS Type 1 membrane, 20°C or 30°C feed temperature, 1.5 kPa permeate pressure; flavour compound concentrations were either the same as, or 50% of, those in the standard multicomponent feed. Data are means (± standard error) of at least two replicates, except for octanoic acid at 20°C, for which only one run was carried out.

permeate mass, with water making up the remainder of the permeate. Therefore, the total flux in each case is negligibly different from the water flux, so Figure 6-1 shows how each compound affected the flux of water.

When the feed solution contained octanoic acid, this compound was found to remain in the system and carry over to the next run. Following overnight cleaning of the pervaporation unit (described in Chapter 3), enough octanoic acid remained in the system that it was detected in the permeate, at a level of 50–90 ppm, after 1.5–3 hours of pervaporation with a feed of distilled water. The permeate concentration of octanoic acid reduced to a stable level (12–13 ppm) after 7.5–9 hours of pervaporation with distilled water. It is likely that the octanoic acid built up in the membrane and contributed to the decline in flux over time, as was discussed in Chapter 4. To avoid influencing the coupling interactions between flavour compounds, runs with the binary octanoic acid/water feed solution were

discontinued part-way through this set of experiments. Figure 6-1 therefore shows only one run with this feed solution at 20°C/standard concentration, and none at 30°C/standard concentration. Experiments with the multicomponent feed solution (which contained octanoic acid) were continued, but a nine-hour run with distilled water was carried out after each run with the multicomponent feed, during the set of experiments in this chapter.

The total flux with a feed of pure water was generally similar to or greater than the total flux with binary or multicomponent feed solutions (Figure 6-1), except that the total flux of a binary ethyl butanoate/water feed at 30°C/standard concentration was 19% greater than the pure water flux, and the total flux of a binary octanoic acid/water feed at 20°C/standard concentration was 10% greater than the pure water flux (although the standard error is unknown for the binary octanoic acid feed because only one replicate was carried out at these conditions).

Total fluxes with most binary feed solutions were similar to the multicomponent feed solution (Figure 6-1), with the following exceptions:

- Binary solutions of 2-heptanone and 2-nonanone both had higher total fluxes (slightly outside standard error limits) than the multicomponent feed at 30°C/50% concentration, but not at standard concentration for either temperature.
- The total flux of a binary ethyl butanoate solution was 55% higher than the multicomponent feed at 30°C/standard concentration.
- The total flux of a binary acetic acid solution was 29% higher than the multicomponent feed at 30°C/standard concentration.
- The total flux of a binary octanoic acid solution was 65% higher than the multicomponent feed at 20°C/standard concentration and 41% higher than the multicomponent feed at 30°C/50% concentration.

There were no obvious trends regarding the operating conditions and flavour compounds for which the total flux of binary feed solutions differed from that of the multicomponent feed. In all cases where there was a difference, binary feed solutions had higher total fluxes than the multicomponent feed. This would normally suggest that the flavour compounds in the multicomponent feed were hindering the flux of water. However, the pure water flux did not confirm this

hypothesis in all cases, as two of the exceptions listed above (ethyl butanoate at 30°C and octanoic acid at 20°C) also had greater total fluxes than the pure water flux at the same conditions. Therefore, at particular operating conditions, some binary feed solutions caused a higher water flux, as opposed to the multicomponent feed solution causing a lower water flux.

An increased water flux could be caused either by increasing the driving force for water, or increasing its mass transfer into and through the membrane. As the feed solution was very dilute, the flavour compounds in the feed are unlikely to have significantly affected the water activity. Therefore, the driving force for water should not have been influenced by which feed solution was used.

As water is a small, hydrophilic molecule, it can be assumed that its diffusion through the membrane would be fast, but its sorption in the hydrophobic membrane would be low. Therefore, the rate-limiting factor for water transport should be sorption rather than diffusion. Any factor that increased the mass transfer of water would have achieved this by increasing its sorption into the membrane.

One explanation for the higher water flux with certain binary feeds is that the sorption of certain flavour compounds in the membrane may have been higher without the competition from other compounds in the multicomponent feed solution. These compounds may have made the membrane more attractive to water, increasing the water sorption. This would explain why, for acetic acid and ethyl butanoate, the difference occurred only at the higher concentration tested (the standard concentration was not tested at 30°C for octanoic acid).

6.3.2 Coupling interactions between different flavour compounds

6.3.2.1 Flavour compound fluxes with binary and multicomponent feed solutions

Figure 6-2 compares the individual fluxes of each flavour compound in binary and multicomponent feed solutions. Fluxes with binary feed solutions were either similar to or higher than multicomponent feed solutions, except for hexanoic acid, which had a higher flux in the multicomponent feed solution at 30°C/standard concentration. Therefore, where coupling occurred, it usually had a negative effect on fluxes achieved (flavour compounds hindered each other's permeation).

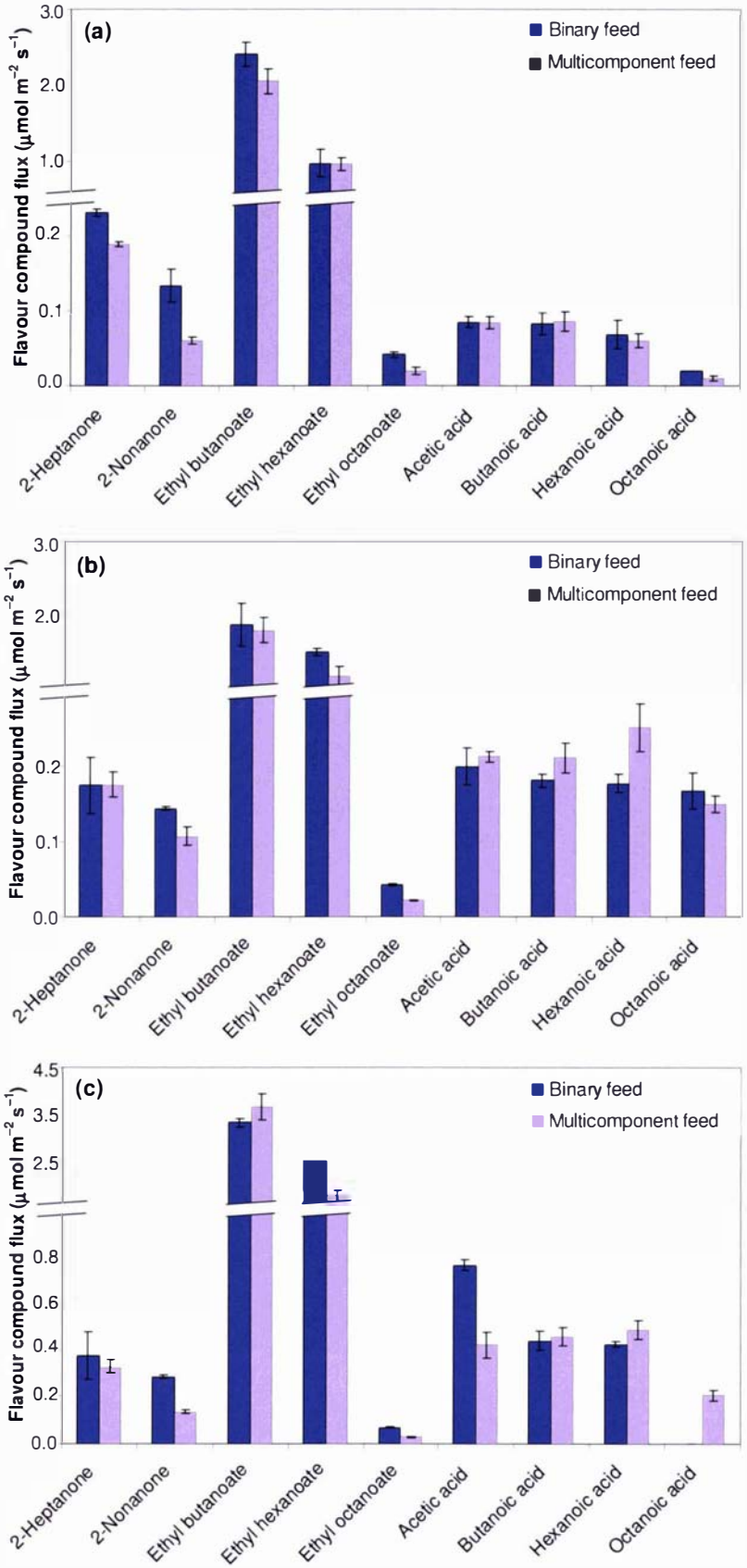


Figure 6-2: Comparison of individual compound fluxes with binary and multicomponent feed solutions. Operating conditions: (a) 20°C feed temperature, standard concentrations; (b) 30°C feed temperature, 50% concentrations; (c) 30°C feed temperature, standard concentrations. All at 1.5 kPa permeate pressure. Data are means (± standard error) of at least two replicates, except octanoic acid single-component feed in graph (a), for which only one replicate was completed.

At 20°C (Figure 6-2a), 2-heptanone, 2-nonanone, ethyl butanoate and ethyl octanoate had 18–116% higher individual fluxes with binary feed solutions than with multicomponent solutions. At 30°C/50% concentration (Figure 6-2b), 2-nonanone, ethyl hexanoate and ethyl octanoate had 27–91% higher fluxes with binary feed solutions, and hexanoic acid had a 28% higher flux with the multicomponent feed solution. At 30°C/standard concentration (Figure 6-2c), 2-nonanone, ethyl hexanoate, ethyl octanoate and acetic acid had 41–131% higher fluxes with binary feed solutions.

Other researchers have also compared the flux of a permeant compound in a binary aqueous feed solution with its flux in a multicomponent feed solution, in order to evaluate coupling between flavour compounds. The range of results obtained by different researchers indicates that each flavour compound will not necessarily display the same coupling behaviour in different feed solutions or at different operating conditions. For example, Peng & Liu (2003) compared an aqueous mixture of six blueberry aroma compounds (1-hexanol, 1-heptanol, *trans*-2-hexenal, ethyl acetate, linalool and d-limonene) with binary aqueous solutions of each compound. The mass transfer coefficient of 1-heptanol was 70% greater, on average, in the mixture than in a binary aqueous solution. Coupling effects between the other flavour compounds they tested were less significant, and were not observed at all operating conditions. Isci et al. (2006) found that the presence of methyl butanoate in an aqueous feed solution did not affect the flux of ethyl butanoate, but the opposite was not true: the flux of methyl butanoate was halved when ethyl butanoate was added to the feed solution. Fluxes of both compounds were further reduced, by approximately two orders of magnitude, in an aqueous solution containing five esters and linalool (Isci et al., 2006). She & Hwang (2006a) did not observe any coupling effects between esters, aldehydes and alcohols (ethyl butanoate, *trans*-2-hexenal, benzaldehyde, *cis*-3-hexenol, phenylethyl alcohol and methyl anthranilate) in dilute feed solutions.

Sampranpiboon et al. (2000b) compared pervaporation of dilute solutions of ethyl butanoate and ethyl hexanoate, separately and together. Under most operating conditions tested, each ester hindered the flux of the other, with ethyl butanoate having a relatively greater effect on the flux of ethyl hexanoate than the other way around. The extent of coupling was affected by the operating conditions; the ratio

of each compound's flux in the mixed solution to its flux in the binary solution either increased or decreased with permeate pressure, depending on the membrane and the compound (Sampranpiboon et al., 2000b). As the permeate pressure affects the driving force rather than the actual mass transfer, their results suggest that these two esters altered each other's driving force. However, Sampranpiboon et al.'s (2000b) feed solution contained 300 ppm of each compound, which is higher than the normal concentration range for flavours. For dilute solutions, it is unlikely that different compounds could affect each other's feed activity (and hence driving force). Instead, permeant compounds affect each other's flux through coupled sorption and/or coupled diffusion.

6.3.2.2 Flavour compound coupling factors

The differences between flavour compound fluxes in binary and multicomponent feed solutions are quantified in Figure 6-3, which gives the coupling factors of each flavour compound in the multicomponent feed solution. The coupling factor for each compound is an overall measure of its coupling to all the other flavour compounds in the multicomponent feed. Lipnizki & Hausmanns (2004) defined

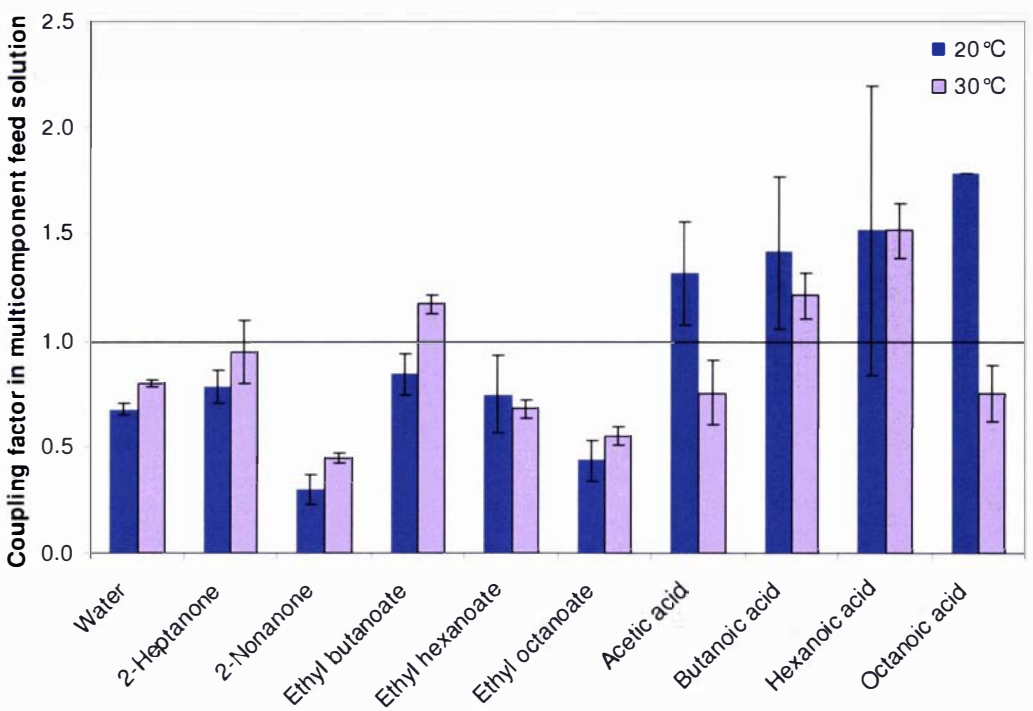


Figure 6-3: Coupling factors (mean ± standard error) of flavour compounds and water in the multicomponent feed solution. Operating conditions: 20°C or 30°C feed temperature (both concentrations combined), 1.5 kPa permeate pressure. The horizontal line indicates the point of no coupling.

the coupling factor for each permeant compound as the ratio between its permeability with the feed solution of interest and its permeability with a reference feed solution in which no coupling occurs. In the current study, the overall mass transfer coefficient was used as an approximation for the permeability (in recognition of the fact that not all the resistance to mass transfer is from the active layer of the membrane), and the reference feed solution was the binary aqueous feed solution for each compound. The coupling factor (C_i) was therefore given by:

$$C_i = \frac{k_{i,ov}(multicomponent\ feed)}{k_{i,ov}(binary\ feed)} \qquad \textbf{(6-1)}$$

where $k_{i,ov}$ is the overall mass transfer coefficient of component i, calculated as described in Appendix B.

The coupling factor represents only coupled mass transfer, not coupled driving forces (Lipnizki & Hausmanns, 2004). In calculating the overall mass transfer coefficients, it was assumed that each compound's feed activity coefficient was equal to literature values for the activity coefficient at infinite dilution, irrespective of which other compounds were in the feed solution. Other researchers have also made this assumption for dilute multicomponent solutions (Baudot & Marin, 1999; Lipnizki & Hausmanns, 2004; Trifunović & Trägårdh, 2006).

A coupling factor of 1.0 indicates that the compound of interest had equal mass transfer coefficients in the binary and multicomponent feed solutions. A coupling factor above 1.0 indicates positive coupling (other compounds in the feed solution enhance the mass transfer of the compound of interest) and a coupling factor below 1.0 indicates negative coupling (other compounds in the feed solution reduce the mass transfer of the compound of interest).

Figure 6-3 shows that in the multicomponent feed solution, the coupling factors of esters and ketones decreased with increasing carbon chain length. In these two homologous series, the smallest compound tested exhibited no coupling or minimal coupling, but larger compounds showed negative coupling, leading to lower fluxes in the multicomponent feed than in binary feeds. This result can also

be seen in the flux comparisons in Figure 6-2. The other compounds in the multicomponent feed therefore decreased the mass transfer of these larger esters and ketones. For the acids, coupling factors increased with increasing molecular weight, apart from octanoic acid, for which the coupling factor was lower than that of hexanoic acid at 30°C only. The greater the molecular weight, the more positive the coupling; that is, the other compounds in the multicomponent feed increased the mass transfer of the larger acids.

The mass transfer of larger compounds within a functional group is more likely to be diffusion-limited than sorption-limited, as discussed in Chapter 5. As larger compounds tended to exhibit more coupling (either positive or negative) under the conditions tested in this study, it appears that coupling mainly affected the diffusion step. A possible mechanism would be that permeant molecules blocked diffusion sites in the membrane (for negative coupling) or dragged other permeant molecules along as they diffused through the membrane (for positive coupling).

In general, the coupling factor followed the same trend as the flavour compound fluxes, within each functional group (Figures 5-3 to 5-5; pages 102–104). Compounds that had low fluxes also had lower coupling factors; that is, these slower-permeating compounds were more sensitive to other compounds in the multicomponent feed, and coupling effects reduced their fluxes relatively more than for faster-permeating compounds. Faster-permeating compounds within each functional group had positive or neutral coupling factors in the multicomponent feed solution. This result contrasts with Peng & Liu's (2003) finding that compounds with low mass transfer coefficients exhibited positive coupling at operating conditions that allowed only low mass transfer, and that compounds with high mass transfer coefficients displayed negative coupling at operating conditions that allowed greater mass transfer.

To clarify which compounds in the multicomponent feed solution were causing coupling, some additional experiments were carried out with feed solutions containing groups of flavour compounds from either the same or different homologous series, as listed in Section 3.1.3 (page 73). These experiments were carried out at 30°C with standard concentrations only. Table 6-1 lists the coupling factors obtained with feed solutions containing two compounds from the same homologous series. The coupling factors were calculated with Equation (6-1) in

Table 6-1: Coupling factors (mean ± standard error) in feed solutions containing either two ketones or two esters. Operating conditions: 30°C feed temperature, 1.5 kPa permeate pressure, standard concentrations.

Feed solution	Compound	Coupling factor
Ketones only	2-Heptanone	1.41 ± 0.22
	2-Nonanone	1.38 ± 0.08
Esters only	Ethyl butanoate	0.98 ± 0.02
	Ethyl octanoate	1.03 ± 0.09

the same way as before, except that the 'multicomponent feed' in this case refers to the feed solution with two flavour compounds, not the standard multicomponent feed. The presence of the other ketone increased the mass transfer of each ketone, whereas the presence of another ester did not significantly affect the mass transfer of ethyl butanoate or ethyl octanoate. Therefore, the negative coupling for the larger esters and ketones in Figure 6-3 could not have been caused by competition with other compounds with the same functional group.

Figure 6-4 shows the coupling factors in feed solutions that contained compounds from two homologous series. When the feed solution contained two ketones plus three esters (Figure 6-4a) or two ketones plus four acids (Figure 6-4b), the coupling factors within each functional group followed a similar pattern as for the multicomponent feed solution (Figure 6-3). Therefore, both positive and negative coupling were caused by interactions between compounds with different functional groups.

Coupling effects were also tested with feed solutions containing only one compound from each homologous series. The fastest-permeating flavour compound (ethyl butanoate) was paired with either the slowest-permeating ketone (2-nonanone) or the slowest-permeating acid (acetic acid). These compounds were chosen because slow-permeating compounds tended to have more negative coupling effects (Figure 6-3). As ethyl butanoate had greater fluxes than any other flavour compound tested, it was chosen as the most likely compound to have an effect on 2-nonanone or acetic acid. However, 2-nonanone (coupling factor of1.08 ± 0.06) was only slightly affected by ethyl butanoate, when the feed

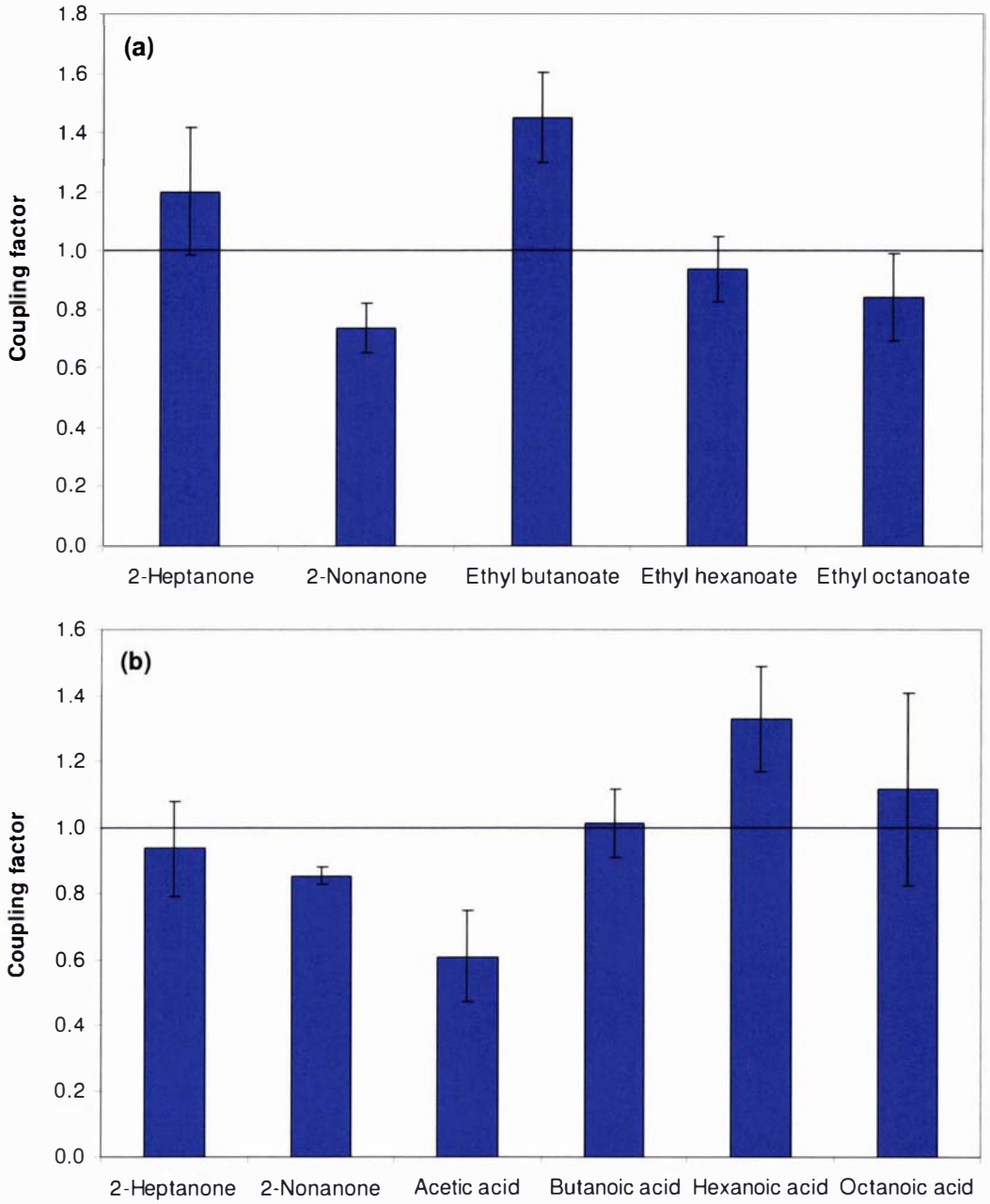


Figure 6-4: Coupling factors (mean ± standard error) in feed solutions containing (a) ketones and esters, (b) ketones and acids. Operating conditions: feed temperature 30°C, permeate pressure 1.5 kPa, standard concentrations. The horizontal line indicates the point of no coupling.

solution contained only these two flavour compounds. Ethyl butanoate was not significantly affected by 2-nonanone (coupling factor of 0.99 ± 0.03). This contrasts with Figure 6-4a, which shows negative and positive coupling respectively for 2-nonanone and ethyl butanoate, when all esters and ketones were present in the feed solution. It therefore appears that coupling effects may partly depend on the total concentration of competing molecules in the feed. Because

2-nonanone was almost at its solubility limit, the effect of concentration was tested for the ethyl butanoate/acetic acid feed solution instead of the ethyl butanoate/2-nonanone feed.

Figure 6-5 shows the extent of coupling between acetic acid and ethyl butanoate at three different acid concentrations. As the concentration of acetic acid increased, its positive effect on ethyl butanoate increased, and the effect of ethyl butanoate on acetic acid changed from positive coupling to negative coupling. Lipnizki & Hausmanns (2004) also observed that coupling factors depended on the feed concentration, when they tested several organic compounds for their effect on the coupling factor of 1-propanol. They found that the extent of negative coupling was greatest when 1-propanol and the second compound had the same molar feed concentration. In the current study, Figure 6-5 shows that the coupling factor of ethyl butanoate (molar concentration 0.86 mmol L^{-1}) was greatest at an acetic acid concentration of 210 ppm (3.49 mmol L^{-1}), indicating that this concentration of acetic acid enhanced the flux of ethyl butanoate. In contrast, ethyl butanoate enhanced the flux of acetic acid by the greatest amount when the acetic acid concentration was 10.5 ppm (0.18 mmol L^{-1}). At an acetic acid concentration of 105 ppm (1.75 mmol L^{-1}), at which the molar concentrations of

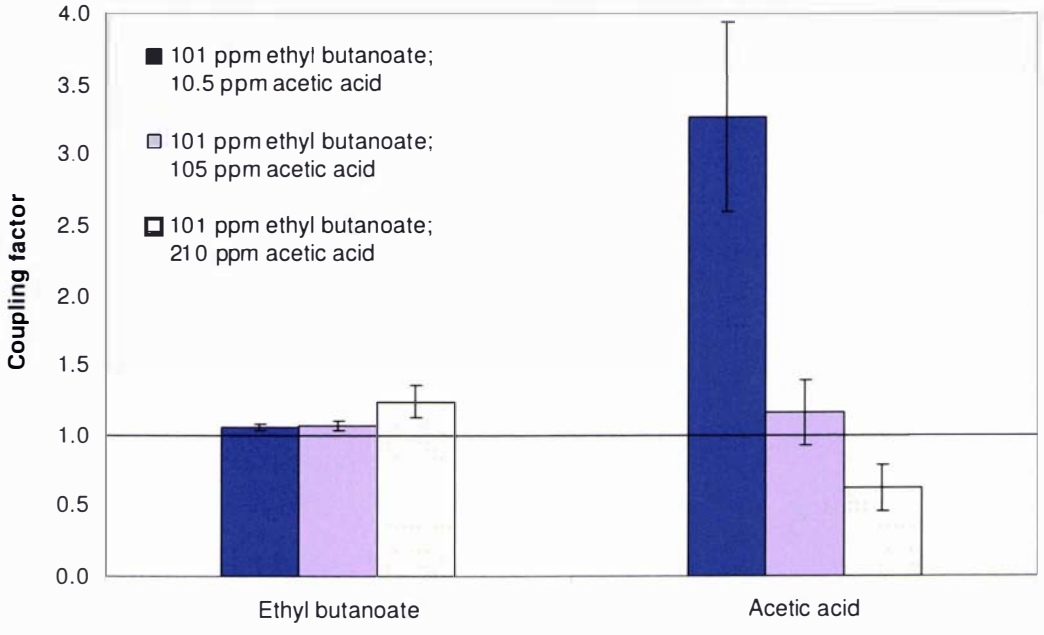


Figure 6-5: Coupling factors (mean ± standard error) in feed solutions containing one ester plus one acid, at the concentrations indicated. Operating conditions: feed temperature 30°C; permeate pressure 1.5 kPa. The horizontal line indicates the point of no coupling.

the two compounds were closest, both compounds had coupling factors close to one. The effect of coupling was therefore smaller when the two compounds had similar concentrations. This contrasts with Lipnizki & Hausmanns (2004), but may be explained by the fact that they observed negative coupling, whereas the coupling factors in Figure 6-5 were positive in all cases except one.

To further examine how coupling factors were affected by the concentration of compounds from other functional groups, Figure 6-6 shows the coupling factors of each flavour compound in all the different feed solutions tested (excluding the feed solutions that contained ethanol). Results for acids (Figure 6-6c) are included for completeness, but from the few data points it is difficult to establish trends. Each compound's coupling factor is its mass transfer ratio between a mixed feed solution (two to nine flavour compounds) and a binary feed solution (one flavour compound plus water). Coupling factors are plotted against the total feed concentration of compounds from homologous series other than the one in question; for example, Figure 6-6a shows the coupling factors of ketones, plotted against the total feed concentration of esters plus acids. Coupling factors did not appear to reach a minimum within the concentration range tested, which again contrasts with Lipnizki & Hausmanns (2004). However, each feed solution contained several flavour compounds, some of which caused positive coupling and some of which caused negative coupling. Figure 6-6 shows only the net overall coupling within each feed mixture. As a result, the data are fairly scattered, but some trends can be observed. Coupling factors of ketones decreased as the total concentration of esters plus acids increased (Figure 6-6a). In Figure 6-6b, the coupling factors of the two larger esters decreased, but the coupling factor of ethyl butanoate increased slightly, as the total concentration of ketones plus acids decreased.

As the feed solutions in Figure 6-6 also contained differing concentrations of other compounds from the same functional group, they can only be interpreted qualitatively. However, the results in Figure 6-6 appear to be consistent with the hypothesis stated earlier, that the observed negative coupling was caused by competition between compounds with different functional groups. This coupling seemed to depend to some extent on the concentration of the competing permeant molecules.

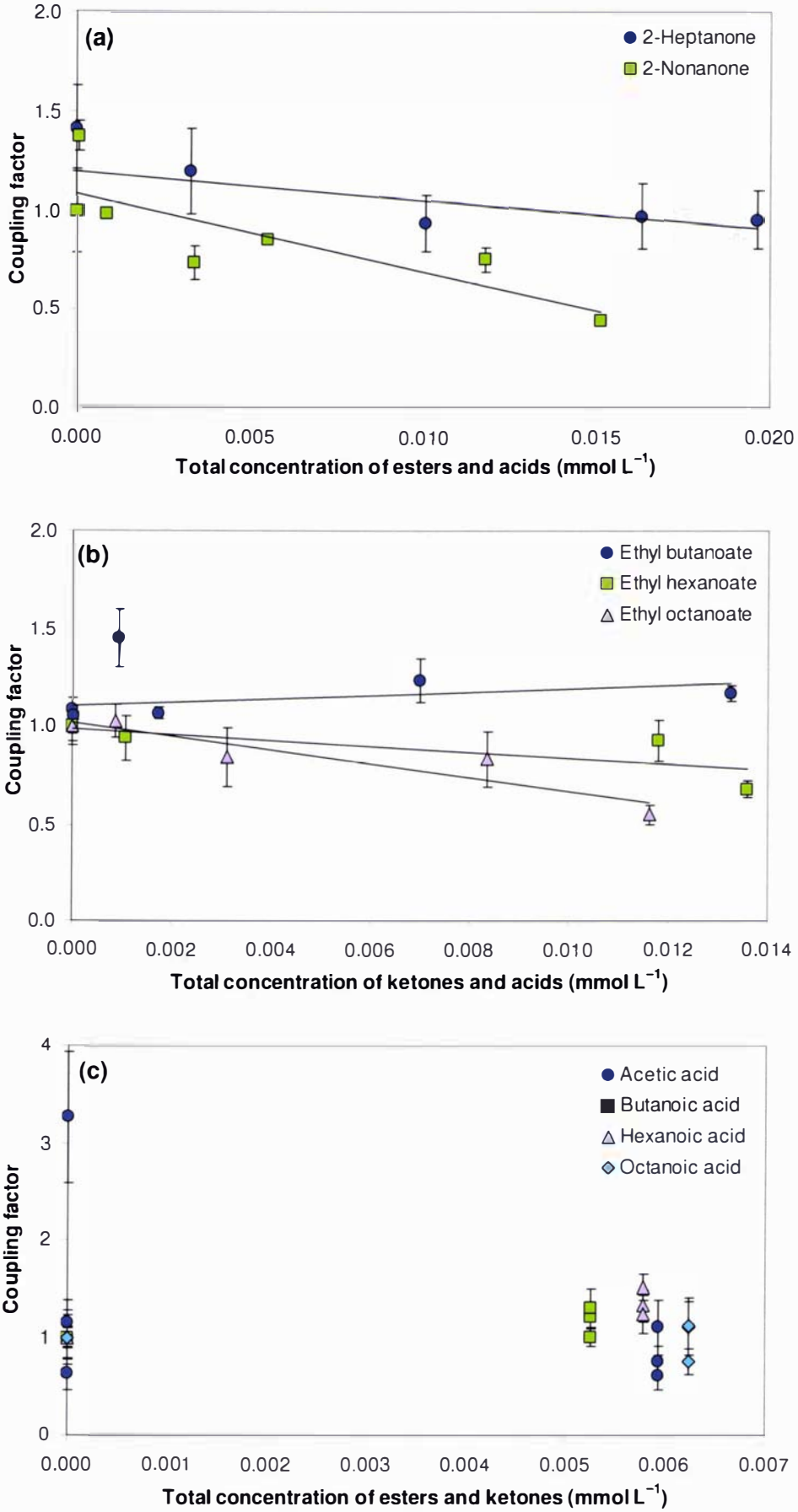


Figure 6-6: Effect of compounds from other functional groups on the coupling factors (mean ± standard error) of (a) ketones, (b) esters and (c) acids.

6.3.3 Effect of ethanol on water flux

When the feed solution contained 5% (v/v) ethanol as well as the standard nine flavour compounds at their standard concentrations, the total flux was 683 ± 6 mg m^{-2} s^{-1} at the conditions tested (30°C feed temperature; 1.5 kPa permeate pressure). This was 20% higher than the total (water) flux for the standard multicomponent feed under the same conditions. Table 6-2 shows that this 20% difference was entirely due to the flux of ethanol, as the water fluxes were similar for both feed solutions. Therefore, this level of ethanol did not appear to swell the membrane enough to affect the water flux.

6.3.4 Coupling interactions between ethanol and flavour compounds

Figure 6-7 shows how the added ethanol affected the fluxes of flavour compounds. The fluxes of 2-nonanone, ethyl hexanoate, acetic acid and octanoic acid increased by 19%, 17%, 20% and 59% respectively when 5% (v/v) ethanol was added to the feed, but the ethanol did not affect the fluxes of the other flavour compounds.

When evaluating the coupling interactions of flavour compounds, there is a key difference between their coupling to ethanol and their coupling to other flavour compounds. In dilute solutions of flavour compounds, it is assumed that the activity coefficients are equal to those at infinite dilution (Baudot & Marin, 1999; Lipnizki & Hausmanns, 2004; Trifunović & Trägårdh, 2006); in other words, the flavour compounds should not affect each other's driving force. This assumption does not hold when the feed solution contains high levels of an organic compound, such as ethanol. For example, Baudot & Marin (1997) calculated that

Table 6-2: Water flux and ethanol flux[a] (mean ± standard error), for feed solutions with and without ethanol.

Feed solution	Water flux[b] (mg m^{-2} s^{-1})	Ethanol flux (mg m^{-2} s^{-1})
Standard multicomponent	570 ± 10	–
Standard multicomponent with 5% (v/v) ethanol	540 ± 40	140 ± 40

[a]Operating conditions: PDMS Type 1 membrane, 30°C feed temperature, 1.5 kPa permeate pressure.

[b]Assumed equal to the total flux for the standard multicomponent feed, and equal to the total flux minus the ethanol flux for the ethanol-containing feed.

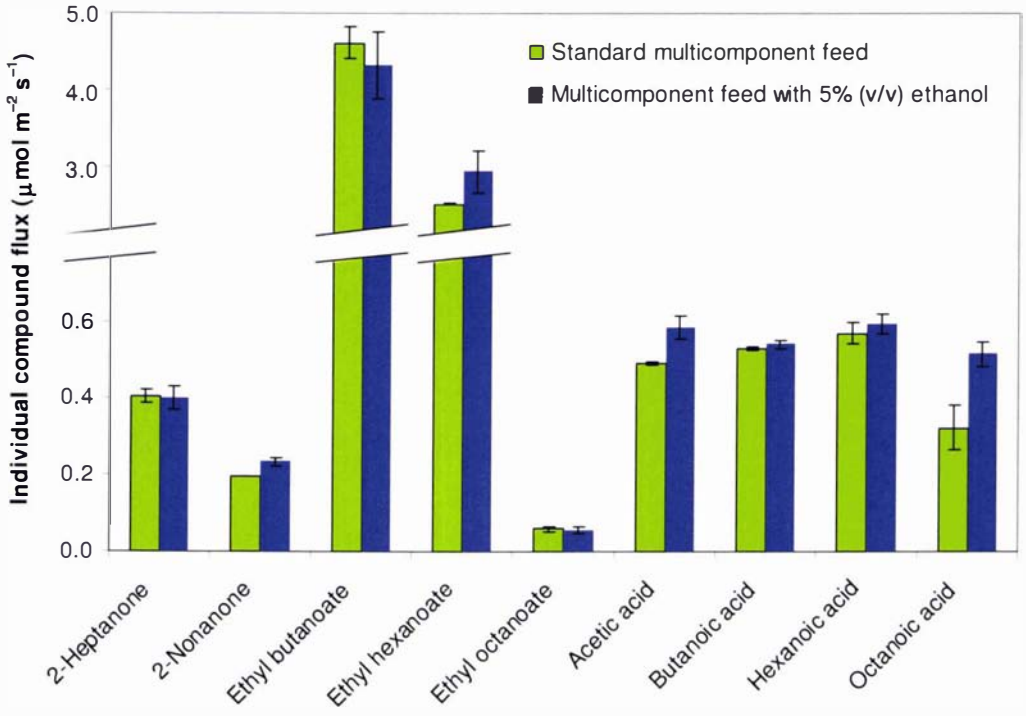


Figure 6-7: Individual fluxes (mean ± standard error) of flavour compounds in feed solutions with and without ethanol. Operating conditions: PDMS Type 1 membrane, feed temperature 30°C, permeate pressure 1.5 kPa.

the activity coefficients of esters and alcohols (at ppm levels) decreased by a factor of 2–3 in the presence of approximately 10% ethanol, compared with their activity coefficients in a purely aqueous solution. This is because the feed solution becomes less hydrophilic in the presence of ethanol, and hence more attractive to hydrophobic flavour compounds (Karlsson & Trägårdh, 1994; Tan et al., 2005). Therefore, whereas dilute flavour compounds may affect each other's permeability in the membrane, percentage levels of ethanol may affect both the permeability and the driving force of flavour compounds.

As a result of these two aspects, researchers have reported both positive and negative effects of ethanol on flavour compound fluxes. For example, fluxes of ethyl acetate, *i*-butanol, *n*-butanol, *i*-amyl alcohol and linalool decreased as the ethanol concentration in the feed increased. Fluxes of 2-methylbutanal and ethyl butanoate increased, whereas methanol, 2-methylpropanal, 1-penten-3-ol and *trans*-2-hexenal were not affected (Beaumelle et al., 1992; Karlsson & Trägårdh, 1994; Tan et al., 2005). Sometimes different researchers have obtained different

results for the same compound; Beaumelle et al. (1992) found that 10% ethanol increased the fluxes of propanol and ethyl acetate, whereas Tan et al. (2005) reported that the flux of propanol remained constant, and the flux of ethyl acetate decreased, as the ethanol content increased from 0% to 40% (mol/mol); and Ferreira (1998) reported no coupling of either propanol or ethyl acetate to ethanol (0–20% w/w). These mixed results may be due to the relative effects of ethanol on the permeability and the driving force in different systems.

In the current study, some flavour compounds had higher fluxes when 5% ethanol was added (Figure 6-7). This finding suggests that the increase in permeability due to ethanol was more significant than the decrease in driving force, leading to a net effect of increased fluxes in the presence of ethanol. However, not all flavour compound fluxes were influenced by the added ethanol.

Figure 6-8 shows the influence of ethanol on the enrichment factor of each flavour compound. Although 5% ethanol had a positive or neutral effect on flavour compound fluxes, the enrichment factors of several compounds (2-heptanone, butanoic acid, hexanoic acid, ethyl butanoate and ethyl octanoate) decreased by

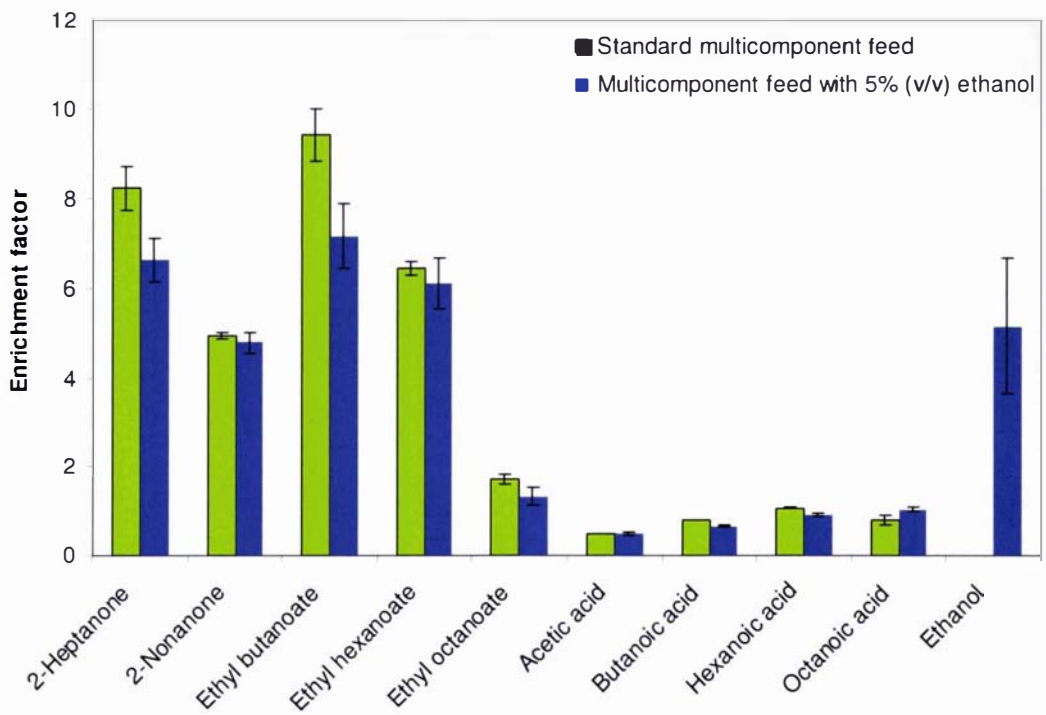


Figure 6-8: Enrichment factors (mean ± standard error) of flavour compounds in feed solutions with and without ethanol. Operating conditions: PDMS Type 1 membrane, feed temperature 30°C, permeate pressure 1.5 kPa.

17–24% in the presence of ethanol. This is because the added ethanol did not significantly affect the fluxes of these compounds (Figure 6-7), but caused a 20% increase in the total flux. Therefore, the collected permeate contained the same amounts of these five compounds, whether or not the feed contained ethanol, but the total amount of permeate was greater in the presence of ethanol. Hence, the flavour compounds listed above had lower permeate concentrations, and thus lower enrichment factors, when the feed contained ethanol.

The enrichment factor of ethanol was 5.2 ± 1.5, which was similar to the enrichment factors of 2-nonanone and ethyl hexanoate. Ethanol has a molecular weight of 46 g mol^{-1}, which is lower than any of the flavour compounds in the model solution. Extrapolation of the ester and ketone homologous series suggests that ethanol would have a lower enrichment factor than esters or ketones of the same molecular weight. Although caution must be used when extrapolating results in this way (as the enrichment factors may increase instead of decrease below a certain molecular weight, as was found for acids in Chapter 5), this observation agrees with other researchers' findings that alcohols generally have lower enrichment factors than esters or ketones (Bengtsson et al., 1992; Vankelecom et al., 1997).

Figure 6-9 compares the coupling factors of each flavour compound in multicomponent feed solutions with and without ethanol. Binary feed solutions (without ethanol) were still used as the reference for calculating coupling factors using Equation (6-1).

The added ethanol caused the coupling factors to increase; that is, it increased the mass transfer of each flavour compound through the membrane. For most flavour compounds, this increase was only slight; both feed solutions were within standard error limits of each other. However, the coupling factors of 2-nonanone, ethyl hexanoate and octanoic acid increased by 84%, 57% and 120% respectively, compared to the standard multicomponent feed. For the latter two compounds, the influence of ethanol was enough to change their coupling effects from negative (coupling factor less than one) to positive (coupling factor greater than one).

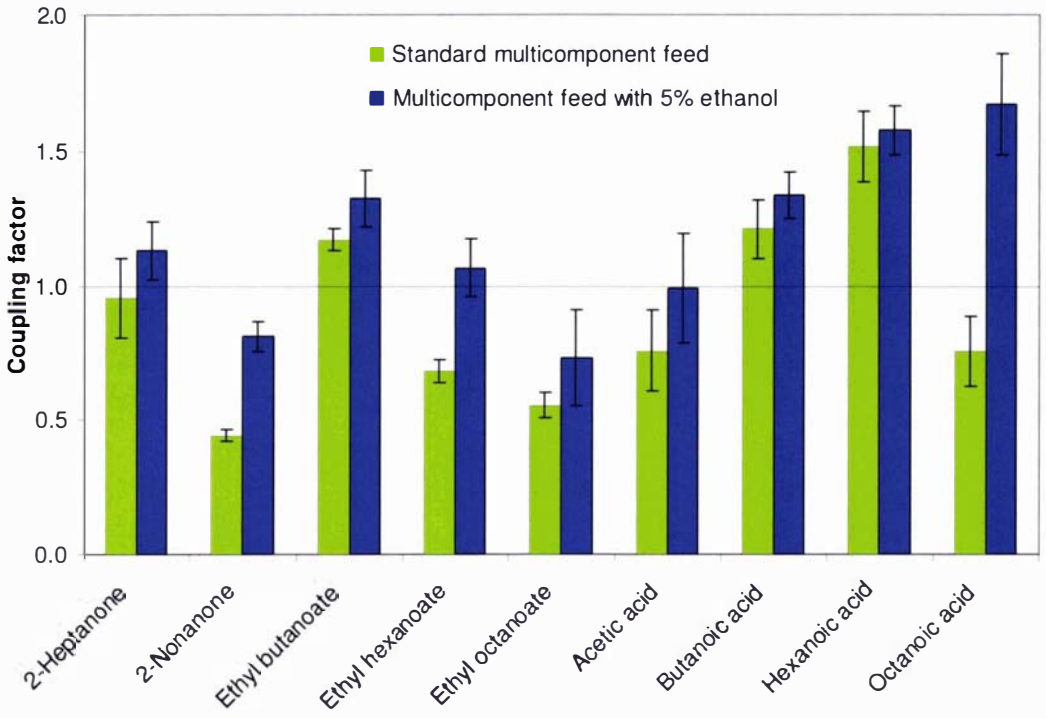


Figure 6-9: Coupling factors (mean ± standard error) of each flavour compound, in feed solutions with and without ethanol. Operating conditions: PDMS Type 1 membrane, feed temperature 30°C, permeate pressure 1.5 kPa. The horizontal line indicates the point of no coupling.

6.4 General discussion

The coupling factors between flavour compounds in this study depended on their molecular weights, and on the concentration of competing permeant compounds. The mechanism of coupling is assumed to be interactions between compounds from different functional groups, in the diffusion step. This hypothesis could be tested by determining the diffusion coefficients of each flavour compound with feed solutions containing other compounds with either the same functional group or different functional groups. Taking ethyl octanoate as an example, the hypothesis would be confirmed if its diffusion coefficient was equal with both a binary aqueous feed solution and a mixed ester feed solution, but lower with a mixed feed solution containing acids or ketones. Unfortunately, diffusion coefficients could not be measured with the available equipment.

In general, the other flavour compounds in the multicomponent feed slowed down the mass transfer rate of fast-permeating compounds (esters and ketones) and increased the mass transfer of slow-permeating compounds (acids). Therefore, coupling caused the different compounds to tend towards the same permeation rate as each other (although they did not reach the same permeation rate; individual compound fluxes still varied by more than an order of magnitude between different flavour compounds). This finding would be beneficial in situations where the aim of pervaporation is to concentrate the total volatile fraction without altering the flavour profile. If all flavour compounds permeated through the membrane to the same degree, they would have the same relative concentrations in the permeate. However, if the aim of pervaporation is to selectively concentrate some volatile compounds without concentrating others, coupling could make it more difficult to achieve this objective.

Under the conditions tested, 5% (v/v) ethanol increased the fluxes of certain flavour compounds, which were mainly the slower-permeating compounds from each homologous series (apart from ethyl hexanoate, which was the second-slowest permeating ester). Other flavour compounds were not affected by this level of ethanol. Therefore, pervaporation may be worth further investigation as a method to concentrate flavours in fermented products. The ethanol permeated through the membrane more easily than water, with an enrichment factor in the same range as the flavour compounds tested.

The results in this chapter show that coupling cannot be ignored, even in dilute feed solutions. However, as the coupling factors were almost always between 0.5 and 1.5, it would be possible to predict fluxes of the studied compounds, in a multicomponent solution, to within about 50% of their true values, using results obtained with binary solutions. It is important to note that this conclusion only applies to dilute solutions; for more concentrated feed solutions the effect is unknown, but permeants may plasticise the membrane and cause more significant coupling effects (Huang & Rhim, 1991).

Chapter 7

Effect of non-volatile dairy components on pervaporation

7.1 Introduction

It is generally agreed that pervaporation results with model feed solutions may differ from results with real feed mixtures, because permeants can interact both with other volatile compounds (coupling) and non-volatile components of the feed (Baudot & Marin, 1996, 1997; Kanani et al., 2003). Chapter 6 covered coupling effects; the present chapter aims to bridge the gap between aqueous model solutions and real dairy flavour systems, by investigating the effect of non-volatile feed components on pervaporation of flavour compounds. Non-volatile substances should not pass through pervaporation membranes (Baudot & Marin, 1996, 1997; Kattenberg & Willemsen, 2001; Aroujalian et al., 2006), but they could nonetheless affect the pervaporation behaviour of volatile compounds by altering their feed side activities.

The major components of milk solids are protein, lactose and fat (Swaisgood, 1996). Apart from their involvement in flavour formation, these non-volatile substances can all potentially interact with flavour compounds, each following a different mechanism.

In a flavour system containing water and fat, a proportion of the flavours will be dissolved in the fat phase (a greater proportion for more hydrophobic compounds) and hence cannot volatilise (Hatchwell, 1996; de Roos, 1997; Leland, 1997). In contrast, proteins bind flavours rather than acting as a solvent (Hatchwell, 1996). Various flavour compounds, including ketones and esters, can bind to milk proteins (Mills & Solms, 1984; Hansen & Booker, 1996; Guichard & Langourieux, 2000; Kühn et al., 2007). Flavours can bind to protein either physically (reversibly, generally through hydrophobic interactions) or chemically (irreversibly, for example via covalent bonding) (Fischer & Widder, 1997; Kühn et al., 2006). Carbohydrates can reduce the volatility of flavour compounds

through intermolecular attractions, or increase their volatility by salting-out (Godshall, 1997). Lactose contains many hydroxyl groups, and is thus able to bind certain flavour compounds through hydrogen bonding (Kellam, 1998; McJarrow, 2008, personal communication).

During pervaporation, flavour compound interactions with milk fat, milk protein or lactose may alter the feed side behaviour of the flavour compounds. The purpose of this study was to show the impact of these interactions on pervaporation performance. Milk also contains minor components such as various minerals and vitamins (Swaisgood, 1996); the impact of these on pervaporation was not specifically tested in the current study. However, most of the non-volatile components tested were in the form of dairy ingredients rather than highly purified chemicals; therefore, some minerals would have been associated with the major non-volatile components being tested.

7.2 Experimental

7.2.1 Partitioning of flavour compounds between fat and water

This experiment was carried out to determine the extent to which the flavour compounds present in the feed stream would partition into the fat phase.

Four feed solutions, containing the standard model flavour compounds and cream, were made as described in Section 3.1.4 (page 74), with 5%, 10%, 20% and 38% fat (w/v) respectively. After holding at room temperature for at least one hour, triplicate samples of each solution (approximately 45 mL) were added to centrifuge tubes. Samples were separated into fat and aqueous phases by centrifuging in a Heraeus Multifuge 1 S-R (Kendro, Germany) at 4700 rpm for one hour at 40°C. Fat and aqueous phases were extracted and analysed separately (following the procedures in Chapter 3) in order to determine the concentration of flavour compounds in each phase. This is a similar procedure to that followed by Hansen & Booker (1996), except that the centrifuging speed was lower due to equipment limitations.

7.2.2 Effect of non-volatile dairy components on flavour compound vapour pressures

The apparatus in Figure 7-1 was used to measure the partial vapour pressures of flavour compounds in the following feed solutions (described in Chapter 3):

- standard model solution
- standard model solution with added cream (5%, 10%, 20% and 38% fat (w/v))
- standard model solution with 4% (w/v) milk protein isolate
- standard model solution with 6% (w/v) lactose (extra pure grade)

The feed container was filled with 50 mL of feed solution. This was first frozen with liquid nitrogen while the headspace above the feed solution was evacuated. The inlet and outlet needle valves were then shut to isolate the feed container from the rest of the system, and the contents of the feed container were thawed at 20°C, stirring with a magnetic stir bar as soon as enough ice had melted to make this possible. Five to ten minutes after the feed solution had completely thawed, the outlet needle valve was opened slightly to draw material from the headspace of the feed container into the cold trap, using the vacuum pump. The air inlet valve was also opened slightly, so that the feed container remained at atmospheric pressure and the feed solution did not boil. Collection was continued until about 1 g of material had been collected in the cold trap. A sample from the cold trap was then extracted and analysed as described in Chapter 3. The measured

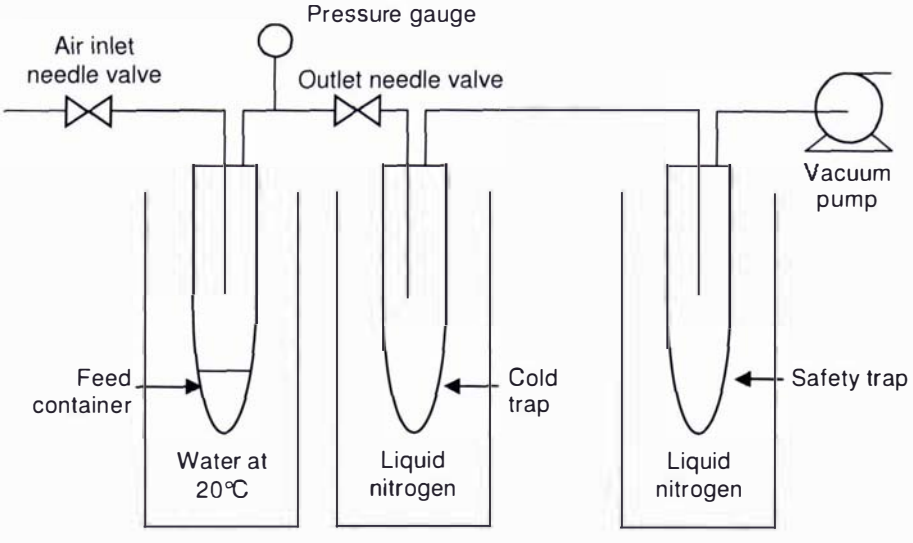


Figure 7-1: Schematic diagram of apparatus for measuring vapour pressures.

concentrations of each compound in the cold trap enabled the mole fraction of each compound in the headspace vapour to be calculated.

Partial vapour pressures in a mixture are the product of the total pressure and the mole fraction of each compound (Silberberg, 2006). In this experiment, the total pressure in the system did not reach a constant equilibrium value, but continued to slowly increase, due to unavoidable small leaks in the system. Therefore, as the volatile fraction of each mixture contained over 99% water, the total pressure was assumed equal to the saturated vapour pressure of water, which is 2.339 kPa at 20°C (Borgnakke & Sonntag, 1997). Calculated partial vapour pressures for each volatile component are therefore approximate, but they can be compared relative to one another.

7.2.3 Effect of non-volatile components on pervaporation performance

Pervaporation runs were carried out following the standard procedure as described in Chapter 3, using the PDMS Type 1 membrane, at a feed temperature of 30°C and a permeate pressure of 2 kPa. The feed solution consisted of nine flavour compounds at their standard concentrations, with cream, milk protein isolate or lactose added as described in Section 3.1.4 (page 74).

A blank run was carried out in triplicate, with a feed solution of pure cream without any flavour compounds added, to test for the presence of any naturally occurring flavour compounds present in cream.

7.2.4 Effect of operating conditions on pervaporation with fat

Using the feed solution containing cream diluted to 20% (w/v) fat (Chapter 3), pervaporation runs were carried out at 20°C/2 kPa, 40°C/2 kPa and 30°C/0.9 kPa, in order to compare with the 30°C/2 kPa run from Section 7.2.3.

7.3 Results and discussion

7.3.1 Effect of fat on pervaporation

7.3.1.1 Effect of fat on total flux

The total flux decreased linearly as the fat level in the feed was increased (Figure 7-2; $R^2 = 0.60$ including all runs; $R^2 = 0.97$ excluding outliers). It is unclear why the fluxes for four runs did not fit the general linear trend (two runs had higher fluxes and two had lower fluxes than expected).

As the majority (>99.5%) of the permeate consisted of water, the total flux in Figure 7-2 can be considered to be equal to the water flux. One of the factors causing a reduced water flux with higher-fat feeds is their greater viscosity, leading to a reduction in diffusivity in the feed side boundary layer. Table 7-1 lists the viscosities of diluted cream with various fat levels, estimated from literature data (Phipps, 1969). Any adsorption of fat to the membrane would also contribute to the decrease in total flux with higher-fat feeds.

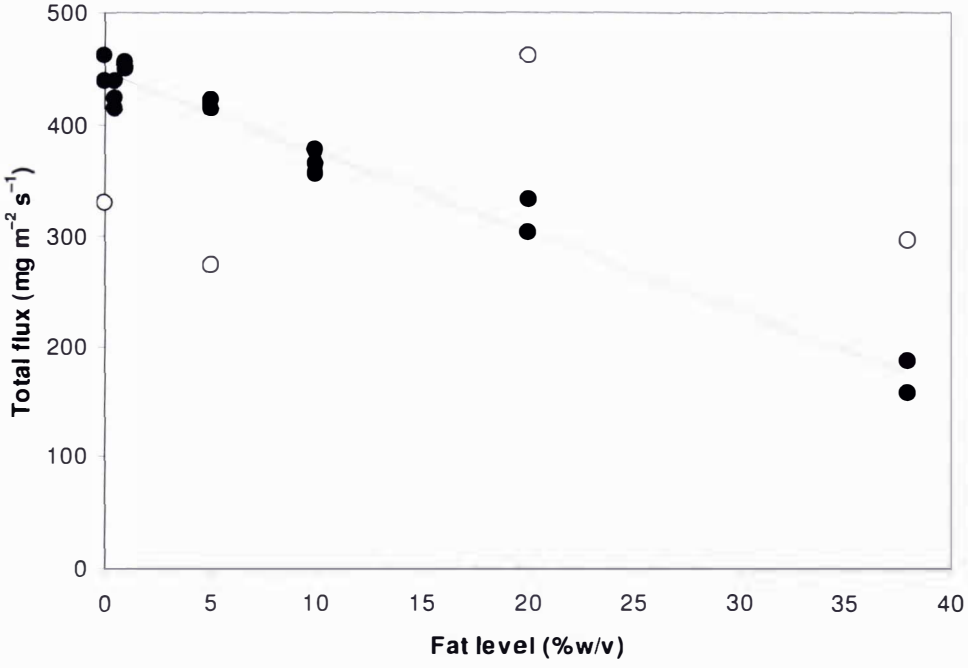


Figure 7-2: Effect of fat on total flux (feed temperature 30°C; permeate pressure 2 kPa). Hollow symbols represent outliers, which were not included in the best fit line calculation.

Table 7-1: Viscosities (at 40°C) of cream/milk mixtures with various levels of fat, estimated from a nomogram by Phipps (1969).

Fat level (%)	Viscosity (mPa s)
0	1.05
5	1.25
10	1.5
20	2.4
38	6.2

During each run, the flux was measured four times at hourly intervals. On average, the flux decreased by about 7% between the first two measurements, but by less than 2% between further measurements. Therefore, most of the fouling occurred in the first two hours of pervaporation. The reduction in total flux between the first two measurements in each run can hence be used to estimate the degree of fouling and/or fat adsorption. In Figure 7-3, this flux reduction is plotted against the fat level. With an aqueous feed solution (0% fat), the flux reduction was (5 ± 2)% after the second hour; higher-fat feeds exhibited more fouling and/or fat adsorption.

The presence of fat should not alter the water activity (Walstra et al., 2006); therefore, the decreasing total flux was not due to a change in driving force.

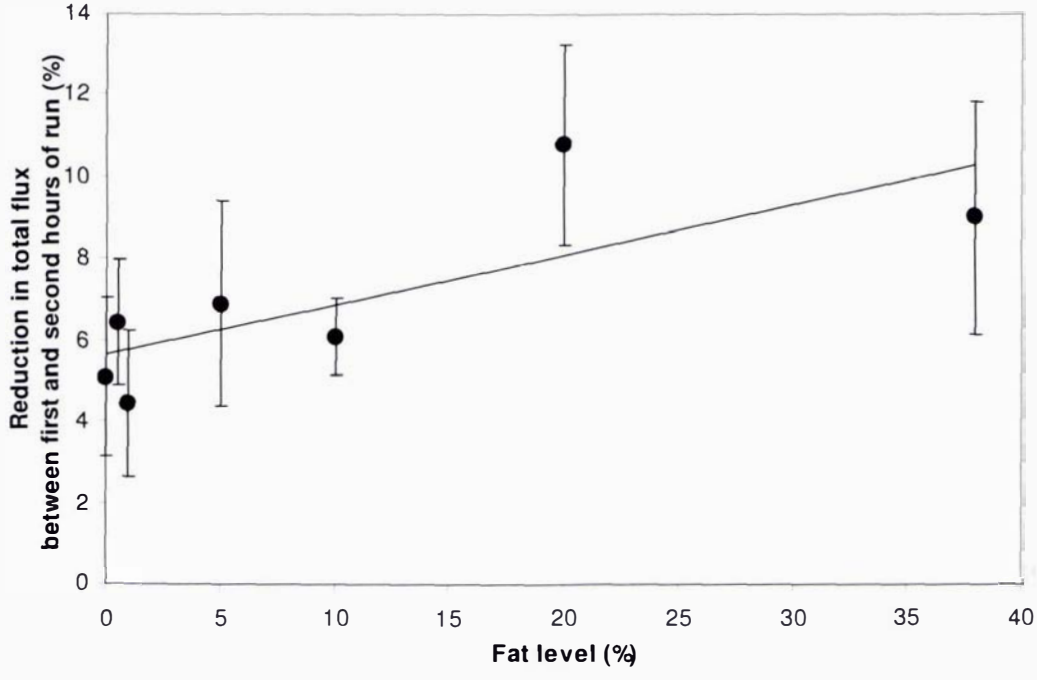


Figure 7-3: Percentage reduction in total flux after two hours, for various fat levels at 30°C and 2 kPa. Data points are the mean (± standard error) of three replicates. R^2 = 0.58.

7.3.1.2 Volatile compounds naturally present in cream

Cream was used merely as a source of fat rather than as a source of flavour compounds. However, the permeate collected from blank runs, carried out with a feed of pure cream, contained low levels of most of the flavour compounds included in the model feed solution (0–12% of their concentrations in the standard multicomponent feed). Table 7-2 gives the concentration of each compound in the permeate from blank cream.

Except for these blank cream runs, feed solutions containing cream were spiked with the model flavour compounds. In order to compare pervaporation runs with different cream levels in the feed, the individual compound fluxes reported in this chapter represent the flux contribution from only the spiked portion of each flavour compound, excluding the flux contribution from the flavour compounds naturally present in cream. The concentrations in Table 7-2 were multiplied by the percentage of cream in each feed solution, then subtracted from the measured permeate concentrations of each compound, to give the permeate concentration of only the spiked portion of each flavour compound. These calculated concentrations were used to determine the individual fluxes.

7.3.1.3 Effect of fat on flavour compound driving forces

Partitioning of flavour compounds between fat and water

Partition coefficients between the fat and water phases, with various levels of fat in the feed solution, are shown in Figure 7-4. Partition coefficients were defined as the ratio of each flavour compound's concentration in the fat phase to its

Table 7-2: Concentrations of model solution compounds in permeate from 100% cream (38% w/v fat). Pervaporation conditions: 30°C feed temperature; 2 kPa permeate pressure. Data are means (± standard error) of three replicates, using different batches of cream.

Compound	Permeate concentration (mg kg^{-1})
2-Heptanone	0.0 ± 0.0
2-Nonanone	0.4 ± 0.1
Acetic acid	12.7 ± 1.0
Butanoic acid	1.8 ± 0.5
Hexanoic acid	7.7 ± 3.4
Octanoic acid	11.2 ± 1.0
Ethyl butanoate	0.7 ± 0.2
Ethyl hexanoate	2.5 ± 0.3
Ethyl octanoate	0.8 ± 0.2

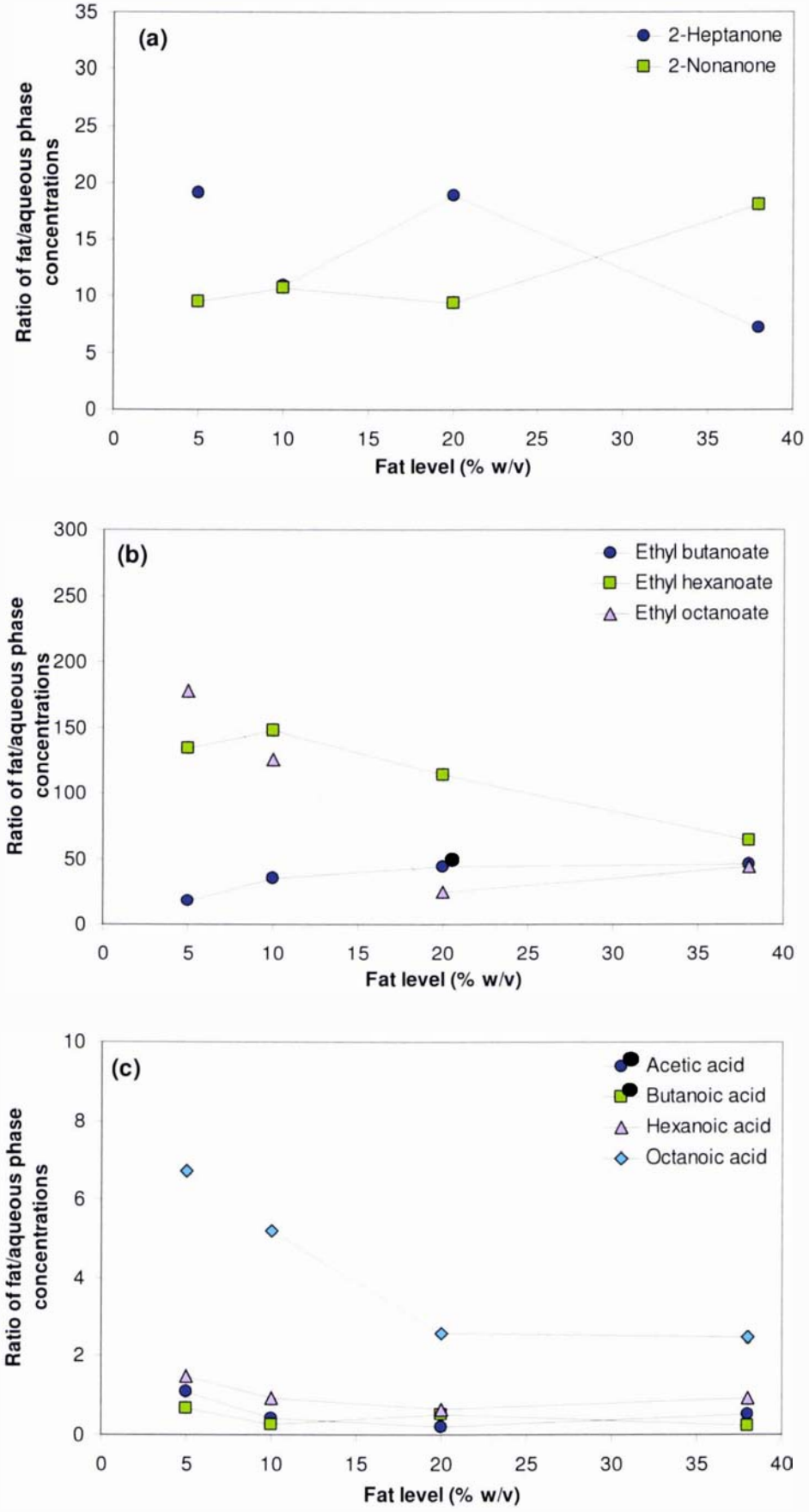


Figure 7-4: Fat/water partition coefficients for (a) ketones, (b) esters and (c) acids, in solutions with various amounts of fat. Data points are the mean (± standard error) of three replicates.

concentration in the aqueous phase. Higher partition coefficients indicated a greater affinity for the fat phase; for example, a partition coefficient of 10 means that the concentration in the fat phase was 10 times the concentration in the aqueous phase.

Esters had the greatest partition coefficients, followed by ketones then acids, reflecting the relative hydrophobicities of these compounds. The larger the compound within a homologous series, the more hydrophobic it is; this is reflected in Figure 7-4, in which larger compounds generally had greater partition coefficients than smaller compounds. Some errors may have been introduced with the 5% fat results, as it was difficult to completely separate this small amount of fat from the aqueous phase before analysis. This is shown with the large standard errors at 5% fat.

The partition coefficients of acids decreased as the fat level increased, meaning that relatively less of each acid was dissolved in the fat phase in high-fat feeds. This result was most probably due to the pH differences between the feed solutions. The pH levels of selected fat-containing feed solutions are given in Table 7-3, showing that the addition of fat (in the form of cream) made the feed solution less acidic. The higher the pH, the greater the proportion of each acid in its dissociated form. The dissociated form is charged, and hence has a greater affinity for water and a lower affinity for fat compared to the undissociated acid.

The partition coefficients of the esters and ketones did not follow any obvious trends with respect to the fat level.

The absolute amounts of most flavour compounds in the fat phase increased with increasing fat level, because there was more fat available to dissolve these compounds. Therefore, the concentration of each compound which was not

Table 7-3: pH values of model feed solutions containing flavour compounds and various amounts of cream.

Fat level (% w/v)	pH
0	3.5
5	4.8
10	5.5
20	6.1
38	6.1

associated with fat, and hence was available for pervaporation, generally decreased as the amount of fat increased (Figure 7-5). There were some anomalies at 5% fat with ketones, which were probably caused by the experimental error mentioned earlier. As flavour compound volatilities tend to be much lower in fat than in water (Landy et al., 1996; Meynier et al., 2003), the portion dissolved in the fat phase should not contribute significantly to the vapour pressure, and therefore the driving force for each compound would mainly be determined by this available concentration.

Effect of fat on flavour compound vapour pressures

Figure 7-6 shows how the level of fat in the feed solution affected the partial vapour pressures of flavour compounds. As mentioned in Section 7.2.2, the absolute values of these partial vapour pressures are approximate because the total vapour pressure was not known exactly, but the measured values are correct relative to each other. The pervaporation driving force can be approximated by the partial pressure difference across the membrane; the higher the partial vapour pressure of a volatile component in the feed, the higher its driving force.

Vapour pressures of ketones and esters (Figure 7-6a and b) decreased as the fat level increased, confirming that, as more of each compound partitioned into the fat phase, less was available to contribute to the driving force. A similar finding was reported by Meynier et al. (2003), who measured the volatility of five esters and aldehydes in water, skim milk, anhydrous milk fat and cream. They observed that air/cream partition coefficients were 94–99% lower than the air/water partition coefficients, indicating that the flavour compounds were less volatile in cream than in water.

Unlike esters and ketones, vapour pressures of all acids, except acetic acid, changed very little between 0% and 38% fat (Figure 7-6c). This result agrees with Roberts & Acree (1996), who found that the volatility of butanoic acid was similar in both water and an oil/water matrix. For one replicate, an anomalously high vapour pressure was recorded for acetic acid at 38% fat, but its average vapour pressure at 38% fat was within standard error limits of the other fat levels.

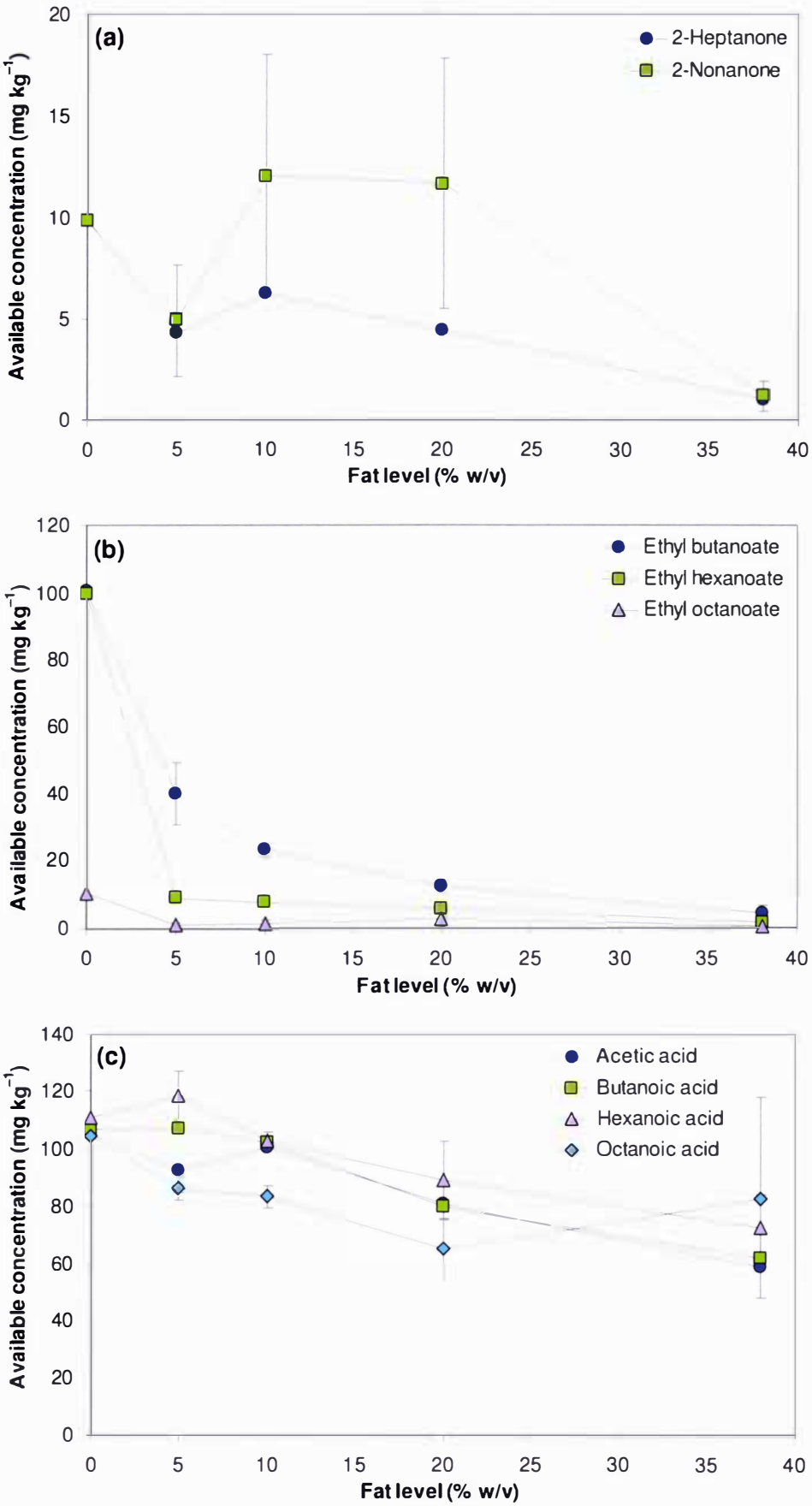


Figure 7-5: Available concentrations (concentration of each compound not associated with fat) of (a) ketones, (b) esters and (c) acids, in feed solutions with various levels of fat. Data are means (± standard error) of three replicates, except for 0% fat, in which the available concentration is the actual amount added to the solution.

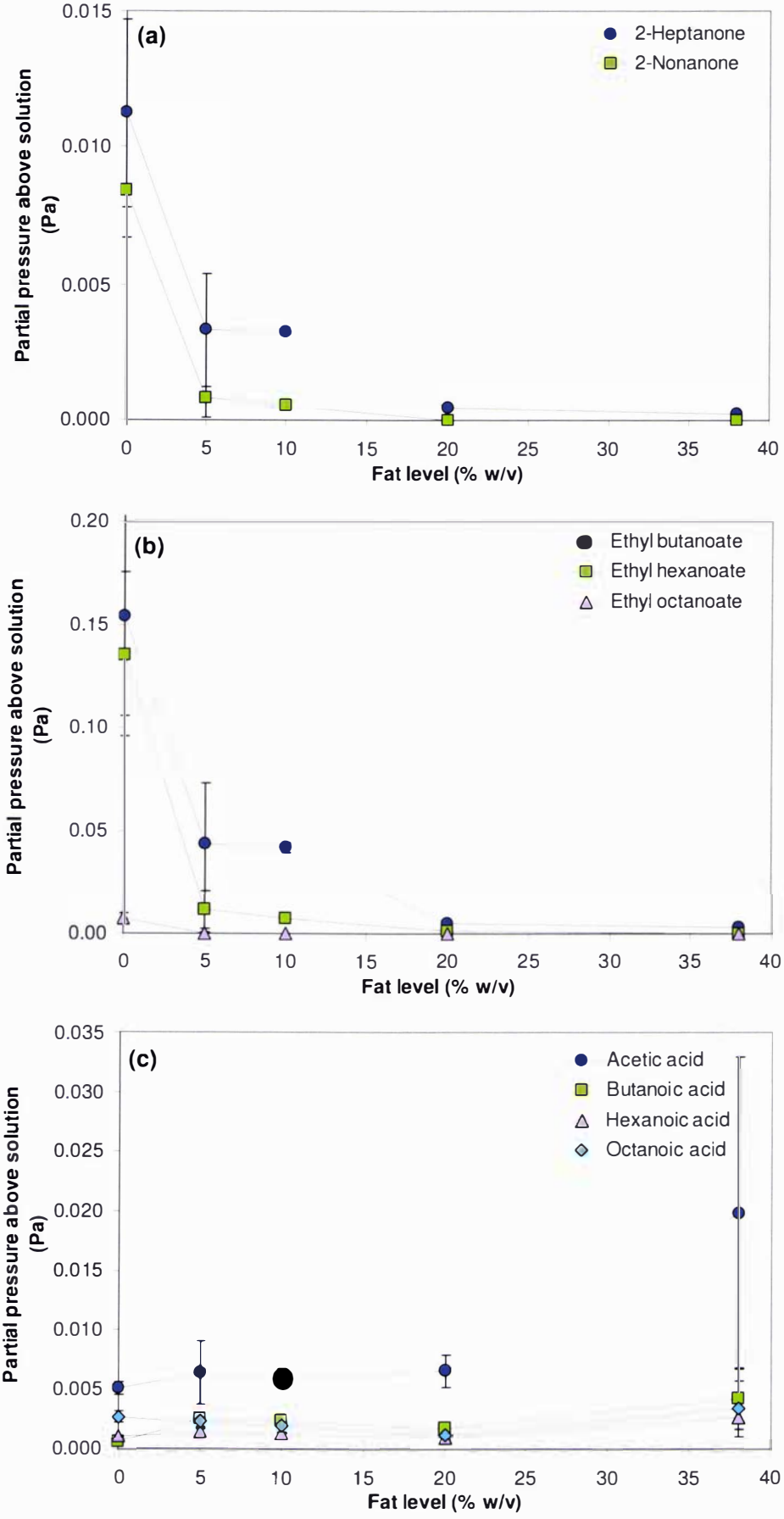


Figure 7-6: Partial pressures of (a) ketones, (b) esters and (c) acids (mean ± standard error of two replicates, measured at 20°C), above feed solutions with various levels of fat.

The partial vapour pressure of each compound depends on its concentration, which is why ethyl butanoate and ethyl hexanoate (approximately 100 ppm each) had much higher partial vapour pressures than ethyl octanoate and the ketones (approximately 10 ppm each). Although acids were approximately 10 times more concentrated than ketones, their vapour pressures were in the same range, reflecting their lower volatility. Notwithstanding the concentration differences, vapour pressures decreased with increasing carbon chain length within each functional group, except that the three largest acids all had similar vapour pressures.

7.3.1.4 Effect of fat on flavour compound fluxes and enrichment factors

With increasing fat levels, flavour compound fluxes (Figure 7-7) decreased by a proportionally greater amount than the total flux (Figure 7-2). The flux of each flavour compound decreased sharply when small amounts of fat were added to the feed, then levelled off as the fat level was increased. As the fat had a greater impact on the flavour compound fluxes than on the water flux, even low levels of fat were detrimental to the enrichment factors (Figure 7-8). The exception was octanoic acid, for which the flux and enrichment did not change much in the presence of fat.

At fat levels of 10% and higher, only 2-heptanone and ethyl butanoate could be concentrated using pervaporation; the enrichment factors of all the other compounds had decreased to less than one. These results confirm Baudot & Marin's (1996) prediction that fat would reduce the pervaporation yield of hydrophobic compounds.

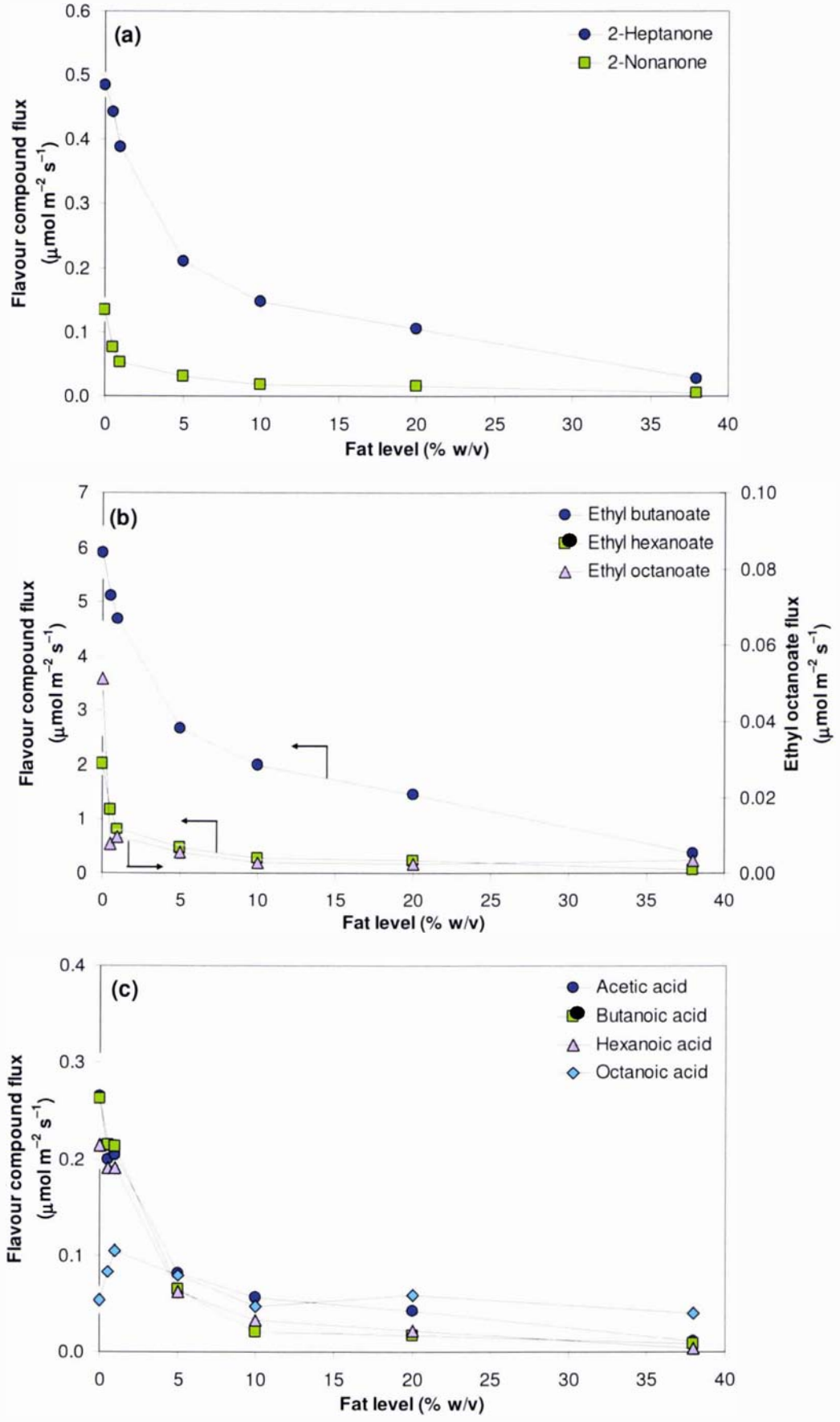


Figure 7-7: Effect of fat on fluxes of (a) ketones, (b) esters and (c) acids (feed temperature 30°C; permeate pressure 2 kPa). Data points are the mean (± standard error) of three replicates.

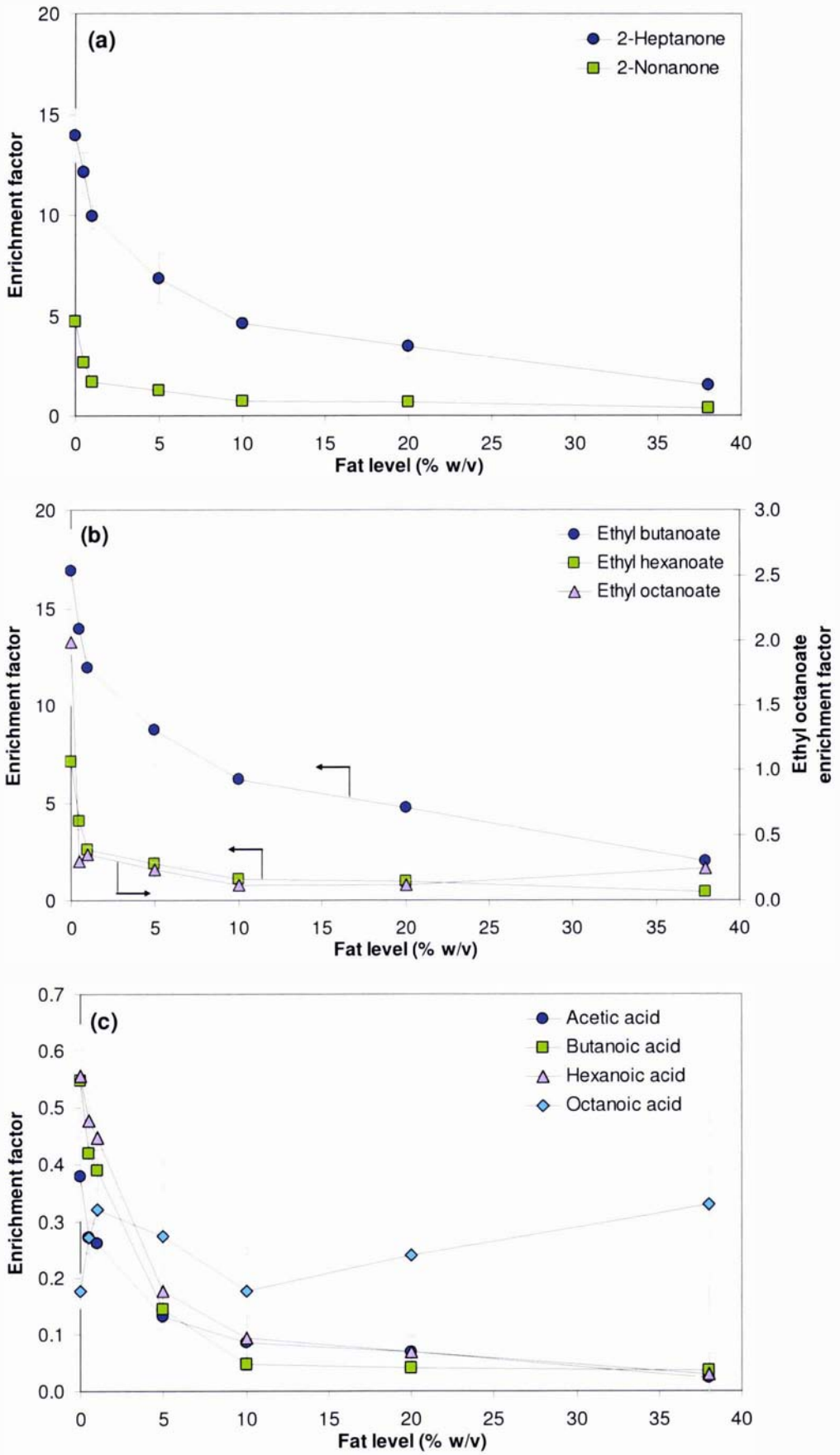


Figure 7-8: Effect of fat on enrichment factors of (a) ketones, (b) esters and (c) acids (feed temperature 30°C; permeate pressure 2 kPa). Data points are the mean (± standard error) of three replicates.

Table 7-4 shows the relative impact of each fat level on the enrichment of each flavour compound, compared with their enrichment in a fat-free feed solution. Within the esters and ketones homologous series, the fat had a greater effect on the larger compounds. Acids, however, showed no such trend. These results reflect the effect of fat on partial vapour pressures of different sized compounds with the same functional group (Figure 7-6), showing that fat reduced the fluxes and enrichment factors of larger, more hydrophobic, esters and ketones by lowering their driving forces.

Other researchers have seen similar trends to those in Figures 7-7 and 7-8, in the context of flavour sorption into polymers (analogous to the first step in pervaporation). van Willige et al. (2000a) showed that the sorption of four flavour compounds into linear low-density polyethylene was decreased when they added glycerol trioctanoate/glycerol tridecanoate oil (up to 5% w/v) to the aqueous flavour mixture. The general trend of sorption versus fat level reflected the trends shown in Figure 7-7 and Figure 7-8, although they found that the sorption of ethyl 2-methylbutanoate increased at very low oil concentrations, then decreased again as the oil level was increased. Compounds of low polarity were more attracted to the oil, so their sorption was affected by oil to a greater extent than more polar compounds (van Willige et al., 2000a). Nielsen et al. (1992) also investigated sorption of flavours into low-density polyethylene, from a solution either in water or in olive oil. Some compounds (aldehydes and large esters) were retained in the oil to a greater extent than in the water. However, they found the opposite effect

Table 7-4: Percentage reduction in enrichment factors[a] caused by various levels of fat (mean of three measurements at 30°C feed temperature and 2 kPa permeate pressure).

Compound	Molecular weight (g mol^{-1})	Reduction in enrichment factor (%) (compared with a feed solution containing no fat)					
		0.5% fat	1% fat	5% fat	10% fat	20% fat	38% fat
2-Heptanone	114	13	29	51	67	75	89
2-Nonanone	142	44	64	73	85	86	93
Ethyl butanoate	116	18	30	49	63	72	88
Ethyl hexanoate	144	43	63	73	85	86	94
Ethyl octanoate	172	85	82	88	94	94	88
Acetic acid	60	29	31	65	78	82	94
Butanoic acid	88	23	29	74	92	93	94
Hexanoic acid	116	14	20	68	83	88	95
Octanoic acid	144	−53	−82	−56	0	−36	−87

[a] $\%\ Reduction = \frac{(enrichment\ factor\ with\ no\ fat) - (enrichment\ factor\ with\ stated\ fat\ level)}{(enrichment\ factor\ with\ no\ fat)} \times 100$

for smaller, more hydrophilic, esters and alcohols. Therefore, although fat decreased the fluxes of all compounds tested in the current study, this may not be the case with different compounds and membrane types.

The effect of fat on pervaporation performance (Figures 7-7 and 7-8) is at least partly due to its lowering of the flavour compound driving forces, which was presented in the previous section. As the fat level increased, the available concentration of each compound decreased (Figure 7-5), and consequently the partial vapour pressure decreased also (Figure 7-6). To account for the changing driving force, flavour compound fluxes were divided by the measured partial vapour pressures (Figure 7-9), which gives an approximation of the mass transfer coefficient or membrane permeability for each compound.

As the mass transfer coefficients were not constant across all fat levels, it can be inferred from Figure 7-9 that the driving force was not the only reason that the added fat decreased the flavour compound fluxes. For esters and ketones, the driving force decreased as the fat level increased, but the mass transfer coefficients generally increased. This means that there was less resistance to mass transfer at higher fat levels. A possible reason is that at higher fat levels, the fluxes were lower, so there was less competition between permeants. For acids, the driving force remained constant across all fat levels, but the mass transfer coefficients decreased as the fat level increased (except for octanoic acid, for which the mass transfer coefficient remained constant). This result can be explained by pH differences. As described in Chapter 5, increasing the feed pH from 3.5 (corresponding to the feed solution with 0% fat) to 4.8 or higher (corresponding to feed solutions with 5% fat or more) reduced the fluxes of acetic acid, butanoic acid and hexanoic acid by more than half, even without any fat.

Despite these differences in the mass transfer resistance at different fat levels, the effect of fat on the driving force of each flavour compound was the main cause of the flux decrease with increasing fat level. Therefore, in many cases the flux could be estimated by multiplying the mass transfer coefficient of each compound, determined at 0% fat, by the calculated driving force at each fat level. Figure 7-10 shows the correlation between the fluxes estimated in this way, and measured fluxes; fluxes could be predicted well for esters, but predictions were not always

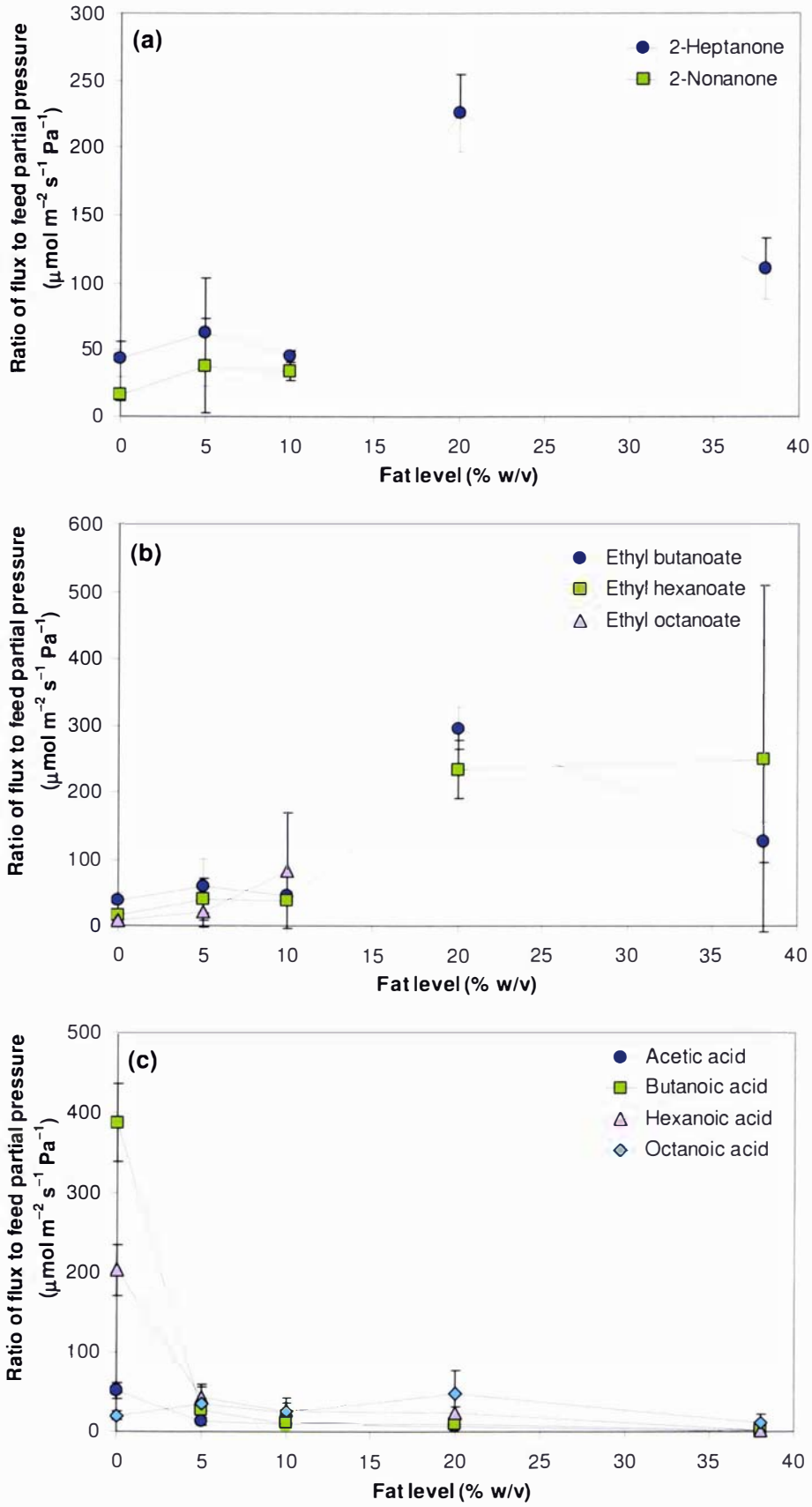


Figure 7-9: Individual compound fluxes (mean ± standard error) of (a) ketones, (b) esters and (c) acids, adjusted by dividing by partial vapour pressures from Figure 7-6. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Values could not be calculated for 2-nonanone or ethyl octanoate in feed solutions above 10% fat, because their partial pressures were too low to measure.

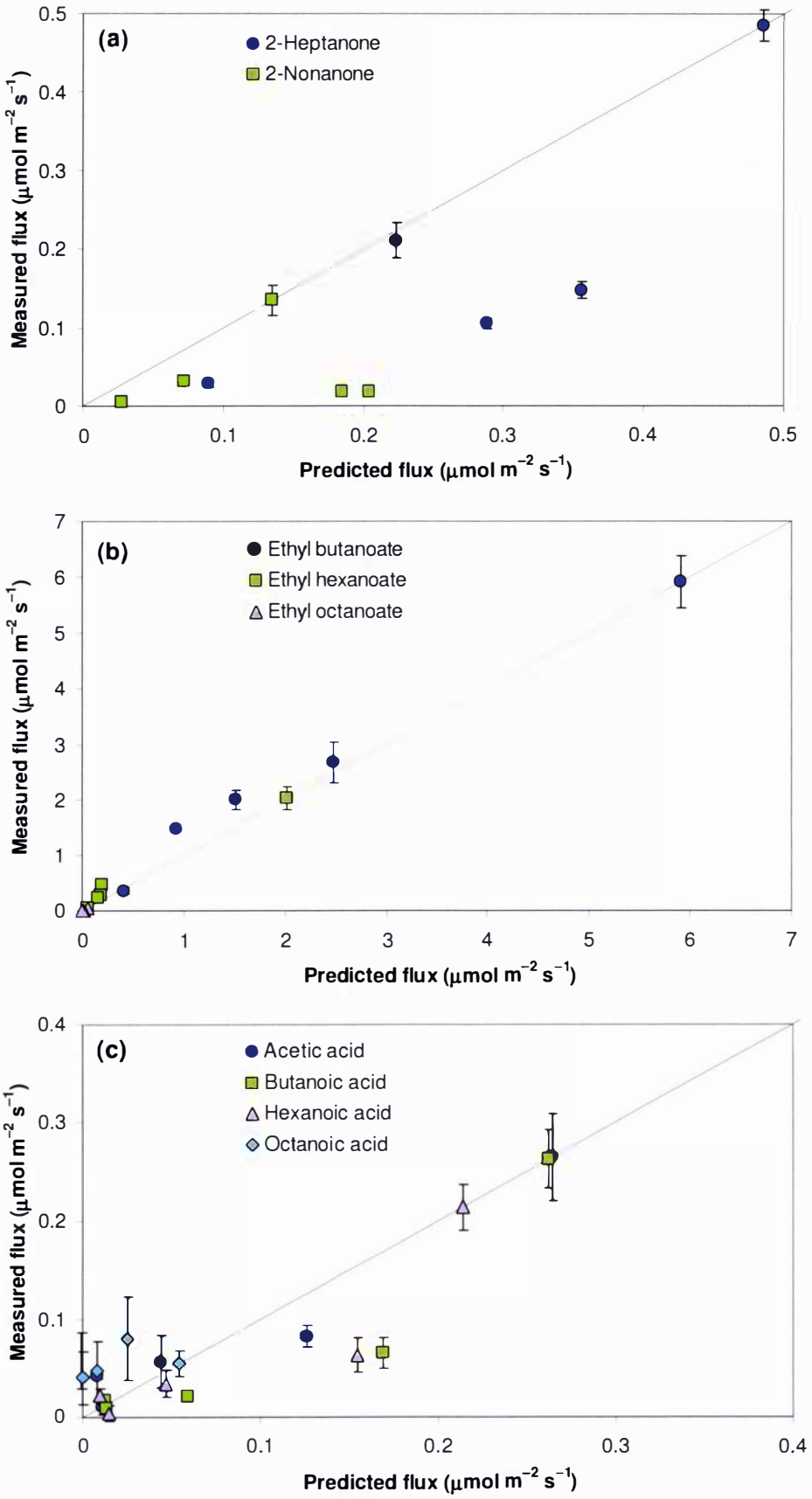


Figure 7-10: Correlation between measured (mean ± standard error) and predicted fluxes (Equation (7-1)) for (a) ketones ($R^2 = 0.67$), (b) esters ($R^2 = 0.99$), and (c) acids ($R^2 = 0.78$). The diagonal line represents an ideal 1:1 relationship.

accurate for ketones or acids. The driving force (*df*) of each compound was defined as the difference in activity between the feed and permeate sides of the membrane:

$$df = x_{i,f}\gamma_{i,f} - \frac{p_{i,p}}{p_i^0} \quad \textbf{(7-1)}$$

where $x_{i,f}$ is the available concentration of compound *i* in the feed, expressed as a mole fraction (for acids, this was defined as the available concentration in the undissociated form, determined from the pH of each feed solution and the pK_a of each acid), $\gamma_{i,f}$ is the activity coefficient of compound *i* in the feed, $p_{i,p}$ is the partial pressure of compound *i* on the permeate side of the membrane, and p_i^0 is the saturated vapour pressure of compound *i*. Calculations are given in Appendix B.

7.3.1.5 Effect of operating conditions on pervaporation of fat-containing feeds

Feed temperature

In the absence of fat, individual compound fluxes increased markedly with increasing temperature, as was presented in Chapter 5. However, when fat was present in the feed, the increase of flux with temperature was much smaller (Figure 7-11), and the fluxes of 2-heptanone, ethyl butanoate and ethyl hexanoate actually decreased between 30°C and 40°C.

Milk fat consists of a mixture of triglycerides and other lipids; at temperatures between −35°C and +35°C, some of the fat is liquid and the remainder is solid (Walstra et al., 2006). At higher temperatures, a greater proportion of the fat is liquid, and liquid oils have been found to retain more flavours than solid fat (Matheis, 1998). Hydrophobic interactions occur to a greater extent at higher temperatures, causing more flavours to be retained in the fat (Nongonierma et al., 2006). Therefore, the expected increase in flux at higher temperatures was offset by the reduction in the driving force caused by increased retention of flavours at 40°C.

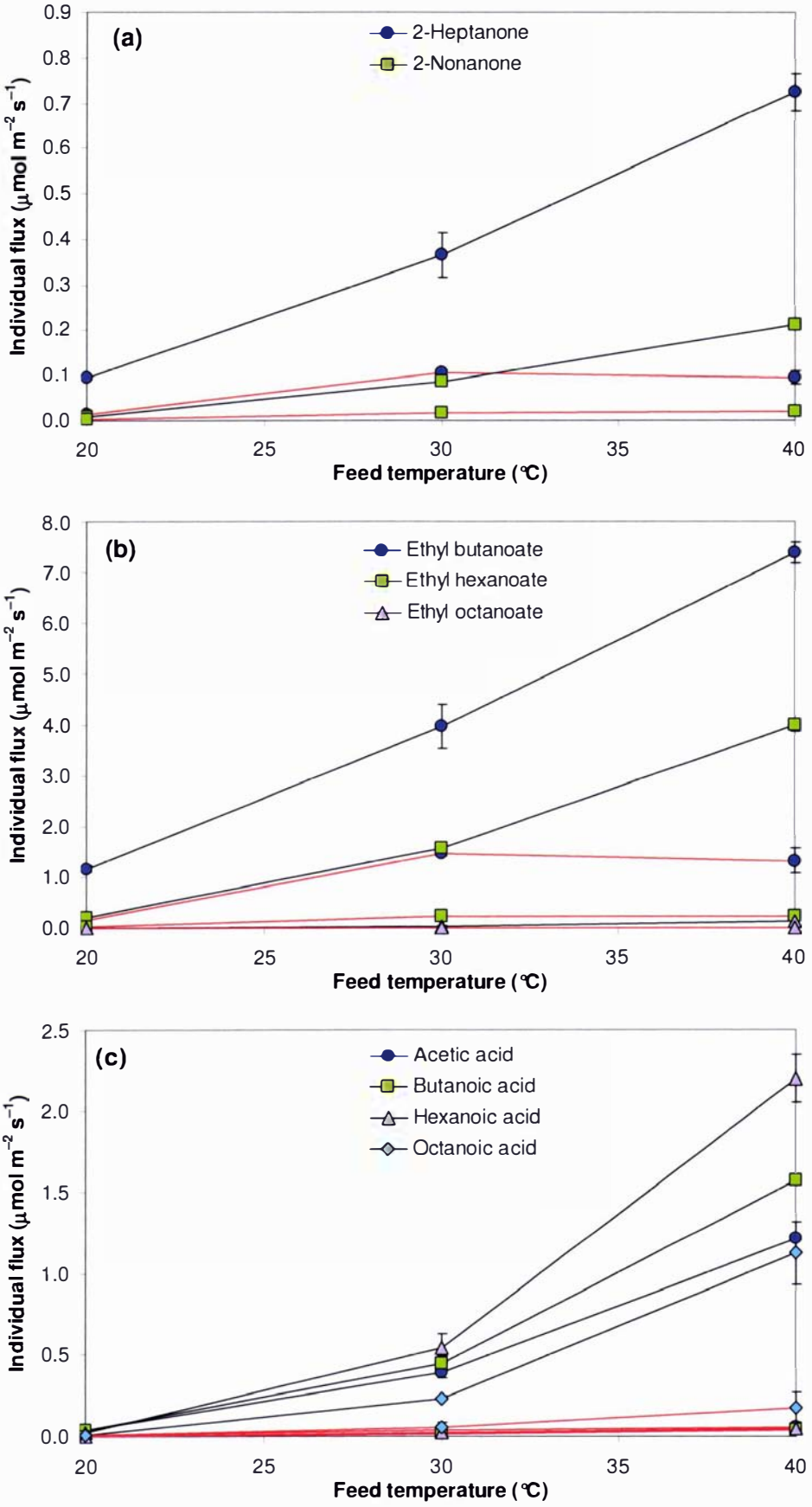


Figure 7-11: Effect of feed temperature on individual fluxes (mean ± standard error) of (a) ketones, (b) esters and (c) acids (2 kPa permeate pressure). Black lines: no fat; red lines: 20% fat.

Permeate pressure

Figure 7-12 shows the effect of permeate pressure on pervaporation fluxes with feeds containing either no fat or 20% fat. Increasing the permeate pressure from 0.9 kPa to 2 kPa lowered the driving force of each compound, causing a reduction in their fluxes. The percentage difference between the two permeate pressures was similar whether or not the feed contained fat. Therefore, the permeate pressure did not seem to influence the interactions of fat with flavour compounds.

As discussed in Section 7.3.1.3, the presence of fat reduced the driving force of flavour compounds. To compensate for this, the driving force could be increased by lowering the permeate pressure. Figure 7-12 shows that the fluxes of all compounds except butanoic acid, in the presence of 20% fat, could be increased to the fluxes achieved without fat, by decreasing the permeate pressure from 2 kPa to 0.9 kPa.

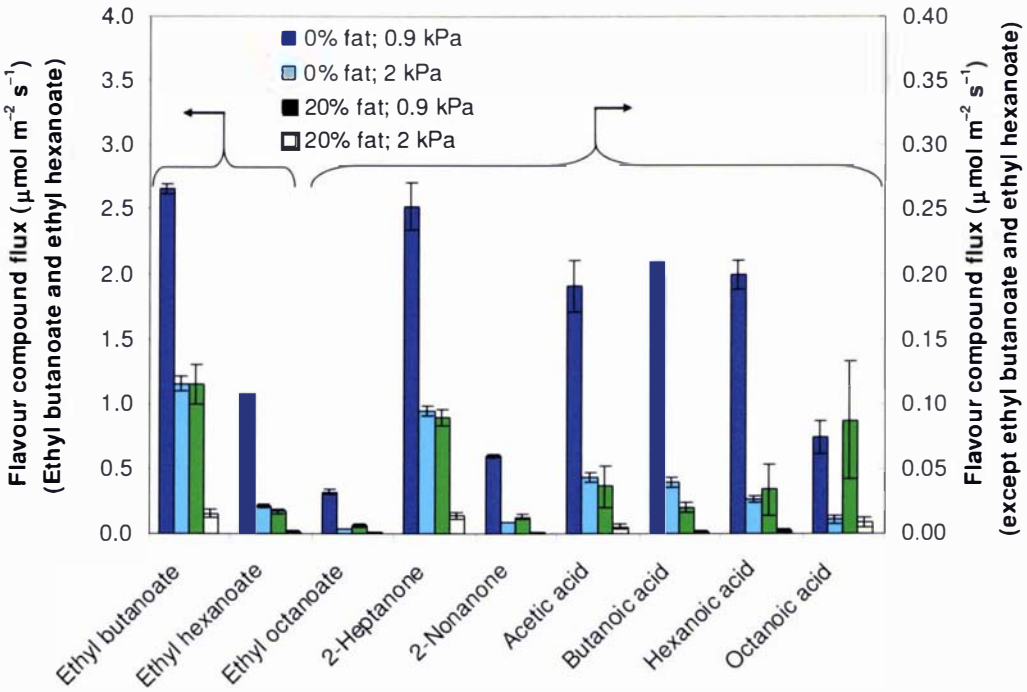


Figure 7-12: Comparison of individual fluxes at with and without fat at two permeate pressures (feed temperature 20°C). Data are means (± standard error) of three replicates.

7.3.2 Effect of milk protein on pervaporation

7.3.2.1 Effect of protein on flavour compound vapour pressures

Figure 7-13 shows how the partial vapour pressures of flavour compounds were affected by the addition of 4% milk protein isolate to the feed solution. The added protein decreased the vapour pressures, and hence the driving forces, of esters, ketones and octanoic acid by 56–94%, but increased the vapour pressures of acetic acid and butanoic acid, and did not affect the vapour pressure of hexanoic acid. Milk proteins are known to bind to both esters and ketones (Kühn et al., 2006), which is consistent with the data in Figure 7-13.

For esters and ketones, the effect of protein depended on the carbon chain length of the flavour compound. Protein caused the vapour pressure to decrease (compared with vapour pressures above a protein-free solution) by 72%, 82% and 94% respectively for ethyl butanoate, ethyl hexanoate and ethyl octanoate, and by 61% and 74% respectively for 2-heptanone and 2-nonanone. Other researchers have also found that milk proteins bound larger compounds to a greater extent than small compounds in the same homologous series (Landy et al., 1995, 1996;

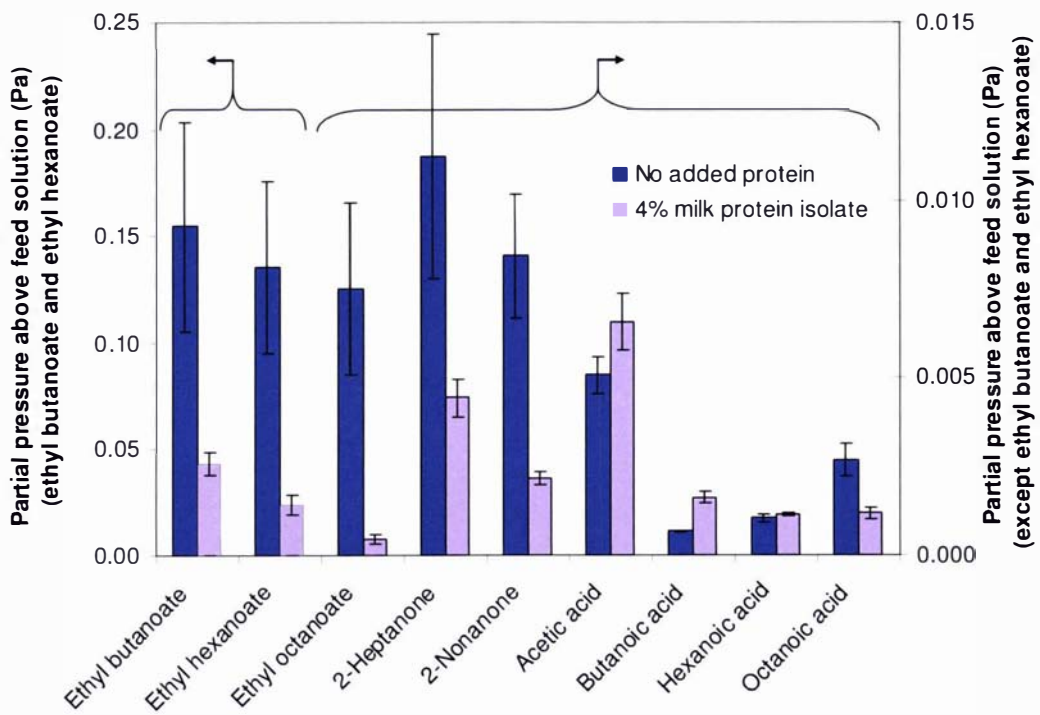


Figure 7-13: Effect of added protein on partial vapour pressures of flavour compounds (measured at 20°C; mean ± standard error of two replicates).

Kühn et al., 2006; Nongonierma et al., 2006). For example, Nongonierma et al. (2006) found that the volatilities of ethyl butanoate, ethyl hexanoate and ethyl octanoate at 10°C in a non-fat milk gel (4.5% protein) were reduced by 4%, 35% and 85% respectively compared with their volatilities in an aqueous solution. The reason was that the hydrophobic interactions between the protein and the flavour compound occured to a greater extent with longer-chain, more hydrophobic flavour compounds than with smaller, more hydrophilic compounds (Nongonierma et al., 2006).

Only the largest acid tested was bound by protein in sufficient amounts to reduce its vapour pressure (Figure 7-13), which is consistent with the above discussion. Milk proteins are known to bind long-chain fatty acids (Kühn et al., 2006), but short-chain acids are more hydrophilic, and hence should not take part in hydrophobic binding. The reason that milk protein isolate increased the vapour pressure of small, hydrophilic acids was probably a salting-out effect. Apart from protein, milk protein isolate also contains small amounts of minerals and sugars, both of which may affect the flavour compound volatilities.

7.3.2.2 Effect of protein on fluxes and enrichment factors

With 4% milk protein isolate in the feed, the total flux was 440 ± 30 mg m^{-2} s^{-1} with no fat, or 370 ± 10 mg m^{-2} s^{-1} with 20% fat. These total fluxes were statistically similar to the total fluxes for feeds without protein, which means that the protein did not cause enough fouling to significantly affect the total flux, nor did it alter the feed water activity enough to reduce the driving force for water.

Figures 7-14 and 7-15 show how the fluxes and enrichment factors of each flavour compound were affected by adding 4% milk protein isolate to the feed, in the presence or absence of 20% fat. In the absence of fat (the blue bars on Figures 7-14 and 7-15), the protein reduced the fluxes of acids by 51–96%, the smallest ester by 41% and the smallest ketone by 31%. Enrichment factors were reduced by similar amounts.

If the effect of protein was purely due to a reduced driving force as a result of flavour binding, flavour compound fluxes with and without protein would follow a similar pattern to the vapour pressures in Figure 7-13. This is clearly not the

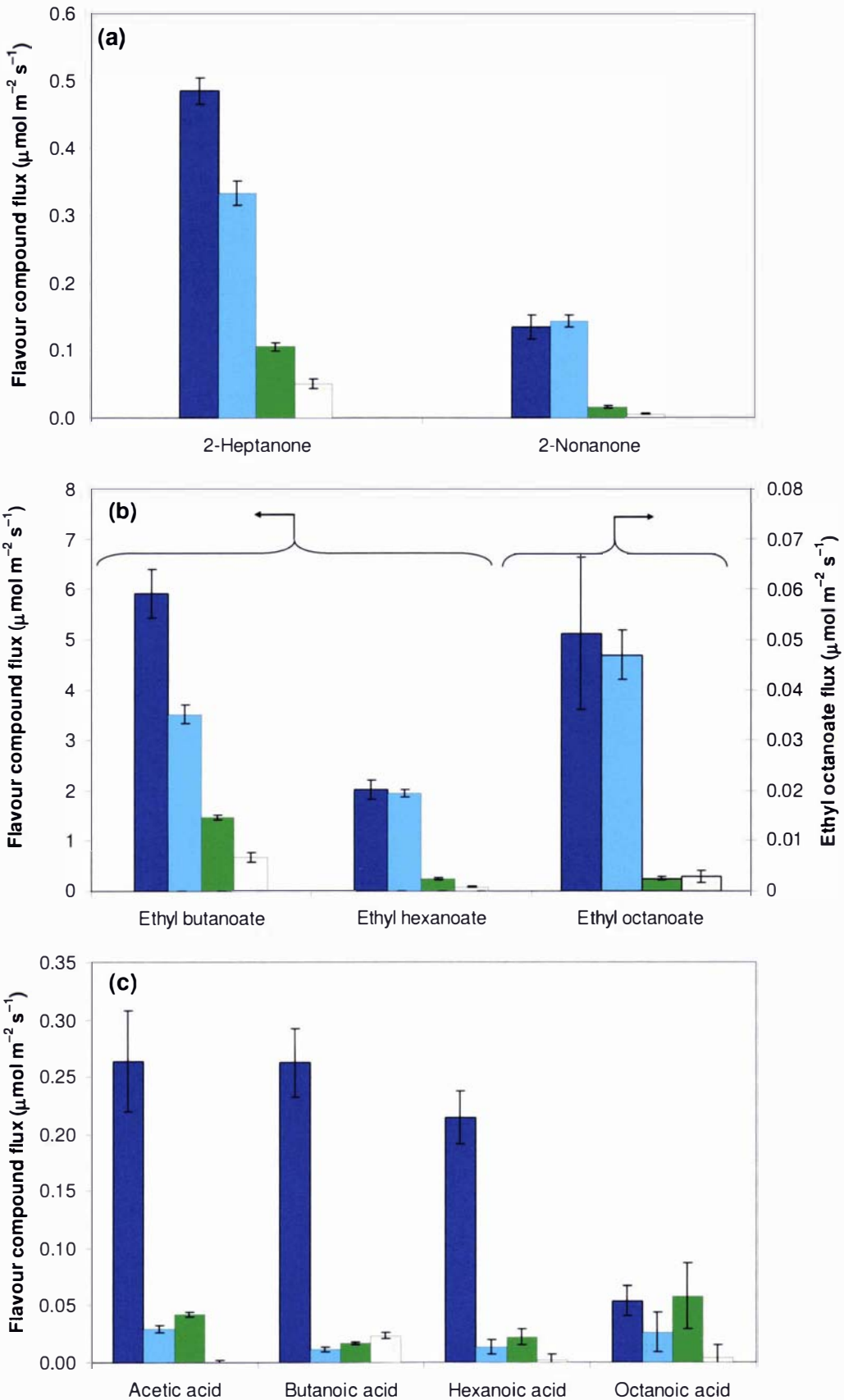


Figure 7-14: Effect of 4% milk protein isolate on fluxes of (a) ketones, (b) esters and (c) acids, in the presence or absence of 20% fat. Data are means (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: ■ 0% fat, 0% milk protein isolate; ■ 0% fat, 4% milk protein isolate; ■ 20% fat, 0% milk protein isolate; 20% fat, 4% milk protein isolate.

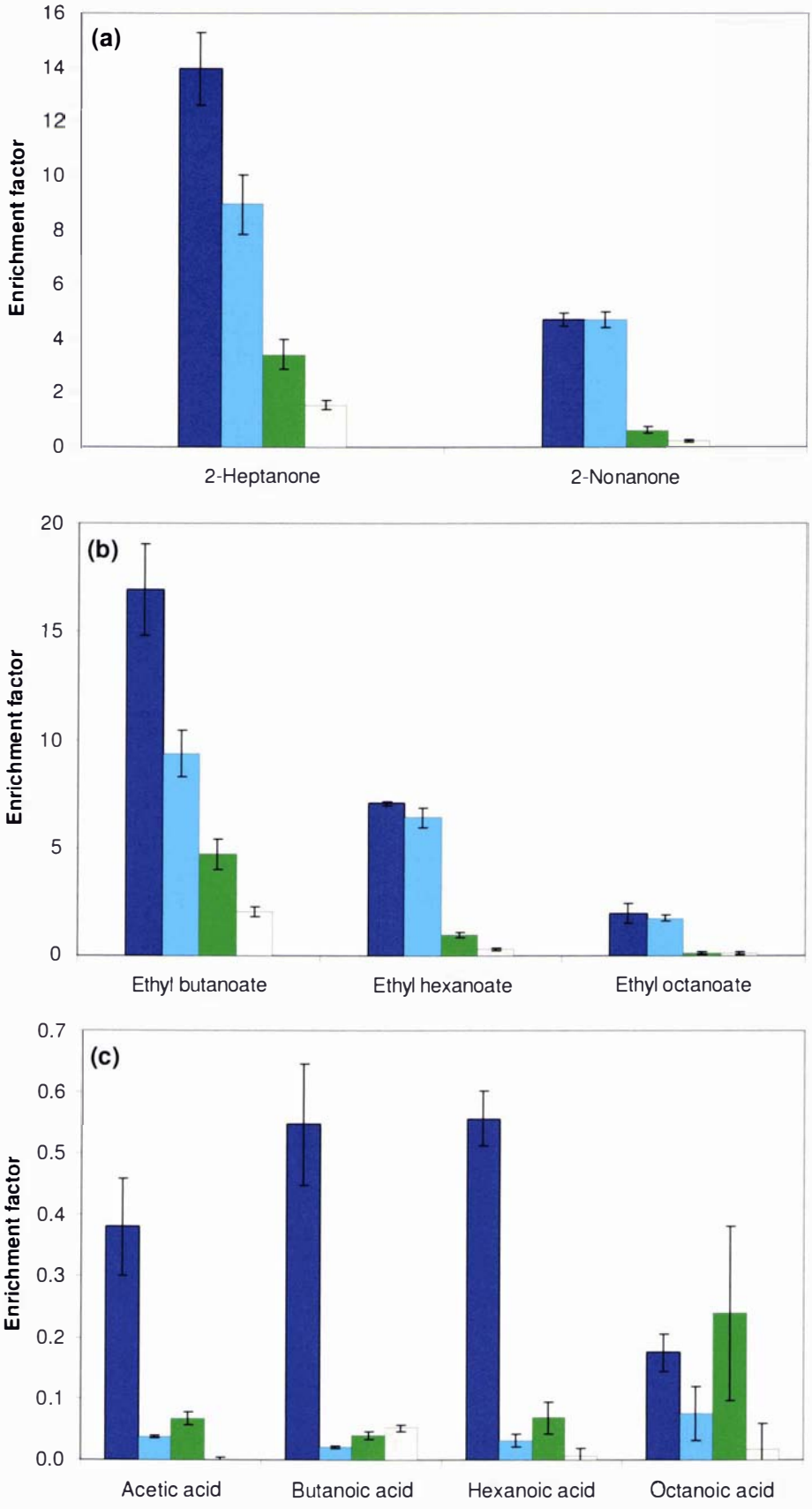


Figure 7-15: Effect of 4% milk protein isolate on enrichment factors of (a) ketones, (b) esters and (c) acids, in the presence or absence of 20% fat. Data are means (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: ■ 0% fat, 0% milk protein isolate; ■ 0% fat, 4% milk protein isolate; ■ 20% fat, 0% milk protein isolate; 20% fat, 4% milk protein isolate.

case. For esters and ketones, protein had a greater effect on the vapour pressures of larger compounds, but affected the flux and enrichment of only the smaller compounds. Protein reduced the vapour pressure of only the largest acid, but reduced the fluxes and enrichment factors of all acids, especially those with low molecular weights.

The result for acids can be attributed to pH differences; the feed pH was 6.3 with 4% milk protein isolate, compared with 3.5 for the standard aqueous feed solution. As explained in Chapter 5, the acids were mostly in the dissociated form at the higher pH, so their fluxes were lower.

The different behaviour between large and small esters and ketones is best explained by the mass transfer mechanism. Mass transfer in pervaporation involves permeant molecules first being transported to and sorbing into the membrane, followed by diffusion through the membrane. As the protein was only present on the feed side of the membrane, it would affect the sorption step only (flavour molecules that are bound to the protein cannot enter the membrane). In Chapter 5, it was discussed how smaller, more hydrophilic compounds have lower sorption coefficients but higher diffusion coefficients than larger compounds. Therefore, smaller compounds are more likely to be sorption-limited, and larger compounds are more likely to be diffusion-limited. If diffusion through the membrane is the rate-limiting step, then the flux should not be affected by how much the protein slows down transport and sorption on the feed side, provided that the rate of molecules sorbing in the membrane does not become slower than the rate of diffusion. Hence, even though the protein bound larger compounds to a greater extent, this binding affected the fluxes of only the smallest esters and ketones, for which sorption was the rate-limiting factor for mass transfer.

Aroujalian et al. (2003) found that 10 g L^{-1} soy protein did not significantly affect the flux or selectivity during pervaporation of an ethanol/water mixture. Soy proteins are known to bind alcohols (Chung & Villota, 1989), but it is unlikely that this level of protein bound enough of the 2% ethanol to see a significant effect. Assuming a molecular weight of at least 150 000 g mol^{-1} for soy protein (Fukushima, 2004), Aroujalian et al.'s (2003) feed solution contained 7×10^{-5} mol L^{-1} protein and 0.43 mol L^{-1} ethanol. Soy protein has been found to contain 18 to 40 binding sites for *n*-butanol and *n*-hexanol per protein molecule

(Chung & Villota, 1989); assuming it has a similar number of binding sites for ethanol, the protein in Aroujalian et al.'s (2003) feed solution would have bound less than 1% of the ethanol present. In contrast, Figure 7-13 shows that 4% milk protein isolate bound the flavour compounds in the present study by up to 94%, as measured by the reduction in their vapour pressures.

van Willige et al. (2000a, 2000b) investigated the effect of milk proteins, skim milk and whole milk on the sorption of flavour compounds into linear low-density polyethylene. Sorption was decreased if the flavour compound bound to milk proteins, which is consistent with the findings in the current study. van Willige et al. (2000a, 2000b) found that the effect depended on both the flavour compound and the type of milk protein.

7.3.2.3 Combined effect of protein and fat

A comparison of the light and dark green bars on Figures 7-14 and 7-15 shows the effect of protein on fluxes and enrichment factors, in the presence of 20% fat. With 20% fat in the feed solution, Figures 7-14a & b and 7-15a & b show that adding 4% milk protein isolate caused ester and ketone fluxes and enrichment factors to decrease by around 50% from their values with a feed solution containing 20% fat but no protein, except for ethyl octanoate, for which the added protein made no difference. Likewise, protein (in the presence of fat) reduced the fluxes and enrichment factors of acids by more than 89%, except for butanoic acid, for which the flux increased slightly (Figures 7-14c and 7-15c). Protein therefore had a greater effect on the fluxes of most flavour compounds when fat was also present in the feed solution.

As noted earlier, protein reduced the fluxes and enrichment factors of only those esters and ketones for which sorption was the rate-limiting factor for mass transfer (2-heptanone and ethyl butanoate). When fat was added to the feed solution, it reduced the sorption of flavour compounds by increasing their affinity for the feed solution compared with the membrane. Therefore, it is plausible that, in a fat-containing feed solution, sorption could become the rate-limiting factor for 2-nonanone and ethyl hexanoate in addition to the smaller compounds. Hence, the protein decreased the fluxes and enrichment factors of the four smallest esters and ketones if fat was present, compared to only the two smallest if no fat was present.

Protein can also reduce the rate at which flavour compounds transfer from the fat phase to the water phase (Guichard & Langourieux, 2000).

The feed mixture with 20% fat had a similar pH to the feed mixture with 4% milk protein isolate (pH 6.1 and 6.3 respectively). The proportion of each acid in the undissociated form differed by only 1.5–2.1% between these two pH values. Therefore, in the presence of fat, the influence of protein on pervaporation of acids was no longer dominated by pH effects, as it was in the absence of fat (Section 7.3.2.2). Instead, interactions between the acids and the protein must have caused the large decreases in the fluxes and enrichment factors of three of the four acids, when protein was added to a feed solution that contained 20% fat (third and fourth bars for each compound in Figures 7-14c and 7-15c).

At first, this explanation appears to contradict the results in Figure 7-13, which showed that octanoic acid was the only acid bound by 4% milk protein isolate in a feed solution with no fat. However, Mills & Solms (1984) have shown that milk fat can increase the binding of some flavour compounds to milk protein. Although Figure 7-13 shows that acetic acid and hexanoic acid did not noticeably bind to protein in the absence of fat, it is possible that binding to protein did occur in the presence of fat, thus causing their fluxes and enrichment factors to be lower in a feed solution with fat plus protein than with fat only (Figures 7-14c and 7-15c).

The feed solution containing both protein and fat caused a greater reduction in flavour compound fluxes and enrichment factors than the feed solutions containing only fat or only protein, for all compounds except butanoic acid and ethyl octanoate. Therefore, both protein and fat interacted with the flavour compounds, and their effects were additive. Hansen & Booker (1996) also found that both flavour binding by protein and partitioning into the fat phase occurred, when they studied how vanillin partitioned between the fat, casein and whey fractions of ice cream (10% fat). The fat phase contained 37% of the vanillin and the casein contained 11%, with the remainder in the whey.

Nevertheless, comparing the middle two bars for each compound in Figures 7-14a & b and 7-15a & b, the effect of fat on fluxes and enrichment factors of esters and ketones was generally much greater than the effect of protein. This is consistent with studies on the release of flavour compounds from milks or milk gels (Roberts

& Pollien, 2000; Nongonierma et al., 2006) and on sorption of flavours into linear low-density polyethylene (van Willige et al., 2000a). Results for acids (Figures 7-14c and 7-15c) appear to contradict these findings, as feed solutions containing either fat or protein tended to give similar results. However, as stated earlier, both 20% fat and 4% milk protein isolate caused the pH to increase by a similar amount, which reduced the permeation of acids compared with an aqueous feed solution.

7.3.3 Effect of lactose on pervaporation

7.3.3.1 Effect of lactose on flavour compound vapour pressures

Figure 7-16 shows how added lactose affected the vapour pressure of each flavour compound. The pattern is very similar to the effect of protein in Figure 7-13, with the vapour pressures of esters and ketones being diminished by 61–94%, and the vapour pressures of acids being either increased or decreased, depending on their molecular weight.

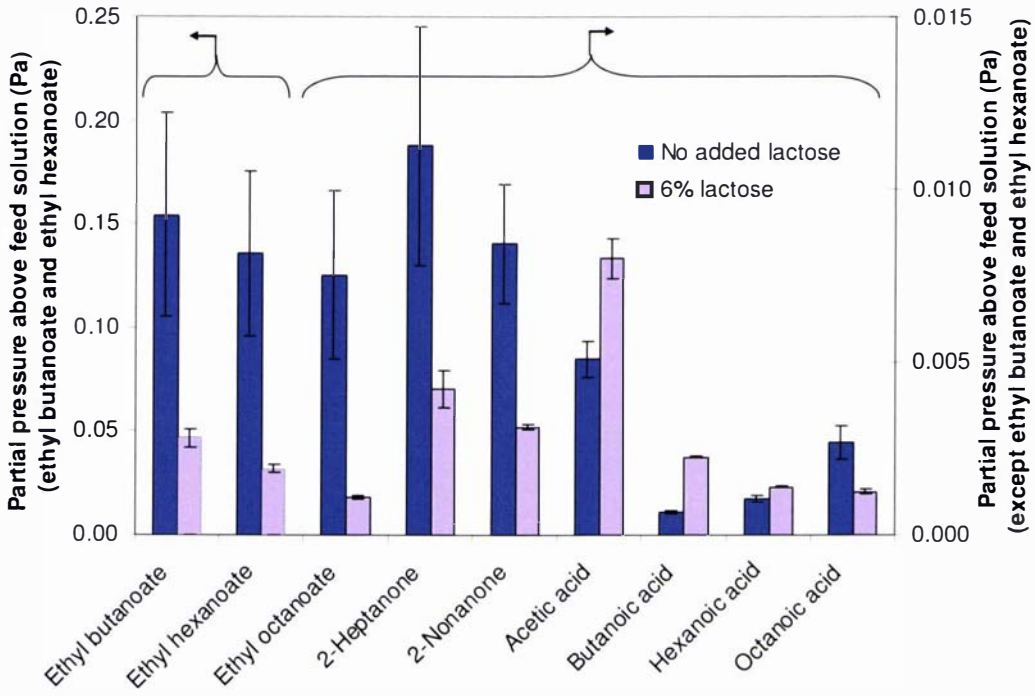


Figure 7-16: Effect of added lactose (extra pure grade) on partial vapour pressures of flavour compounds (measured at 20°C; mean ± standard error of two replicates).

Lactose is known to bind certain flavour compounds (Kellam, 1998), but the mechanism of flavour binding by sugars is unclear (Solms & Guggenbuehl, 1990; Matheis, 1998; Reineccius, 2006). Lactose, like all sugars, contains hydroxyl groups which can hydrogen-bond with other compounds. However, this does not explain why it had a greater negative influence on long-chain compounds, which are more hydrophobic than smaller compounds. The most plausible explanation parallels a hypothesis for the same effect with sucrose: when the sugar is dissolved, the solution becomes more hydrophobic, and hence more favourable to hydrophobic flavour compounds and less favourable to short-chain, hydrophilic compounds (Reineccius, 2006).

7.3.3.2 Effect of lactose on fluxes and enrichment factors

Like protein, lactose (6% or 12% edible grade, or 6% extra pure grade) did not have a significant effect on the total flux, but did influence the individual fluxes and enrichment factors of most flavour compounds (Figures 7-17 and 7-18). With edible grade lactose (the blue bars on Figures 7-17 and 7-18), fluxes of the smaller flavour compounds (2-heptanone, ethyl butanoate, acetic acid, butanoic acid and hexanoic acid) decreased with increasing lactose concentration. Edible grade lactose had a lesser effect on the fluxes of larger compounds (2-nonanone, ethyl hexanoate, ethyl octanoate and octanoic acid); their fluxes increased or did not change (within standard error limits) between 0% and 6% edible grade lactose, then decreased or stayed the same between 6% and 12%.

These results parallel the findings with protein in the feed solution (Section 7.3.2), and can therefore be explained in the same way. Although Figure 7-16 shows that lactose bound larger flavour compounds to a greater extent, it only reduced the fluxes and enrichment factors of smaller compounds, for which sorption into the membrane was the rate-limiting factor for mass transfer. However, it is less clear why lactose increased the vapour pressures of the three smallest acids, yet it decreased their fluxes and enrichment factors. Unlike protein, lactose affected the feed pH only slightly (the feed solution with 6% edible grade lactose had a pH of 3.9, compared with 3.5 for the standard aqueous feed), but this small difference may still have caused the fluxes of acids to decrease.

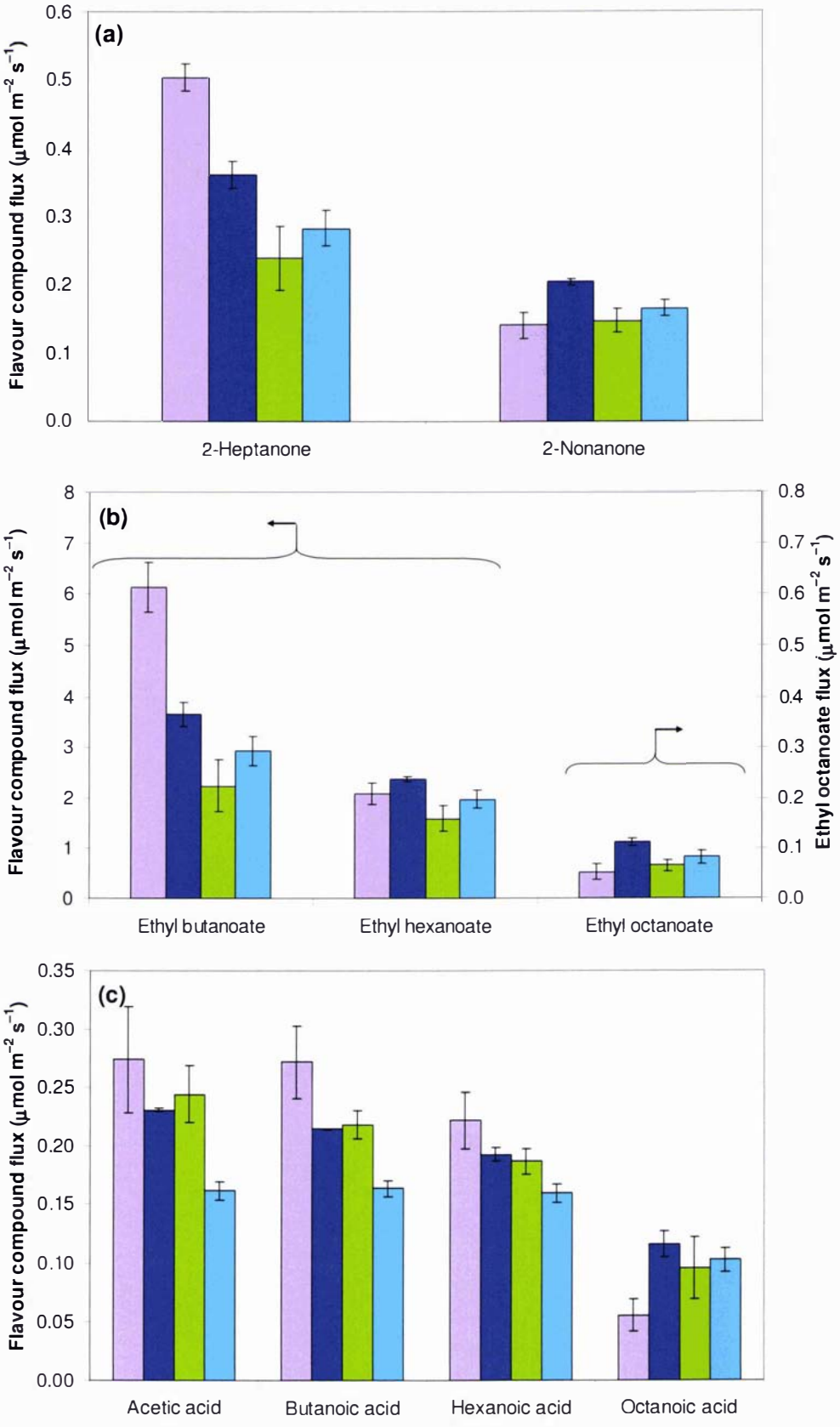


Figure 7-17: Effect of edible grade and extra pure lactose on the fluxes of (a) ketones, (b) esters and (c) acids. Data points show the mean (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: no lactose; 6% lactose (edible grade); 6% lactose (extra pure grade); 12% lactose (edible grade).

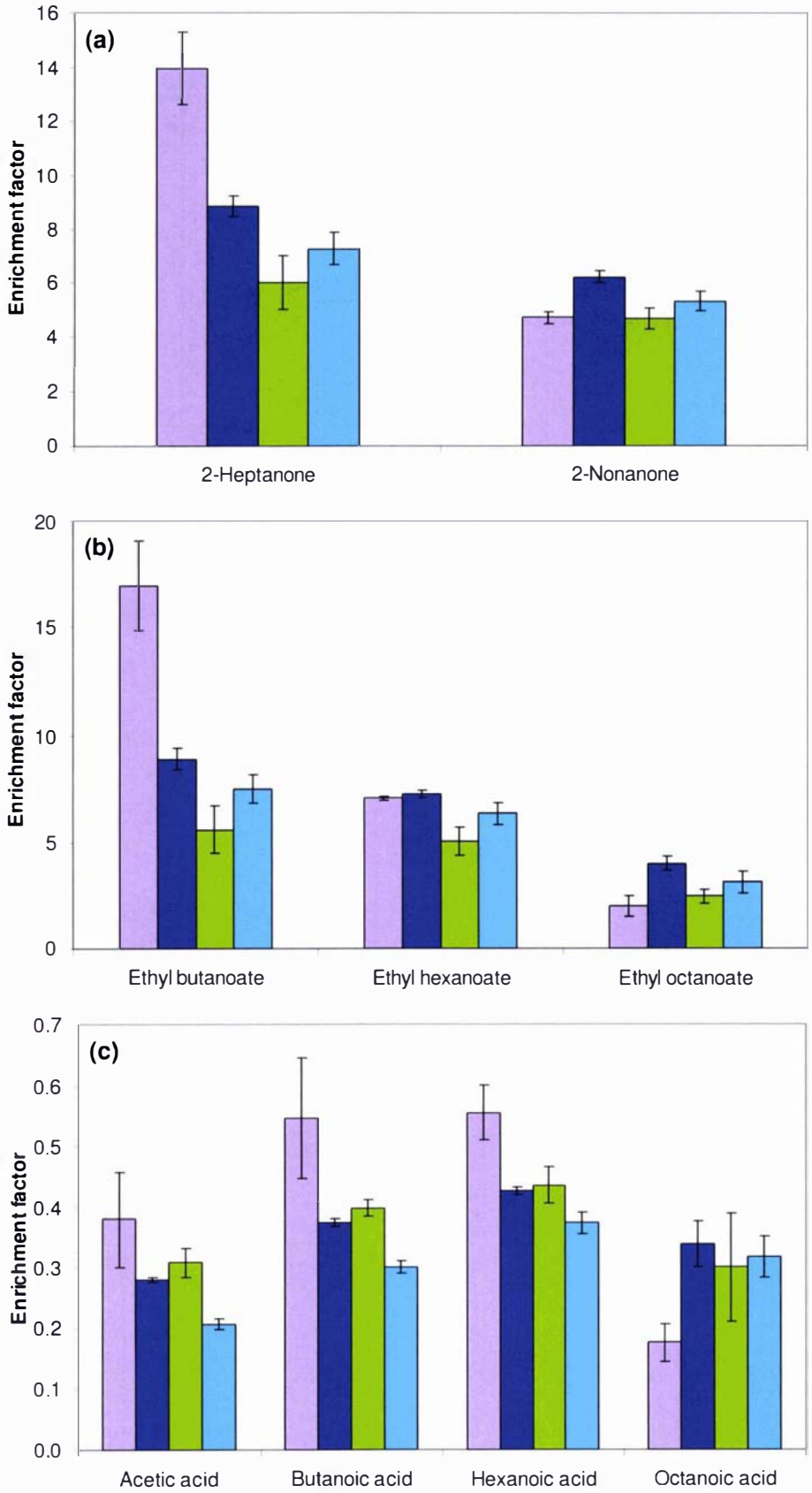


Figure 7-18: Effect of edible grade and extra pure grade lactose on enrichment factors of (a) ketones, (b) esters and (c) acids. Data points show the mean (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: no lactose; 6% lactose (edible grade); 6% lactose (extra pure grade); 12% lactose (edible grade).

Other researchers have found that sugars and sugar alcohols may have positive, negative or neutral effects on pervaporation. Aroujalian et al. (2006) studied the effects of glucose and xylose on pervaporation of a 2% ethanol/water solution. Both sugars caused the total flux to decrease, with the effect being greater at high permeate pressures. Glucose also lowered the ethanol selectivity, but xylose increased the selectivity under certain conditions. Ikegami et al. (1999) also found that glucose, lactose, *myo*-inositol and xylitol all caused the total flux of an ethanol/water solution to decrease. Glucose, lactose and *myo*-inositol caused a slight decrease in the ethanol flux and a larger decrease in the water flux, resulting in an increased separation factor. However, xylitol caused the ethanol flux to decrease more than the water flux, so that the selectivity was lowered. In contrast, lactose did not significantly affect the flux or selectivity of methylthiobutanoate (Baudot et al., 1996) or diacetyl (Rajagopalan et al., 1994). These results suggest that the effect of sugars on pervaporation may depend on the operating conditions and type of permeant as well as the type of sugar.

Aroujalian et al. (2006) explained the flux decrease in terms of sugars increasing the vapour pressure of ethanol and decreasing the vapour pressure of water. Although a higher selectivity would be normally be expected if this were the case, they explained that the addition of sugars raised the ethanol concentration in the PDMS membrane, causing the selectivity to be lowered in some instances due to membrane plasticisation. Unlike Aroujalian et al. (2006), Ikegami et al. (1999) assumed that sugars reduced water sorption into the silicalite membrane, rather than affecting the vapour pressure in the feed.

Two grades of lactose were compared at the 6% level (Figures 7-17 and 7-18). Ester and ketone fluxes and enrichment factors were 33–70% higher with edible grade than with extra pure grade, but both grades gave similar results for acids. Some of the non-lactose components in whey, such as riboflavin, lactose phosphates and lactic acid, are known to bind to lactose crystals (Kellam, 1998). These impurities in the edible grade lactose may have associated with the lactose in the feed solution, causing its ester- and ketone-binding capacity to decrease relative to extra pure grade lactose. A possible reason for the acid fluxes not depending on the grade of lactose is that lactose bound the impurities in preference to esters and ketones, but bound the acids in preference to impurities.

This hypothesis is plausible because acids have greater hydrogen-bonding capacities than esters or ketones, and hence may bind to lactose via a different mechanism.

7.3.3.3 Combined effect of lactose and fat

Figures 7-19 and 7-20 compare the effect of 6% edible grade lactose, in the presence or absence of 20% fat, on the fluxes and enrichment factors of flavour compounds. When 20% fat was present in the feed solution, lactose decreased the fluxes and enrichment factors of all flavour compounds (although not beyond standard error limits in the case of ethyl octanoate, butanoic acid and octanoic acid). This result differs from feed solutions containing lactose but no fat (blue bars on Figures 7-19 and 7-20), in which the lactose reduced the fluxes and enrichment factors of only the smaller compounds. The same explanation applies as for the combined effect of protein and fat (Section 7.3.2.3); lactose affected the pervaporation performance for only those compounds for which sorption was the rate-limiting factor for mass transfer, and the presence of fat in the feed solution caused more compounds to be sorption-limited rather than diffusion-limited.

7.4 General discussion

In most cases, interactions between flavours and food components have been studied from a sensory perspective; if flavour compounds bind to non-volatile substances, consumers' perception of these flavours will be reduced (McGorrin & Leland, 1996; Leland, 1997). The same principle applies to pervaporation: flavours that are bound to non-volatile feed components will not be able to pass into the membrane.

In pervaporation, the flux is the product of the driving force and the mass transfer coefficient. Non-volatile feed components affect both these factors, by altering the affinity of the permeant for the feed solution. This affects the feed-side activities and partial pressures of permeant compounds (which determine the driving force) and the partitioning of permeants between the feed solution and the membrane (the sorption coefficient, which affects the mass transfer). Through these

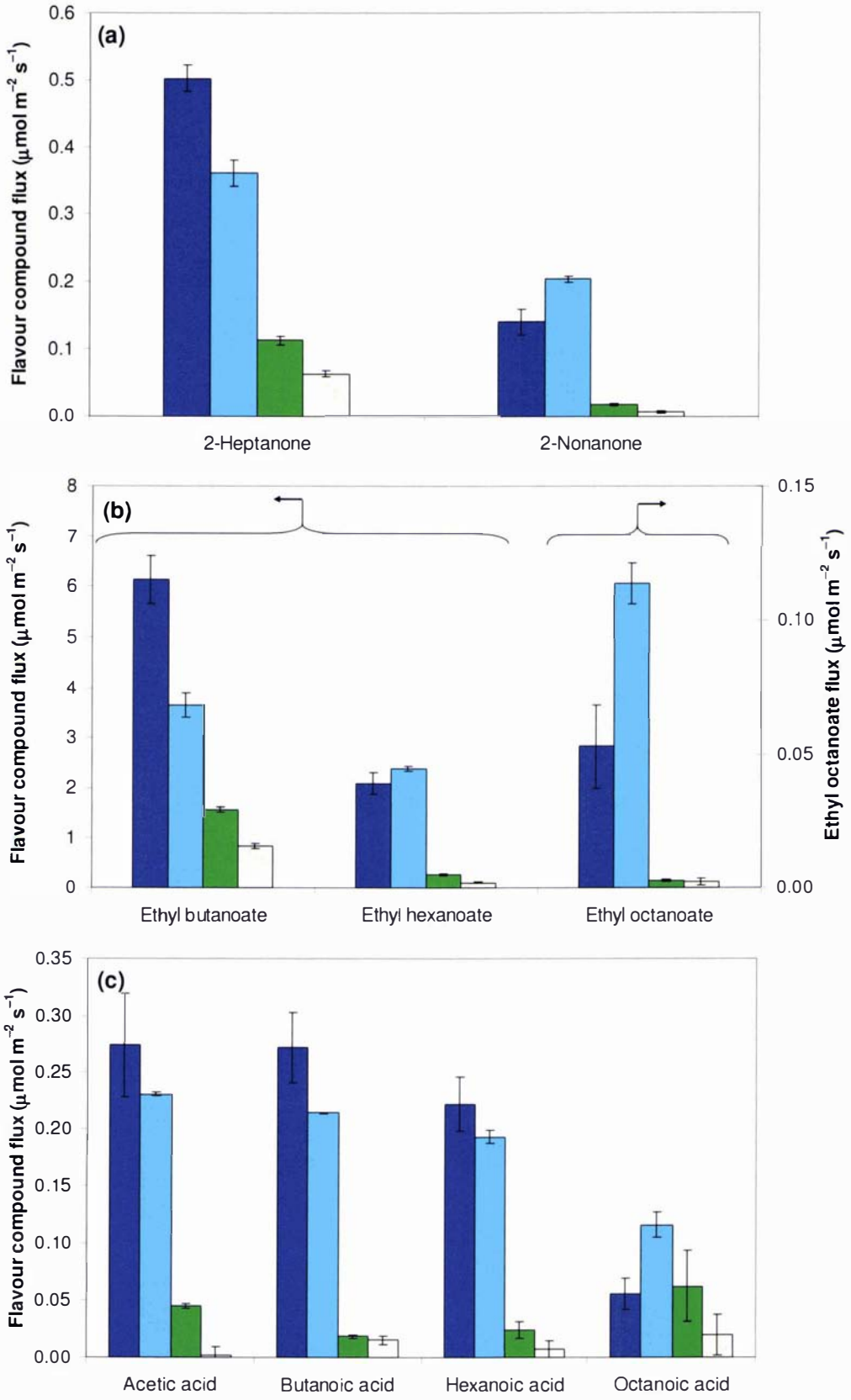


Figure 7-19: Effect of 6% edible grade lactose on fluxes of (a) ketones, (b) esters and (c) acids, in the presence or absence of 20% fat. Data are the mean (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: 0% fat, 0% lactose; 0% fat, 6% lactose; 20% fat, 0% lactose; 20% fat, 6% lactose.

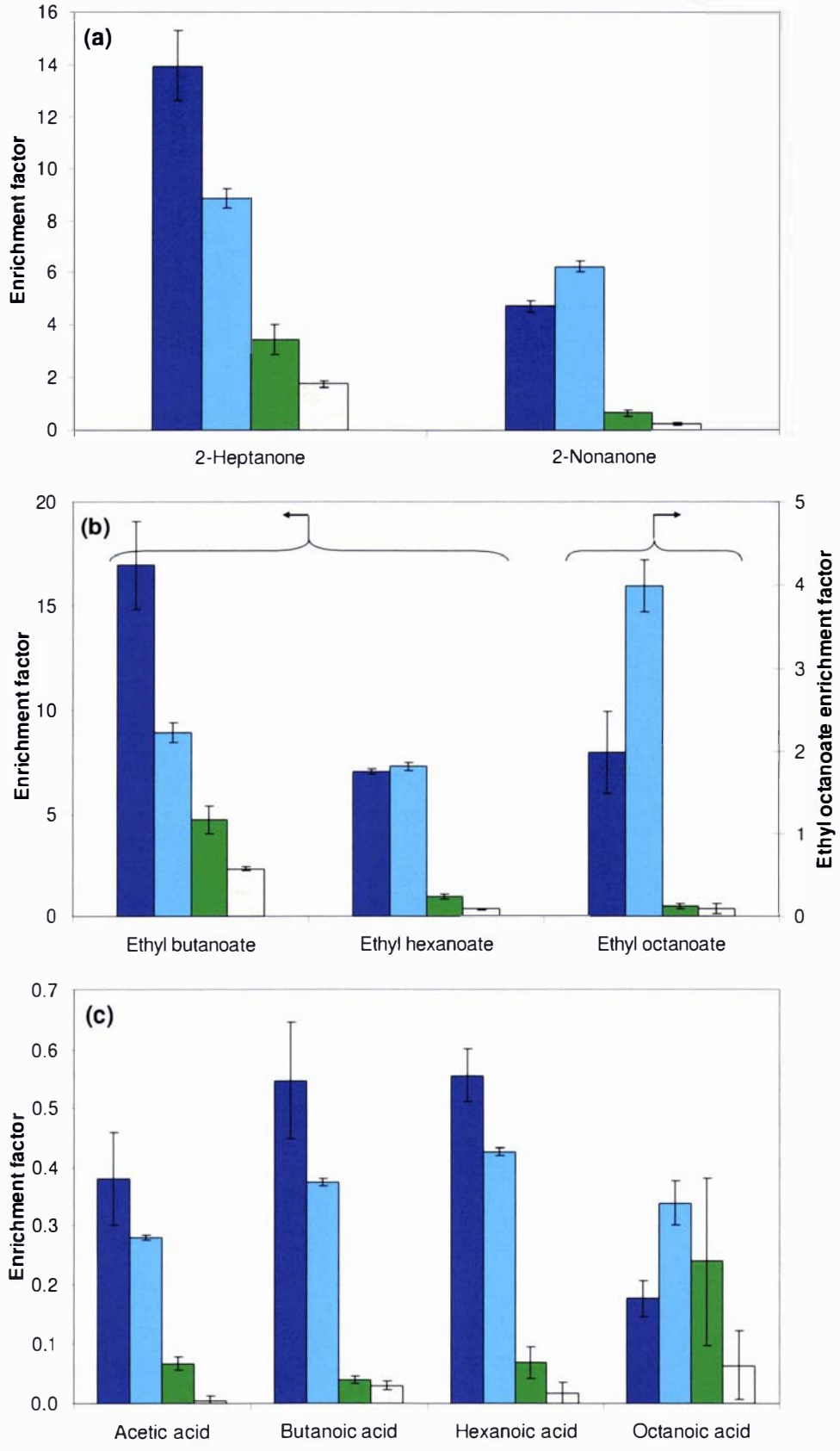


Figure 7-20: Effect of 6% edible grade lactose on enrichment of (a) ketones, (b) esters and (c) acids, in the presence or absence of 20% fat. Data are the mean (± standard error) of three replicates. Operating conditions: 30°C feed temperature, 2 kPa permeate pressure. Legend: 0% fat, 0% lactose; 0% fat, 6% lactose; 20% fat, 0% lactose; 20% fat, 6% lactose.

mechanisms, the non-volatile dairy components tested in this study tended to reduce the effectiveness of pervaporation as a flavour concentration process.

Out of the three non-volatile dairy components tested (fat, protein and lactose), only fat had any effect on the total flux. Therefore, protein and lactose were not able to reduce the feed side mass transfer under the conditions tested in this study, meaning that their effects on pervaporation performance were purely due to their interactions with the flavour compounds. Fat, however, reduced the mass transfer on the feed side as well as reducing the amounts of flavour compounds available for pervaporation.

The addition of protein (in the form of milk protein isolate) or fat (in the form of cream) caused the feed pH to increase, thereby decreasing the fluxes and enrichment factors of acids. This result could potentially be reversed, or at least reduced, by manipulating the feed pH. However, too low a pH could lead to denaturation of the proteins as the isoelectric point is approached. Denaturation can either increase or decrease the flavour binding capacity of proteins (Matheis, 1998; Kühn et al., 2006).

Normally, the sorption coefficient in pervaporation relates to the partitioning of flavour compounds between the membrane and the aqueous feed solution. When fat is added to the feed, the flavour compounds need to distribute between three phases: the fat, the water and the membrane. The partitioning experiment in this study confirmed that hydrophobic compounds partitioned into the fat to a greater degree than hydrophilic compounds. This resulted in the fluxes and enrichment factors of all flavour compounds tested, especially the more hydrophobic compounds, being reduced in the presence of fat. For this reason, pervaporation is only suitable for recovering flavours from feeds containing high levels of fat if the permeate pressure can be lowered enough to compensate for the reduced driving force.

Because interactions between the flavour compounds and the fat occurred to a greater degree at higher temperatures, the increase in fluxes with increasing temperature was minimal when the feed solution contained fat, compared with a fat-free feed solution. Therefore, it would probably be more economical to operate pervaporation at a lower temperature if the feed stream contains fat. The binding

of flavours to proteins can be influenced by temperature (Matheis, 1998; Kühn et al., 2006), so it is possible that added protein would also modify how pervaporation fluxes are affected by temperature.

Each flavour compound was affected in a similar way by both protein and lactose, suggesting that both interacted with flavours via a binding mechanism. However, binding of a flavour compound to protein or lactose (as evidenced by the reduction in that compound's vapour pressure when protein or lactose were present in the feed) did not automatically mean that the flux or enrichment of that compound would be lowered. Added protein or lactose affected the sorption of permeants into the membrane, but not their diffusion through the membrane. Hence, these dairy components only reduced the fluxes and enrichment factors of flavour compounds for which sorption was the rate-limiting factor for mass transfer.

When the feed solution contained fat as well as either protein or lactose, the influence of fat dominated the effects of the other non-volatile feed components. The presence of fat affected sorption of the flavour compounds, meaning that more compounds were sorption-limited rather than diffusion-limited, compared with an aqueous feed solution. Hence, added fat increased the number of flavour compounds for which protein or lactose reduced the pervaporation performance.

Protein and lactose both had a greater impact on the pervaporation performance of smaller, sorption-limited compounds than larger compounds, but fat had a greater effect on larger, more hydrophobic compounds. This finding presents an opportunity to manipulate the permeate composition by varying the non-volatile components of the feed, although this technique would need to be verified in an industrial setting.

The results in this chapter show that the composition of the feed mixture has a significant effect on flavour compound pervaporation. For this reason, in some cases it could be beneficial to combine pervaporation with other flavour recovery techniques, to first separate the flavours from the dairy matrix, followed by concentration of the flavours using pervaporation.

With the exception of extra pure grade lactose, the non-volatile feed components tested in this study were not pure chemical compounds, but were chosen to reflect typical dairy systems. This means that other possible interactions with minor non-volatile components may also have influenced the results.

Chapter 8

Pervaporation of real dairy products

8.1 Introduction

To investigate pervaporation of flavours in a real-world situation, experiments were carried out using real dairy products as the feed. Two Fonterra flavour products, starter distillate and ester cream, were chosen.

Starter distillate is an aqueous product manufactured by fermenting a dairy medium with lactic acid bacteria, then distilling the flavours produced. Diacetyl (2,3-butanedione) is the main flavour compound in starter distillate. Diacetyl is a low molecular weight diketone (86.09 g mol^{-1}) with a buttery/caramel flavour, and is a key flavour compound in dairy products such as butter and cultured milks (Schieberle et al., 1993; Rajagopalan et al., 1994; Urbach, 1995; Keen, 1998). An ingredient with increased buttery flavour could be created by combining starter distillate with natural diacetyl from another source. A potential alternative would be to concentrate the diacetyl using pervaporation, instead of adding extra diacetyl.

The model feed solutions used in previous chapters did not contain diacetyl, but they contained two higher molecular weight ketones (2-heptanone and 2-nonanone).

Ester cream is a high-fat liquid product produced from the enzymatic reaction of ethanol with triglycerides found in cream; this reaction produces many of the same flavour compounds as in the model solutions used in previous chapters (acids and ethyl esters) as well as longer-chain acids and esters which were not included in the model solution. Short-chain ethyl esters are best known for their fruity flavours, and are commonly found in dairy products such as cheese, where their flavour contribution is positive at low concentrations but detrimental at high concentrations (Liu et al., 2004). However, the free fatty acids and long chain esters in ester cream are undesirable because they give soapy, waxy and metallic

flavours (Keen, 1998; Crow, 2005, personal communication). Pervaporation could potentially be used to fractionate this flavour mixture into desirable and undesirable flavours.

The pervaporation system used for the current study could concentrate esters by a factor of up to approximately 30 (Chapter 5), with short-chain esters being concentrated to a greater extent than longer-chain esters under the conditions tested. PDMS and POMS membranes did not concentrate acids to a great degree, and in many cases the permeate was reduced in concentration of acids compared to the feed. Therefore, pervaporation using these membranes appeared to be an ideal method of concentrating the desirable flavours in ester cream, without concentrating the less desirable flavours from the acids and long chain esters. However, ester cream contains 20% fat; ester enrichment factors with a model solution containing this level of fat were reduced by more than 70%, compared with a non-fat feed (Chapter 7).

Few researchers have studied pervaporation as a means of concentrating flavours in a dairy-based feed. Sibeijn et al. (2004) found that most aldehydes and ketones they studied had lower pervaporation enrichment factors with a yoghurt fermentation than with an aqueous feed solution; they explained that this effect was partly caused by concentration differences between the two feed mixtures, but did not report how results were influenced by non-volatile substances in the yoghurt. Rajagopalan et al. (1994) briefly reported trials with whey permeate and lactose as feed solutions, which were spiked with flavour compounds before pervaporation, rather than using pervaporation to concentrate flavours already present in the dairy product. Apart from flavour concentration, several researchers have successfully used pervaporation to recover ethanol or butanol from microbial fermentations of lactose-based dairy substrates (Shabtai & Mandel, 1993; Lewandowska & Kujawski, 2007; Staniszewski et al., 2007).

The objective of this work was to conduct trials with both ester cream and starter distillate, in order to investigate the feasibility of pervaporation for concentrating and fractionating flavours in dairy products. Where possible, results were compared to those with model feed solutions.

8.2 Experimental

8.2.1 Pervaporation experiments

Pervaporation runs were carried out in duplicate at both 20°C and 40°C, following the procedure in Chapter 3, with either ester cream or starter distillate as the feed. The PDMS Type 1 membrane was used for all runs, with a permeate pressure of 2 kPa.

With these feed mixtures, enrichment factors were calculated slightly differently from enrichment factors in previous chapters. Ester cream enrichment factors were evaluated as the ratio of permeate concentration to retentate concentration (both averaged over the four hours of each run). The ester cream did not remain homogeneous during each run; the retentate represented the portion of the feed actually flowing past the membrane on the feed side, so it was more valid to use the retentate concentration than the concentration in the bulk feed. In starter distillate, the diacetyl enrichment factor was calculated in the same way as in previous chapters (permeate concentration divided by feed concentration), but the concentrations of other compounds were not measured, so their enrichment factors were estimated from the ratio of their peak areas in chromatograms of permeate and retentate samples.

8.2.2 Extent of fat separation in ester cream

During pervaporation runs with ester cream, a creamy layer rose to the top of the feed tank instead of being pumped past the membrane. To estimate the extent of this separation, three 0.8 mL retentate samples from each run (taken after zero, two and four hours) were centrifuged at 13 000 rpm for 3 min in a Heraeus Biofuge Pico centrifuge (Bio-Strategy Ltd, Auckland, New Zealand). The fat appeared as a liquid layer, and its volume was visually compared with that of the aqueous phase.

8.3 Results and discussion

8.3.1 Pervaporation of starter distillate

The main aim of starter distillate pervaporation was to concentrate diacetyl. Hence, this was the only compound quantified in retentate and permeate samples. The average time zero retentate concentration of diacetyl in starter distillate (equivalent to the feed concentration) was 2200 ± 400 mg kg^{-1}, which agreed well with the concentration of 2.2 mg mL^{-1} reported by Fonterra (Crow, 2007, personal communication). Starter distillate also contained many other flavour compounds, but GC chromatograms of starter distillate extracts (using the method in Section 3.5.4; data not shown) indicated that the diacetyl peak was more than twice as large as any other peak, and contributed an average of 42% of the total peak area (excluding the solvent peak).

8.3.1.1 Total flux

Table 8-1 lists the total flux achieved for starter distillate at 20°C and 40°C. Diacetyl contributed approximately 1% of the total flux (1.13 ± 0.02 mg m^{-2} s^{-1} at 20°C and 15 ± 7 mg m^{-2} s^{-1} at 40°C). As diacetyl was the most abundant compound in starter distillate, most of the remaining ~99% can be considered to be water. Table 8-1 also gives the total (water) flux of the standard multicomponent feed measured in Chapter 5 at the same operating conditions.

Starter distillate and the aqueous model solution had similar total fluxes (within standard error limits) at 40°C, but at 20°C starter distillate had about double the total flux of the model solution. One reason for the difference between the two feed solutions at 20°C could be membrane plasticisation (swelling), caused by a high concentration of hydrophilic diacetyl molecules. When hydrophilic

Table 8-1: Comparison of total fluxes[a] between starter distillate and the standard multicomponent feed solution.

Feed temperature (°C)	Total flux[b] (mg m^{-2} s^{-1})	
	Starter distillate	Standard multicomponent feed
20	108 ± 6	55 ± 2
40	1030 ± 80	986 ± 11

[a]Operating conditions: PDMS Type 1 membrane, 2 kPa permeate pressure

[b]Mean ± standard error of two replicates

compounds plasticise a membrane, the membrane becomes more hydrophilic, and hence better able to permeate water (Aroujalian et al., 2006). Plasticisation is not usually an issue in flavour compound pervaporation, because it does not occur to a great extent in rubbery polymers (Dole et al., 2006) or at low feed concentrations typical of flavour systems (Peng et al., 2003; Pereira et al., 2006). However, the concentration of diacetyl in starter distillate was 2200 mg kg^{-1}, more than triple the total concentration of flavour compounds in the model solution used in previous chapters. At high concentrations like this, membrane plasticisation can occur. For example, Rajagopalan et al. (1994) found that high concentrations of diacetyl plasticised a PDMS-polycarbonate membrane, causing the total flux to be 55% greater than expected when the diacetyl concentration was increased from 2000 mg L^{-1} to 20,000 mg L^{-1}. In the current study, plasticisation was more noticeable at 20°C than at 40°C, probably because more hydrogen bonding occurs at lower temperatures (Liang & Ruckenstein, 1996). Diacetyl molecules sorbed in the membrane were thus better able to hydrogen-bond with water, thereby increasing the water flux, at the lower temperature.

8.3.1.2 Enrichment of diacetyl

Table 8-2 gives the diacetyl enrichment factors obtained with a feed of starter distillate, as well as the enrichment factors of the two ketones in the standard multicomponent feed solution at the same operating conditions (Chapter 5). Other researchers have also shown that diacetyl can be effectively concentrated using pervaporation. Rajagopalan et al. (1994) achieved diacetyl enrichment factors of 33–41 with a PDMS-polycarbonate copolymer membrane, a feed temperature of 24–43.5°C, and a permeate pressure of 0.7–2.5 kPa; and Baudot & Marin (1996) obtained enrichment factors of 12–21 using silicalite-filled PDMS membranes and PEBA membranes, a feed temperature of 30–50°C, and a permeate pressure of 0.19–2.5 kPa.

Table 8-2: Comparison of diacetyl enrichment factor[a] with model solution ketones.

Feed temperature (°C)	Enrichment factor[b]		
	Diacetyl (in starter distillate)	2-Heptanone (in model solution)	2-Nonanone (in model solution)
20	4.8 ± 0.1	19.7 ± 0.1	2.3 ± 0.1
40	6.3 ± 2.8	8.5 ± 0.4	3.1 ± 0.1

[a]Operating conditions: PDMS Type 1 membrane, 2 kPa permeate pressure

[b]Mean ± standard error of 2–3 replicates

The above researchers achieved diacetyl enrichment factors several times greater than those in this study (Table 8-2), but the high enrichment factors were offset by much lower fluxes. At comparable temperatures to those in the current work, Baudot & Marin (1996) and Rajagopalan et al. (1994) obtained total fluxes of less than 31 mg m^{-2} s^{-1}. The higher fluxes and lower enrichment factors in the present study are due to the different membranes used; thin, high-flux membranes generally have lower selectivity than membranes with thicker active layers (Baudot & Marin, 1997). Baudot & Marin (1996) and Rajagopalan et al. (1994) used membranes that were more than 50 times thicker than those in the current study, as well as having different polymer compositions.

The smaller of the two model solution ketones, 2-heptanone, had a greater enrichment factor than 2-nonanone (Table 8-2). Contrary to this trend, diacetyl's enrichment factor lay between those for 2-heptanone and 2-nonanone, although diacetyl is a smaller molecule than these two ketones; the molecular weights of diacetyl, 2-heptanone and 2-nonanone are 86.09 g mol^{-1}, 114.19 g mol^{-1} and 142.24 g mol^{-1} respectively. Baudot & Marin (1997) also found that the enrichment factor of diacetyl did not fit with larger ketones. They compared literature data for pervaporation enrichment with vapour-liquid equilibria for many compounds, including ketones. Pervaporation was more selective than using a vapour-liquid equilibrium for concentrating large ketones, such as 2-heptanone and 2-nonanone, but less selective than a vapour-liquid equilibrium for small ketones such as diacetyl (Baudot & Marin, 1997).

Diacetyl differs from 2-heptanone and 2-nonanone in two ways: it has a lower molecular weight, and it has two carbonyl groups instead of one. Also, diacetyl's feed concentration in starter distillate (2200 mg kg^{-1}) was far greater than the concentrations of ketones in the model solution (each 9.8 mg kg^{-1}). The enrichment factor of diacetyl depends on its flux relative to the total flux (approximately equal to the water flux), normalised for its concentration in the feed. Therefore, a lower enrichment factor than expected is a result of either a lower driving force and/or mass transfer coefficient for diacetyl, or a higher driving force and/or mass transfer coefficient for water.

When the permeate pressure is low (so that the permeate activity tends towards zero), the driving force of each compound depends mainly on its activity in the

feed, which is the product of the feed concentration and the activity coefficient. Diacetyl had a high driving force because of its high feed concentration in starter distillate, so its driving force cannot directly be compared with the driving forces of the ketones in the model feed solution. However, if all three ketones had the same feed concentration, any differences in their driving forces would be due to their different activity coefficients in the feed. The presence of a second functional group may have increased the affinity of diacetyl for water. This is reflected in its low infinite dilution activity coefficient of 13 in the temperature range used for these experiments (Baudot & Marin, 1996). With the same number of carbons as diacetyl but only one ketone functional group, 2-butanone has an infinite dilution activity coefficient of 27–37 (calculated using a correlation from Poling et al. (2001)). Diacetyl therefore has a lower activity coefficient than would be expected from its carbon chain length. The model solution ketones, 2-heptanone and 2-nonanone, have infinite dilution activity coefficients of 1560–1785 and 26 500–28 100 respectively (Poling et al., 2001). Therefore, after accounting for concentration differences, diacetyl had a lower feed activity and a lower driving force than the model solution ketones.

Mass transfer coefficients of the three ketones (flux divided by activity difference across membrane) are given in Table 8-3. Diacetyl fits with the trend expected from 2-heptanone and 2-nonanone; the mass transfer coefficients decreased with increasing molecular weight. The high affinity of diacetyl for water means that it would have a low degree of sorption in the hydrophobic membrane; Vankelecom et al. (1997) noted that the sorption of diacetyl in PDMS was only about 5% of that exhibited by 2-hexanone. However, diacetyl's low sorption was cancelled out by its high rate of diffusion, so that its mass transfer coefficient was greater than that of 2-heptanone or 2-nonanone.

Table 8-3: Comparison of diacetyl mass transfer coefficient[a] with model solution ketones.

Feed temperature (°C)	Mass transfer coefficient[b] (μmol m^{-2} s^{-1})		
	Diacetyl (in starter distillate)	2-Heptanone (in model solution)	2-Nonanone (in model solution)
20	2 440 ± 40	47.2 ± 1.9	0.273 ± 0.010
40	30 000 ± 16 000	266 ± 15	6.08 ± 0.09

[a]Operating conditions: PDMS Type 1 membrane, 2 kPa permeate pressure

[b]Mean ± standard error of 2–3 replicates

The enrichment factor depends on the relative fluxes of water (approximated by the total flux) and diacetyl. At 20°C, the water flux from starter distillate was higher than from the model solution. This would cause diacetyl to have a lower enrichment factor than expected. However, at 40°C the water flux was similar with both feed solutions, yet diacetyl still had a lower enrichment factor than expected (Table 8-2). Diacetyl's lower enrichment factor was therefore caused by its lower relative driving force as discussed above (accounting for concentration differences), not by the difference in mass transfer coefficients.

In pervaporation studies, there is generally a trade-off between flux and selectivity; conditions under which high enrichment factors are possible usually do not allow high fluxes (Huang & Rhim, 1991; Sampranpiboon et al., 2000a). Diacetyl appears to be an exception to this rule when comparing different temperatures with the same membrane. In the current study as well as other studies (Rajagopalan et al., 1994; Baudot & Marin, 1996), the enrichment factor of diacetyl through a PDMS-based membrane increased by 24–31% when the temperature was increased by 20°C.

As the temperature is increased, both the driving force and the membrane permeability should increase for each permeant compound (Peng et al., 2003). The enrichment factor normally decreases with increasing temperature, but may also increase, depending on the relative effect of temperature on the driving force and permeability of water compared with the flavour compound of interest. If the permeation rate of a flavour compound increases more than that of water as the temperature is raised (due to either an increased permeability or an increased driving force), the enrichment factor of the flavour compound will increase with temperature.

The feed temperature influences the driving force by altering the activity of each compound (related to the partial pressure) on the feed side of the membrane. In the present study, the feed partial pressure of diacetyl at 40°C was 2.8 times as great compared with 20°C, whereas the partial pressure of water rose by a factor of 3.2 over this temperature range (calculations in Appendix F). The driving force of water therefore increased more than the driving force of diacetyl as the temperature increased, meaning that driving force differences cannot explain the higher enrichment factor of diacetyl at 40°C.

As the driving force differences could not explain the enrichment factor increase, it can be concluded that the temperature had a greater effect on the permeability of the membrane to diacetyl than to water. In other words, as the temperature was increased, the membrane became much more permeable to diacetyl but only slightly more permeable to water. Baudot & Marin (1996) also found that diacetyl permeability, with a silicalite-filled PDMS membrane, increased more than the water permeability as the temperature increased.

These results can also be interpreted by comparison with those found earlier in this study. In the standard multicomponent feed, the enrichment factors of esters and ketones either decreased or had no trend with temperature, whereas those of acids tended to increase with temperature (Chapter 5). Diacetyl is a ketone, but it is more hydrophilic than the ketones in the model solution; its infinite dilution activity coefficient (13) was closer to acids in the model solution (Appendix B). An increased temperature therefore seemed to have a positive effect on enrichment of hydrophilic compounds. The most likely explanation is that hydrogen bonding between the hydrophilic compounds and water decreases at a higher temperature (Liang & Ruckenstein, 1996). This would result in hydrophilic compounds having a lower affinity for the feed solution, and therefore passing into the membrane more easily, at raised temperatures.

In summary, pervaporation could be used to concentrate diacetyl in starter distillate. Diacetyl had a lower enrichment factor than the ketones in the model solution, due to its lower activity coefficient. The mass transfer of diacetyl increased more than that of water as the temperature increased, leading to a higher enrichment factor at 40°C than at 20°C.

8.3.1.3 Enrichment of other compounds in starter distillate

Figure 8-1 shows the volatile profile in the headspace of starter distillate retentate and permeate, as determined by GCMS. Compared to the retentate chromatogram, the volatile profile of the permeate appeared similar, but more concentrated overall. However, some of the higher esters (peaks 31, 35 and 38) were less concentrated in the permeate, and were not detected in all permeate samples.

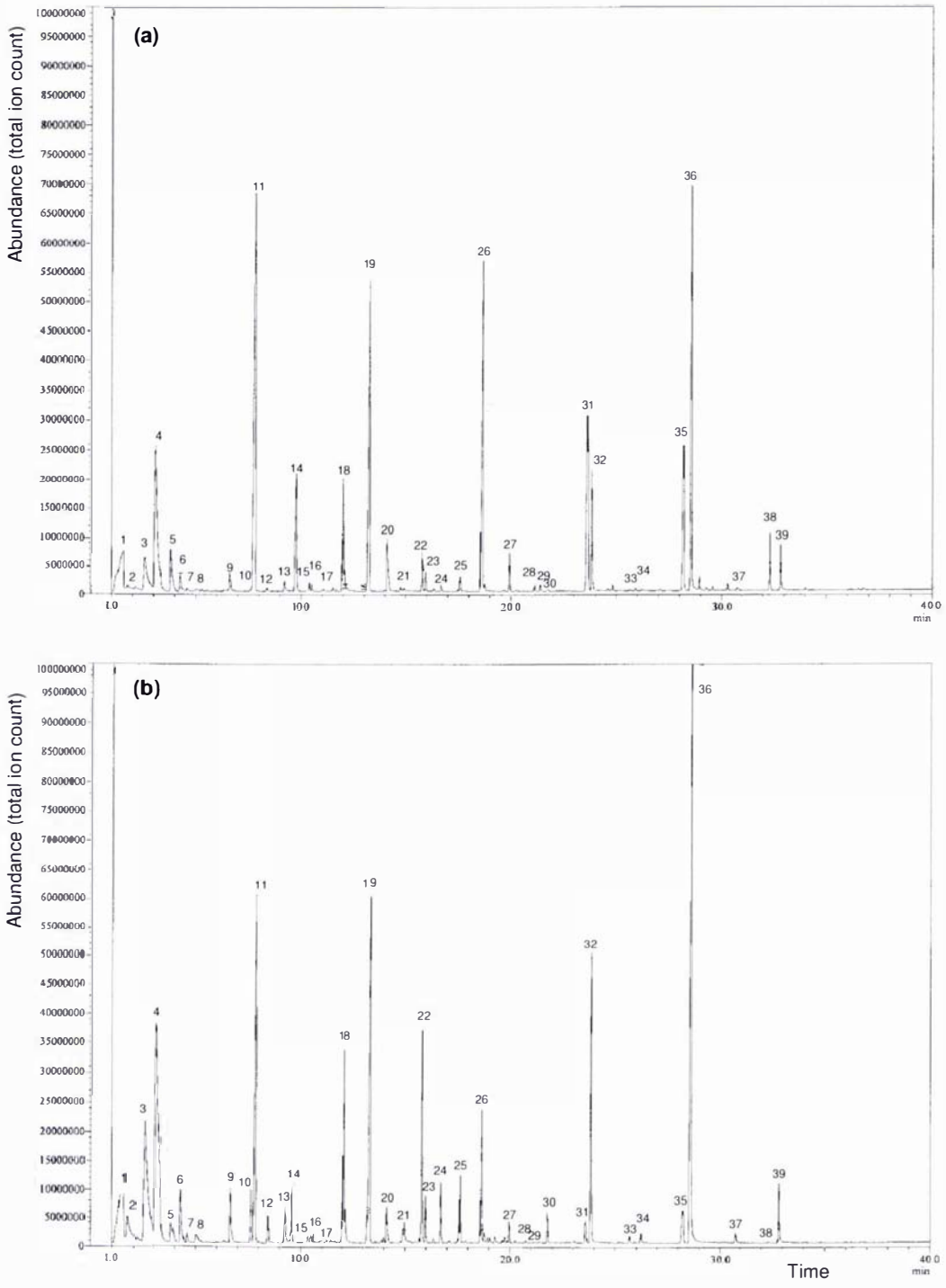


Figure 8-1: Representative GCMS chromatograms of the headspace of (a) starter distillate retentate (collected after two hours of pervaporation) and (b) starter distillate permeate (collected after three hours of pervaporation). Pervaporation conditions: PDMS Type 1 membrane, 40°C feed temperature, 2 kPa permeate pressure. Tentative identities of numbered peaks: 1. oxygen, 2. acetone, 3. ethanol, 4. diacetyl, 5. ethyl butanoate, 6. 2,3-pentanedione, 7. hexanal, 8. 2-methyl-1-propanol, 9. 4-methyl- or 5-methyl-hexanone, 10. 3-methyl-1-butanol, 11. ethyl hexanoate, 12. styrene, 13. octanal, 14. 3-hydroxy-2-butanone, 15. 2-heptenal, 16. ethyl heptanoate, 17. 1-hexanol, 18. 2-octanone, 19. ethyl octanoate, 20. acetic acid, 21. 2-octanol, 22. benzaldehyde, 23. 2-decenal, 24. 1-octanol, 25. 2-undecanone, 26. ethyl decanoate, 27. unsaturated ethyl ester, 28. ethyl ester, 29. unsaturated aldehyde, 30. 1-decanol, 31. ethyl ester, 32. hexanoic acid, 33. indole, 34. heptanoic acid, 35. ethyl ester, 36. octanoic acid, 37. nonanoic acid, 38. ethyl ester, 39. decanoic acid.

Diacetyl does not appear to have the largest peak in the GCMS chromatograms in Figure 8-1, contrary to GC analyses (using a different temperature programme; not shown) which showed it to be the most abundant compound in starter distillate. The difference is that Figure 8-1 is an analysis of the headspace, rather than the starter distillate itself. The headspace, rather than a solvent extract, was analysed in order to avoid obscuring peaks behind the solvent peak. As diacetyl has a high affinity for water, its headspace concentration would be low compared with the concentration in the liquid starter distillate.

Estimated enrichment factors of selected compounds in starter distillate are shown in Figure 8-2. These 26 compounds were chosen because they are known dairy flavour compounds, could be identified with a reasonable degree of confidence in nearly all retentate and permeate samples, and did not overlap significantly with other peaks. As the absolute concentration of each compound was unknown, these enrichment factors were estimated from the peak areas of retentate and permeate samples. Therefore, they may not be equal to the true enrichment factors, and

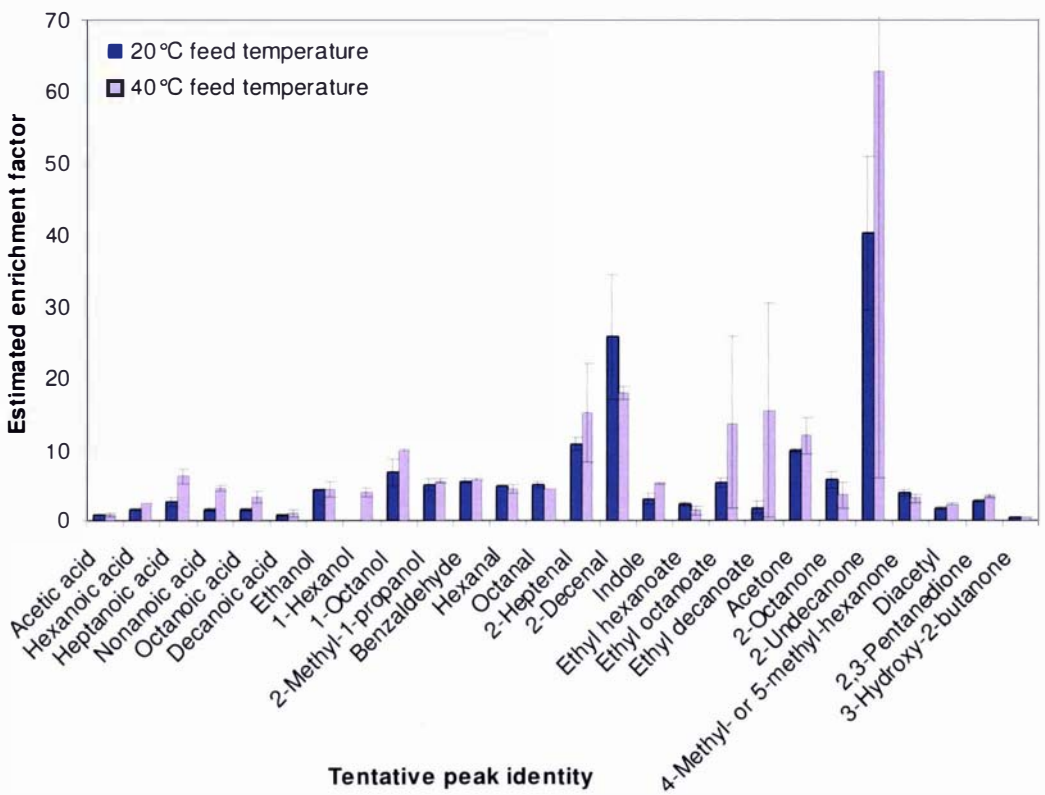


Figure 8-2: Estimated enrichment factors (ratio of peak areas in permeate and retentate samples) for selected compounds identified in starter distillate. Data are the mean ± standard error of two replicates.

cannot be quantitatively compared with model solution results, but can still be used to give an indication of possible trends. The estimated enrichment factor of diacetyl in Figure 8-2 (1.7–2.1) is lower than its true enrichment factor (4.8–6.3) in Table 8-2.

Figure 8-2 shows that many of the flavour compounds in starter distillate were enriched by a factor of 3–6 using pervaporation. Certain compounds had higher estimated enrichment factors than this, particularly unsaturated aldehydes and some esters and ketones. The most highly enriched compound was 2-undecanone, with an enrichment factor of 40–63. In contrast, some compounds were not enriched at all. Acetic acid, decanoic acid and 3-hydroxy-2-butanone had estimated enrichment factors of 0.4–0.9, indicating that these compounds were not preferentially transported through the membrane.

Figure 8-2 includes many compounds with different molecular sizes and functional groups, enabling some general trends to be observed. Overall, compounds from the various homologous series can be placed in order of decreasing estimated enrichment factors: unsubstituted ketones > unsaturated aldehydes > esters > saturated aldehydes > alcohols > substituted or branched ketones > acids. This order is similar to that found in several previous studies: esters > aldehydes > alcohols (Bengtsson et al., 1992), esters > aldehydes/ketones > alcohols > diketone (Vankelecom et al., 1997), or esters/ketones > acids (Overington et al., 2008).

Trends within the acid, ester and unsubstituted ketone functional groups can also be compared with model solution results using the same pervaporation system (Chapter 5). Acids in starter distillate behaved in the same way as in a model solution; their enrichment factors increased with increasing molecular weight up to a point, then decreased. However, esters and ketones did not follow the same trend. In the model solution, enrichment factors of esters (ethyl butanoate, ethyl hexanoate and ethyl octanoate) and ketones (2-heptanone and 2-nonanone) decreased with increasing molecular size. In contrast, estimated enrichment factors of the three esters shown in Figure 8-2 increased with increasing molecular weight at 40°C, or increased then decreased at 20°C. For ketones, acetone and 2-octanone followed the trend found in the model solution experiments, but 2-undecanone had an extremely high enrichment factor in starter distillate.

As there were so many different compounds in starter distillate, it is possible that there were complex interactions between permeants, which changed the order of selectivity. It was observed in Chapter 6 that larger esters and ketones were relatively more affected by coupling interactions than smaller compounds within these functional groups; hence, the order of selectivity within a functional group could change depending on the other compounds in the feed. Alternatively, the differences could have arisen in the analysis rather than during pervaporation. The large number of compounds in starter distillate may have meant that some extra compounds were obscured under the observed chromatogram peaks, altering their perceived peak areas.

As some compounds passed through the membrane more easily than others, the volatile composition of the permeate differed from the feed (Figure 8-1). Compared with the feed, the permeate contained relatively more 2-undecanone, which has a floral or herbaceous flavour (Molimard & Spinnler, 1996), and less of certain acids, as well as being more concentrated overall. Therefore, pervaporation may have altered the flavour profile of starter distillate; however, any differences were not obvious. No sensory tests were carried out, but starter distillate was informally observed to have a diacetyl-like odour, which had a similar character but stronger intensity in the permeate than in the feed.

8.3.2 Pervaporation of ester cream

8.3.2.1 Total flux

Ester cream contained 20% fat, which corresponded to one of the fat-containing model solutions tested in Chapter 7. As cream was the only dairy ingredient in ester cream, fat was the main non-volatile component. The total flux with ester cream was 1.5–2.2 times greater than the total flux with a model solution containing the same amount of fat (Table 8-4). The difference is partly because ester cream contains 5% ethanol, which permeates relatively easily through pervaporation membranes, and hence contributed to the total flux. Earlier in this study (Chapter 6), it was shown than this concentration of ethanol increased the total flux of an aqueous model solution by 20%.

However, even allowing for a 20% flux increase, the total flux with ester cream was still higher than expected from model solution results. One explanation for

Table 8-4: Comparison of ester cream total flux with model solution (20% fat) at the same operating conditions (PDMS Type 1 membrane; 2 kPa permeate pressure).

Temperature (°C)	Total flux (mg m^{-2} s^{-1}) (mean ± standard error)	
	Ester cream (2 replicates)	Model solution (20% fat) (3 replicates)
20	118 ± 1	52 ± 6
40	950 ± 140	620 ± 160

the remaining difference is that the ester cream feed did not remain homogeneous. During each run, the ester cream partially separated into aqueous and fat phases, with the majority of the fat rising to the top of the feed tank (creaming) and therefore not being pumped past the membrane. Creaming was not apparent with model solutions, except for those with very low levels of fat. Therefore, in the model solution in Table 8-4, the 20% fat was distributed evenly throughout the feed, including the portion passing over the membrane. In contrast, the portion of ester cream passing the membrane would have contained less than 20% fat.

This hypothesis was confirmed by centrifuging ester cream retentate samples to separate the fat from the aqueous phase. Retentate samples were taken from the bottom of the feed tank, and hence represented the portion passing over the membrane. Samples from runs at 40°C contained less than 10% fat, and most of the samples from runs at 20°C did not contain any visible fat. Therefore, the total flux of ester cream was greater than that of the model solution with 20% fat, because the mass transfer would not have been affected by fouling or concentration polarisation to the same extent as the fat-containing model solution. Creaming was more prevalent at 20°C than at 40°C, which is the most likely explanation for the difference in total flux between ester cream and the fat-containing model solution being relatively greater at 20°C.

8.3.2.2 Enrichment factors of flavour compounds

The aim of this study was to investigate the pervaporation behaviour of ester cream, compared with a fat-containing model solution. The discussion in this section therefore focuses mainly on the flavour compounds that were quantified in both ester cream and the fat-containing model solution, namely ethyl butanoate, ethyl hexanoate, ethyl octanoate, acetic acid and butanoic acid. However, ester

cream contains some additional flavour compounds, which were not present in the model solution. Some of these additional compounds were also quantified, if standards could be easily obtained.

Flavour compound concentrations in ester cream retentate varied widely between runs. This was partly due to batch variations in the feed (as ester cream is a fermented product, some variation is inevitable), and partly because the ester cream composition varied within the feed tank due to creaming. Most of the fat in ester cream remained at the top of the feed tank, whereas the feed was pumped to the membrane from the base of the feed tank. Retentate samples, as well as the portion of feed being pumped past the membrane, therefore consisted mainly of the aqueous fraction. Different flavour compounds partitioned between the fat and aqueous phases to different extents (Chapter 7), so the amount of fat in the retentate samples would have affected the measured concentrations of each compound.

As the retentate varied between runs, this caused the permeate composition to vary also, so that each run gave very different pervaporation results. Results from each run are therefore given separately in the following figures (note that each graph has a different scale). Figure 8-3 shows the concentrations of selected esters and acids in ester cream retentate and permeate, and their enrichment factors, for runs at 20°C; Figure 8-4 shows corresponding data for runs at 40°C. The large amount of variation between replicates at each temperature meant that it was not possible to draw conclusions about the effect of temperature.

At a feed temperature of 20°C (Figure 8-3), retentate concentrations were lower in Run 20B than in Run 20A, but the relative proportions of each flavour compound were similar for both runs. However, permeate concentrations and enrichment factors were greater in Run 20B than in Run 20A.

In the retentate of both runs, butanoic acid was the main flavour compound out of those measured; its concentration was more than double that of any other compound measured. The compound with the next highest concentration was ethyl oleate in Run 20A and ethyl butanoate in Run 20B. For both runs, the permeate composition was quite different from the retentate, consisting mainly of ethyl butanoate, with smaller amounts of other esters. The two largest esters

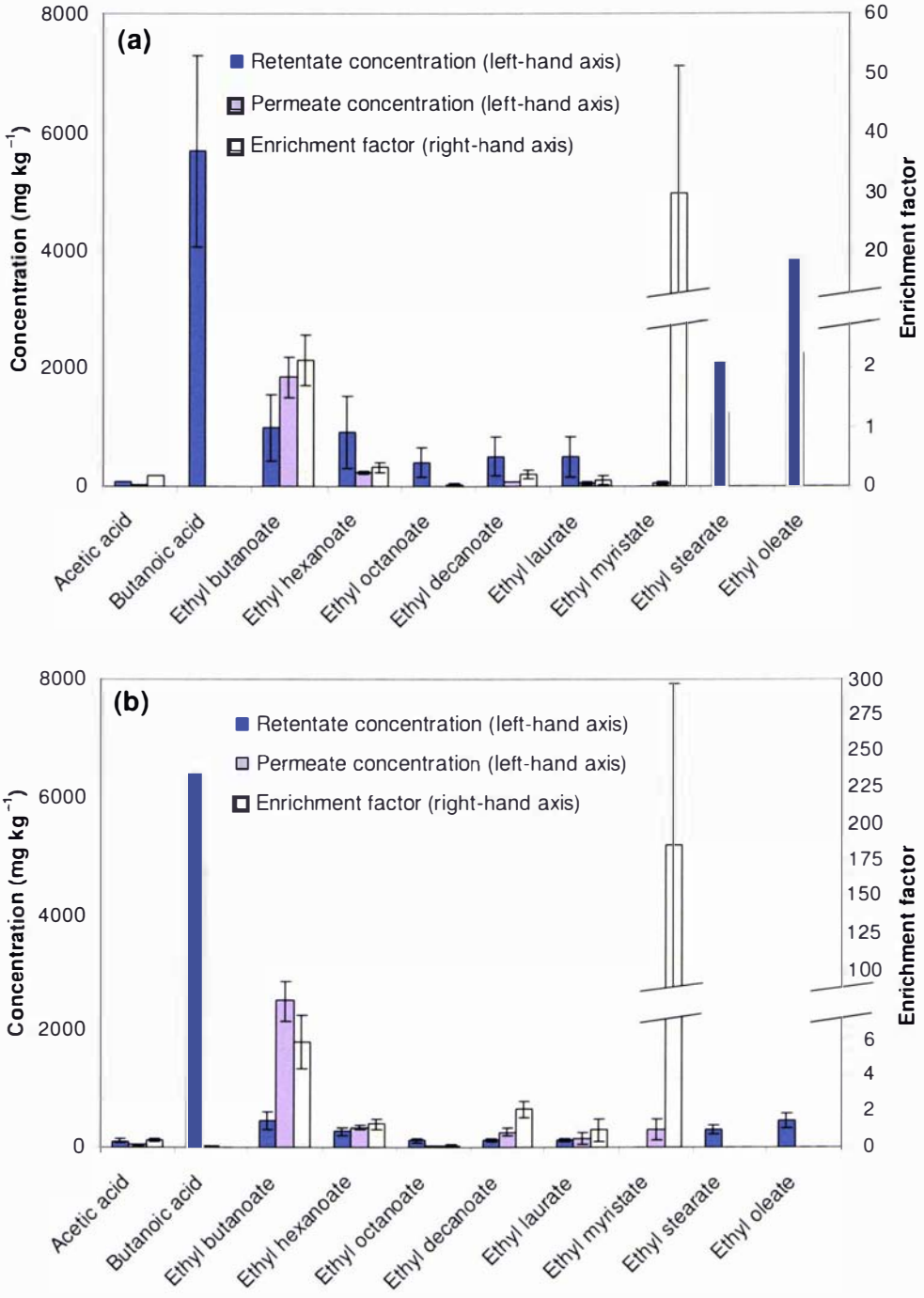


Figure 8-3: Ester cream retentate and permeate concentrations, and enrichment factors, for (a) Run 20A and (b) Run 20B at 20°C (PDMS Type 1 membrane, permeate pressure 2 kPa). Data are means ± standard error of four permeate samples or three retentate samples.

measured, ethyl stearate and ethyl oleate, were not detected in the permeate of either run.

Ethyl myristate appeared to have an extremely high enrichment factor (30 ± 21 in Run 20A and 190 ± 110 in Run 20B), but large standard errors, coupled with the

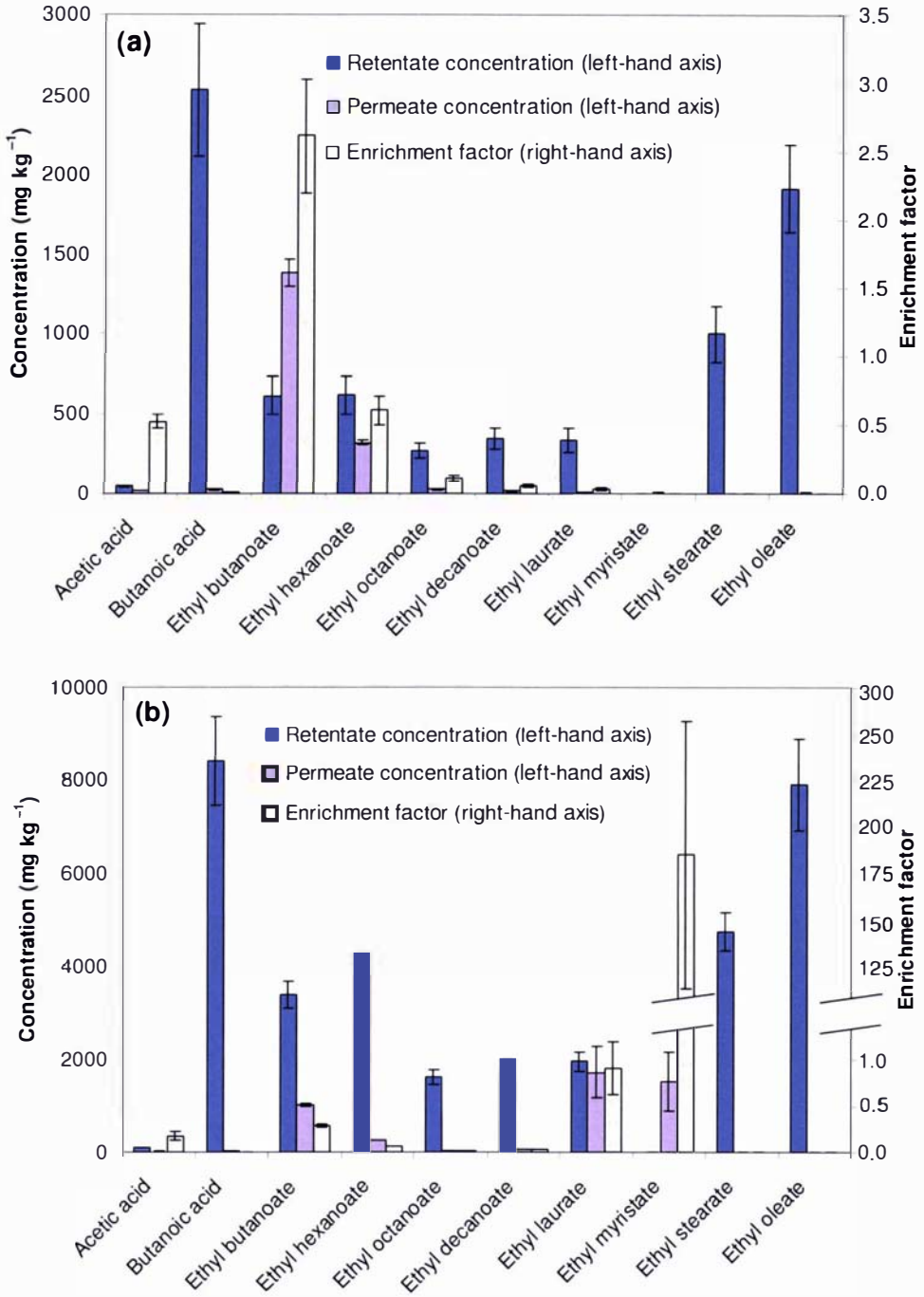


Figure 8-4: Ester cream retentate and permeate concentrations, and enrichment factors, for (a) Run 40A and (b) Run 40B at 40°C (PDMS Type 1 membrane, permeate pressure 2 kPa). Data are means ± standard error of four permeate samples or three retentate samples.

fact that this compound was only detected in half of all permeate samples from these two runs, mean that this result must be viewed with caution. Ethyl myristate was present at very low levels in the retentate, so that even with this high enrichment factor, it made up only 2% and 8% of the total measured compounds in the permeate for Run 20A and Run 20B respectively.

Aside from ethyl myristate, the compound with the highest enrichment factor was ethyl butanoate. In Run 20A, ethyl butanoate and ethyl myristate were the only compounds of those tested that were actually enriched (enrichment factors greater than one), but ethyl hexanoate, ethyl decanoate and ethyl laurate were also enriched in Run 20B.

Figure 8-4 shows results from the two runs at 40°C. Although retentate concentrations in Run 40B were 2–6 times greater than those in Run 40A, Figure 8-4 shows that the relative proportions of each compound in the retentate were similar for both runs. Butanoic acid was still the main compound in the retentate, but it did not dominate the retentate composition as in runs at 20°C; at 40°C, ethyl oleate was almost as concentrated as butanoic acid, followed by ethyl stearate. These long-chain esters would have been mainly associated with the fat phase. They appeared less concentrated in the retentate at 20°C, because the fat phase was mostly at the top of the feed tank. Consequently, the portion of the retentate that was sampled and analysed (and the portion that came in contact with the membrane) had a lower level of fat, and therefore a lower level of fat-soluble flavour compounds. At 40°C, less creaming occurred, so retentate samples contained more fat and consequently more long-chain esters.

In Run 40A, the permeate was dominated by ethyl butanoate with a smaller amount of ethyl hexanoate, as for runs at 20°C. However, in Run 40B, ethyl laurate and ethyl myristate had slightly higher concentrations than ethyl butanoate, although ethyl butanoate and ethyl hexanoate were still in similar proportions to each other.

In Run 40A, ethyl myristate was not detected in the retentate, so its enrichment factor could not be determined for this run. Ethyl butanoate was the only compound with an enrichment factor greater than one. In Run 40B, ethyl myristate had an enrichment factor of 190 ± 70 (although it was not detected in the permeate sample taken after the first hour of pervaporation, only in samples taken after two, three and four hours). In Run 40B, ethyl myristate was one of the most concentrated compounds in the permeate, so its high enrichment factor cannot be disregarded in this case. In this run, ethyl laurate also had a higher enrichment factor than ethyl butanoate; however, no compound had an enrichment factor greater than one.

Results were more consistent between duplicate runs at 20°C than at 40°C. This is probably because creaming occurred to a greater extent at the lower temperature, causing the ratio of fat to water in the retentate samples to be more constant. The retentate from runs at 20°C contained almost no fat, whereas the amount of fat was more variable in samples from 40°C runs.

Some general results were evident across all four runs. Although ethyl myristate appeared to have an extremely high enrichment factor in three out of four runs, this result was not reproducible, and it was not detected in all permeate samples. In most cases ethyl butanoate was the only other flavour compound that was enriched by pervaporation, and it was the main flavour compound in the permeate in three out of four runs. Its permeate concentration was 4–8 times that of ethyl hexanoate. The two largest esters tested for, ethyl oleate and ethyl stearate, did not pass through the membrane at all; the permeate also had very low levels of acetic and butanoic acids.

8.3.2.3 Comparison of ester cream with model solutions

Earlier experiments with model solutions containing ethanol (Chapter 6) or fat (Chapter 7) showed that the fat in ester cream (20%) would have a far greater negative impact on flavour compound enrichment factors than the ethanol (5%). Ester cream enrichment factors should therefore be comparable with a model solution containing 20% fat. In model solution trials, ethanol was not tested in the presence of fat; as ethanol is miscible with both fat and water, it probably would have altered how flavour compounds partitioned between the two phases.

Figure 8-5 compares enrichment factors achieved with ester cream to those achieved at the same operating conditions with a model solution containing 20% fat (Chapter 7), for the five compounds that could be quantified in both feed solutions. It is more meaningful to compare enrichment factors than fluxes in this case, because the fat-containing model solution had different feed concentrations from the ester cream, and the feed concentration in ester cream differed between runs as well. In most cases, ester cream results were similar to those obtained with the fat-containing model solution. However, ester cream Run 40B had lower enrichment factors for esters (Figure 8-5b). This was probably due to batch differences in the feed; Figure 8-4 shows that this run had higher retentate

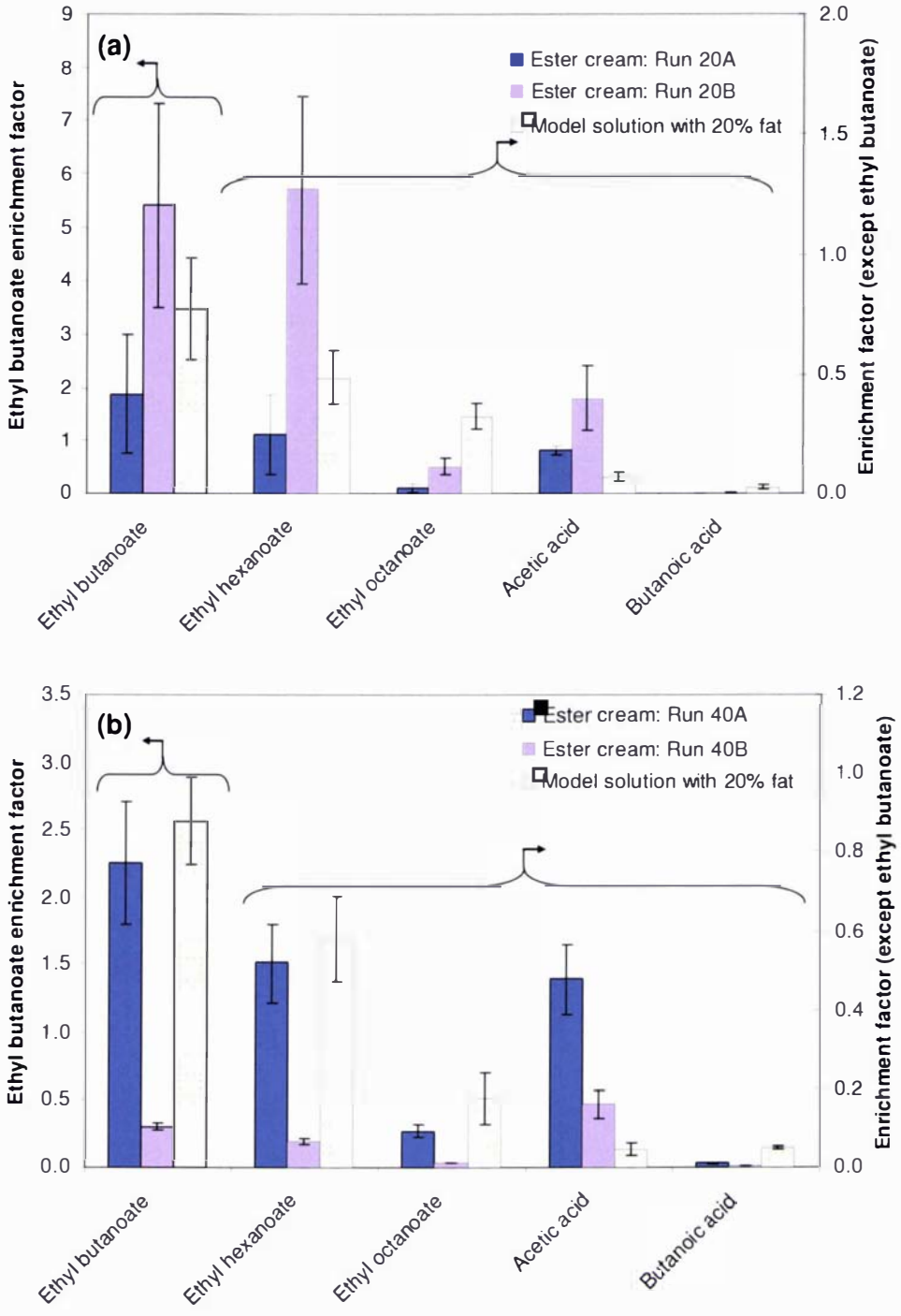


Figure 8-5: Comparison of enrichment factors between ester cream and model solution (20% fat). Operating conditions: PDMS Type 1 membrane, permeate pressure 2 kPa, feed temperatures (a) 20°C and (b) 40°C. Data are means (± standard error) of three runs for model solutions, or four measurements within one run for ester cream.

concentrations than the other runs. In some cases, a higher concentration leads to a lower enrichment factor (Sampranpiboon et al., 2000b).

In both ester cream and the model solution, enrichment factors followed the order: ethyl butanoate >> ethyl hexanoate/acetic acid/ethyl octanoate > butanoic acid.

Ester cream had a pH of 4.8, which is less acidic than the aqueous model solution in previous chapters (pH 3.5), but more acidic than the model solution with 20% fat (pH 6.1). As discussed in previous chapters, the feed pH had a significant effect on acid permeation. This means that the enrichment factors of acids in ester cream should be higher than those obtained in Chapter 7. Figure 8-5 shows that this is true for acetic acid, but butanoic acid was enriched less in ester cream (enrichment factors of less than 0.01) than in the model solution with 20% fat (enrichment factors of 0.03 at 20°C or 0.05 at 40°C). The difference may be due to the fact that the feed concentration of butanoic acid in ester cream was more than 60 times greater than in the model solution. When the feed concentration differs by this much, the enrichment factor may not be independent of the concentration. Concentration polarisation could become more significant at the higher concentration, leading to the enrichment factor being lower than expected. Also, activity coefficients may decrease at higher concentrations, as the feed solution is no longer infinitely dilute (Sampranpiboon et al., 2000b). If activity coefficients do not remain constant, the driving force is not directly proportional to the feed concentration over a very large concentration range.

8.4 Implications and commercial aspects

8.4.1 Commercial aspects of starter distillate pervaporation

Pervaporation was an effective method of concentrating the flavours in starter distillate. Both the flux and enrichment factor of diacetyl were greater at 40°C than at 20°C; a higher temperature than those tested may provide an even more efficient separation. If this trend continues beyond the two temperatures tested, it would be beneficial to run commercially at the highest temperature possible without damaging the feed solution.

The starter distillate used in this study contained 2200 ppm diacetyl. Some applications require a diacetyl concentration of 30 000 ppm, which could potentially be achieved using pervaporation, with the advantage that many of the minor flavour compounds in starter distillate would also be concentrated. Under

the conditions tested, the permeate concentration of diacetyl ranged from 7400 to 20 500 ppm. Therefore, pervaporation permeate could be used, along with some added natural diacetyl, to achieve the target concentration. The required amount of natural diacetyl would be 30–40% lower if it was used in conjunction with starter distillate permeate rather than untreated starter distillate. This amount could be further reduced by using a more selective membrane; diacetyl enrichment factors up to eight times higher than those in the current study have been reported using different membranes (Rajagopalan et al., 1994; Baudot & Marin, 1996).

In the 40°C experiments reported in this chapter, only about 2% of the total starter distillate feed was removed as permeate during each four-hour run. This meant that the retentate and permeate concentrations did not change significantly over the run time (data not shown), in contrast to ester cream. Under these conditions, about 50 L of starter distillate would be needed to produce 1 L of permeate. This ratio could be changed by altering the membrane area or the length of each run.

With a constant flux, the amount of permeate is proportional to both the membrane area and the run time. If either of these were increased so that 10% of the feed was removed as permeate, only 10 L of starter distillate would be needed to produce 1 L of permeate, with approximately 10 800 ppm diacetyl (at 40°C). The 9 L of retentate would still contain approximately 1200 ppm diacetyl. The greater the proportion of the feed removed as permeate, the lower the retentate concentration would become. Assuming a constant enrichment factor, this would lead to the permeate concentration decreasing as the run time or membrane area was increased. The cost of pervaporation would have to be balanced with the cost of adding natural diacetyl to a product along with starter distillate. Mass balance calculations are given in Appendix G.

8.4.2 Commercial aspects of ester cream pervaporation

Using pervaporation, it was possible to recover the desirable ethyl butanoate flavour from ester cream, while recovering only small amounts of the less desirable acids and long chain esters. The permeate did not consist of only ethyl butanoate, but also contained other flavour compounds. This is one of the major advantages in using a separation process to concentrate natural flavours, rather than creating flavours using the pure flavour chemical of interest: the other

background flavour compounds add complexity to the flavour and make it more well-rounded. Single esters generally have too much of a chemical flavour (Crow, 2005, personal communication).

However, ester cream does not seem to be a very suitable feed for pervaporation. Although ethyl butanoate could be enriched using pervaporation, its concentration in the permeate was only about double that in the feed. Model solution trials (Chapter 7) have shown that pervaporation is most effective when the feed stream does not contain any fat. Therefore, it may be better to separate the flavour compounds from the ester cream matrix using a different aroma recovery technique, such as distillation, before using pervaporation to concentrate and fractionate the flavours. This would also reduce the inconsistencies between runs, caused by ester cream not remaining as a stable dispersion.

8.4.3 Conclusions

Pervaporation trials with model solutions can be used to estimate general trends expected with real dairy products. However, some unexpected results were obtained with both starter distillate and ester cream, which shows that it is necessary to test pervaporation with actual process streams.

In starter distillate, diacetyl did not have a higher enrichment factor than both model solution ketones, contrary to expectations. This highlights the fact that a trend established within a homologous series cannot be extrapolated to include compounds from a different homologous series, even if they are closely related.

Starter distillate was a more suitable feed stream than ester cream, which gave low enrichment factors and variable results.

Both dairy products showed that pervaporation performance is highly dependent on the feed composition. With starter distillate, the effect of a high feed concentration was shown; this led to membrane plasticisation, and also may have lowered the enrichment factor of diacetyl. By comparing ester cream with a fat-containing model solution, it was shown that fluxes and enrichment factors are affected not only by the type and level of non-volatile components in the feed, but also by whether they are distributed evenly throughout the feed mixture. This is important to consider when evaluating pervaporation for complex feed streams

that may not be evenly dispersed, such as fermentation broths or aqueous dispersions of solid foods. For some feed streams, it would be helpful to have an agitator in the feed tank.

Chapter 9

Empirical modelling of mass transfer coefficients

9.1 Introduction

Many researchers have presented models for pervaporation (reviewed by Lipnizki & Trägårdh (2001) and Karlsson & Trägårdh (1993)), with most based on the solution-diffusion model. However, mass transfer rates can vary depending on the membrane, module and process used (Lipnizki & Trägårdh, 2001), making it difficult to compare results obtained by different researchers. Hence, it is hard to predict pervaporation performance without at least some experimental data on the pervaporation system in question.

The objective of this chapter was to empirically model the pervaporation fluxes of the nine flavour compounds in the standard multicomponent feed, based on the overall mass transfer coefficient for each compound under different operating conditions (membrane type, feed temperature and permeate pressure). The data in Chapter 5, with the standard multicomponent feed solution only, were used to develop the model. In the current chapter, the model is first applied to the same data from which it was developed, then it is used to predict fluxes in experiments with feed solutions other than those used to develop the model.

This chapter forms the basis for a peer-reviewed paper (Overington et al., 2009).

9.2 Theory

For steady-state transport processes, fluxes are proportional to the driving force (Mulder, 1996), with the proportionality constant defined as the mass transfer coefficient (Zydney, 1997):

$$J_i = k_i \times df \quad \textbf{(9-1)}$$

where J_i is the flux, k_i is the overall mass transfer coefficient, and *df* is the driving force of component *i*. The mass transfer coefficient includes mass transfer through all steps in the pervaporation process: mass transfer through the feed boundary layer, through the membrane and out into the permeate side (Karlsson & Trägårdh, 1994). This can be described using a resistance-in-series model (Karlsson & Trägårdh, 1994; Karlsson et al., 1995; Mulder, 1996):

$$\frac{1}{k_i} = \frac{1}{k_{i,bl}} + \frac{1}{k_{i,m}} + \frac{1}{k_{i,p}} \qquad \textbf{(9-2)}$$

In Equation (9-2), $k_{i,bl}$ is the mass transfer coefficient of compound *i* through the feed boundary layer, $k_{i,m}$ is the mass transfer coefficient through the membrane and $k_{i,p}$ is the mass transfer coefficient on the permeate side. All of these depend on the pervaporation system, the operating conditions, and the permeant compound.

In the absence of an electrical potential driving force, all common driving forces in membrane processes can be reduced to a gradient in chemical potential across the membrane (Wijmans & Baker, 1995; Mulder, 1996). The solution-diffusion model, which is the most commonly used model to describe pervaporation, assumes that this chemical potential gradient is expressed as a concentration or activity gradient (rather than a total pressure gradient as in the pore flow model) (Wijmans & Baker, 1995). Several expressions for the pervaporation driving force are used in the literature, with the most common being partial pressure difference (Baker et al., 1997; Baudot et al., 1999; Trifunović & Trägårdh, 2006), activity difference (Jiraratananon et al., 2002a; Lipnizki et al., 2004) and concentration difference (Karlsson et al., 1995) between the feed and permeate sides of the membrane. Partial pressure and activity driving forces are closely related, with partial pressure being the product of activity and saturated vapour pressure (Lee, 1999). The mass transfer coefficient with a partial pressure driving force may be divided by the saturated vapour pressure, in order to express the effective mass transfer coefficient in terms of an activity driving force (Trifunović & Trägårdh, 2005).

Concentration difference as a driving force does not take into account any non-ideal effects, and therefore is a poor approximation of the true driving force,

because aqueous solutions containing organic compounds of low solubility frequently show non-ideal behaviour (Pereira et al., 1998; Pereira et al., 2006). Hence, Pereira et al. (1998) concluded that a chemical potential driving force (based on logarithmic activity difference) led to more accurate results than an approximation based on concentration difference.

In this study, the driving force was approximated by the activity difference between the upstream and downstream sides of the membrane. Activities on the feed and permeate sides were estimated from Equations (9-3) and (9-4) respectively (Baudot et al., 1999; Trifunović & Trägårdh, 2005):

$$a_{i,f} = x_{i,f}\gamma_{i,f} \tag{9-3}$$

$$a_{i,p} = \frac{p_{i,p}}{p_i^0(T_f)} \tag{9-4}$$

where $a_{i,f}$ and $a_{i,p}$ are the activities of compound i in the feed and permeate respectively, $x_{i,f}$ is the mole fraction of compound i in the feed, $\gamma_{i,f}$ is the activity coefficient of compound i, $p_{i,p}$ is the partial pressure of compound i on the permeate side, and $p_i^0(T_f)$ is the saturated vapour pressure of compound i at the feed temperature. The flux was thus given by the following expression, based on Trifunović et al. (2006):

$$J_i = k_i\left(\gamma_i x_{i,f} - \frac{p_{i,p}}{p_i^0}\right) \tag{9-5}$$

9.3 Determination of model parameters

The model was developed from all the flux data using the standard multicomponent feed under various operating conditions (Chapter 5). The water flux was assumed equal to the total flux.

Using Equation (9-5) as the starting point, flavour compound driving forces at each set of operating conditions were calculated from their concentrations and literature data for their activity coefficients and saturated vapour pressures, as demonstrated in Appendix B. Activity coefficients of flavour compounds were

assumed to be equal to those at infinite dilution, as the feed solution was very dilute (no compound had a concentration greater than 111 ppm). This is a common assumption for pervaporation with dilute aqueous feeds (Baudot & Marin, 1999; Lipnizki & Hausmanns, 2004; Trifunović & Trägårdh, 2006). The dilute feed also meant that the activity coefficient of water could be assumed to be unity (Olsson & Trägårdh, 1999).

Once the driving force was calculated in this way for each compound, the overall effective mass transfer coefficient could be determined for each compound with each membrane and each temperature (Equation (9-5)). Mass transfer coefficients do not usually vary with the permeate pressure (Baudot et al., 1999); hence, the effective mass transfer coefficient was taken as the mean for all runs at a particular temperature.

9.4 Results and discussion

9.4.1 Effect of temperature on mass transfer

Fluxes increased with temperature by about one order of magnitude, on average, between 20°C and 40°C (Chapter 5). This well-known trend is due to an increased membrane permeability at raised temperatures, as well as an increase in feed activity creating a higher driving force (Feng & Huang, 1996; Lipnizki et al., 1999; Peng et al., 2003). Changes in the driving force due to temperature can be estimated by examining literature data for saturated vapour pressures of permeants over the temperature range of interest, and using Equation (9-5). However, the mass transfer coefficient is more difficult to predict for different systems, as it depends on both the permeant and the membrane (Börjesson et al., 1996).

Both the driving force and the permeability contribute to the increase in flux with temperature, but the relative importance of these two factors can vary. Olsson & Trägårdh (1999) found that the increase in water flux with increasing temperature (through a POMS membrane) was largely due to the increased driving force; however, for aroma compounds, they found that the increased permeability at higher temperatures influenced flux enhancement to a similar or greater degree than the increased driving force. Similar results were found in the current study:

the driving force of water increased more than three-fold from 20°C to 40°C, but driving forces of other compounds increased only slightly (Appendix B).

When activation energies for pervaporation are reported in the literature, they are normally calculated from the slope of a plot of ln(J) versus 1/T. To distinguish the effect of temperature on permeability from its effect on the driving force, Feng & Huang (1996) recommended plotting ln(P) (where P is the permeability) instead of ln(J), to calculate the activation energy for permeation. This is similar to the method followed in this study, except that effective mass transfer coefficients (defined as $J/\Delta a$) were used instead of membrane thickness-normalised permeabilities (defined by Feng & Huang (1996) as $J/\Delta p$, where Δp is the partial pressure difference across the membrane).

Effective mass transfer coefficients increased with temperature according to an Arrhenius-type relationship:

$$\ln(k_i) = \ln(k_0) - \frac{E_a}{RT} \qquad \textbf{(9-6)}$$

where k_0 is the pre-exponential factor, E_a is the activation energy and R is the gas constant. It is well known that the diffusion of small molecules in polymers is an activated process (Barrer, 1939; Yampolskii et al., 1998; Zheng et al., 2007), being described by an Arrhenius-type equation as long as the temperature range is not too large.

Figure 9-1 shows the Arrhenius relationship for each compound, with the PDMS Type 1 membrane. Arrhenius plots for the other two membranes are given in Appendix H. Within each class of compounds, the effective mass transfer coefficients decreased with increasing molecular weight. Both PDMS membranes gave linear Arrhenius plots, and it was therefore assumed that the POMS membrane would also follow an Arrhenius-type relationship (only two temperatures were tested with this membrane). Other researchers have also found linear Arrhenius relationships, using various membranes including POMS (Karlsson et al., 1995; Feng & Huang, 1996; Olsson & Trägårdh, 1999). Activation energies are shown in Figure 9-2, in relation to the molecular weight of each flavour compound.

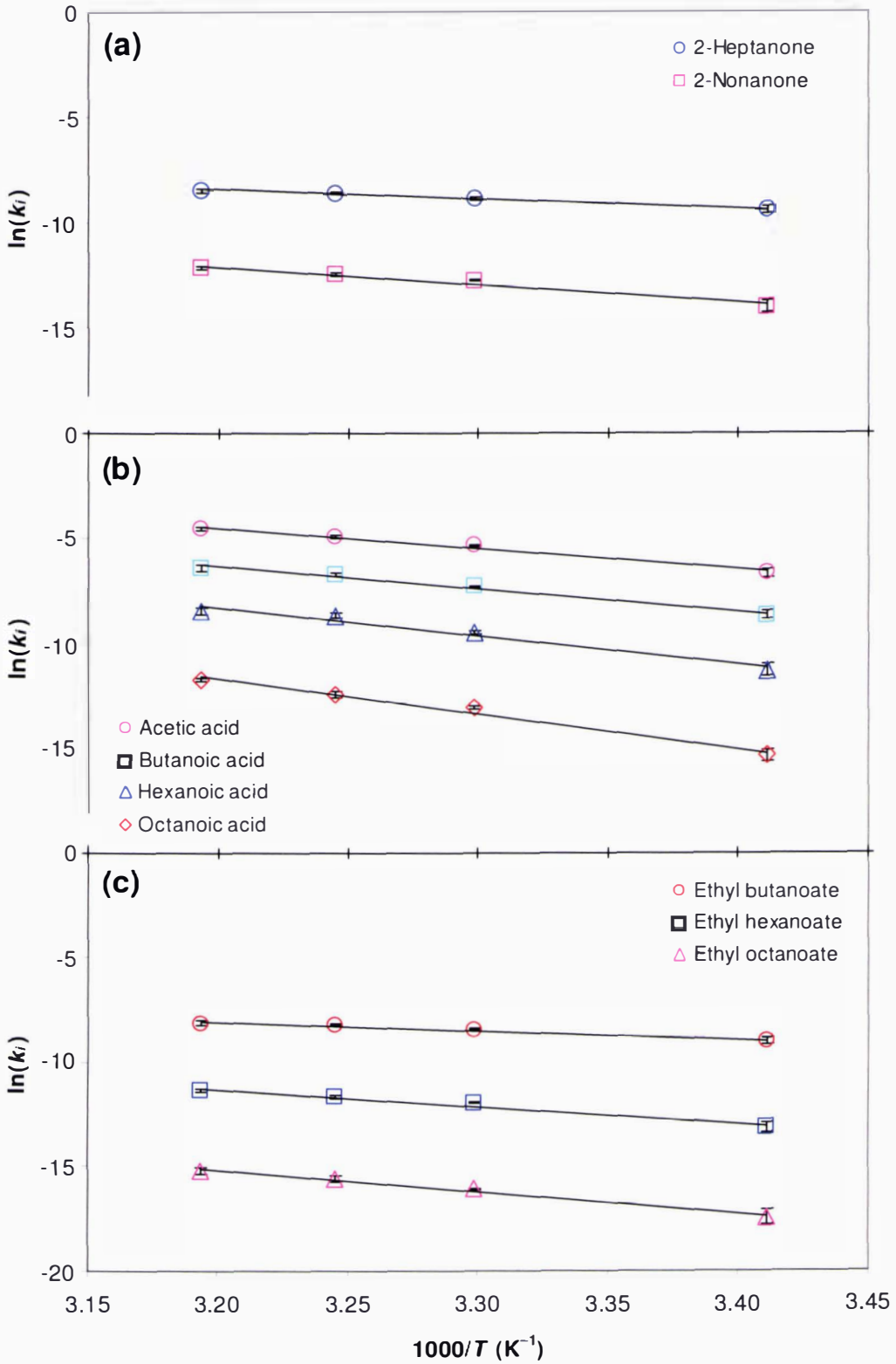


Figure 9-1: Arrhenius plots of (a) ketone, (b) acid and (c) ester effective mass transfer coefficients (PDMS Type 1 membrane). Data points are means (± standard errors) of 3–17 measurements at each temperature.

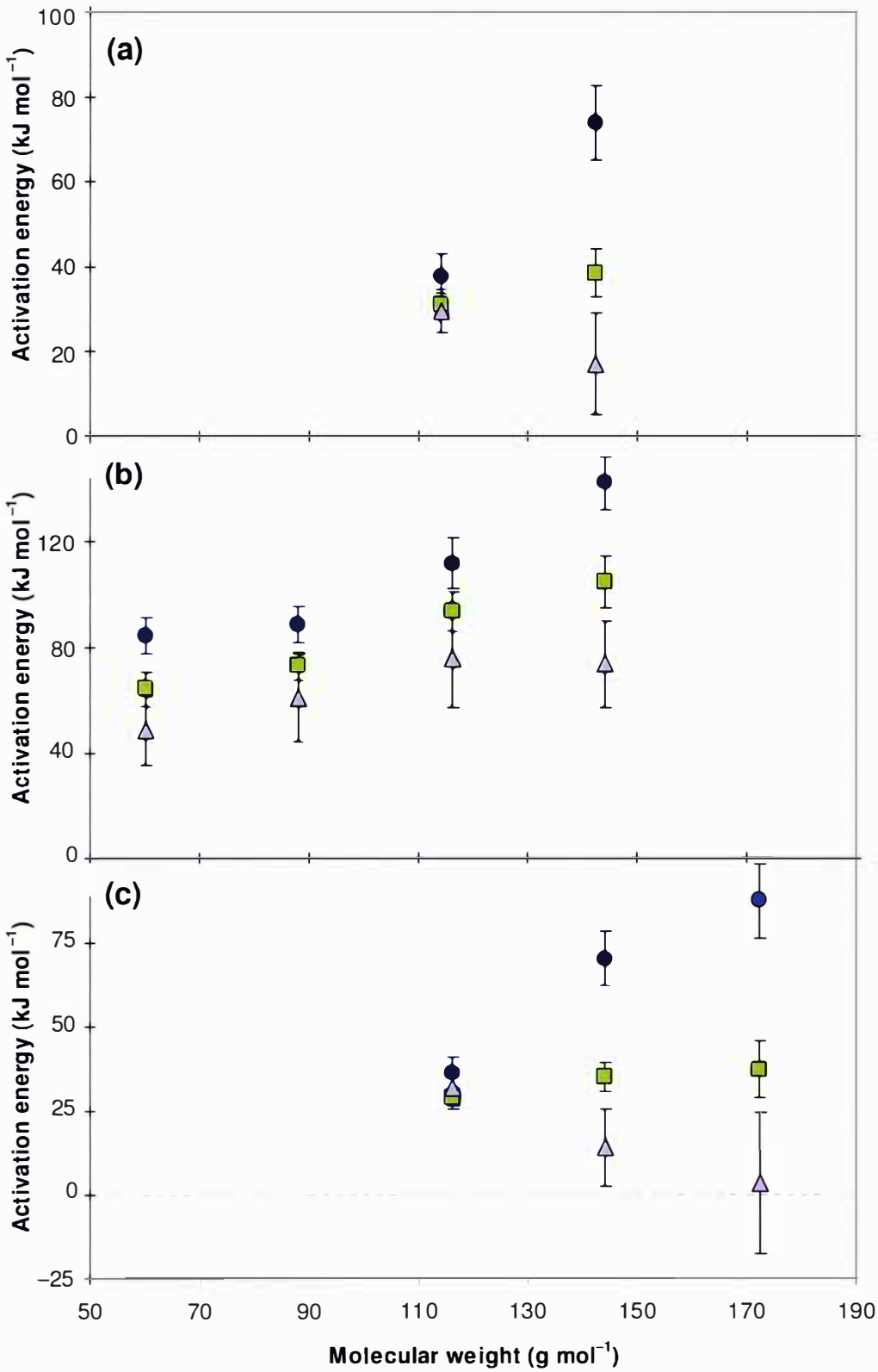


Figure 9-2: Relationships between activation energy for permeation (mean ± standard error) and molecular weight, for (a) ketones, (b) acids and (c) esters. Activation energies were calculated from Arrhenius plots with 27–35 data points. Legend: ● PDMS Type 1; ■ PDMS Type 2; ▲ POMS.

9.4.2 Effect of compound and membrane type on activation energy

The activation energy for molecular diffusion through a polymer corresponds to the energy required for permeant molecules to jump from one free volume hole to the next one in the polymer (van Krevelen, 1990; Aminabhavi et al., 1996). This means that the activation energy required for diffusion should increase with molecular size (van Krevelen, 1990). However, in pervaporation, other parameters besides diffusion influence the rate of movement through the membrane, and thus the dependence of activation energy on molecular size is more complex. This is shown by Figure 9-2, in which activation energies showed different behaviour with increasing size within each homologous series, depending on the membrane used.

The membrane type had a significant effect on the activation energy of some compounds, but not others. The activation energies of small permeants (with molecular weights lower than about 120 g mol^{-1}), especially esters and ketones, were not influenced by the type of membrane. In contrast, the activation energies of larger compounds varied widely between the three membranes tested, with compounds needing the greatest activation energy to pass through PDMS Type 1, followed by PDMS Type 2 then POMS. This corresponded to PDMS Type 1 having the highest fluxes, followed by PDMS Type 2 then POMS, indicating that membranes with higher fluxes had a greater temperature dependence.

This distinction between small and large permeants was also observed by Dole et al. (2006), who analysed their own and literature data on activation energies for diffusion of various compounds in several packaging polymers. They suggested that polymer mobility may be important for the diffusion of large molecules only, whereas for small molecules the intrinsic mobility of the permeant is more important regardless of polymer type.

Tikhomirov et al. (1968) discussed the differences in activation energies of diffusion above and below the glass transition temperature of the polymer. In general, diffusion below the glass transition temperature involves the permeant moving between pre-existing holes, whereas at higher temperatures it normally also involves creation of larger holes as a result of polymer chain movement. Which of these two mechanisms is rate-limiting above the glass transition

temperature depends on the permeant size as well as the polymer type (Tikhomirov et al., 1968). In the current study, all experiments were carried out well above the glass transition temperature of −121°C for PDMS (Bicerano, 2002) (no glass transition data were available for POMS, but it is a similar polymer to PDMS), and the change at approximately 120 g mol^{-1} in Figure 9-2 fits with the theory that there is a change in the rate-limiting factor for permeants above a certain molecular size.

Below 120 g mol^{-1}, the activation energy increased with increasing molecular weight within the acids (this trend could not be confirmed for the other functional groups, because only one ester and one ketone below this critical size were tested). Kabra et al. (1995) found that the activation energy was greater for pervaporation of butanoic acid than for propanoic acid, which fits with the trends in Figure 9-2. The larger the permeant, the lower its diffusivity in the membrane. Consequently, as the permeants move through the membrane, it is less likely that larger permeating molecules will find a free volume hole in the polymer of appropriate size to jump into, and therefore the activation energy should increase with molecular size, consistent with the trend for small acids in Figure 9-2.

In an apparent contradiction, the fluxes of small acids (acetic acid, butanoic acid and usually hexanoic acid, depending on the operating conditions) increased with increasing molecular weight (Chapter 5), even though, as the activation energy increases (that is, as permeation becomes more difficult), the flux would be expected to decrease. One reason for this is that the flux depends on both the mass transfer coefficient and the driving force. As the molecular weight increased within each class of compounds, the overall effective mass transfer coefficient decreased but the activity difference across the membrane increased, leading to the flux either increasing or decreasing, depending on whether the effective mass transfer coefficient or the driving force was the dominant factor. Liang & Ruckenstein (1996) found that membranes for which the flux was lower had a higher activation energy. However, their activation energy was calculated based on the flux rather than the mass transfer coefficient. This means that it represented the effect of temperature on both the mass transfer coefficient and the driving force together, rather than considering them separately as in the current study.

Ketones and esters had similar activation energies for the same molecular weight, whereas the activation energies of acids were considerably higher. This was reflected in the relative fluxes of each class of compound; after normalising for different feed concentrations, the ketones and esters had fluxes several times higher than the acids.

To further explain the differences in activation energy given in Figure 9-2, it is necessary to split the total activation energy into its constituent parts. The apparent activation energy for permeation is a combination of the energy required for sorption and the energy required for diffusion (van Krevelen, 1990; Feng & Huang, 1996):

$$E_a = \Delta H_S + E_D \tag{9-7}$$

where E_a is the apparent activation energy of permeation, ΔH_S is the molar heat of sorption and E_D is the activation energy of diffusion.

Barrer (1939) calculated that the activation energy for diffusion through a lattice is a function of the displacement of molecules making up the lattice (i.e., the strain), and depends on whether the lattice is elastic or rigid. Pönitsch & Kirchheim (1996) (following a derivation by Zener (1951)) applied this theory to diffusion in polymers, using the elastic modulus as a measure of elasticity, to create the equation:

$$E_D = M_0 f(\varepsilon) \tag{9-8}$$

where M_0 is the elastic modulus extrapolated to a reference temperature (taken in this study to be −121°C, the glass transition temperature of PDMS), and $f(\varepsilon)$ is a function of the average strain encountered as the permeant moves from site to site within the polymer. According to Pönitsch & Kirchheim (1996), the principle applies equally to rubbery and glassy polymers, as long as the strain does not relax during the time period in which a permeant jumps between sites in the polymer. Substituting Equation (9-8) into Equation (9-7) gives the following equation:

$$E_a = \Delta H_S + f(\varepsilon) M_0 \tag{9-9}$$

As the elastic moduli of PDMS films have been found to increase with decreasing film thickness (Wang et al., 1997), it therefore follows that thinner membranes should require greater activation energies. This was indeed found to be the case for compounds with molecular weights greater than 120 g mol^{-1} (Figure 9-2). Shishatskii et al. (1996) also showed that the density of polymer films increased as their thickness decreased, meaning that the cohesive energy density, and hence the activation energy for diffusion, was greater with thinner membranes.

Estimated M_0 values for PDMS Type 1, PDMS Type 2 and POMS membranes were 102 MPa, 34 MPa and 10 MPa respectively. M_0 for PDMS was estimated by taking values for the elastic modulus of the bulk polymer at a range of temperatures (Lötters et al., 1997), then accounting for the membrane thickness by extrapolating Wang et al.'s (1997) elasticity data for various film thicknesses (at their lowest measured strain of 5%). No literature data were available for the elastic modulus of POMS, but it was estimated to be approximately 2.2 times that of PDMS (in the bulk polymer), using a group contribution method explained by van Krevelen (1990). Assuming that the elastic modulus of POMS and PDMS were both influenced by membrane thickness in the same way, Wang et al.'s (1997) PDMS data were again extrapolated to estimate the elastic modulus of POMS at the membrane thickness used.

Figure 9-3, which shows Equation (9-9) graphically, has y-intercepts equal to ΔH_S (assuming that this is similar for both PDMS and POMS) and slopes depending on $f(\varepsilon)$. Therefore, this figure can be used to distinguish between the two components of apparent activation energy: heat of sorption and activation energy of diffusion. Slopes of the best fit lines in Figure 9-3 are large and positive for compounds greater than 120 g mol^{-1}, and closer to zero for compounds below this critical molecular weight (especially water, 2-heptanone and ethyl butanoate). This means that for small compounds, the total activation energy was almost entirely determined by the heat of sorption, with the activation energy of diffusion having very little influence. In contrast, the activation energy for larger compounds was strongly influenced by the energy required to diffuse through the polymer matrix.

The y-intercepts of Figure 9-3 are given in Figure 9-4, which shows two distinct groups. In the acids (including water) homologous series, ΔH_S increased with

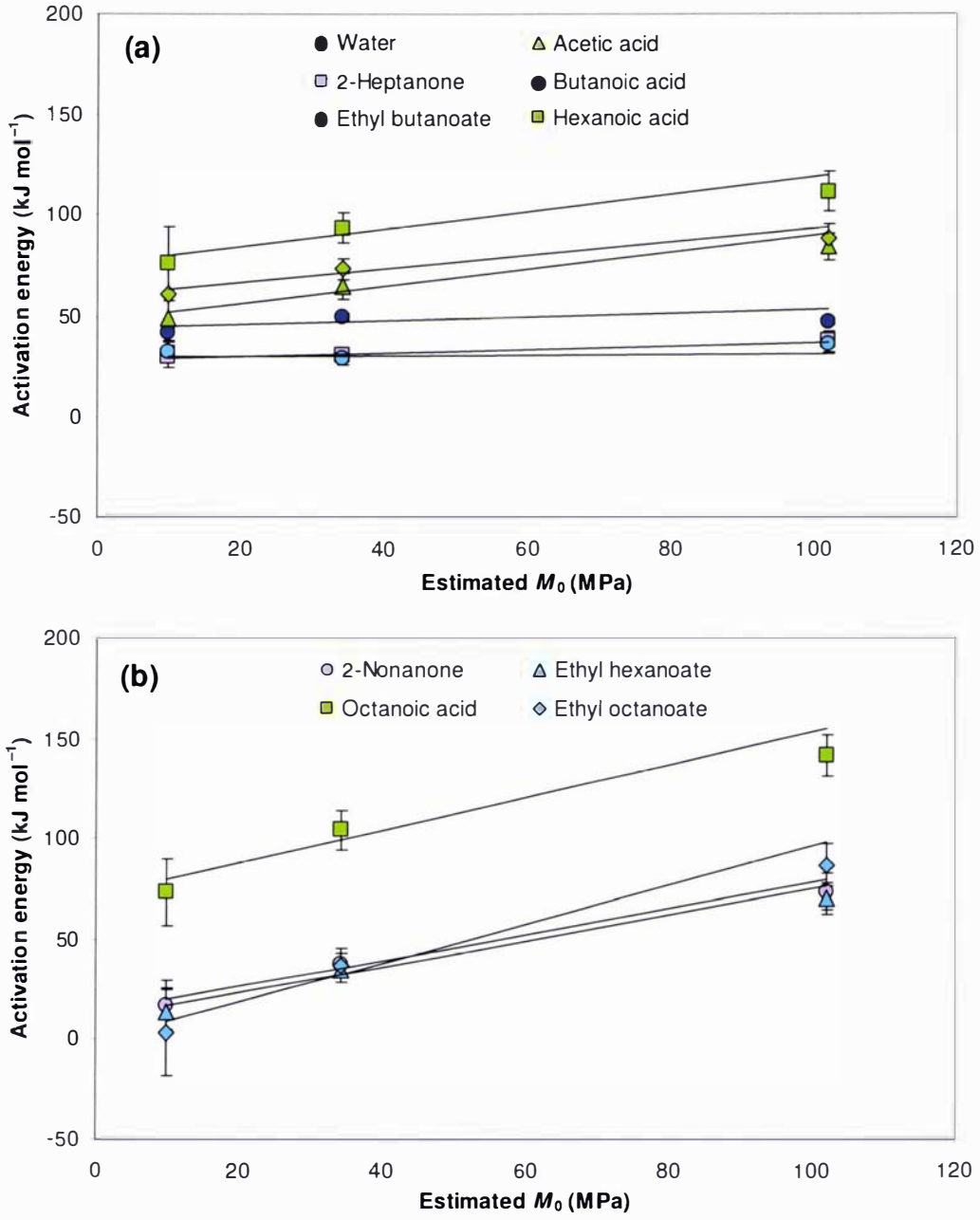


Figure 9-3: Activation energy versus estimated elastic modulus: (a) compounds with molecular weights less than 120 g mol^{-1}; (b) compounds with molecular weights greater than 120 g mol^{-1}.

increasing molecular weight, except for octanoic acid. In the esters and ketones series, ΔH_S was lower than for acids, and decreased linearly with increasing molecular weight. The heat of sorption is a combination of the energy required to make a void in the polymer and the energy given off when that void is filled by a permeant molecule (ten Hulscher & Cornelissen, 1996). Larger compounds would require a larger void, so the former quantity would increase with molecular

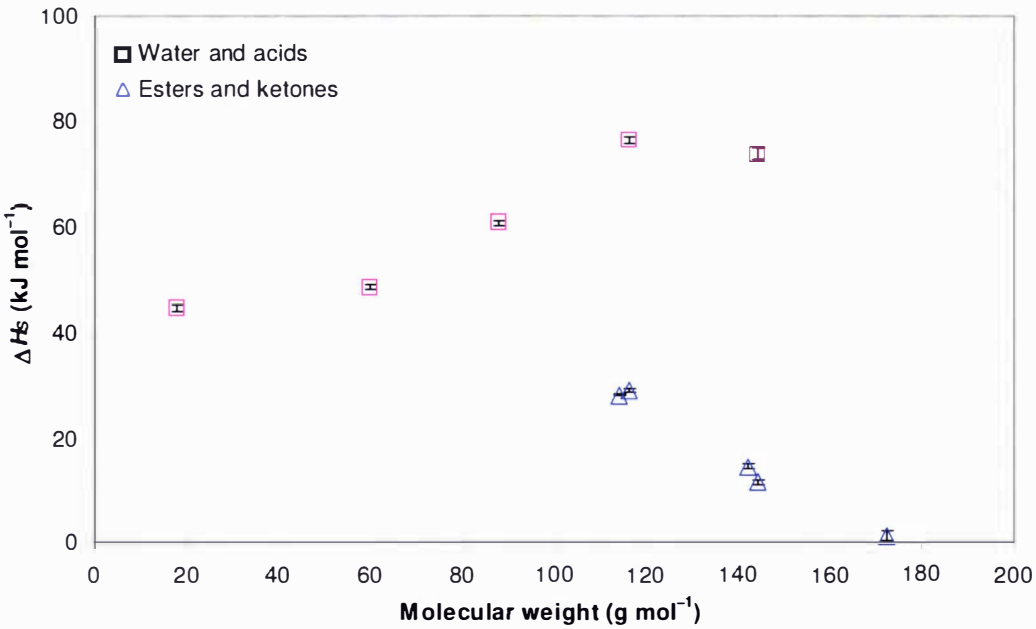


Figure 9-4: Heat of sorption (mean ± standard error of the intercept of Figure 9-3) versus molecular weight, for water, acids, esters and ketones.

weight. However, larger compounds of the functional groups tested here are also more hydrophobic, so would be expected to release more energy when associating with the hydrophobic polymers making up these membranes. Figure 9-4 seems to indicate that of these two factors, the hydrophobicity effect was more important for esters and ketones, but the molecular size effect was more important for acids (except for octanoic acid).

Literature data regarding the heats of sorption of flavour compounds in the polymers studied here are scarce, so the ΔH_S values in Figure 9-4 could only be verified for those compounds for which sorption coefficients were available in the literature at more than one temperature (ethyl butanoate and ethyl hexanoate). For these two compounds, ΔH_S could be estimated from the following Arrhenius-type equation (van Krevelen, 1990):

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \qquad \textbf{(9-10)}$$

in which S is the sorption coefficient and S_0 is the pre-exponential factor for sorption. Table 9-1 shows that the heats of sorption in Figure 9-4 are similar to those calculated from independent data. Their similarity increases confidence in

Table 9-1: Heats of sorption calculated from literature data (Equation (9-10)) and from Figure 9-4.

Compound	Sorption coefficient			Heat of sorption (kJ mol^{-1})	
	18°C in POMS[a]	20°C in POMS[b]	25°C in silicone rubber[c]	Equation (9-10)	Figure 9-4[d]
Ethyl butanoate		21.4	29.3	45.7	29.1 ± 0.3
Ethyl hexanoate	241.3		264.6	9.5	11.6 ± 0.5

[a]Schäfer et al. (2005)

[b]Calculated from Trifunović & Trägårdh (2003)

[c]Lamer et al. (1994)

[d]Mean ± standard error

the data in Figure 9-4 and Equation (9-9). However, Equation (9-10) must be used with some caution in this case because sorption coefficients at only two temperatures, with slightly different polymers, were used in the calculation. The heat of sorption of water in non-polar polymers has been reported to be around 25 kJ mol^{-1} (van Krevelen, 1990), somewhat lower than the value from Figure 9-4.

Olsson & Trägårdh (1999) suggested that it could be possible to predict pervaporation activation energies from each permeant's functional group, its activity coefficient at infinite dilution in water (which influences hydrophobicity and therefore solubility in the membrane) and its liquid molar volume (which influences diffusivity in the membrane). Figures 9-3 and 9-4 support their hypothesis that the activation energy of each compound is influenced by its functional group and its molecular size (evaluated as molecular weight in the current study), but also show that the membrane thickness is an important factor affecting the activation energies of certain compounds. Djebbar et al. (1998) found no obvious relationship between activation energy and compound or membrane type, but their apparent activation energies were determined based on the increase of flux with temperature, rather than the increase of mass transfer coefficient with temperature as recommended by Feng & Huang (1996).

9.4.3 Relationship between activation energy and pre-exponential factor

The pre-exponential factor in Equation (9-6) was calculated from the y-intercepts in Figure 9-1. Logarithms of pre-exponential factors normalised for membrane thickness ($k_0 \times l$) varied with compound and membrane in a similar pattern to activation energies, suggesting that there was a relationship between the two. A linear relationship has been observed between the logarithm of the pre-exponential factor and the activation energy (or between the entropy change and enthalpy change) for many different chemical processes (Liu & Guo, 2001), including diffusion in polymers (Barrer & Skirrow, 1948; Kwei & Arnheim, 1962; Prabhakar et al., 2005; Zheng et al., 2007) and sorption in foods (Aguerre et al., 1986) and solvents (Bell, 1937). This relationship is generally referred to as the compensation effect. According to transition state theory, the logarithm of the pre-exponential factor is proportional to the activation entropy in a process, and the activation energy is related to the enthalpy difference between the activated and normal states (Zheng et al., 2007). Accordingly, compensation between entropy and enthalpy will lead to a relationship between the activation energy and the pre-exponential factor. However, in the case of diffusion, the pre-exponential factor also depends on the length of each activated jump within the polymer (Zheng et al., 2007), meaning that the compensation effect in this situation is not fully explained by entropy-enthalpy compensation.

Although there has been some debate over whether the compensation effect is real or a mathematical artefact (Liu & Guo, 2001; Philibert, 2006), Pönitsch & Kirchheim (1996) (following a derivation by Zener (1951)) proposed a physical reason for the compensation effect for diffusion in polymers, relating both the activation energy and the pre-exponential factor to the elastic modulus of the polymer.

Figure 9-5 shows the compensation effect between $\ln(k_0 \times l)$ and E_a/R plotted from the results of the current study, for which the slopes were similar for all compounds, but the intercepts varied between different compounds. The average slope of this graph was 0.0031 K^{-1} (standard error of $\pm$ 0.0001 K^{-1}). When the slope of each compound's line was fixed to this average value, the intercepts varied depending on the molecular weight, as shown by Figure 9-6. The following empirical relationship gave a good fit for the data in Figure 9-6 (R^2 = 0.998):

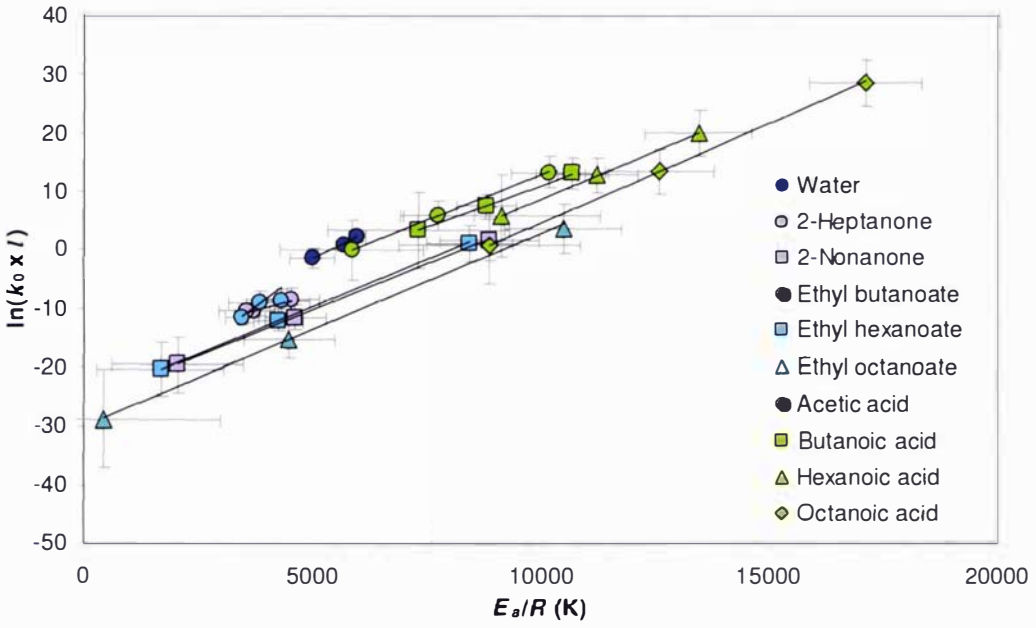


Figure 9-5: Compensation effect between activation energy and pre-exponential factor. Error bars show standard errors of the slope and intercept of Arrhenius plots.

$$\ln(-y_{\text{intercept}}) = 4.00\times10^{-5} M^{1.87} + 2.80 \qquad \textbf{(9-11)}$$

where $y_{\text{intercept}}$ is the y-intercept of Figure 9-5 ($\ln(k_0 \times l)$ when $E_a/R = 0$) and M is the molecular weight of the flavour compound. This relationship was also tested

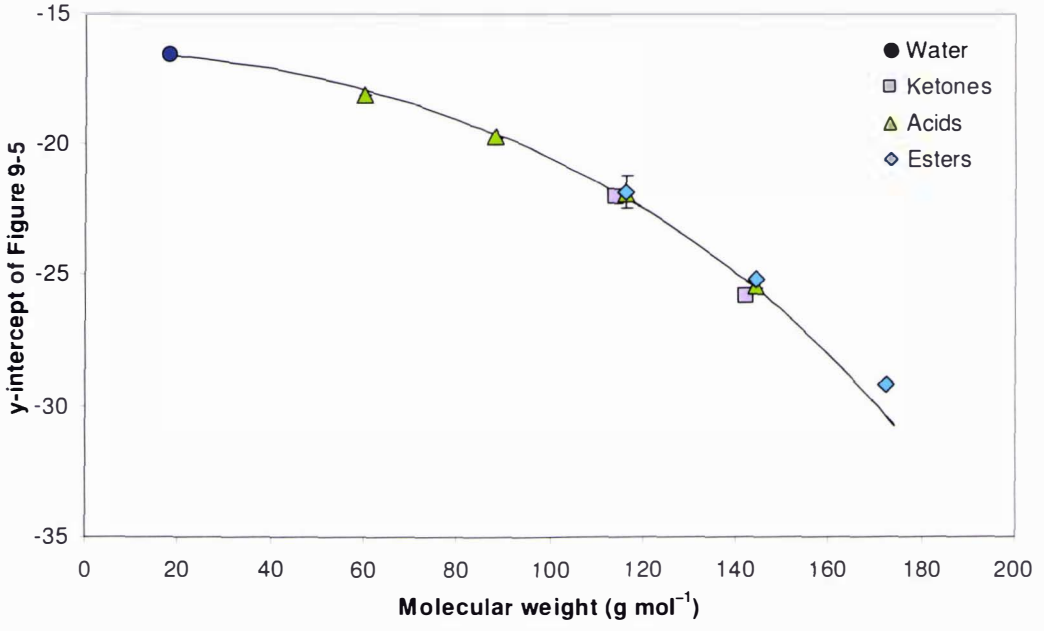


Figure 9-6: Variation of compensation effect between compounds (mean ± standard error of the y-intercept of Figure 9-5; three data points per compound).

using literature data for liquid molar volumes, molecular volumes or molecular cross-sections in place of molecular weights (data not shown). Molecular weights proved to give a better correlation than the other measures of molecular size tested. However, it seems intuitive that $f(\varepsilon)$ should depend on the size of each permeant molecule, not only on its molecular weight. This hypothesis could potentially be investigated by using isomers with the same molecular weight but different molecular sizes.

As there was a relationship between activation energies and pre-exponential factors, this means that if the activation energy could be predicted based on knowledge of ΔH_S, $f(\varepsilon)$ and M_0, then the pre-exponential factor could be empirically predicted as well. Therefore, predicted values for the effective mass transfer coefficient and hence the flux could be calculated for different compounds and different operating conditions.

van Krevelen (1990) postulated the following relationship between activation energy and pre-exponential factor for permeation in rubbery polymers (converted to natural logarithm units instead of $\log_{10}$ as given by van Krevelen (1990)):

$$\ln(k_0) = 0.0023\frac{E_a}{R} - 23.2 \qquad \textbf{(9-12)}$$

The constants in Equation (9-12) are slightly different from those determined in this study (on Figure 9-5, the slope of each line was close to 0.0031 K^{-1}, and intercepts ranged from −29.8 to −18.3). In this study, the slope of Figure 9-5 was close to the inverse of the average operating temperature. Kirchheim & Huang (1987) explained how, in the case of diffusion, this result arises mathematically from the form of the compensation equation rather than for any physical reason, provided that the difference in diffusivity between matrices (different membranes in this case) is small compared with the difference in activation energies. They argued that, although the compensation effect works mathematically in this situation, it could not be used to explain the physical diffusion mechanism when applied to an individual permeant diffusing in different matrices (as opposed to different permeants diffusing in the same matrix).

However, there is a stronger physical basis to explain why the compensation effect for sorption, rather than diffusion, depends on temperature. Liu & Guo (2001) summarised a theory relating the compensation effect to entropy and enthalpy changes occurring when a solute dissolves in a solvent. This is relevant to pervaporation, because sorption into the membrane is one of the contributing factors to the permeability. According to the theory (Liu & Guo, 2001), when a species X dissolves in a solvent A, two processes occur at once: the nominal process, in which X is transferred from its own environment into the solvent environment $X\backslash a$; and the environmental process, in which some A molecules, which were surrounded by other A molecules in the environment $A\backslash a$, are transferred into the environment of the solute $A\backslash x$. The environmental process may involve enthalpy and entropy changes, but the free energy change for the environmental process is zero (Liu & Guo, 2001). This means that the enthalpy (ΔH) and entropy changes (ΔS) must offset each other, so that:

$$\Delta H - T\Delta S = 0$$
$$\frac{\Delta H}{\Delta S} = T \qquad \textbf{(9-13)}$$

If the entropy and enthalpy changes for the environmental process are much larger than their counterparts for the nominal process, then the proportionality constant in the compensation effect equation will therefore be approximately the inverse temperature (Liu & Guo, 2001), since ΔH is related to the activation energy and ΔS is related to the logarithm of the pre-exponential factor.

The compensation effect has not been reported before for pervaporation, but it has been observed for permeabilities of gases in polymers (van Krevelen, 1990; Yampolskii et al., 1998) (although not described mechanistically, as opposed to diffusion). Permeability is a combination of two processes, sorption and diffusion. Budrugeac & Segal (1998) discussed how, for a two-step process, an apparent compensation effect occurs if an apparent rate constant is used rather than evaluating each process separately. This implies that the compensation effect observed in the current study is an apparent effect.

A false compensation effect occurs if there are experimental errors in the data such that the estimated values for k_0 and E_a are correlated, even though their true

values are not (Liu & Guo, 2001). Correlation between the estimated values occurs because k_0 and E_a are not determined independently, so that any experimental errors in the data used to calculate them will translate into correlated errors in both k_0 and E_a. To establish whether an apparent compensation effect is real or false, Liu and Guo (2001) recommended drawing error bars on the compensation plot. Standard errors on each point in Figure 9-5 were relatively small compared to the variation between data points; hence, the overall linear relationship between $\ln(k_0 \times l)$ and E_a/R exists even when errors are taken into account. Therefore, in this case the compensation effect is not likely to be caused by experimental error.

Independent of whether the compensation effect observed in the current study has a true physical origin, the observed correlation in Figure 9-5 can be used practically to estimate the pre-exponential factor from the activation energy.

9.4.4 Estimation of effective mass transfer coefficients using correlations

Activation energies for each compound and each membrane were determined from Equation (9-9), taking values of ΔH_S from Figure 9-4 and using the slope of Figure 9-3 as $f(\varepsilon)$. Each compound's molecular weight was substituted into Equation (9-11), to obtain a value for the y-intercept of Figure 9-5. The activation energy and y-intercept were then used to calculate the pre-exponential factor, using Equation (9-14), in which 0.0031 was the average slope from Figure 9-5.

$$\ln(k_0) = 0.0031\frac{E_a}{R} + y_{\text{intercept}} \qquad \textbf{(9-14)}$$

Effective mass transfer coefficients at each temperature could then be estimated by substituting the calculated pre-exponential factors and activation energies into the Arrhenius equation. Predicted effective mass transfer coefficients are compared with experimental effective mass transfer coefficients in Figure 9-7 (water), Figure 9-8 (ketones), Figure 9-9 (acids) and Figure 9-10 (esters). These figures show that the accuracy of predictions varied for different compounds. Activation energies were close to the experimental values, which meant that the slopes of the lines in Figures 9-7 to Figure 9-10 (that is, the influence of temperature on the effective mass transfer coefficient) could be predicted well.

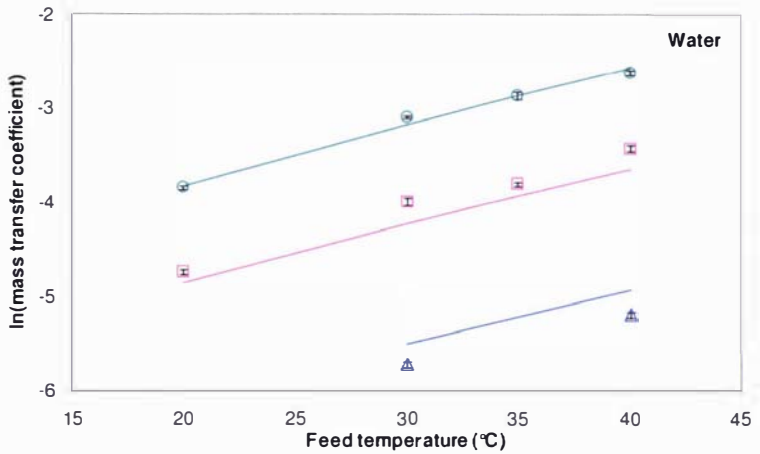


Figure 9-7: Effective mass transfer coefficients for water. Symbols are experimental values (mean ± standard error of at least three replicates) and lines show model predictions. Legend: ○ PDMS Type 1; □ PDMS Type 2; Δ POMS.

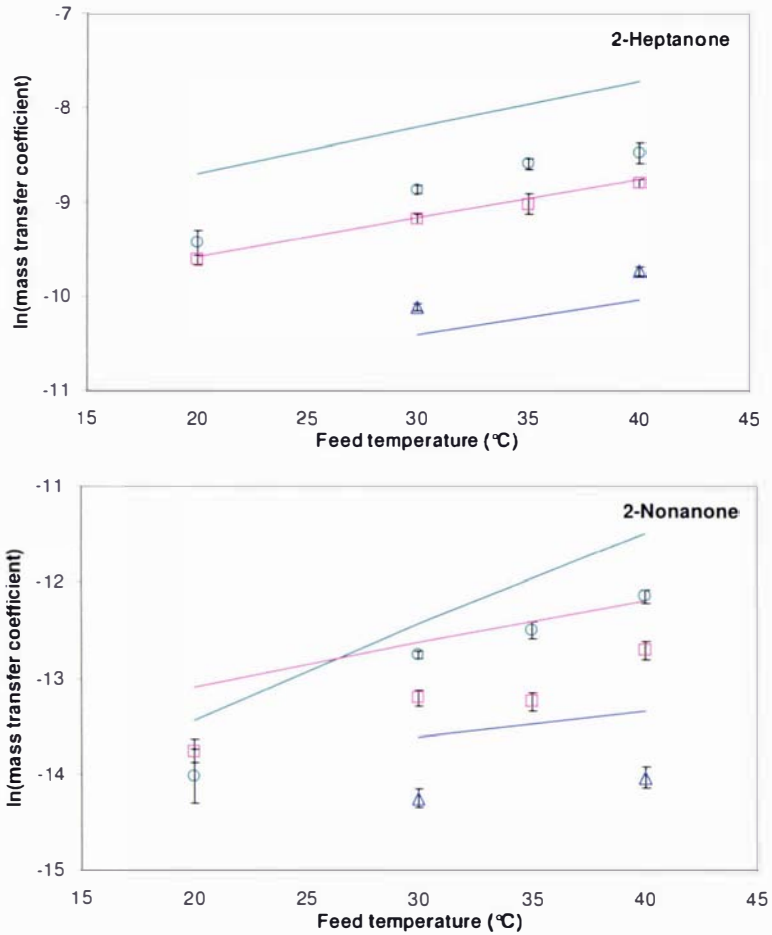


Figure 9-8: Effective mass transfer coefficients for ketones. Symbols are experimental values (mean ± standard error of at least three replicates) and lines show model predictions. Legend: ○ PDMS Type 1; □ PDMS Type 2; Δ POMS.

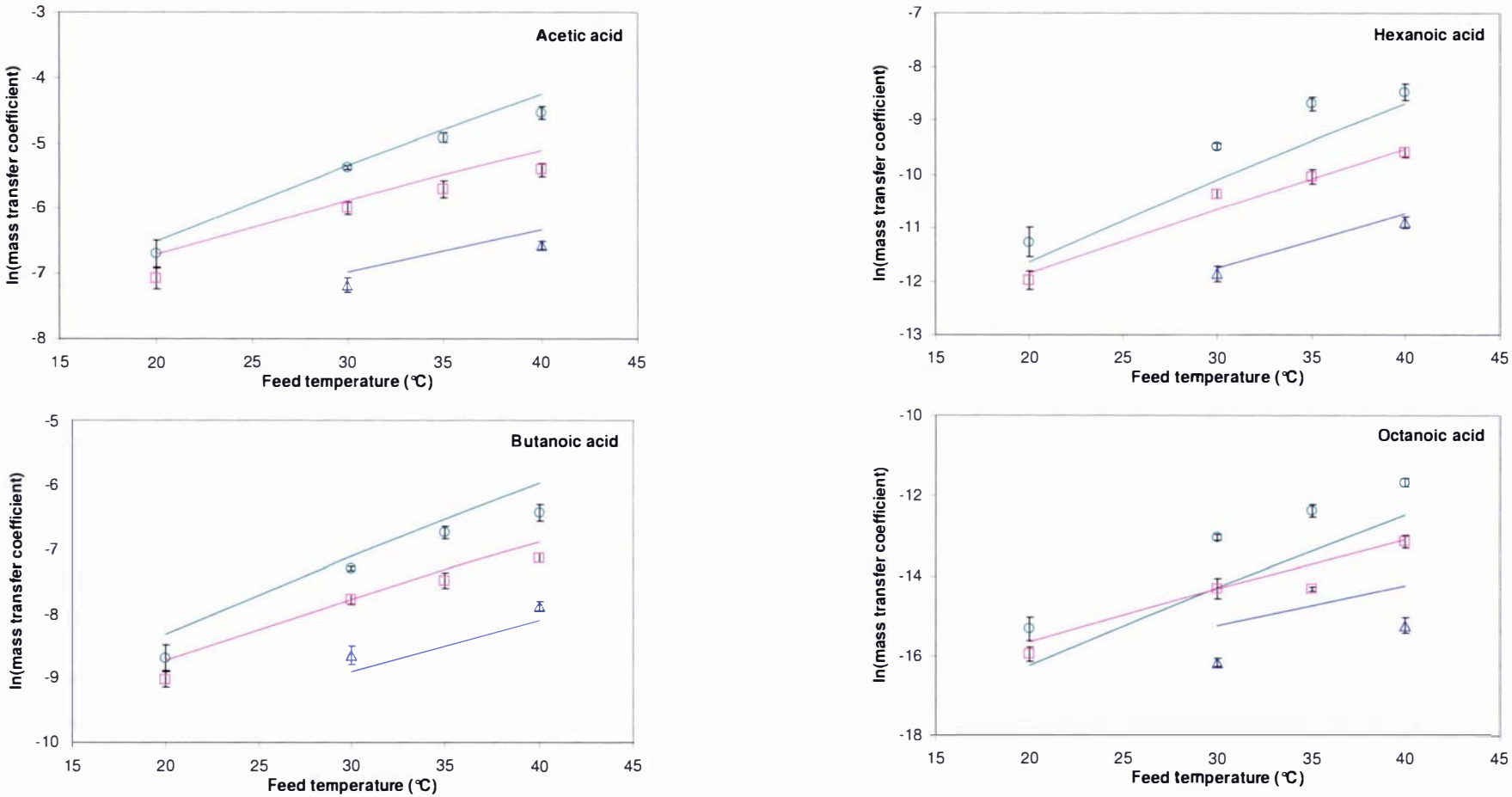


Figure 9-9: Mass transfer coefficients for acids. Symbols are experimental values (mean ± standard error of at least three replicates) and lines show model predictions. Legend: ○ PDMS Type 1; □ PDMS Type 2; Δ POMS.

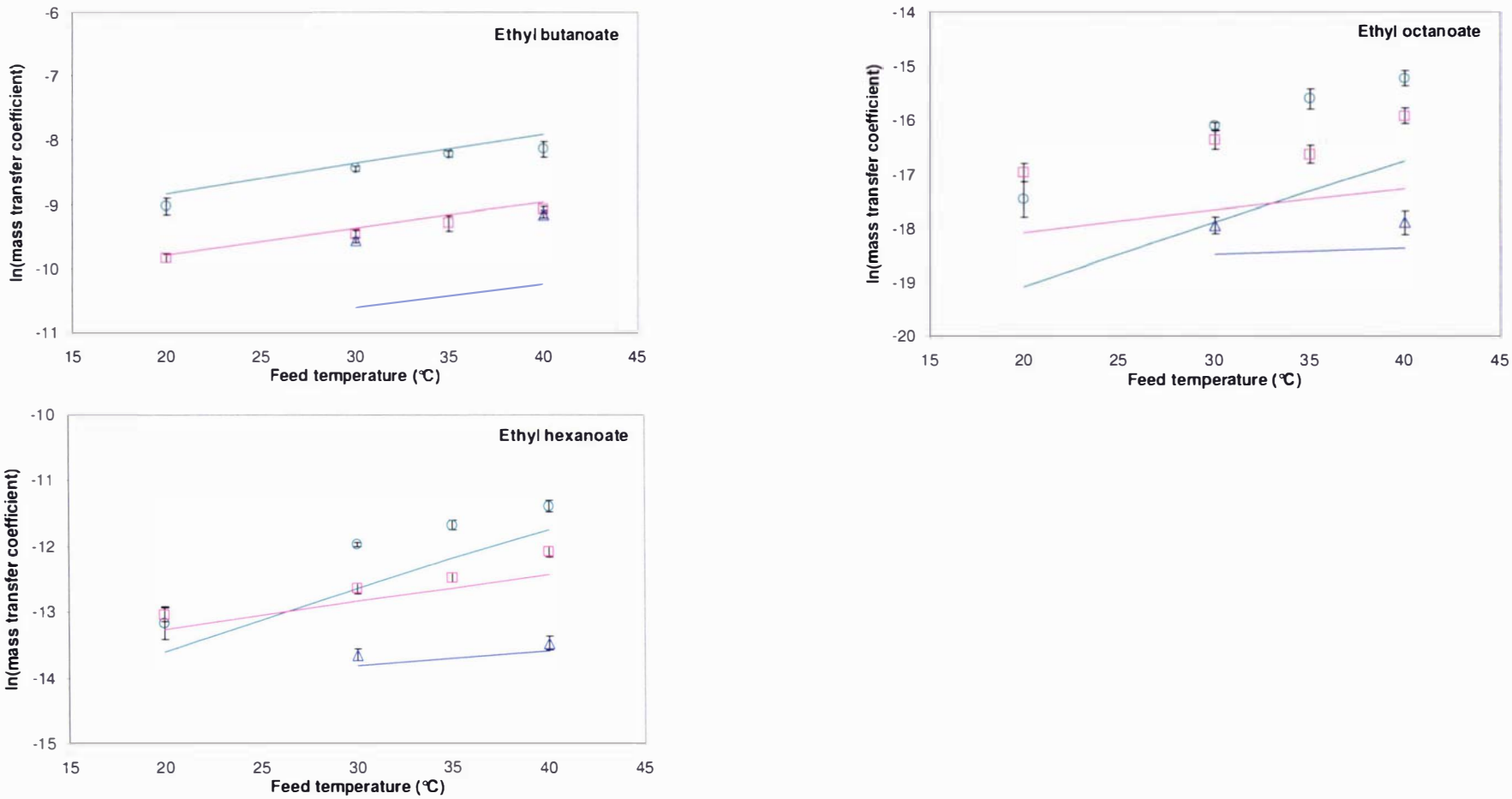


Figure 9-10: Mass transfer coefficients for esters. Symbols are experimental values (mean ± standard error of at least three replicates) and lines show model predictions. Legend: ○ PDMS Type 1; □ PDMS Type 2; Δ POMS.

However, predicted effective mass transfer coefficients were often above or below the experimental values by up to 1.5 logarithmic units. This is due to the difficulty in accurately calculating the pre-exponential factor from the activation energy. The best predictions were for those compounds that had correlation coefficients close to one in Figure 9-5 as well as lying on the best fit line in Figure 9-6 (water, ethyl hexanoate, acetic acid, butanoic acid and hexanoic acid). Ethyl butanoate and 2-heptanone were the only compounds with R^2 less than 0.99 on Figure 9-5; more membranes of different thicknesses would be needed to improve this correlation. Predicted effective mass transfer coefficients were then multiplied by the calculated activity driving force in order to predict fluxes. Predicted fluxes were compared to actual measured fluxes for the total flux (Figure 9-11a) and for all the individual flavour compound fluxes (Figure 9-11b). Figure 9-11 shows that, although there was some scatter, total and individual fluxes were well predicted overall. Therefore, this method could be used to gain an estimate of the flux for flavour compounds with these functional groups.

9.4.5 Extension of model to predict results with different feed mixtures

9.4.5.1 Flavour compound fluxes in fat-containing feed mixture

The procedure in Section 9.4.4 was followed, to predict the flux of each flavour compound in a model solution containing 20% (w/v) fat (Chapter 7). These flux data had not been used in the model development. All model parameters, except the driving force, were assumed to be identical in both fat-containing and fat-free feed mixtures. The driving force was calculated as described in Appendix B, using the available feed concentrations determined in Chapter 7 (for acids, the available undissociated concentrations were used, because approximately 95% of each acid was in the dissociated form in this feed mixture, compared with less than 5% in the standard multicomponent feed). Figure 9-12 shows a good correlation between predicted and measured fluxes for water and esters ($R^2 = 0.95$ and 0.82 respectively), but fluxes were over-predicted for ketones ($R^2 = 0.45$), and poorly predicted for acids ($R^2 = 0.01$). Negative fluxes were predicted for octanoic acid at 20°C and 30°C (-0.0016 μmol m^{-2} s^{-1} and -0.0006 μmol m^{-2} s^{-1} respectively); these negative values could not be shown with the logarithmic scale in Figure 9-12. Corresponding (positive) measured fluxes for octanoic acid were

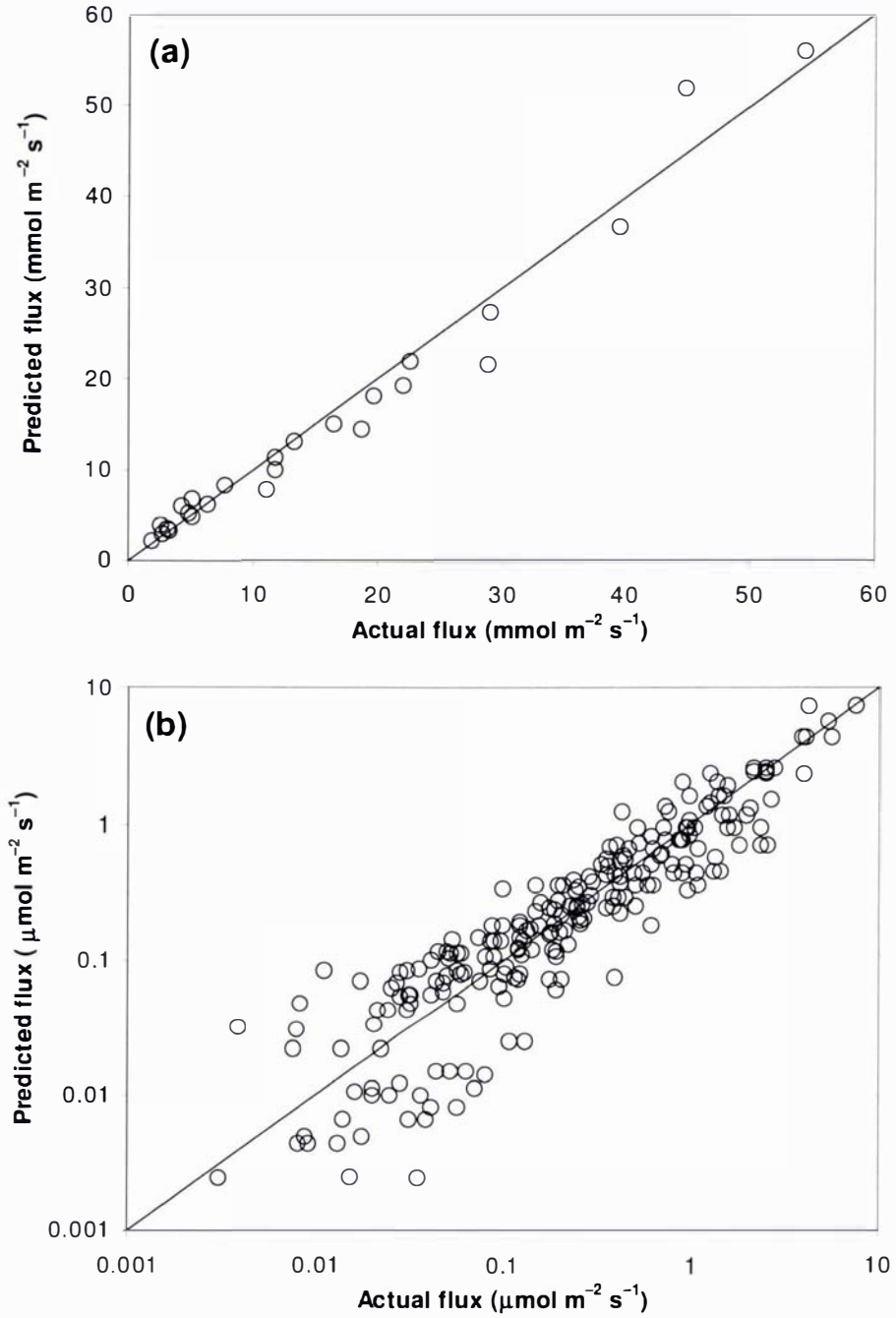


Figure 9-11: Predicted versus experimental fluxes for (a) water (total flux; $R^2 = 0.97$) and (b) flavour compounds ($R^2 = 0.85$). The diagonal line shows an ideal 1:1 relationship between the two.

0.009 ± 0.004 μmol m^{-2} s^{-1} and 0.058 ± 0.029 μmol m^{-2} s^{-1}, at 20°C and 30°C respectively.

As the model was developed using a fat-free feed solution, it was necessary to assume that the fat influenced only the driving forces of flavour compounds, not their effective mass transfer coefficients. Chapter 7 showed that this assumption

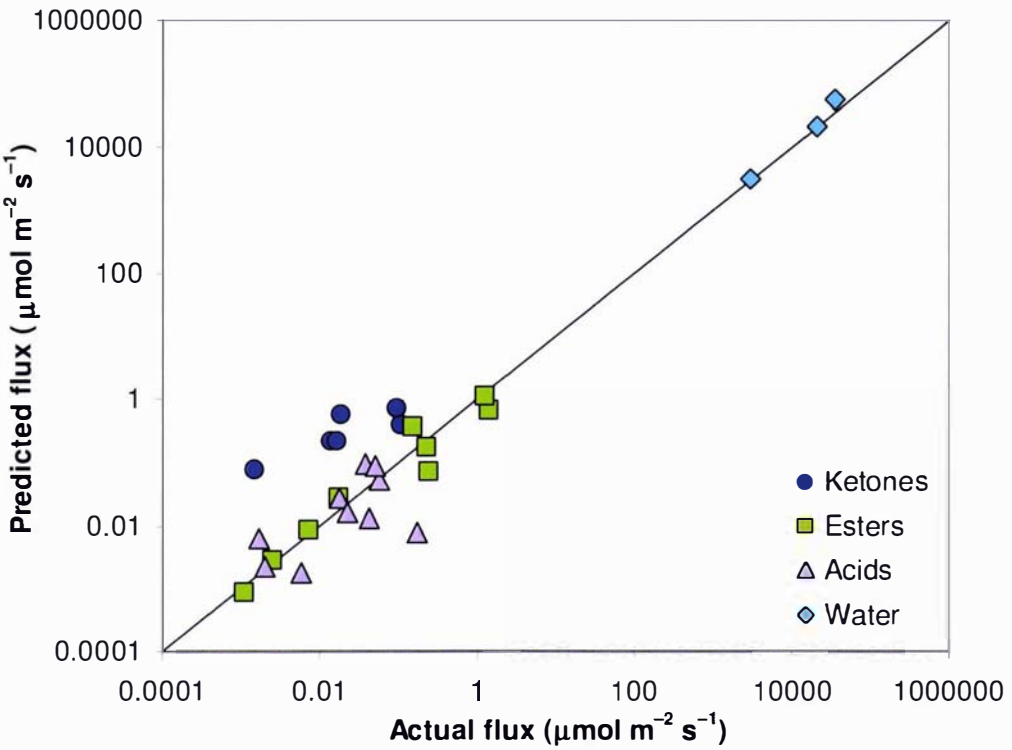


Figure 9-12: Predicted and actual fluxes for flavour compounds and water in a feed solution containing 20% fat. The diagonal line shows an ideal 1:1 relationship between the two. Operating conditions: PDMS Type 1 membrane; 20°C, 30°C or 40°C feed temperature; 2 kPa permeate pressure. Graph excludes negative predicted fluxes for octanoic acid at 20°C and 30°C.

was not always valid, which is one reason for the imperfect agreement between the predicted and measured fluxes in Figure 9-12. As well as possibly decreasing the mass transfer through the feed boundary layer, the added fat would have altered the partitioning of the flavour compounds between the feed and the membrane (sorption). The heat of sorption is one contributor to the activation energy (Equation (9-9)), which is an essential part of the model.

For the feed solution with 20% fat, fluxes were measured at three temperatures (Chapter 7). The effective mass transfer coefficients were calculated at each temperature, and activation energies of permeation were determined in the same way as in Section 9.4.1. These are shown in Table 9-2, along with the corresponding activation energies using the standard multicomponent feed (taken from Figure 9-2). For most compounds, the activation energies were statistically similar for both feed solutions. However, this similarity is mainly due to the large

Table 9-2: Activation energies of permeation (mean ± standard error) for flavour compounds and water, in feed solutions with and without fat. Membrane: PDMS Type 1.

Compound	Molecular weight ($g\ mol^{-1}$)	Activation energy ($kJ\ mol^{-1}$)	
		Standard multicomponent feed	Model feed mixture with 20% fat
Water	18.0	47 ± 1	33 ± 10
2-Heptanone	114.2	38 ± 5	66 ± 45
2-Nonanone	142.2	74 ± 9	96 ± 46
Ethyl butanoate	116.2	36 ± 5	74 ± 49
Ethyl hexanoate	144.2	70 ± 8	99 ± 57
Ethyl octanoate	172.3	87 ± 11	74 ± 7
Acetic acid	60.1	84 ± 7	83 ± 36
Butanoic acid	88.1	89 ± 7	116 ± 31
Hexanoic acid	116.2	112 ± 10	123 ± 31
Octanoic acid	144.2	142 ± 10	108 ± 10

standard errors in the fat-containing model feed mixture, because the activation energy for this feed mixture was calculated from comparatively few data points (nine data points spread across three temperatures, compared with 35 data points and four temperatures for the standard multicomponent feed).

For most of the low molecular weight flavour compounds, the fat-containing feed mixture had greater activation energies than the standard multicomponent feed, although the difference was generally not significant. This trend can be explained in terms of the two terms making up the total activation energy (Equation (9-7)). In Section 9.4.2, it was shown that the heat of sorption was the main contributor to the activation energy for compounds with molecular weights lower than $120\ g\ mol^{-1}$, whereas the activation energy of diffusion was relatively more important for larger compounds. Added fat is not expected to affect the activation energy of diffusion, as it is assumed not to penetrate into the membrane.

The heat of sorption is a measure of the ease with which permeants pass from the feed solution into the membrane. Adding fat makes the feed solution more hydrophobic, so that hydrophobic permeants are more attracted to the feed and do not pass into the membrane as easily. Hence, for hydrophobic permeants, the heat of sorption should be greater when the feed solution contains fat, than with an aqueous feed solution. For sorption-controlled compounds (those with molecular weights lower than $120\ g\ mol^{-1}$), this should lead to the activation energy being

higher in a fat-containing feed solution. Table 9-2 shows that this was true for all compounds with molecular weights less than 120 g mol^{-1}, apart from acetic acid (for which the activation energies were almost identical in both feed solutions) and water. Acetic acid and water are both hydrophilic, which means that they should be less attracted to a fat-containing feed than an aqueous feed. Hence, their overall energy requirement to pass from the feed into the membrane was lower with a fat-containing feed than with an aqueous feed.

For compounds larger than the critical molecular weight of 120 g mol^{-1}, the heat of sorption was not the main contributor to the activation energy; therefore, the addition of fat should not have had a strong influence on the activation energy. Two of these compounds (2-nonanone and ethyl hexanoate) had greater activation energies when fat was added, and the other two (ethyl octanoate and octanoic acid) had lower activation energies (Table 9-2).

9.4.5.2 Diacetyl flux in starter distillate

In Section 9.4.5.1 above, the model was applied to the same nine flavour compounds from which it was developed, in a different feed solution. In this section, the model is applied to a different flavour compound: diacetyl. The fluxes of diacetyl and water, with a feed of starter distillate, were modelled and compared to the measured data in Chapter 8.

In contrast to the flavour compounds in the previous section, the activation energy for diacetyl was unknown. Equation (9-9) was therefore used as a starting point. The heat of sorption for diacetyl was calculated from Vankelecom et al.'s (1997) data for the influence of temperature on sorption in PDMS (calculation shown in Appendix I), and its strain function ($f(\varepsilon)$) was estimated as the mean of all $f(\varepsilon)$ values for model solution compounds with molecular weights lower than 120 g mol^{-1}. After determining the activation energy using Equation (9-9), the fluxes were predicted for diacetyl and water in starter distillate, following the procedure described in Section 9.4.4.

Table 9-3 shows that the model predicted the fluxes reasonably well, except for the case of diacetyl at 40°C. For water at 20°C, the flux was also higher than predicted; this can be attributed to plasticisation of the membrane as discussed in Chapter 8. Diacetyl's predicted and experimental fluxes at 20°C were remarkably

Table 9-3: Comparison of experimental and predicted fluxes for starter distillate.

Compound	Feed temperature (°C)	Experimental flux[a] (μmol m^{-2} s^{-1})	Predicted flux (μmol m^{-2} s^{-1})
Diacetyl	20	13.1 ± 0.3	13.5
	40	171 ± 85	20
Water	20	5960 ± 300	3460
	40	57300 ± 4300	59500

[a]Mean ± standard error

close, given that the data for diacetyl were not used at all in the model development.

9.5 Conclusions

Fluxes could be estimated for this pervaporation system, as a function of the elastic modulus of the membrane, experimental values of each compound's heat of sorption and $f(\varepsilon)$, and the empirical relationship between activation energy and pre-exponential factor.

The activation energy of diffusion was only an important contributor to the total apparent activation energy for compounds larger than a certain critical molecular weight. For these compounds, thinner membranes had higher activation energies due to their greater elastic moduli. For smaller compounds, thermodynamic factors, such as the heat of sorption, were more important than the activation energy of diffusion.

Chapter 10

Pervaporation of dairy flavours: Overall discussion, conclusions and recommendations

10.1 Overall discussion: Using pervaporation to concentrate dairy flavours

Some applications of hydrophobic pervaporation have been studied extensively; for example, aroma recovery from fruit juices or juice by-products (reviewed by Pereira et al., 2006), environmental applications (reviewed by Kujawski, 2000; Peng et al., 2003) and product recovery from fermentation systems (reviewed by Vane, 2005). The first two of these applications have now reached industrial scale (Jonquières et al., 2002; Willemsen, 2005).

The current work has focussed on using pervaporation to concentrate flavours in dairy streams, for which the accumulated knowledge has not yet reached the level of the above applications. This study builds on the foundations laid by other researchers; for example, Sibeijn et al. (2004) highlighted the potential of pervaporation for downstream processing of dairy flavour process streams. Earlier, Baudot & Marin (1996) investigated pervaporation for the recovery of some dairy flavour compounds, and discussed its application to real dairy products. Rajagopalan et al. (1994) showed that pervaporation could be used to recover diacetyl (a butter-flavoured compound) either from an aqueous solution, or from a mixture containing lactose or whey permeate. The current study has shown that pervaporation has potential as a method for concentrating or fractionating flavours in dairy process streams. Its effectiveness depends on the flavour compounds being concentrated, the operating conditions, and the characteristics of the feed mixture.

10.1.1 Comparison of dairy flavour compounds with respect to their pervaporation behaviour

When pervaporation is used for flavour concentration, the desired product may be either a flavour concentrate with a similar but stronger flavour than the feed, or a

concentrate with a different flavour character from the feed. The first of these is achieved if all the important flavour compounds in the feed have similar enrichment factors, and the second is achieved by selectively concentrating some of the flavour compounds. In the current study, the enrichment factors of model dairy flavour compounds (homologous series of acids, esters and ketones, in an aqueous solution) varied from less than one to greater than 30, depending on their functional groups and molecular weights (Chapter 5). This finding suggests that if the feed is a dairy flavour stream containing a variety of different flavour compounds, the second of the two goals listed above is the more realistic.

With the three membranes tested, esters and ketones were concentrated more effectively than acids, partly due to their higher vapour pressures resulting in a higher driving force, and partly due to their greater affinity for the hydrophobic membrane compared with the aqueous feed. For the smallest ester and ketone, this was especially true with the POMS membrane, which is more hydrophobic than PDMS (Trifunović & Trägårdh, 2006). Within each homologous series, the enrichment factors and normalised fluxes of smaller acids increased with increasing molecular weight, whereas those of larger compounds (acids, esters and ketones) decreased. The transition between increasing and decreasing flux occurred at approximately 120 g mol^{-1}, depending on the membrane, feed temperature and permeate pressure (Chapter 5). This finding indicated that, in this pervaporation system, the permeation of smaller, more hydrophilic compounds depended mainly on their sorption into the membrane, and the permeation of larger, more hydrophobic compounds was controlled mainly by their diffusion through the membrane.

As the enrichment factors of flavour compounds varied both within and between the three homologous series tested, the permeate from pervaporation of a dairy stream would be expected to have a different flavour profile from the original dairy stream. This observation creates an opportunity to use pervaporation to fractionate a flavour mixture into desirable and undesirable flavours.

10.1.2 Effect of operating conditions on pervaporation of flavour compounds

Three different hydrophobic membranes were tested for pervaporation of the standard multicomponent feed solution, at a range of feed temperatures and permeate pressures (Chapter 5). Although it is generally accepted that pervaporation fluxes increase with increasing feed temperature and decrease with increasing permeate pressure, the magnitude of fluxes was not known for this particular system. Therefore, the objective was to gather baseline data for the flux of each compound at a range of operating conditions.

Pervaporation fluxes are a function of the driving force and the overall mass transfer coefficient (which includes sorption in and diffusion through the membrane, as well as mass transfer in the feed boundary layer). The permeate pressure directly influences the driving force by determining the activity of each permeant compound downstream of the membrane, which is why fluxes decreased with increasing permeate pressure (Chapter 5).

The choice of membrane influences the mass transfer coefficient rather than the driving force. In this study, the total flux with the PDMS Type 1 membrane (0.5 μm) was approximately an order of magnitude greater than that with the POMS membrane (5–6 μm), with the PDMS Type 2 membrane (1.5 μm) in between. Although the fluxes clearly depended on the membrane thickness, the relationship was not inversely proportional, as would be expected if the membranes were identical and all other factors were equal (Spitzen et al., 1988; Baker et al., 1997; Pereira et al., 1998). After normalising for the active layer thickness, the PDMS membranes still achieved higher fluxes than the POMS membrane, due to their different polymeric structures. Of the two PDMS membranes, the thicker membrane achieved 30% greater thickness-normalised fluxes, which suggests that concentration polarisation occurred on the feed side, presenting a mass transfer resistance which was not negligible with the thinner membrane (Chapter 5).

The feed temperature has two main effects on pervaporation: both the driving force and the mass transfer coefficient are greater at higher temperatures. The temperature influences the driving force through its effect on the feed vapour pressure of each permeant compound (Lipnizki et al., 1999). The influence of

temperature on mass transfer was expressed in terms of the Arrhenius activation energy, which differed depending on the flavour compound. For compounds with molecular weights lower than 120 g mol^{-1}, the activation energy was mainly a function of the heat of sorption; for larger compounds, both the heat of sorption and the activation energy of diffusion contributed to the total activation energy (Chapter 9). This finding confirms the interpretation of the results in Chapter 5: that the permeation of small flavour compounds was sorption-controlled and that of larger compounds was diffusion-controlled.

When 20% (w/v) fat was present in the feed mixture, the temperature had a lesser effect on the flux (Chapter 7), but a greater effect on the effective mass transfer coefficients of some flavour compounds (Chapter 9), compared with a fat-free feed. Raising the temperature increased the the affinity of the flavour compounds for the feed mixture, by increasing the hydrophobic interactions between the fat and the flavour compounds (Nongonierma et al., 2006). This meant that with a fat-containing feed mixture, the driving force of each compound did not increase as much with temperature as when the feed solution contained no fat.

The activation energy of permeation for most sorption-controlled flavour compounds was higher when 20% (w/v) fat was present, compared with an aqueous feed (Chapter 9). A greater activation energy means that the temperature had relatively more influence on the effective mass transfer coefficient. It can be assumed that more energy was required for hydrophobic flavour compounds to sorb into the membrane from a fat-containing (more hydrophobic) feed than an aqueous (less hydrophobic) feed, which caused the activation energy to increase for those compounds that were sorption-controlled (small) but still relatively hydrophobic.

Higher temperatures allow a higher flux, but also mean that more energy must be supplied to the process. To optimise the cost-effectiveness, the feed temperature must be chosen to maximise the flux while keeping the energy input at an acceptable level, as well as optimising enrichment factors and ensuring that the product is not thermally damaged. Practically, the findings discussed above mean that less of a flux advantage is gained by raising the temperature, if the feed contains fat. Therefore, the most cost-effective feed temperature may be lower for fat-containing feed streams.

10.1.3 Influence of the feed mixture on pervaporation of flavour compounds

The characteristics of the feed mixture proved to be very important in determining the effectiveness of pervaporation for concentrating flavours. As different dairy products and process streams have widely varying compositions, some would be better candidates than others for further processing with pervaporation. Several aspects of the feed mixture were studied: the pH, the volatile composition, and the presence of non-volatile dairy components.

The permeation of acids through the membrane could be manipulated by altering the pH of the feed (Chapter 5). This result provides a simple way of controlling whether the acids in a flavour mixture will pass through the membrane, provided that the pH is kept within a range that will not cause denaturation of any proteins in the feed mixture. In situations where acid flavours are desired in the permeate, the feed pH should be kept low; conversely, if acids are undesirable, the feed pH should be close to neutral (depending on the pK_a values of the particular acids in the feed). It has previously been found that the feed pH determined the affinity of an acid for a hydrophobic membrane material (Ikegami et al., 2005), but manipulation of the feed pH has not been used before as a way to control the permeate composition in flavour pervaporation.

Fluxes sometimes differed between feed solutions with different volatile compositions, due to coupling interactions between the flavour compounds (Chapter 6). Coupling between flavour compounds was difficult to predict, but it had either a neutral or negative effect on fluxes in most cases. It appears that coupling mainly occurred as a result of competition between compounds from different functional groups, and that the extent of this coupling depended on the total concentration of compounds from different functional groups. Coupling seemed to affect the water flux as well as the flavour compound fluxes; most flavour compounds caused the water flux to be lower in a binary or multicomponent feed solution than with a pure water feed. In contrast, it appeared that ethyl butanoate and octanoic acid increased the mass transfer of water when they were present in a binary feed solution, but not in a multicomponent feed. Further experiments with different combinations of flavour compounds, at

different concentrations, would be needed to fully explain these complex coupling effects.

Many dairy flavour ingredients are produced via fermentation, for which ethanol is a common by-product. The effect of ethanol on the pervaporation of some alcohols, aldehydes and esters has been investigated previously (Beaumelle et al., 1992; Karlsson & Trägårdh, 1994; Tan et al., 2005). The current study adds more flavour compounds (acids and ketones) to the existing body of literature. When ethanol was added to the feed at a typical concentration for a fermented dairy product (5% v/v), it increased the fluxes of four of the flavour compounds tested (by up to 59%), but did not affect the water flux or the fluxes of the other five flavour compounds. The increase in permeability caused by ethanol addition compensated for any reduction of the driving forces in the presence of ethanol, so that the net effect on flux was positive or neutral (Chapter 6). Ethanol permeated through the membrane more easily than water, so it diluted the flavour compound concentrations in the permeate. Therefore, if pervaporation is used to concentrate flavours in an ethanol-containing dairy fermentation, the resulting permeate flavour may be weaker than if ethanol was not present, even though the fluxes of some compounds may be higher.

As well as volatile compounds, dairy flavour products generally contain fat, protein and lactose. In this study, these non-volatile components affected the pervaporation of esters and ketones through their interactions in the feed, whereas they affected the pervaporation of acids through their influence on the feed pH (Chapter 7).

When either milk protein or lactose was present in the feed mixture, these non-volatile components bound the esters and ketones as well as octanoic acid, but the three smaller acids were not observed to bind to the protein or lactose. This binding would have decreased the sorption of esters and ketones into the membrane. Therefore, milk protein isolate (4% w/v) or lactose (6% or 12% w/v) decreased the fluxes, and hence the enrichment factors, of sorption-limited (short-chain) esters and ketones, but did not affect diffusion-limited (longer-chain) compounds (Chapter 7).

In feed mixtures that contained fat, the flavour compounds partitioned between the fat and water phases. This reduced the driving forces of esters and ketones, which caused their fluxes and enrichment factors to decrease as the fat level in the feed was increased from 0% to 38% (w/v).

When 20% fat (w/v) was added to the feed together with either 4% (w/v) milk protein isolate or 6% (w/v) lactose, it appeared that a larger number of compounds became sorption-controlled instead of diffusion-controlled. This is plausible because the fat-containing feed mixture would have been more favourable to the hydrophobic flavour compounds than an aqueous feed solution, thereby lowering the sorption coefficient between the membrane and the feed. Therefore, when fat was present, protein or lactose reduced the permeation of esters and ketones with molecular weights less than approximately 150 g mol^{-1}, compared with approximately 120 g mol^{-1} in the absence of fat (Chapter 7).

In contrast to esters and ketones, the non-volatile dairy components generally did not reduce the vapour pressures of acids in the feed. However, the added fat and protein, and to a lesser extent lactose, caused the feed to become less acidic. As previously discussed, increasing the feed pH led to the acids having lower fluxes and enrichment factors.

The influence of the feed mixture means that potential feed streams must be chosen very carefully. Ideally, feed mixtures should not contain any low-volatility compounds that may reduce the membrane performance over time (Chapter 4). For applications in which the aim is to achieve high permeate concentrations of all flavour compounds, the negative effects of feed components on flavour compound enrichment factors should be minimised. High-fat process streams are not recommended for pervaporation, unless the fat could be removed upstream of the membrane without removing the flavour compounds. Feed streams containing protein or lactose would be appropriate if the permeation of the most important flavour compounds was diffusion-limited. In other words, the key flavour compounds should have relatively high molecular weights, in order for their permeation to be unaffected by protein or lactose.

For other applications, where the aim is to fractionate a mixture of flavours, there is an opportunity to deliberately manipulate the feed characteristics, in order to

control which feed components pass through the membrane. For example, permeation of acids could be minimised by raising the pH of the feed solution (Chapter 5). If relatively more diffusion-controlled (larger) flavour compounds were desired in the permeate compared with sorption-controlled compounds, a substance that binds flavour compounds, such as lactose or protein, could be added to the feed (Chapter 7). However, the economic feasibility of this practice would need to be determined.

10.1.4 Application to real dairy process streams

To investigate actual pervaporation applications relevant to the flavours sector of the dairy industry, studies were carried out with either starter distillate or ester cream as the feed (Chapter 8).

Starter distillate, as produced, contains a lower level of diacetyl than is desired for use as a flavour ingredient in some applications. Using pervaporation, it was possible to concentrate the diacetyl in starter distillate from 2200 ppm to 20 500 ppm. However, a large amount of starter distillate would be needed to produce a relatively small amount of permeate, so the economic benefits of this alternative process should be weighed against its costs before it is developed further.

Pervaporation was useful for partially fractionating the flavours in ester cream, but did not concentrate the flavours to any great degree. Compared with the feed, the permeate contained relatively more short-chain esters, which have desirable fruity flavours, and relatively less long-chain esters and acids, which have soapy, waxy or metallic characteristics. However, ester cream was not an ideal feed stream because it contained 20% fat, which meant that most flavour compounds permeated poorly through the membrane and were not enriched using pervaporation. The results were not consistent between runs, because the ester cream feed did not remain homogeneous.

Many of the results with starter distillate or ester cream could be estimated based on the results obtained with model feed mixtures. The enrichment factors of five flavour compounds in ester cream (acids and esters) were close to their enrichment factors in a model feed mixture containing the same amount of fat. In

starter distillate, esters and ketones had greater enrichment factors than acids, which is the same trend as found with model solutions. However, the real dairy products were more complex than the model feed mixtures, in terms of both the mixture composition and the distribution of components throughout the mixture. These complexities influenced some of the results. Within each homologous series, the trend of enrichment factors increasing or decreasing with molecular weight sometimes differed between starter distillate and model solutions; the difference may be caused by interactions between the many volatile compounds in starter distillate. The total flux of starter distillate was double that of a model feed solution at 20°C, possibly because the high concentration of diacetyl promoted membrane plasticisation. The total flux of ester cream was also greater than that of a model solution containing the same amount of fat, because with ester cream the fat was not evenly distributed throughout the feed. These findings emphasise the importance of the feed composition in determining the pervaporation performance.

10.1.5 Prediction of pervaporation fluxes

It is advantageous to be able to predict the relative effects of temperature on the different flavour compounds in the feed. If the feed contains compounds with very different activation energies, altering the temperature will alter the composition of the permeate. In this case, the permeate composition could potentially be manipulated by changing the operating conditions.

An empirical model was developed to estimate the activation energies and pre-exponential factors, and thus the effective mass transfer coefficients, for pervaporation of flavour compounds (Chapter 9). Models that had originally been developed for the diffusion of gases in polymers, relating the activation energy to the polymer's elastic modulus and to the pre-exponential factor (Pönitsch & Kirchheim, 1996; Liu & Guo, 2001), were combined with a pervaporation model relating the total activation energy to the heat of sorption and the activation energy for diffusion (Feng & Huang, 1996). The activation energy for permeation of each flavour compound was thus a function of its heat of sorption in the membrane and the elastic modulus of the membrane. The empirical constant in this relationship depended on the strain encountered during diffusion, and it

differed for each flavour compound. This constant was close to zero for sorption-controlled compounds.

In order to determine the effective mass transfer coefficient of a particular compound at a particular temperature, two Arrhenius parameters were required: the activation energy and the pre-exponential factor. These two parameters were related through an empirical equation based on the compensation effect. One of the empirical constants in this equation was related to the molecular weight of the flavour compound. The diffusion of small molecules in polymers is known to follow the compensation effect (Barrer & Skirrow, 1948; Kwei & Arnheim, 1962; Prabhakar et al., 2005; Zheng et al., 2007). However, this is the first time that the compensation effect has been reported for pervaporation. Using the compensation effect gives this model the advantage that the pre-exponential factor does not need to be modelled separately from the activation energy.

The resulting correlations could be used to predict the fluxes of flavour compounds, based on the operating conditions, the permeant properties and the elastic modulus of the membrane. Although the model is empirical and hence applies only to this particular pervaporation system, it is expected that similar models could be developed for other pervaporation systems, by changing the empirical constants.

10.2 Conclusions

Pervaporation could be used to concentrate and fractionate dairy flavours in certain feed mixtures. Of the flavour compounds tested, esters and ketones, especially those with low molecular weights, were concentrated to a greater degree than acids. In the pervaporation system tested, the mass transfer was dominated by sorption for flavour compounds with molecular weights lower than approximately 120 g mol^{-1}, and dominated by diffusion for larger compounds.

Fluxes could be estimated through empirical correlations, which depended on the operating conditions and the properties of the flavour compound and membrane. A high feed temperature and a low permeate pressure led to the greatest fluxes. Of the three membranes tested, the highest fluxes were achieved with PDMS Type 1. The effect of the operating conditions on the enrichment factors was dependent on

the flavour compound: acids had the highest enrichment factors at high-flux conditions, sorption-limited esters and ketones had the highest enrichment factors at low-flux conditions, and the enrichment factors of diffusion-limited esters and ketones did not appear to depend on the operating conditions.

The feed characteristics (its pH, and the mixture of permeants and non-volatile substances) had a major impact on the pervaporation of flavour compounds. The enrichment factor of each flavour compound was strongly influenced by whether it was in a simple model solution or a more complex feed mixture. Milk fat, milk protein and lactose all reduced the permeation of at least some flavour compounds. Therefore, in applying pervaporation to dairy products, it is important to understand how each flavour compound will interact with the feed mixture.

Of the two real dairy products tested, the flavours in starter distillate could be concentrated more effectively than those in ester cream.

10.3 Recommendations for future research

The decline of membrane performance over time needs to be addressed, to reduce the frequency at which membranes need to be replaced. Firstly, which compounds caused the flux decline should be confirmed, by measuring the rate of flux decline with single-component feed solutions. The design of the pervaporation unit (including the membrane) should be improved, to prevent condensation of these compounds in the membrane.

Future research could focus on manipulating the feed characteristics with the objective of obtaining the desired permeate composition. This would involve defining the ideal flavour composition of the permeate, and then altering the feed pH or adding non-permeating components in order to enhance or hinder the permeation of each flavour compound.

A more extensive study of coupling effects between a range of flavour compounds could be another avenue for future research. In order to attain a better understanding of the coupling mechanism, the sorption and diffusion coefficients of flavour compounds should be compared for various mixtures of compounds

with the same functional group or different functional groups, at a range of concentrations.

Research to refine and validate the empirical model in Chapter 9 is also recommended. For example, work could focus on independently verifying each of the model parameters (heats of sorption, $f(\varepsilon)$ and membrane elastic modulus). The model also needs to be validated using independently generated data sets with different membranes and flavour compounds.

In this study, the permeate was analysed in terms of the flavour compound concentrations. Commercially, the next step would be to determine the usefulness of pervaporation permeate as a flavouring ingredient. This would involve first choosing appropriate process streams for the feed, taking into account the feed characteristics as discussed earlier, as well as the cost-effectiveness. A sensory panel should assess the permeate, to ensure that it had an acceptable flavour. Trials should also be carried out using the permeate as an ingredient in a potential product. It is recommended that these further trials be carried out using a pilot-scale pervaporation unit, which would enable adequate amounts of permeate to be collected in a shorter time than with a laboratory-scale unit, as well as allowing any problems with upscaling to be resolved before proceeding to industrial scale. Pilot-scale trials should be carried out as a continuous rather than batch process, to reflect the likely industrial-scale process.

Pervaporation is not recommended as a method to concentrate flavours in high-fat dairy process streams, such as ester cream. Low-fat process streams, such as starter distillate, are more promising. The process should be analysed from an economic point of view, comparing it with other flavour concentration techniques, before a decision can be made on whether to adopt pervaporation as a method for flavour concentration in the dairy industry.

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Appendix A

Extraction efficiencies of flavour compounds

The apparent extraction efficiency of each flavour compound is a measure of how well it could be extracted for GC analysis, compared with the internal standard (propyl butanoate). Samples of known composition were extracted, and the apparent concentration of each flavour compound was determined using GC (internal standard method). The apparent extraction efficiency for each compound was defined as the ratio between its known concentration in the sample and its apparent concentration. Those compounds with apparent extraction efficiencies greater than one were extracted more easily than propyl butanoate.

The extraction efficiencies of flavour compounds in aqueous solutions, using direct extraction with diethyl ether, are given in Table A-1 (compounds in the standard multicomponent feed) and Table A-2 (extra flavour compounds).

Table A-1: Apparent extraction efficiencies of flavour compounds in the standard multicomponent feed.

Compound	Apparent extraction efficiency
2-Heptanone	0.85
2-Nonanone	0.89
Ethyl butanoate	0.99
Ethyl hexanoate	1.16
Ethyl octanoate	1.32
Acetic acid	0.95
Butanoic acid	0.49
Hexanoic acid	0.41
Octanoic acid	0.33

Table A-2: Apparent extraction efficiencies of flavour compounds additional to those in the standard multicomponent feed.

Compound	Apparent extraction efficiency
Ethyl decanoate	1.47
Propanoic acid	0.47
Pentanoic acid	0.44
Heptanoic acid	0.43

Table A-3 gives the apparent extraction efficiencies using an SPE extraction method (for samples that contained non-volatile substances).

Table A-3: Apparent extraction efficiencies of flavour compounds with an SPE extraction method, for mixtures with various levels of fat.

Compound	Apparent extraction efficiency				
	No fat	5% fat	10% fat	20% fat	38% fat
2-Heptanone	2.01	1.57	2.18	2.36	0.90
2-Nonanone	3.56	1.57	2.15	2.11	1.07
Ethyl butanoate	3.30	2.50	3.05	4.07	1.12
Ethyl hexanoate	4.01	2.08	3.05	3.86	1.15
Ethyl octanoate	1.71	1.27	1.91	2.18	0.90
Acetic acid	1.46	1.54	1.62	2.04	1.09
Butanoic acid	1.87	2.05	2.23	3.26	1.10
Hexanoic acid	2.50	2.23	2.68	3.36	1.10
Octanoic acid	3.09	1.60	2.30	2.80	0.66

Appendix B

Calculation of driving forces and effective mass transfer coefficients

This appendix describes the calculations involved in determining the effective mass transfer coefficients of flavour compounds. The example calculations shown throughout are for acetic acid, with the PDMS Type 1 membrane, a feed temperature of 30°C and a permeate pressure of 1.5 kPa. Data for the other flavour compounds and operating conditions are shown at the end in Table B-1.

The effective mass transfer coefficient is defined as the proportionality constant between the flux and the driving force:

$$J_i = k_{i,ov}(a_{i,f} - a_{i,p}) \qquad \textbf{(B-1)}$$

where J_i is the flux of compound i, $k_{i,ov}$ is the overall effective mass transfer coefficient of compound i, and $a_{i,f}$ and $a_{i,p}$ are the activities of compound i on the feed and permeate sides of the membrane respectively. The driving force is given by the term inside the brackets.

B.1 Feed activity

The activity of compound i on the feed side of the membrane is the product of its mole fraction in the feed ($x_{i,f}$) and its activity coefficient ($\gamma_{i,f}$):

$$a_{i,f} = x_{i,f}\gamma_{i,f} \qquad \textbf{(B-2)}$$

B.1.1 Mole fraction in feed

For aqueous model solutions, the molar concentration of each flavour compound was negligible compared to the molar concentration of water (55.56 mol L^{-1}). Known molar concentrations of flavour compounds were therefore converted to mole fractions by dividing by the molar concentration of water:

$$x_{i,f} = \frac{c_{i,f}}{c_{w,f}} \quad \textbf{(B-3)}$$

where $c_{i,f}$ and $c_{w,f}$ are the feed concentrations (mol L^{-1}) of permeant compound i and water respectively.

Example

In the standard multicomponent feed solution, the concentration of acetic acid was 1.75×10^{-3} mol L^{-1} (104.9 mg L^{-1}).

$$x_{i,f} = \frac{1.75 \times 10^{-3} \text{ mol L}^{-1}}{55.56 \text{ mol L}^{-1}}$$
$$x_{i,f} = 3.15 \times 10^{-5}$$

For feed solutions that contained fat, $x_{i,f}$ was the available mole fraction in the feed solution (the portion not associated with fat). For acids, only the portion in the undissociated form was counted.

$$x_{i,f} = \frac{c_{i,f(avail)}}{c_{fat,f} + c_{w,f}} \quad \textbf{(B-4)}$$

where $c_{i,f(avail)}$ is the available molar concentration of compound i (calculated from partitioning experiments), $c_{w,f}$ is the molar concentration of water in the feed mixture, and $c_{fat,f}$ is the molar concentration of fat in the feed mixture (the average molecular weight of milk fat triglycerides was calculated as approximately 715 g mol^{-1}, using data from Swaisgood (1996) for the distribution of fatty acids in milk fat).

Example

The feed mixture with 20% fat (200 g fat per litre of feed mixture) had a pH of 6.1. The pK_a of acetic acid is 4.75 (James & Lord, 1992). The densities of milk fat

and water are approximately 918 g L^{-1} and 998 g L^{-1} respectively (Walstra et al., 2006).

$$c_{fat,f} = \frac{200\ \text{g L}^{-1}}{715\ \text{g mol}^{-1}}$$

$$= 0.28\ \text{mol L}^{-1}$$

$$\text{Volume of fat in 1 L feed} = \frac{200\ \text{g}}{918\ \text{g L}^{-1}}$$

$$= 0.218\ \text{L}$$

$$\text{Volume of water in 1 L feed} = 1\ \text{L} - 0.218\ \text{L}$$

$$= 0.782\ \text{L}$$

$$\text{Mass of water in 1 L feed} = 0.782\ \text{L} \times 998\ \text{g L}^{-1}$$

$$= 780.4\ \text{g}$$

$$c_{w,f} = \frac{780.4\ \text{g L}^{-1}}{18.02\ \text{g mol}^{-1}}$$

$$= 43.3\ \text{mol L}^{-1}$$

When the fat and water phases were separated by centrifuging, the average concentration of acetic acid in the water phase was 101.3 mg L^{-1} (1.69×10^{-3} mol L^{-1}).

$c_{i,f(avail)}$ = concentration in water phase × volume fraction of water in feed

$$= 1.69 \times 10^{-3}\ \text{mol L}^{-1} \times 0.782\ \text{L L}^{-1}$$

$$= 1.32 \times 10^{-3}\ \text{mol L}^{-1}$$

[HA] = Available undissociated concentration

$$= 1.32 \times 10^{-3}\ \text{mol L}^{-1} - [\text{A}^-]$$

Henderson-Hasselbach equation:

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(\text{pH}-\text{pK}_a)}$$

$$\frac{1.32\times10^{-3}\ \text{mol L}^{-1} - [\text{HA}]}{[\text{HA}]} = 10^{(6.1-4.75)}$$

$$[\text{HA}] = 5.6\times10^{-5}\ \text{mol L}^{-1}$$

$$= c_{i,f(avail)}\ \text{(undissociated form)}$$

$$x_{i,f} = \frac{5.6\times10^{-5}\ \text{mol L}^{-1}}{0.28\ \text{mol L}^{-1} + 43.3\ \text{mol L}^{-1}}$$

$$= 1.28\times10^{-6}$$

B.1.2 Activity coefficient in feed

The activity coefficients of flavour compounds in the feed solution were assumed equal to their activity coefficients at infinite dilution. For ethyl butanoate, experimental infinite dilution activity coefficients were taken from Carelli et al. (1991). For all the other compounds, the infinite dilution activity coefficients were calculated from correlations at specific temperatures (Poling et al., 2001):

Acids: $$\log\gamma_i^{\infty} = \omega + \in N_i + \frac{\zeta}{N_i} + \frac{\theta}{N_w} \quad \textbf{(B-5)}$$

Esters and ketones: $$\log\gamma_i^{\infty} = \omega + \in N_i + \zeta\left(\frac{1}{N_i'} + \frac{1}{N_i''}\right) + \lambda(N_i - N_w)^2 \quad \textbf{(B-6)}$$

where ω, $\in$, ζ, θ and λ are empirical constants which depend on the temperature and the homologous series, N is the total number of carbon atoms, N' and N'' are the number of carbon atoms in respective branches of branched compounds, and the subscripts i and w refer to the flavour compound and water respectively.

Activity coefficients at each required temperature were interpolated from these literature data, except for ethyl hexanoate and ethyl octanoate, because constants to calculate the activity coefficients of these compounds were only given at 20°C in Poling et al. (2001). However, Carelli et al. (1991) showed that the activity coefficient for ethyl butanoate varied by only 10% over the temperature range of 25–65°C, so 20°C values from Poling et al. (2001) were assumed to give a satisfactory estimate for the activity coefficients of ethyl hexanoate and ethyl

octanoate between 20°C and 40°C. Poling et al. (2001) state that the variation of activity coefficients with temperature is usually much smaller than the variation of saturated vapour pressure, and therefore it is acceptable to disregard the temperature dependence of the activity coefficient in calculations of this type. This assumption was also applied to pervaporation by Olsson & Trägårdh (1999).

Example

For *n*-acids at infinite dilution in water, Poling et al. (2001) lists constants for Equation (B-5) at three temperatures:

	25°C	50°C	100°C
ω	−1.00	−0.80	−0.62
$\in$	0.622	0.590	0.517
ζ	0.490	0.290	0.140
θ	0	0	0

Substituting these constants in Equation (B-5), γ_i^∞ for acetic acid ($N_i = 2$) is 3.08, 3.35 and 3.05 at 25°C, 50°C and 100°C respectively. A plot of $\log(\gamma_i^\infty)$ against absolute temperature fits the polynomial equation:

$$\log \gamma_i^\infty = -3.01\times10^{-5}T^2 + 2.02\times10^{-2}T - 2.84$$

Therefore, at 30°C (303 K), $\gamma_i^\infty = 3.16$ for acetic acid.

B.2 Permeate activity

The activity of each compound in the permeate is the ratio of its partial pressure on the permeate side of the membrane ($p_{i,p}$) to its saturated vapour pressure (p_i^0):

$$a_{i,p} = \frac{p_{i,p}}{p_i^0} \qquad \textbf{(B-7)}$$

B.2.1 Partial pressure in permeate

The partial pressure of each compound on the permeate side of the membrane is the product of its mole fraction ($x_{i,p}$) and the total permeate pressure (p_T):

$$p_{i,p} = x_{i,p} p_T \quad \textbf{(B-8)}$$

Mole fractions were calculated using Equation (B-9), assuming that the total number of moles in the permeate was negligibly different from the number of moles of water.

$$x_{i,p} = \frac{c_{i,p}}{c_{w,p}} \quad \textbf{(B-9)}$$

where $c_{i,p}$ and $c_{w,p}$ are the permeate concentrations (mol L^{-1}) of permeant compound *i* and water respectively.

Example

Using the PDMS Type 1 membrane, with a feed temperature of 30°C and a permeate pressure of 1.5 kPa, the average permeate concentration of acetic acid was 51.5 mg L^{-1} (8.6×10^{-4} mol L^{-1}).

$$x_{i,p} = \frac{8.6 \times 10^{-4} \text{ mol L}^{-1}}{55.56 \text{ mol L}^{-1}}$$

$$= 1.55 \times 10^{-5}$$

$$p_{i,p} = 1.55 \times 10^{-5} \times 1500 \text{ Pa}$$

$$= 0.023 \text{ Pa}$$

B.2.2 Saturated vapour pressure

Saturated vapour pressures of water, esters and ketones were interpolated from literature data (Borgnakke & Sonntag, 1997; Speight, 2003; Lide, 2005), and interpolated over the temperature range of interest (20–40°C). Vapour pressures

of acids were estimated using the Wagner equation (Equation (B-10)), using constants tabulated in Poling et al. (2001).

$$\ln p_i^0 = \ln p_c + \left(\frac{T_c}{T}\right)\left(a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5\right) \quad \textbf{(B-10)}$$

In Equation (B-10), p_i^0 is the vapour pressure in bars; p_c is the critical pressure in bars; T is the feed temperature; T_c is the critical temperature; a, b, c and d are empirical constants and τ is given by the equation:

$$\tau = 1 - \frac{T}{T_c} \quad \textbf{(B-11)}$$

Example

For acetic acid at 30°C (303 K), using values of p_c, T_c, a, b, c and d from Poling et al. (2001):

$$\tau = 1 - \frac{303.15\,\text{K}}{592.71\,\text{K}}$$

$$= 0.489$$

$$\ln p_i^0 = \ln(57.86) + \left(\frac{592.71}{303.15}\right)\left(-8.294 \times 0.489 + 0.979 \times 0.489^{1.5} - 0.217 \times 0.489^{2.5} - 5.724 \times 0.489^5\right)$$

$$= -3.59$$

$$p_i^0 = 0.028 \text{ bar}$$

$$= 2.8 \text{ kPa}$$

B.3 Effective mass transfer coefficients

Rearranging Equation (B-1) and substituting in Equations (B-2) and (B-7) leads to an expression for the overall effective mass transfer coefficient of compound *i*:

$$k_{i,ov} = \frac{J_i}{x_{i,f}\gamma_{i,f} - \frac{x_{i,p}p_T}{p_i^0}} \quad \textbf{(B-12)}$$

This equation was used to calculate the overall effective mass transfer coefficient for each flavour compound at each set of operating conditions.

Example

With the PDMS Type 1 membrane, a feed temperature of 30°C, and a permeate pressure of 1.5 kPa, the mean flux of acetic acid was 5.3×10^{-7} mol m^{-2} s^{-1}.

$$k_{i,ov} = \frac{5.3\times10^{-7}\ \text{mol m}^{-2}\ \text{s}^{-1}}{3.15\times10^{-5}\times3.16 - \dfrac{0.023\ \text{Pa}}{2800\ \text{Pa}}}$$

$$= 5.8 \times 10^{-3}\ \text{mol m}^{-2}\ \text{s}^{-1}$$

Table B-1: Activities and effective mass transfer coefficients of permeant compounds under various operating conditions.

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Water	20	0.9	PDMS Type 1	1000000	1.00	1.00	1000000	2353	0.40	0.60	15285	25332
Water	20	1.5	PDMS Type 1	1000000	1.00	1.00	1000000	2353	0.62	0.38	9789	25985
Water	20	2.0	PDMS Type 1	1000000	1.00	1.00	1000000	2353	0.85	0.15	3590	23916
Water	30	1.5	PDMS Type 1	1000000	1.00	1.00	1000000	4221	0.35	0.65	34253	52494
Water	30	2.0	PDMS Type 1	1000000	1.00	1.00	1000000	4221	0.47	0.53	27754	52747
Water	30	2.4	PDMS Type 1	1000000	1.00	1.00	1000000	4221	0.57	0.43	23127	53609
Water	35	2.0	PDMS Type 1	1000000	1.00	1.00	1000000	5612	0.36	0.64	42570	66138
Water	40	2.0	PDMS Type 1	1000000	1.00	1.00	1000000	7428	0.27	0.73	63916	87463
Water	40	2.4	PDMS Type 1	1000000	1.00	1.00	1000000	7428	0.32	0.68	55031	81293
Water	20	0.5	PDMS Type 2	1000000	1.00	1.00	1000000	2353	0.23	0.77	7300	9439
Water	20	0.9	PDMS Type 2	1000000	1.00	1.00	1000000	2353	0.40	0.60	5421	8984
Water	20	1.3	PDMS Type 2	1000000	1.00	1.00	1000000	2353	0.57	0.43	4067	9383
Water	30	0.9	PDMS Type 2	1000000	1.00	1.00	1000000	4221	0.22	0.78	14155	18174
Water	30	1.3	PDMS Type 2	1000000	1.00	1.00	1000000	4221	0.32	0.68	12785	18688
Water	30	2.0	PDMS Type 2	1000000	1.00	1.00	1000000	4221	0.47	0.53	11494	21844
Water	35	1.3	PDMS Type 2	1000000	1.00	1.00	1000000	5612	0.24	0.76	17908	23487
Water	40	1.3	PDMS Type 2	1000000	1.00	1.00	1000000	7428	0.18	0.82	27688	33744
Water	40	2.0	PDMS Type 2	1000000	1.00	1.00	1000000	7428	0.27	0.73	26424	36158
Water	40	3.3	PDMS Type 2	1000000	1.00	1.00	1000000	7428	0.45	0.55	18481	33522
Water	30	0.3	POMS	1000000	1.00	1.00	1000000	4221	0.06	0.94	2916	3113
Water	30	1.3	POMS	1000000	1.00	1.00	1000000	4221	0.32	0.68	2508	3666

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Water	30	2.0	POMS	1000000	1.00	1.00	1000000	4221	0.47	0.53	1952	3709
Water	40	0.5	POMS	1000000	1.00	1.00	1000000	7428	0.07	0.93	5105	5500
Water	40	1.3	POMS	1000000	1.00	1.00	1000000	7428	0.18	0.82	4286	5223
Water	40	2.0	POMS	1000000	1.00	1.00	1000000	7428	0.27	0.73	4371	5981
2-Heptanone	20	0.9	PDMS Type 1	1.55	1560	0.00242	19.3	144	0.00012	0.00230	0.29	128.3
2-Heptanone	20	1.5	PDMS Type 1	1.55	1560	0.00242	25.9	144	0.00026	0.00216	0.25	117.5
2-Heptanone	20	2.0	PDMS Type 1	1.55	1560	0.00242	30.7	144	0.00042	0.00200	0.11	55.1
2-Heptanone	30	1.5	PDMS Type 1	1.55	1693	0.00263	12.4	269	0.00007	0.00256	0.42	165.5
2-Heptanone	30	2.0	PDMS Type 1	1.55	1693	0.00263	15.4	269	0.00011	0.00252	0.43	169.6
2-Heptanone	30	2.4	PDMS Type 1	1.55	1693	0.00263	18.5	269	0.00017	0.00246	0.43	173.7
2-Heptanone	35	2.0	PDMS Type 1	1.55	1745	0.00271	13.5	367	0.00007	0.00264	0.57	217.7
2-Heptanone	40	2.0	PDMS Type 1	1.55	1785	0.00277	13.2	500	0.00005	0.00272	0.85	310.8
2-Heptanone	40	2.4	PDMS Type 1	1.55	1785	0.00277	9.5	500	0.00005	0.00273	0.52	192.4
2-Heptanone	20	0.5	PDMS Type 2	1.55	1560	0.00242	24.9	144	0.00009	0.00233	0.18	78.1
2-Heptanone	20	0.9	PDMS Type 2	1.55	1560	0.00242	30.1	144	0.00019	0.00223	0.16	73.3
2-Heptanone	20	1.3	PDMS Type 2	1.55	1560	0.00242	32.4	144	0.00030	0.00212	0.13	62.0
2-Heptanone	30	0.9	PDMS Type 2	1.55	1693	0.00263	20.0	269	0.00007	0.00256	0.28	110.8
2-Heptanone	30	1.3	PDMS Type 2	1.55	1693	0.00263	21.4	269	0.00011	0.00252	0.27	108.3
2-Heptanone	30	2.0	PDMS Type 2	1.55	1693	0.00263	24.3	269	0.00018	0.00245	0.28	113.9
2-Heptanone	35	1.3	PDMS Type 2	1.55	1745	0.00271	19.2	367	0.00007	0.00264	0.34	130.2
2-Heptanone	40	1.3	PDMS Type 2	1.55	1785	0.00277	16.2	500	0.00004	0.00273	0.45	163.9
2-Heptanone	40	2.0	PDMS Type 2	1.55	1785	0.00277	15.9	500	0.00006	0.00271	0.42	155.0

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
2-Heptanone	40	3.3	PDMS Type 2	1.55	1785	0.00277	23.7	500	0.00016	0.00262	0.44	167.1
2-Heptanone	30	0.3	POMS	1.55	1693	0.00263	38.9	269	0.00004	0.00259	0.11	43.7
2-Heptanone	30	1.3	POMS	1.55	1693	0.00263	41.1	269	0.00020	0.00243	0.10	42.5
2-Heptanone	30	2.0	POMS	1.55	1693	0.00263	38.5	269	0.00029	0.00234	0.08	32.1
2-Heptanone	40	0.5	POMS	1.55	1785	0.00277	33.2	500	0.00004	0.00274	0.17	61.9
2-Heptanone	40	1.3	POMS	1.55	1785	0.00277	34.5	500	0.00009	0.00268	0.15	55.1
2-Heptanone	40	2.0	POMS	1.55	1785	0.00277	38.3	500	0.00015	0.00262	0.17	63.8
2-Nonanone	20	0.9	PDMS Type 1	1.25	26503	0.03305	4.59	73	0.00006	0.03299	0.07	2.12
2-Nonanone	20	1.5	PDMS Type 1	1.25	26503	0.03305	4.38	73	0.00009	0.03297	0.04	1.30
2-Nonanone	20	2.0	PDMS Type 1	1.25	26503	0.03305	2.93	73	0.00008	0.03297	0.01	0.32
2-Nonanone	30	1.5	PDMS Type 1	1.25	27788	0.03466	3.68	126	0.00004	0.03461	0.13	3.64
2-Nonanone	30	2.0	PDMS Type 1	1.25	27788	0.03466	3.61	126	0.00006	0.03460	0.10	2.89
2-Nonanone	30	2.4	PDMS Type 1	1.25	27788	0.03466	4.74	126	0.00009	0.03457	0.11	3.17
2-Nonanone	35	2.0	PDMS Type 1	1.25	28079	0.03502	3.62	165	0.00004	0.03498	0.15	4.41
2-Nonanone	40	2.0	PDMS Type 1	1.25	28122	0.03507	3.89	217	0.00004	0.03504	0.25	7.10
2-Nonanone	40	2.4	PDMS Type 1	1.25	28122	0.03507	3.49	217	0.00004	0.03503	0.19	5.49
2-Nonanone	20	0.5	PDMS Type 2	1.25	26503	0.03305	5.75	73	0.00004	0.03301	0.04	1.27
2-Nonanone	20	0.9	PDMS Type 2	1.25	26503	0.03305	7.77	73	0.00010	0.03295	0.04	1.28
2-Nonanone	20	1.3	PDMS Type 2	1.25	26503	0.03305	8.40	73	0.00015	0.03290	0.03	1.04
2-Nonanone	30	0.9	PDMS Type 2	1.25	27788	0.03466	6.36	126	0.00005	0.03461	0.09	2.60
2-Nonanone	30	1.3	PDMS Type 2	1.25	27788	0.03466	4.91	126	0.00005	0.03460	0.06	1.81
2-Nonanone	30	2.0	PDMS Type 2	1.25	27788	0.03466	4.94	126	0.00008	0.03458	0.06	1.64

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
2-Nonanone	35	1.3	PDMS Type 2	1.25	28079	0.03502	3.71	165	0.00003	0.03499	0.07	1.90
2-Nonanone	40	1.3	PDMS Type 2	1.25	28122	0.03507	4.89	217	0.00003	0.03504	0.14	3.86
2-Nonanone	40	2.0	PDMS Type 2	1.25	28122	0.03507	4.98	217	0.00005	0.03503	0.13	3.76
2-Nonanone	40	3.3	PDMS Type 2	1.25	28122	0.03507	4.51	217	0.00007	0.03500	0.08	2.38
2-Nonanone	30	0.3	POMS	1.25	27788	0.03466	8.86	126	0.00002	0.03464	0.03	0.75
2-Nonanone	30	1.3	POMS	1.25	27788	0.03466	10.44	126	0.00011	0.03455	0.03	0.76
2-Nonanone	30	2.0	POMS	1.25	27788	0.03466	8.99	126	0.00014	0.03451	0.02	0.51
2-Nonanone	40	0.5	POMS	1.25	28122	0.03507	5.14	217	0.00001	0.03506	0.03	0.75
2-Nonanone	40	1.3	POMS	1.25	28122	0.03507	8.94	217	0.00005	0.03502	0.04	1.09
2-Nonanone	40	2.0	POMS	1.25	28122	0.03507	5.73	217	0.00005	0.03502	0.03	0.72
Acetic Acid	20	0.9	PDMS Type 1	31.5	3.00	0.00009	14.58	1549	0.00001	0.00009	0.22	2602
Acetic Acid	20	1.5	PDMS Type 1	31.5	3.00	0.00009	14.48	1549	0.00001	0.00008	0.14	1756
Acetic Acid	20	2.0	PDMS Type 1	31.5	3.00	0.00009	14.15	1549	0.00002	0.00008	0.05	667
Acetic Acid	30	1.5	PDMS Type 1	31.5	3.16	0.00010	15.43	2752	0.00001	0.00009	0.53	5803
Acetic Acid	30	2.0	PDMS Type 1	31.5	3.16	0.00010	16.47	2752	0.00001	0.00009	0.46	5233
Acetic Acid	30	2.4	PDMS Type 1	31.5	3.16	0.00010	16.71	2752	0.00001	0.00008	0.39	4560
Acetic Acid	35	2.0	PDMS Type 1	31.5	3.22	0.00010	18.34	3607	0.00001	0.00009	0.78	8564
Acetic Acid	40	2.0	PDMS Type 1	31.5	3.27	0.00010	22.23	4680	0.00001	0.00009	1.42	15195
Acetic Acid	40	2.4	PDMS Type 1	31.5	3.27	0.00010	17.50	4680	0.00001	0.00009	0.96	10241
Acetic Acid	20	0.5	PDMS Type 2	31.5	3.00	0.00009	16.18	1549	0.00001	0.00009	0.12	1329
Acetic Acid	20	0.9	PDMS Type 2	31.5	3.00	0.00009	13.81	1549	0.00001	0.00009	0.07	870
Acetic Acid	20	1.3	PDMS Type 2	31.5	3.00	0.00009	10.50	1549	0.00001	0.00009	0.04	500

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction × 10^6	Activity coefficient	Activity	Mole fraction × 10^6	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux ($\mu mol\ m^{-2}\ s^{-1}$)	Effective mass transfer coefficient ($\mu mol\ m^{-2}\ s^{-1}$)
Acetic Acid	30	0.9	PDMS Type 2	31.5	3.16	0.00010	16.19	2752	0.00001	0.00009	0.23	2442
Acetic Acid	30	1.3	PDMS Type 2	31.5	3.16	0.00010	19.34	2752	0.00001	0.00009	0.25	2749
Acetic Acid	30	2.0	PDMS Type 2	31.5	3.16	0.00010	22.13	2752	0.00002	0.00008	0.25	3055
Acetic Acid	35	1.3	PDMS Type 2	31.5	3.22	0.00010	18.87	3607	0.00001	0.00009	0.34	3581
Acetic Acid	40	1.3	PDMS Type 2	31.5	3.27	0.00010	23.19	4680	0.00001	0.00010	0.64	6659
Acetic Acid	40	2.0	PDMS Type 2	31.5	3.27	0.00010	15.47	4680	0.00001	0.00010	0.41	4239
Acetic Acid	40	3.3	PDMS Type 2	31.5	3.27	0.00010	18.70	4680	0.00001	0.00009	0.35	3853
Acetic Acid	30	0.3	POMS	31.5	3.16	0.00010	33.65	2752	0.00000	0.00010	0.10	1021
Acetic Acid	30	1.3	POMS	31.5	3.16	0.00010	20.25	2752	0.00001	0.00009	0.05	567
Acetic Acid	30	2.0	POMS	31.5	3.16	0.00010	14.81	2752	0.00001	0.00009	0.03	326
Acetic Acid	40	0.5	POMS	31.5	3.27	0.00010	31.52	4680	0.00000	0.00010	0.16	1618
Acetic Acid	40	1.3	POMS	31.5	3.27	0.00010	32.18	4680	0.00001	0.00009	0.14	1469
Acetic Acid	40	2.0	POMS	31.5	3.27	0.00010	25.17	4680	0.00001	0.00009	0.11	1192
Butanoic Acid	20	0.9	PDMS Type 1	21.8	39.7	0.00086	15.13	68	0.00021	0.00066	0.23	353
Butanoic Acid	20	1.5	PDMS Type 1	21.8	39.7	0.00086	13.45	68	0.00029	0.00057	0.13	230
Butanoic Acid	20	2.0	PDMS Type 1	21.8	39.7	0.00086	12.98	68	0.00038	0.00048	0.05	97
Butanoic Acid	30	1.5	PDMS Type 1	21.8	41.7	0.00091	17.38	149	0.00017	0.00074	0.60	806
Butanoic Acid	30	2.0	PDMS Type 1	21.8	41.7	0.00091	18.76	149	0.00025	0.00066	0.52	791
Butanoic Acid	30	2.4	PDMS Type 1	21.8	41.7	0.00091	19.26	149	0.00031	0.00060	0.45	743
Butanoic Acid	35	2.0	PDMS Type 1	21.8	42.4	0.00092	23.12	217	0.00021	0.00071	0.98	1385
Butanoic Acid	40	2.0	PDMS Type 1	21.8	42.8	0.00093	28.81	311	0.00019	0.00075	1.84	2462
Butanoic Acid	40	2.4	PDMS Type 1	21.8	42.8	0.00093	20.17	311	0.00016	0.00078	1.11	1428

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Butanoic Acid	20	0.5	PDMS Type 2	21.8	39.7	0.00086	17.41	68	0.00014	0.00073	0.13	175
Butanoic Acid	20	0.9	PDMS Type 2	21.8	39.7	0.00086	14.74	68	0.00020	0.00066	0.08	121
Butanoic Acid	20	1.3	PDMS Type 2	21.8	39.7	0.00086	12.39	68	0.00024	0.00062	0.05	81
Butanoic Acid	30	0.9	PDMS Type 2	21.8	41.7	0.00091	23.71	149	0.00015	0.00076	0.34	441
Butanoic Acid	30	1.3	PDMS Type 2	21.8	41.7	0.00091	23.55	149	0.00021	0.00070	0.30	431
Butanoic Acid	30	2.0	PDMS Type 2	21.8	41.7	0.00091	24.80	149	0.00033	0.00058	0.29	494
Butanoic Acid	35	1.3	PDMS Type 2	21.8	42.4	0.00092	25.71	217	0.00016	0.00077	0.46	601
Butanoic Acid	40	1.3	PDMS Type 2	21.8	42.8	0.00093	31.19	311	0.00013	0.00080	0.86	1080
Butanoic Acid	40	2.0	PDMS Type 2	21.8	42.8	0.00093	22.63	311	0.00015	0.00079	0.60	759
Butanoic Acid	40	3.3	PDMS Type 2	21.8	42.8	0.00093	26.60	311	0.00029	0.00065	0.49	759
Butanoic Acid	30	0.3	POMS	21.8	41.7	0.00091	69.41	149	0.00012	0.00079	0.20	258
Butanoic Acid	30	1.3	POMS	21.8	41.7	0.00091	29.05	149	0.00026	0.00065	0.07	112
Butanoic Acid	30	2.0	POMS	21.8	41.7	0.00091	19.60	149	0.00026	0.00065	0.04	59
Butanoic Acid	40	0.5	POMS	21.8	42.8	0.00093	74.13	311	0.00013	0.00081	0.38	469
Butanoic Acid	40	1.3	POMS	21.8	42.8	0.00093	56.92	311	0.00024	0.00069	0.24	354
Butanoic Acid	40	2.0	POMS	21.8	42.8	0.00093	47.70	311	0.00031	0.00063	0.21	333
Hexanoic Acid	20	0.9	PDMS Type 1	17.2	645	0.0111	15.21	3.41	0.0042	0.0069	0.23	33.6
Hexanoic Acid	20	1.5	PDMS Type 1	17.2	645	0.0111	11.95	3.41	0.0051	0.0060	0.12	19.7
Hexanoic Acid	20	2.0	PDMS Type 1	17.2	645	0.0111	8.62	3.41	0.0051	0.0060	0.03	5.1
Hexanoic Acid	30	1.5	PDMS Type 1	17.2	653	0.0112	20.04	9.08	0.0032	0.0080	0.69	85.9
Hexanoic Acid	30	2.0	PDMS Type 1	17.2	653	0.0112	22.87	9.08	0.0050	0.0062	0.63	102.5
Hexanoic Acid	30	2.4	PDMS Type 1	17.2	653	0.0112	22.17	9.08	0.0059	0.0054	0.51	95.5

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Hexanoic Acid	35	2.0	PDMS Type 1	17.2	650	0.0112	31.65	14.40	0.0044	0.0068	1.35	198.7
Hexanoic Acid	40	2.0	PDMS Type 1	17.2	642	0.0110	40.17	22.41	0.0036	0.0075	2.57	344.0
Hexanoic Acid	40	2.4	PDMS Type 1	17.2	642	0.0110	26.22	22.41	0.0028	0.0082	1.44	175.1
Hexanoic Acid	20	0.5	PDMS Type 2	17.2	645	0.0111	13.35	3.41	0.0021	0.0090	0.10	10.8
Hexanoic Acid	20	0.9	PDMS Type 2	17.2	645	0.0111	9.88	3.41	0.0027	0.0084	0.05	6.4
Hexanoic Acid	20	1.3	PDMS Type 2	17.2	645	0.0111	6.11	3.41	0.0024	0.0087	0.02	2.9
Hexanoic Acid	30	0.9	PDMS Type 2	17.2	653	0.0112	25.17	9.08	0.0026	0.0086	0.36	41.2
Hexanoic Acid	30	1.3	PDMS Type 2	17.2	653	0.0112	20.20	9.08	0.0030	0.0083	0.26	31.2
Hexanoic Acid	30	2.0	PDMS Type 2	17.2	653	0.0112	18.80	9.08	0.0041	0.0071	0.22	30.5
Hexanoic Acid	35	1.3	PDMS Type 2	17.2	650	0.0112	23.44	14.40	0.0022	0.0090	0.42	46.6
Hexanoic Acid	40	1.3	PDMS Type 2	17.2	642	0.0110	33.26	22.41	0.0020	0.0091	0.92	101.5
Hexanoic Acid	40	2.0	PDMS Type 2	17.2	642	0.0110	22.95	22.41	0.0020	0.0090	0.61	67.4
Hexanoic Acid	40	3.3	PDMS Type 2	17.2	642	0.0110	24.01	22.41	0.0036	0.0075	0.44	59.3
Hexanoic Acid	30	0.3	POMS	17.2	653	0.0112	37.39	9.08	0.0011	0.0101	0.11	10.8
Hexanoic Acid	30	1.3	POMS	17.2	653	0.0112	15.99	9.08	0.0023	0.0089	0.04	4.5
Hexanoic Acid	30	2.0	POMS	17.2	653	0.0112	10.13	9.08	0.0022	0.0090	0.02	2.2
Hexanoic Acid	40	0.5	POMS	17.2	642	0.0110	47.57	22.41	0.0011	0.0099	0.24	24.5
Hexanoic Acid	40	1.3	POMS	17.2	642	0.0110	41.32	22.41	0.0025	0.0086	0.18	20.6
Hexanoic Acid	40	2.0	POMS	17.2	642	0.0110	25.73	22.41	0.0023	0.0088	0.11	12.9
Octanoic Acid	20	0.9	PDMS Type 1	13.1	11041	0.144	5.65	0.28	0.019	0.125	0.09	0.69
Octanoic Acid	20	1.5	PDMS Type 1	13.1	11041	0.144	3.33	0.28	0.018	0.127	0.03	0.26
Octanoic Acid	20	2.0	PDMS Type 1	13.1	11041	0.144	3.57	0.28	0.026	0.119	0.01	0.11

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Octanoic Acid	30	1.5	PDMS Type 1	13.1	10666	0.140	10.52	0.86	0.018	0.122	0.36	2.96
Octanoic Acid	30	2.0	PDMS Type 1	13.1	10666	0.140	9.90	0.86	0.023	0.117	0.27	2.36
Octanoic Acid	30	2.4	PDMS Type 1	13.1	10666	0.140	8.12	0.86	0.023	0.117	0.19	1.61
Octanoic Acid	35	2.0	PDMS Type 1	13.1	10358	0.135	13.79	1.47	0.019	0.117	0.59	5.03
Octanoic Acid	40	2.0	PDMS Type 1	13.1	9979	0.131	20.58	2.45	0.017	0.114	1.32	11.56
Octanoic Acid	40	2.4	PDMS Type 1	13.1	9979	0.131	17.95	2.45	0.018	0.113	0.99	8.75
Octanoic Acid	20	0.5	PDMS Type 2	13.1	11041	0.144	3.76	0.28	0.007	0.137	0.03	0.20
Octanoic Acid	20	0.9	PDMS Type 2	13.1	11041	0.144	3.06	0.28	0.010	0.134	0.02	0.12
Octanoic Acid	20	1.3	PDMS Type 2	13.1	11041	0.144	1.88	0.28	0.009	0.135	0.01	0.06
Octanoic Acid	30	0.9	PDMS Type 2	13.1	10666	0.140	15.21	0.86	0.016	0.123	0.22	1.75
Octanoic Acid	30	1.3	PDMS Type 2	13.1	10666	0.140	4.69	0.86	0.007	0.132	0.06	0.45
Octanoic Acid	30	2.0	PDMS Type 2	13.1	10666	0.140	4.06	0.86	0.009	0.130	0.05	0.36
Octanoic Acid	35	1.3	PDMS Type 2	13.1	10358	0.135	4.69	1.47	0.004	0.131	0.08	0.64
Octanoic Acid	40	1.3	PDMS Type 2	13.1	9979	0.131	13.43	2.45	0.007	0.123	0.37	3.02
Octanoic Acid	40	2.0	PDMS Type 2	13.1	9979	0.131	10.95	2.45	0.009	0.122	0.29	2.38
Octanoic Acid	40	3.3	PDMS Type 2	13.1	9979	0.131	8.21	2.45	0.011	0.119	0.15	1.27
Octanoic Acid	30	0.3	POMS	13.1	10666	0.140	5.09	0.86	0.002	0.138	0.01	0.11
Octanoic Acid	30	1.3	POMS	13.1	10666	0.140	7.64	0.86	0.012	0.128	0.02	0.15
Octanoic Acid	30	2.0	POMS	13.1	10666	0.140	3.65	0.86	0.008	0.131	0.01	0.05
Octanoic Acid	40	0.5	POMS	13.1	9979	0.131	7.96	2.45	0.002	0.129	0.04	0.32
Octanoic Acid	40	1.3	POMS	13.1	9979	0.131	10.86	2.45	0.006	0.125	0.05	0.37
Octanoic Acid	40	2.0	POMS	13.1	9979	0.131	4.09	2.45	0.003	0.127	0.02	0.14

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Ethyl Butanoate	20	0.9	PDMS Type 1	15.6	1050	0.01639	203	1210	0.00016	0.01623	3.10	191.3
Ethyl Butanoate	20	1.5	PDMS Type 1	15.6	1050	0.01639	279	1210	0.00034	0.01605	2.73	170.4
Ethyl Butanoate	20	2.0	PDMS Type 1	15.6	1050	0.01639	376	1210	0.00062	0.01576	1.35	85.6
Ethyl Butanoate	30	1.5	PDMS Type 1	15.6	1179	0.01841	137	2316	0.00009	0.01832	4.68	255.4
Ethyl Butanoate	30	2.0	PDMS Type 1	15.6	1179	0.01841	167	2316	0.00014	0.01826	4.63	253.4
Ethyl Butanoate	30	2.4	PDMS Type 1	15.6	1179	0.01841	207	2316	0.00021	0.01819	4.79	263.2
Ethyl Butanoate	35	2.0	PDMS Type 1	15.6	1220	0.01904	142	3179	0.00009	0.01896	6.06	319.5
Ethyl Butanoate	40	2.0	PDMS Type 1	15.6	1245	0.01944	135	4341	0.00006	0.01937	8.62	445.0
Ethyl Butanoate	40	2.4	PDMS Type 1	15.6	1245	0.01944	95	4341	0.00005	0.01938	5.21	268.6
Ethyl Butanoate	20	0.5	PDMS Type 2	15.6	1050	0.01639	140	1210	0.00006	0.01632	1.02	62.7
Ethyl Butanoate	20	0.9	PDMS Type 2	15.6	1050	0.01639	172	1210	0.00013	0.01625	0.93	57.5
Ethyl Butanoate	20	1.3	PDMS Type 2	15.6	1050	0.01639	199	1210	0.00022	0.01617	0.81	50.2
Ethyl Butanoate	30	0.9	PDMS Type 2	15.6	1179	0.01841	112	2316	0.00005	0.01836	1.59	86.6
Ethyl Butanoate	30	1.3	PDMS Type 2	15.6	1179	0.01841	115	2316	0.00007	0.01834	1.47	80.3
Ethyl Butanoate	30	2.0	PDMS Type 2	15.6	1179	0.01841	133	2316	0.00012	0.01829	1.53	83.8
Ethyl Butanoate	35	1.3	PDMS Type 2	15.6	1220	0.01904	106	3179	0.00004	0.01900	1.90	99.9
Ethyl Butanoate	40	1.3	PDMS Type 2	15.6	1245	0.01944	88	4341	0.00003	0.01941	2.43	125.3
Ethyl Butanoate	40	2.0	PDMS Type 2	15.6	1245	0.01944	85	4341	0.00004	0.01940	2.25	116.0
Ethyl Butanoate	40	3.3	PDMS Type 2	15.6	1245	0.01944	135	4341	0.00010	0.01933	2.49	128.9
Ethyl Butanoate	30	0.3	POMS	15.6	1179	0.01841	485	2316	0.00006	0.01835	1.41	77.0
Ethyl Butanoate	30	1.3	POMS	15.6	1179	0.01841	515	2316	0.00030	0.01811	1.29	71.4
Ethyl Butanoate	30	2.0	POMS	15.6	1179	0.01841	510	2316	0.00044	0.01797	1.00	55.4

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction × 10^6	Activity coefficient	Activity	Mole fraction × 10^6	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Ethyl Butanoate	40	0.5	POMS	15.6	1245	0.01944	432	4341	0.00005	0.01938	2.21	113.8
Ethyl Butanoate	40	1.3	POMS	15.6	1245	0.01944	448	4341	0.00014	0.01930	1.92	99.5
Ethyl Butanoate	40	2.0	POMS	15.6	1245	0.01944	487	4341	0.00022	0.01921	2.13	110.9
Ethyl Hexanoate	20	0.9	PDMS Type 1	12.5	23085	0.2883	82.1	116	0.0007	0.2877	1.25	4.36
Ethyl Hexanoate	20	1.5	PDMS Type 1	12.5	23085	0.2883	86.7	116	0.0011	0.2872	0.85	2.95
Ethyl Hexanoate	20	2.0	PDMS Type 1	12.5	23085	0.2883	70.4	116	0.0012	0.2871	0.25	0.88
Ethyl Hexanoate	30	1.5	PDMS Type 1	12.5	23085	0.2883	65.4	216	0.0004	0.2879	2.24	7.78
Ethyl Hexanoate	30	2.0	PDMS Type 1	12.5	23085	0.2883	65.7	216	0.0006	0.2877	1.82	6.34
Ethyl Hexanoate	30	2.4	PDMS Type 1	12.5	23085	0.2883	89.8	216	0.0010	0.2873	2.08	7.23
Ethyl Hexanoate	35	2.0	PDMS Type 1	12.5	23085	0.2883	67.5	293	0.0005	0.2879	2.87	9.98
Ethyl Hexanoate	40	2.0	PDMS Type 1	12.5	23085	0.2883	72.6	395	0.0004	0.2880	4.64	16.12
Ethyl Hexanoate	40	2.4	PDMS Type 1	12.5	23085	0.2883	56.9	395	0.0003	0.2880	3.13	10.88
Ethyl Hexanoate	20	0.5	PDMS Type 2	12.5	23085	0.2883	97.1	116	0.0004	0.2879	0.71	2.46
Ethyl Hexanoate	20	0.9	PDMS Type 2	12.5	23085	0.2883	129.3	116	0.0010	0.2873	0.70	2.44
Ethyl Hexanoate	20	1.3	PDMS Type 2	12.5	23085	0.2883	163.8	116	0.0019	0.2865	0.67	2.33
Ethyl Hexanoate	30	0.9	PDMS Type 2	12.5	23085	0.2883	91.1	216	0.0004	0.2880	1.29	4.48
Ethyl Hexanoate	30	1.3	PDMS Type 2	12.5	23085	0.2883	71.3	216	0.0004	0.2879	0.91	3.17
Ethyl Hexanoate	30	2.0	PDMS Type 2	12.5	23085	0.2883	73.3	216	0.0007	0.2877	0.84	2.93
Ethyl Hexanoate	35	1.3	PDMS Type 2	12.5	23085	0.2883	65.2	293	0.0003	0.2880	1.17	4.05
Ethyl Hexanoate	40	1.3	PDMS Type 2	12.5	23085	0.2883	69.5	395	0.0002	0.2881	1.92	6.67
Ethyl Hexanoate	40	2.0	PDMS Type 2	12.5	23085	0.2883	69.9	395	0.0004	0.2880	1.85	6.41
Ethyl Hexanoate	40	3.3	PDMS Type 2	12.5	23085	0.2883	81.4	395	0.0007	0.2877	1.50	5.23

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Ethyl Hexanoate	30	0.3	POMS	12.5	23085	0.2883	122.7	216	0.0002	0.2882	0.36	1.24
Ethyl Hexanoate	30	1.3	POMS	12.5	23085	0.2883	172.0	216	0.0011	0.2873	0.43	1.50
Ethyl Hexanoate	30	2.0	POMS	12.5	23085	0.2883	161.6	216	0.0015	0.2868	0.32	1.10
Ethyl Hexanoate	40	0.5	POMS	12.5	23085	0.2883	68.9	395	0.0001	0.2883	0.35	1.22
Ethyl Hexanoate	40	1.3	POMS	12.5	23085	0.2883	128.5	395	0.0004	0.2879	0.55	1.91
Ethyl Hexanoate	40	2.0	POMS	12.5	23085	0.2883	86.3	395	0.0004	0.2879	0.38	1.31
Ethyl Octanoate	20	0.9	PDMS Type 1	1.09	429042	0.46708	2.47	22.7	0.00010	0.46698	0.04	0.08
Ethyl Octanoate	20	1.5	PDMS Type 1	1.09	429042	0.46708	1.94	22.7	0.00013	0.46696	0.02	0.04
Ethyl Octanoate	20	2.0	PDMS Type 1	1.09	429042	0.46708	1.17	22.7	0.00010	0.46698	0.00	0.01
Ethyl Octanoate	30	1.5	PDMS Type 1	1.09	429042	0.46708	1.70	44.5	0.00006	0.46703	0.06	0.12
Ethyl Octanoate	30	2.0	PDMS Type 1	1.09	429042	0.46708	1.52	44.5	0.00007	0.46701	0.04	0.09
Ethyl Octanoate	30	2.4	PDMS Type 1	1.09	429042	0.46708	2.77	44.5	0.00015	0.46693	0.06	0.14
Ethyl Octanoate	35	2.0	PDMS Type 1	1.09	429042	0.46708	2.18	61.9	0.00007	0.46701	0.09	0.20
Ethyl Octanoate	40	2.0	PDMS Type 1	1.09	429042	0.46708	2.52	85.6	0.00006	0.46702	0.16	0.34
Ethyl Octanoate	40	2.4	PDMS Type 1	1.09	429042	0.46708	2.05	85.6	0.00006	0.46703	0.11	0.24
Ethyl Octanoate	20	0.5	PDMS Type 2	1.09	429042	0.46708	3.17	22.7	0.00007	0.46701	0.02	0.05
Ethyl Octanoate	20	0.9	PDMS Type 2	1.09	429042	0.46708	5.04	22.7	0.00021	0.46688	0.03	0.06
Ethyl Octanoate	20	1.3	PDMS Type 2	1.09	429042	0.46708	5.52	22.7	0.00032	0.46676	0.02	0.05
Ethyl Octanoate	30	0.9	PDMS Type 2	1.09	429042	0.46708	4.29	44.5	0.00009	0.46699	0.06	0.13
Ethyl Octanoate	30	1.3	PDMS Type 2	1.09	429042	0.46708	3.16	44.5	0.00009	0.46699	0.04	0.09
Ethyl Octanoate	30	2.0	PDMS Type 2	1.09	429042	0.46708	2.44	44.5	0.00011	0.46697	0.03	0.06
Ethyl Octanoate	35	1.3	PDMS Type 2	1.09	429042	0.46708	1.68	61.9	0.00004	0.46705	0.03	0.06

Compound	Operating conditions			Feed side			Permeate side			Overall		
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Mole fraction $\times 10^6$	Activity coefficient	Activity	Mole fraction $\times 10^6$	Saturated vapour pressure (Pa)	Activity	Activity difference across membrane	Mean flux (μmol m^{-2} s^{-1})	Effective mass transfer coefficient (μmol m^{-2} s^{-1})
Ethyl Octanoate	40	1.3	PDMS Type 2	1.09	429042	0.46708	2.87	85.6	0.00004	0.46704	0.08	0.17
Ethyl Octanoate	40	2.0	PDMS Type 2	1.09	429042	0.46708	2.78	85.6	0.00006	0.46702	0.07	0.16
Ethyl Octanoate	40	3.3	PDMS Type 2	1.09	429042	0.46708	2.14	85.6	0.00008	0.46700	0.04	0.08
Ethyl Octanoate	30	0.3	POMS	1.09	429042	0.46708	3.49	44.5	0.00002	0.46706	0.01	0.02
Ethyl Octanoate	30	1.3	POMS	1.09	429042	0.46708	3.61	44.5	0.00011	0.46697	0.01	0.02
Ethyl Octanoate	30	2.0	POMS	1.09	429042	0.46708	3.01	44.5	0.00013	0.46695	0.01	0.01
Ethyl Octanoate	40	0.5	POMS	1.09	429042	0.46708	1.21	85.6	0.00001	0.46708	0.01	0.01
Ethyl Octanoate	40	1.3	POMS	1.09	429042	0.46708	3.89	85.6	0.00006	0.46702	0.02	0.04
Ethyl Octanoate	40	2.0	POMS	1.09	429042	0.46708	1.35	85.6	0.00003	0.46705	0.01	0.01

Appendix C

Mass balance for flavour compounds in standard multicomponent feed

To confirm that there were no significant losses of flavour compounds during each pervaporation run, a mass balance for each flavour compound was carried out for runs with the standard multicomponent feed. If no losses occurred, the mass of each flavour compound in the feed should equal the mass remaining in the retentate at the end of the run, plus the mass removed in the permeate. Table C-1 shows that the mass of each flavour compound in the feed was always statistically similar to the mass in the retentate plus the mass in the permeate (95% confidence). Therefore, no significant losses occurred.

For each compound:

Mass in feed (mg) = measured feed concentration (mg kg^{-1}) × total feed mass (5 kg)

Mass in retentate (mg) = final retentate concentration (mg kg^{-1}) × retentate mass (5 kg − total permeate mass)

Mass in permeate (mg) = sum of [permeate concentration (mg kg^{-1}) × permeate mass (kg)] for the four permeate samples during each run

The values in Table C-1 are 95% confidence intervals for at least three replicates at each set of operating conditions.

Table C-1: Mass balance of flavour compounds during pervaporation runs with the standard multicomponent feed (95% confidence intervals).

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
2-Heptanone	20	0.9	PDMS Type 1	48 ± 10	47 ± 22	5.3 ± 2.0	52 ± 22
2-Heptanone	20	1.5	PDMS Type 1	46 ± 17	51 ± 42	4.6 ± 2.0	55 ± 42
2-Heptanone	20	2.0	PDMS Type 1	46 ± 4	47 ± 6	2.0 ± 0.1	49 ± 6
2-Heptanone	30	1.5	PDMS Type 1	43 ± 5	35 ± 4	7.9 ± 0.6	43 ± 4
2-Heptanone	30	2.0	PDMS Type 1	47 ± 11	43 ± 13	7.6 ± 2.7	50 ± 14
2-Heptanone	30	2.4	PDMS Type 1	45 ± 25	40 ± 17	7.6 ± 3.6	47 ± 17
2-Heptanone	35	2.0	PDMS Type 1	47 ± 21	41 ± 10	9.1 ± 1.2	50 ± 10
2-Heptanone	40	2.0	PDMS Type 1	53 ± 28	44 ± 9	12.7 ± 2.5	56 ± 9
2-Heptanone	40	2.4	PDMS Type 1	48 ± 18	35 ± 12	9.9 ± 3.4	45 ± 12
2-Heptanone	20	0.5	PDMS Type 2	43 ± 8	41 ± 7	3.2 ± 0.8	44 ± 7
2-Heptanone	20	0.9	PDMS Type 2	39 ± 4	40 ± 18	3.0 ± 0.9	43 ± 18
2-Heptanone	20	1.3	PDMS Type 2	45 ± 13	39 ± 12	2.4 ± 0.7	42 ± 12
2-Heptanone	30	0.9	PDMS Type 2	46 ± 9	38 ± 4	5.3 ± 3.6	44 ± 6
2-Heptanone	30	1.3	PDMS Type 2	36 ± 14	38 ± 18	5.1 ± 0.6	43 ± 18
2-Heptanone	30	2.0	PDMS Type 2	41 ± 6	35 ± 6	5.2 ± 0.7	40 ± 6
2-Heptanone	35	1.3	PDMS Type 2	39 ± 32	34 ± 18	5.0 ± 2.4	39 ± 18
2-Heptanone	40	1.3	PDMS Type 2	39 ± 13	31 ± 9	8.4 ± 4.3	40 ± 10
2-Heptanone	40	2.0	PDMS Type 2	40 ± 34	31 ± 15	7.9 ± 3.3	39 ± 16
2-Heptanone	40	3.3	PDMS Type 2	43 ± 10	23 ± 49	7.2 ± 0.3	30 ± 49

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
2-Heptanone	30	0.3	POMS	42 ± 4	40 ± 4	1.7 ± 0.2	41 ± 4
2-Heptanone	30	1.3	POMS	40 ± 13	36 ± 5	1.3 ± 0.3	37 ± 5
2-Heptanone	30	2.0	POMS	41 ± 3	38 ± 2	1.1 ± 0.4	40 ± 2
2-Heptanone	40	0.5	POMS	39 ± 1	34 ± 3	2.4 ± 1.3	36 ± 4
2-Heptanone	40	1.3	POMS	40 ± 11	35 ± 2	2.8 ± 0.3	37 ± 2
2-Heptanone	40	2.0	POMS	41 ± 4	38 ± 4	2.4 ± 1.1	41 ± 4
2-Nonanone	20	0.9	PDMS Type 1	32 ± 8	31 ± 15	1.6 ± 0.4	33 ± 15
2-Nonanone	20	1.5	PDMS Type 1	31 ± 13	33 ± 27	1.0 ± 0.7	34 ± 27
2-Nonanone	20	2.0	PDMS Type 1	32 ± 5	32 ± 6	0.2 ± 0.1	32 ± 6
2-Nonanone	30	1.5	PDMS Type 1	30 ± 4	24 ± 2	3.0 ± 0.4	27 ± 2
2-Nonanone	30	2.0	PDMS Type 1	32 ± 9	28 ± 5	2.3 ± 1.1	30 ± 6
2-Nonanone	30	2.4	PDMS Type 1	32 ± 12	27 ± 13	2.4 ± 1.0	29 ± 13
2-Nonanone	35	2.0	PDMS Type 1	30 ± 17	25 ± 6	3.0 ± 0.9	28 ± 6
2-Nonanone	40	2.0	PDMS Type 1	32 ± 14	27 ± 4	4.6 ± 0.5	31 ± 4
2-Nonanone	40	2.4	PDMS Type 1	33 ± 18	23 ± 9	4.5 ± 2.1	28 ± 9
2-Nonanone	20	0.5	PDMS Type 2	35 ± 8	32 ± 4	0.9 ± 0.4	33 ± 4
2-Nonanone	20	0.9	PDMS Type 2	31 ± 12	33 ± 11	1.0 ± 0.6	34 ± 12
2-Nonanone	20	1.3	PDMS Type 2	36 ± 11	31 ± 6	0.8 ± 0.8	32 ± 6
2-Nonanone	30	0.9	PDMS Type 2	36 ± 14	32 ± 6	2.1 ± 2.0	34 ± 6
2-Nonanone	30	1.3	PDMS Type 2	28 ± 9	29 ± 11	1.5 ± 0.4	31 ± 11

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
2-Nonanone	30	2.0	PDMS Type 2	34 ± 3	28 ± 6	1.3 ± 0.4	30 ± 6
2-Nonanone	35	1.3	PDMS Type 2	29 ± 26	25 ± 17	1.2 ± 0.6	26 ± 17
2-Nonanone	40	1.3	PDMS Type 2	31 ± 9	23 ± 7	3.2 ± 1.7	26 ± 7
2-Nonanone	40	2.0	PDMS Type 2	32 ± 24	29 ± 35	3.1 ± 2.8	32 ± 35
2-Nonanone	40	3.3	PDMS Type 2	33 ± 5	15 ± 33	1.7 ± 0.5	17 ± 33
2-Nonanone	30	0.3	POMS	40 ± 4	38 ± 5	0.5 ± 0.1	39 ± 5
2-Nonanone	30	1.3	POMS	39 ± 12	34 ± 2	0.4 ± 0.4	35 ± 2
2-Nonanone	30	2.0	POMS	41 ± 6	37 ± 4	0.3 ± 0.1	38 ± 4
2-Nonanone	40	0.5	POMS	38 ± 7	32 ± 4	0.5 ± 0.2	33 ± 4
2-Nonanone	40	1.3	POMS	38 ± 10	33 ± 2	0.9 ± 0.5	34 ± 2
2-Nonanone	40	2.0	POMS	39 ± 6	35 ± 4	0.4 ± 0.3	36 ± 4
Ethyl butanoate	20	0.9	PDMS Type 1	480 ± 140	470 ± 270	56 ± 24	520 ± 270
Ethyl butanoate	20	1.5	PDMS Type 1	460 ± 220	500 ± 390	50 ± 22	550 ± 400
Ethyl butanoate	20	2.0	PDMS Type 1	460 ± 60	460 ± 80	25 ± 3	490 ± 80
Ethyl butanoate	30	1.5	PDMS Type 1	450 ± 60	370 ± 40	89 ± 7	460 ± 40
Ethyl butanoate	30	2.0	PDMS Type 1	490 ± 80	440 ± 40	84 ± 26	530 ± 50
Ethyl butanoate	30	2.4	PDMS Type 1	470 ± 170	400 ± 160	86 ± 34	480 ± 170
Ethyl butanoate	35	2.0	PDMS Type 1	450 ± 190	400 ± 70	97 ± 12	500 ± 70
Ethyl butanoate	40	2.0	PDMS Type 1	530 ± 210	440 ± 40	131 ± 10	570 ± 40
Ethyl butanoate	40	2.4	PDMS Type 1	450 ± 150	330 ± 100	99 ± 36	420 ± 110

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Ethyl butanoate	20	0.5	PDMS Type 2	210 ± 50	200 ± 40	18 ± 4	220 ± 40
Ethyl butanoate	20	0.9	PDMS Type 2	190 ± 20	190 ± 60	17 ± 3	210 ± 60
Ethyl butanoate	20	1.3	PDMS Type 2	230 ± 50	190 ± 40	15 ± 6	210 ± 40
Ethyl butanoate	30	0.9	PDMS Type 2	220 ± 30	180 ± 20	30 ± 25	210 ± 30
Ethyl butanoate	30	1.3	PDMS Type 2	170 ± 70	170 ± 50	28 ± 5	200 ± 50
Ethyl butanoate	30	2.0	PDMS Type 2	200 ± 60	170 ± 50	29 ± 5	200 ± 50
Ethyl butanoate	35	1.3	PDMS Type 2	200 ± 160	170 ± 100	28 ± 14	200 ± 100
Ethyl butanoate	40	1.3	PDMS Type 2	190 ± 100	150 ± 50	47 ± 27	200 ± 50
Ethyl butanoate	40	2.0	PDMS Type 2	180 ± 170	130 ± 40	43 ± 14	180 ± 50
Ethyl butanoate	40	3.3	PDMS Type 2	200 ± 40	110 ± 230	42 ± 7	150 ± 230
Ethyl butanoate	30	0.3	POMS	470 ± 50	440 ± 40	22 ± 3	460 ± 40
Ethyl butanoate	30	1.3	POMS	440 ± 150	390 ± 60	16 ± 4	410 ± 60
Ethyl butanoate	30	2.0	POMS	440 ± 60	410 ± 70	14 ± 3	420 ± 70
Ethyl butanoate	40	0.5	POMS	420 ± 30	380 ± 30	32 ± 18	410 ± 30
Ethyl butanoate	40	1.3	POMS	460 ± 120	400 ± 10	36 ± 6	440 ± 20
Ethyl butanoate	40	2.0	POMS	450 ± 60	400 ± 100	31 ± 11	430 ± 100
Ethyl hexanoate	20	0.9	PDMS Type 1	480 ± 120	470 ± 180	28 ± 4	490 ± 180
Ethyl hexanoate	20	1.5	PDMS Type 1	470 ± 210	490 ± 430	20 ± 14	510 ± 430
Ethyl hexanoate	20	2.0	PDMS Type 1	450 ± 90	450 ± 70	6 ± 2	460 ± 70
Ethyl hexanoate	30	1.5	PDMS Type 1	450 ± 50	360 ± 40	54 ± 6	410 ± 40

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Ethyl hexanoate	30	2.0	PDMS Type 1	490 ± 140	420 ± 70	42 ± 15	460 ± 70
Ethyl hexanoate	30	2.4	PDMS Type 1	480 ± 180	400 ± 160	46 ± 20	450 ± 160
Ethyl hexanoate	35	2.0	PDMS Type 1	460 ± 230	390 ± 120	57 ± 12	450 ± 120
Ethyl hexanoate	40	2.0	PDMS Type 1	520 ± 190	420 ± 40	88 ± 8	510 ± 40
Ethyl hexanoate	40	2.4	PDMS Type 1	480 ± 220	340 ± 40	75 ± 31	420 ± 50
Ethyl hexanoate	20	0.5	PDMS Type 2	440 ± 140	410 ± 90	16 ± 6	420 ± 90
Ethyl hexanoate	20	0.9	PDMS Type 2	380 ± 70	400 ± 120	16 ± 9	420 ± 120
Ethyl hexanoate	20	1.3	PDMS Type 2	480 ± 150	400 ± 120	15 ± 14	420 ± 120
Ethyl hexanoate	30	0.9	PDMS Type 2	440 ± 80	360 ± 50	30 ± 22	390 ± 50
Ethyl hexanoate	30	1.3	PDMS Type 2	320 ± 180	320 ± 40	22 ± 6	340 ± 40
Ethyl hexanoate	30	2.0	PDMS Type 2	380 ± 180	320 ± 170	20 ± 5	340 ± 170
Ethyl hexanoate	35	1.3	PDMS Type 2	400 ± 300	340 ± 190	21 ± 7	360 ± 190
Ethyl hexanoate	40	1.3	PDMS Type 2	370 ± 250	300 ± 80	46 ± 28	340 ± 90
Ethyl hexanoate	40	2.0	PDMS Type 2	370 ± 340	260 ± 90	44 ± 33	300 ± 90
Ethyl hexanoate	40	3.3	PDMS Type 2	440 ± 80	220 ± 480	31 ± 11	250 ± 480
Ethyl hexanoate	30	0.3	POMS	460 ± 50	420 ± 50	7 ± 2	430 ± 50
Ethyl hexanoate	30	1.3	POMS	440 ± 120	380 ± 40	7 ± 5	390 ± 40
Ethyl hexanoate	30	2.0	POMS	440 ± 20	400 ± 20	6 ± 2	410 ± 20
Ethyl hexanoate	40	0.5	POMS	410 ± 80	350 ± 40	6 ± 2	350 ± 40
Ethyl hexanoate	40	1.3	POMS	460 ± 180	390 ± 30	13 ± 6	410 ± 30

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Ethyl hexanoate	40	2.0	POMS	440 ± 80	390 ± 60	7 ± 3	390 ± 60
Ethyl octanoate	20	0.9	PDMS Type 1	34 ± 18	32 ± 28	1.0 ± 0.2	33 ± 28
Ethyl octanoate	20	1.5	PDMS Type 1	31 ± 11	30 ± 21	0.5 ± 0.6	30 ± 22
Ethyl octanoate	20	2.0	PDMS Type 1	34 ± 14	29 ± 6	0.1 ± 0.1	29 ± 6
Ethyl octanoate	30	1.5	PDMS Type 1	28 ± 5	21 ± 4	1.7 ± 0.3	22 ± 4
Ethyl octanoate	30	2.0	PDMS Type 1	28 ± 11	23 ± 6	1.2 ± 0.6	24 ± 6
Ethyl octanoate	30	2.4	PDMS Type 1	35 ± 24	27 ± 21	1.7 ± 0.8	28 ± 21
Ethyl octanoate	35	2.0	PDMS Type 1	27 ± 18	21 ± 6	2.2 ± 1.5	24 ± 6
Ethyl octanoate	40	2.0	PDMS Type 1	34 ± 14	29 ± 15	3.6 ± 0.7	32 ± 15
Ethyl octanoate	40	2.4	PDMS Type 1	28 ± 12	20 ± 16	3.1 ± 2.6	23 ± 16
Ethyl octanoate	20	0.5	PDMS Type 2	28 ± 10	25 ± 8	0.6 ± 0.4	26 ± 8
Ethyl octanoate	20	0.9	PDMS Type 2	25 ± 16	26 ± 10	0.8 ± 0.4	27 ± 10
Ethyl octanoate	20	1.3	PDMS Type 2	30 ± 14	26 ± 11	0.6 ± 1.1	27 ± 11
Ethyl octanoate	30	0.9	PDMS Type 2	25 ± 10	26 ± 20	1.7 ± 1.7	27 ± 20
Ethyl octanoate	30	1.3	PDMS Type 2	30 ± 39	31 ± 46	1.2 ± 1.6	32 ± 46
Ethyl octanoate	30	2.0	PDMS Type 2	28 ± 23	26 ± 39	0.8 ± 1.2	27 ± 39
Ethyl octanoate	35	1.3	PDMS Type 2	26 ± 25	20 ± 15	0.7 ± 0.5	21 ± 15
Ethyl octanoate	40	1.3	PDMS Type 2	23 ± 19	18 ± 14	2.3 ± 1.5	21 ± 14
Ethyl octanoate	40	2.0	PDMS Type 2	25 ± 30	23 ± 43	2.1 ± 1.9	25 ± 43
Ethyl octanoate	40	3.3	PDMS Type 2	28 ± 10	12 ± 25	1.0 ± 0.7	13 ± 25

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Ethyl octanoate	30	0.3	POMS	20 ± 4	18 ± 3	0.2 ± 0.1	18 ± 3
Ethyl octanoate	30	1.3	POMS	18 ± 5	15 ± 4	0.2 ± 0.2	15 ± 4
Ethyl octanoate	30	2.0	POMS	19 ± 7	16 ± 5	0.1 ± 0.1	17 ± 5
Ethyl octanoate	40	0.5	POMS	17 ± 3	13 ± 7	0.1 ± 0.1	13 ± 7
Ethyl octanoate	40	1.3	POMS	18 ± 13	15 ± 1	0.5 ± 0.4	15 ± 1
Ethyl octanoate	40	2.0	POMS	17 ± 2	15 ± 3	0.1 ± 0.1	15 ± 3
Acetic acid	20	0.9	PDMS Type 1	600 ± 210	660 ± 340	2.1 ± 0.6	660 ± 340
Acetic acid	20	1.5	PDMS Type 1	590 ± 130	670 ± 400	1.3 ± 0.5	670 ± 400
Acetic acid	20	2.0	PDMS Type 1	610 ± 50	620 ± 70	0.5 ± 0.1	620 ± 70
Acetic acid	30	1.5	PDMS Type 1	570 ± 70	540 ± 60	5.3 ± 0.5	550 ± 60
Acetic acid	30	2.0	PDMS Type 1	590 ± 180	650 ± 100	4.4 ± 1.9	660 ± 100
Acetic acid	30	2.4	PDMS Type 1	610 ± 210	610 ± 200	3.6 ± 1.9	610 ± 200
Acetic acid	35	2.0	PDMS Type 1	610 ± 240	590 ± 550	6.5 ± 1.2	590 ± 550
Acetic acid	40	2.0	PDMS Type 1	760 ± 590	710 ± 190	11.2 ± 0.5	720 ± 190
Acetic acid	40	2.4	PDMS Type 1	650 ± 300	590 ± 200	9.6 ± 5.2	600 ± 200
Acetic acid	20	0.5	PDMS Type 2	620 ± 110	680 ± 240	1.1 ± 0.4	680 ± 240
Acetic acid	20	0.9	PDMS Type 2	470 ± 180	580 ± 330	0.7 ± 0.2	580 ± 330
Acetic acid	20	1.3	PDMS Type 2	470 ± 900	480 ± 820	0.4 ± 0.3	480 ± 820
Acetic acid	30	0.9	PDMS Type 2	640 ± 150	610 ± 140	2.3 ± 1.6	610 ± 140
Acetic acid	30	1.3	PDMS Type 2	600 ± 380	730 ± 940	2.4 ± 1.1	740 ± 940

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Acetic acid	30	2.0	PDMS Type 2	740 ± 720	750 ± 780	2.5 ± 2.9	750 ± 780
Acetic acid	35	1.3	PDMS Type 2	510 ± 390	510 ± 280	2.6 ± 1.4	510 ± 280
Acetic acid	40	1.3	PDMS Type 2	600 ± 470	490 ± 210	6.3 ± 2.7	490 ± 210
Acetic acid	40	2.0	PDMS Type 2	490 ± 610	480 ± 300	4.0 ± 1.9	490 ± 300
Acetic acid	40	3.3	PDMS Type 2	590 ± 80	390 ± 880	3.0 ± 0.5	390 ± 880
Acetic acid	30	0.3	POMS	500 ± 100	530 ± 90	0.8 ± 0.2	530 ± 90
Acetic acid	30	1.3	POMS	440 ± 230	420 ± 60	0.3 ± 0.1	420 ± 60
Acetic acid	30	2.0	POMS	410 ± 80	420 ± 80	0.2 ± 0.1	420 ± 80
Acetic acid	40	0.5	POMS	470 ± 130	500 ± 50	1.2 ± 0.7	500 ± 50
Acetic acid	40	1.3	POMS	600 ± 230	590 ± 20	1.4 ± 0.1	590 ± 20
Acetic acid	40	2.0	POMS	460 ± 120	490 ± 170	0.8 ± 0.3	490 ± 170
Butanoic acid	20	0.9	PDMS Type 1	480 ± 140	530 ± 300	3.2 ± 1.2	530 ± 300
Butanoic acid	20	1.5	PDMS Type 1	460 ± 170	570 ± 350	1.8 ± 1.0	570 ± 350
Butanoic acid	20	2.0	PDMS Type 1	500 ± 60	520 ± 50	0.7 ± 0.2	520 ± 50
Butanoic acid	30	1.5	PDMS Type 1	460 ± 50	440 ± 50	8.6 ± 0.6	440 ± 50
Butanoic acid	30	2.0	PDMS Type 1	510 ± 90	540 ± 120	7.2 ± 3.2	550 ± 120
Butanoic acid	30	2.4	PDMS Type 1	500 ± 80	520 ± 130	6.1 ± 2.2	520 ± 130
Butanoic acid	35	2.0	PDMS Type 1	530 ± 210	560 ± 170	12.0 ± 3.8	570 ± 170
Butanoic acid	40	2.0	PDMS Type 1	600 ± 310	600 ± 60	21.3 ± 3.0	630 ± 60
Butanoic acid	40	2.4	PDMS Type 1	490 ± 190	440 ± 120	16.1 ± 6.2	460 ± 120

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Butanoic acid	20	0.5	PDMS Type 2	490 ± 70	560 ± 200	1.7 ± 0.5	560 ± 200
Butanoic acid	20	0.9	PDMS Type 2	420 ± 20	470 ± 240	1.1 ± 0.4	470 ± 240
Butanoic acid	20	1.3	PDMS Type 2	490 ± 170	490 ± 60	0.7 ± 0.4	490 ± 60
Butanoic acid	30	0.9	PDMS Type 2	550 ± 150	510 ± 170	4.8 ± 3.4	510 ± 170
Butanoic acid	30	1.3	PDMS Type 2	440 ± 200	540 ± 530	4.3 ± 2.2	540 ± 530
Butanoic acid	30	2.0	PDMS Type 2	540 ± 320	540 ± 320	4.1 ± 3.0	550 ± 320
Butanoic acid	35	1.3	PDMS Type 2	420 ± 340	420 ± 220	5.2 ± 2.6	420 ± 220
Butanoic acid	40	1.3	PDMS Type 2	450 ± 230	410 ± 180	12.5 ± 4.9	420 ± 180
Butanoic acid	40	2.0	PDMS Type 2	390 ± 480	370 ± 250	8.6 ± 4.4	380 ± 250
Butanoic acid	40	3.3	PDMS Type 2	500 ± 110	310 ± 700	6.3 ± 0.4	320 ± 700
Butanoic acid	30	0.3	POMS	420 ± 60	450 ± 60	2.4 ± 0.4	450 ± 60
Butanoic acid	30	1.3	POMS	390 ± 160	370 ± 70	0.7 ± 0.2	370 ± 70
Butanoic acid	30	2.0	POMS	360 ± 50	370 ± 60	0.4 ± 0.2	380 ± 60
Butanoic acid	40	0.5	POMS	400 ± 30	410 ± 20	4.2 ± 3.2	410 ± 20
Butanoic acid	40	1.3	POMS	480 ± 120	480 ± 40	3.5 ± 0.3	480 ± 40
Butanoic acid	40	2.0	POMS	400 ± 70	420 ± 80	2.3 ± 0.9	420 ± 80
Hexanoic acid	20	0.9	PDMS Type 1	450 ± 190	470 ± 160	4.2 ± 1.6	470 ± 160
Hexanoic acid	20	1.5	PDMS Type 1	400 ± 200	540 ± 120	2.1 ± 0.8	540 ± 120
Hexanoic acid	20	2.0	PDMS Type 1	540 ± 150	430 ± 70	0.6 ± 0.2	430 ± 70
Hexanoic acid	30	1.5	PDMS Type 1	450 ± 70	390 ± 70	12.9 ± 1.2	410 ± 70

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Hexanoic acid	30	2.0	PDMS Type 1	610 ± 920	480 ± 290	11.5 ± 7.1	490 ± 290
Hexanoic acid	30	2.4	PDMS Type 1	490 ± 10	500 ± 30	9.2 ± 3.8	510 ± 30
Hexanoic acid	35	2.0	PDMS Type 1	550 ± 160	660 ± 550	21.6 ± 8.9	680 ± 550
Hexanoic acid	40	2.0	PDMS Type 1	620 ± 390	600 ± 110	39.2 ± 13.4	640 ± 110
Hexanoic acid	40	2.4	PDMS Type 1	460 ± 160	510 ± 610	27.3 ± 9.9	540 ± 610
Hexanoic acid	20	0.5	PDMS Type 2	360 ± 60	390 ± 80	1.7 ± 0.6	390 ± 80
Hexanoic acid	20	0.9	PDMS Type 2	310 ± 40	360 ± 180	1.0 ± 0.4	360 ± 180
Hexanoic acid	20	1.3	PDMS Type 2	350 ± 150	370 ± 100	0.5 ± 0.2	370 ± 100
Hexanoic acid	30	0.9	PDMS Type 2	400 ± 120	380 ± 110	6.8 ± 5.1	380 ± 110
Hexanoic acid	30	1.3	PDMS Type 2	310 ± 140	370 ± 320	4.9 ± 2.8	380 ± 320
Hexanoic acid	30	2.0	PDMS Type 2	390 ± 210	380 ± 200	4.1 ± 1.8	380 ± 200
Hexanoic acid	35	1.3	PDMS Type 2	370 ± 340	330 ± 180	6.2 ± 3.3	330 ± 180
Hexanoic acid	40	1.3	PDMS Type 2	360 ± 210	300 ± 150	17.5 ± 8.3	320 ± 150
Hexanoic acid	40	2.0	PDMS Type 2	290 ± 380	270 ± 220	11.6 ± 5.4	280 ± 220
Hexanoic acid	40	3.3	PDMS Type 2	340 ± 60	230 ± 520	7.4 ± 1.2	240 ± 520
Hexanoic acid	30	0.3	POMS	390 ± 60	390 ± 60	1.7 ± 0.3	390 ± 60
Hexanoic acid	30	1.3	POMS	400 ± 150	350 ± 100	0.5 ± 0.2	350 ± 100
Hexanoic acid	30	2.0	POMS	320 ± 50	320 ± 60	0.3 ± 0.2	320 ± 60
Hexanoic acid	40	0.5	POMS	370 ± 110	370 ± 40	3.6 ± 3.4	380 ± 40
Hexanoic acid	40	1.3	POMS	440 ± 180	420 ± 20	3.4 ± 0.3	430 ± 20

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Hexanoic acid	40	2.0	POMS	350 ± 50	350 ± 100	1.7 ± 1.1	350 ± 100
Octanoic acid	20	0.9	PDMS Type 1	300 ± 100	330 ± 270	2.0 ± 1.7	330 ± 270
Octanoic acid	20	1.5	PDMS Type 1	310 ± 190	340 ± 250	0.8 ± 0.6	340 ± 250
Octanoic acid	20	2.0	PDMS Type 1	340 ± 120	320 ± 50	0.3 ± 0.3	320 ± 50
Octanoic acid	30	1.5	PDMS Type 1	310 ± 40	290 ± 50	8.7 ± 1.6	290 ± 50
Octanoic acid	30	2.0	PDMS Type 1	330 ± 60	340 ± 110	6.3 ± 3.6	350 ± 110
Octanoic acid	30	2.4	PDMS Type 1	310 ± 70	310 ± 60	4.2 ± 2.0	310 ± 60
Octanoic acid	35	2.0	PDMS Type 1	370 ± 100	320 ± 50	11.7 ± 5.9	330 ± 50
Octanoic acid	40	2.0	PDMS Type 1	460 ± 330	400 ± 100	25 ± 19.8	430 ± 100
Octanoic acid	40	2.4	PDMS Type 1	340 ± 260	260 ± 160	23.2 ± 12.6	290 ± 160
Octanoic acid	20	0.5	PDMS Type 2	260 ± 90	270 ± 50	0.6 ± 0.3	270 ± 50
Octanoic acid	20	0.9	PDMS Type 2	230 ± 50	260 ± 130	0.4 ± 0.2	260 ± 130
Octanoic acid	20	1.3	PDMS Type 2	240 ± 220	280 ± 340	0.2 ± 0.0	280 ± 340
Octanoic acid	30	0.9	PDMS Type 2	310 ± 210	300 ± 160	5.1 ± 7.4	300 ± 160
Octanoic acid	30	1.3	PDMS Type 2	180 ± 90	200 ± 80	1.4 ± 0.1	200 ± 80
Octanoic acid	30	2.0	PDMS Type 2	230 ± 140	220 ± 80	1.1 ± 0.6	220 ± 80
Octanoic acid	35	1.3	PDMS Type 2	160 ± 110	160 ± 80	1.5 ± 0.4	160 ± 80
Octanoic acid	40	1.3	PDMS Type 2	250 ± 230	210 ± 120	8.9 ± 2.0	220 ± 120
Octanoic acid	40	2.0	PDMS Type 2	190 ± 170	170 ± 90	6.9 ± 3.6	180 ± 90
Octanoic acid	40	3.3	PDMS Type 2	270 ± 30	180 ± 400	3.2 ± 2.2	190 ± 400

Compound	Operating Conditions			Mass of flavour compound (mg)			
	Feed temperature (°C)	Permeate pressure (kPa)	Membrane	Feed	Retentate	Permeate	Retentate + Permeate
Octanoic acid	30	0.3	POMS	270 ± 20	300 ± 30	0.3 ± 0.0	300 ± 30
Octanoic acid	30	1.3	POMS	330 ± 490	420 ± 350	0.3 ± 0.5	420 ± 350
Octanoic acid	30	2.0	POMS	260 ± 110	260 ± 70	0.1 ± 0.2	260 ± 70
Octanoic acid	40	0.5	POMS	250 ± 150	240 ± 150	0.7 ± 0.7	240 ± 150
Octanoic acid	40	1.3	POMS	310 ± 50	300 ± 80	1.1 ± 0.8	300 ± 80
Octanoic acid	40	2.0	POMS	330 ± 180	280 ± 50	0.4 ± 0.7	280 ± 50

Appendix D

Flavour compound enrichment factors at various operating conditions

With each membrane, the enrichment factors of flavour compounds were measured at a range of feed temperatures and permeate pressures (using the standard multicomponent feed). Tables D-1 and D-2 give the results obtained with the POMS and PDMS Type 2 membranes respectively.

Table D-1: Enrichment factors (mean ± standard error) of flavour compounds at various operating conditions (POMS membrane; standard multicomponent feed).

	Enrichment factor					
Feed temperature	30°C			40°C		
Permeate pressure	0.3 kPa	1.3 kPa	2 kPa	0.5 kPa	1.3 kPa	2 kPa
2-Heptanone	25.12 ± 0.81	26.49 ± 0.3	25.52 ± 0.56	21.35 ± 1.09	22.16 ± 0.55	22.57 ± 2.75
2-Nonanone	6.99 ± 0.91	8.67 ± 1.52	7.94 ± 1.49	4.11 ± 0.47	7.19 ± 0.97	4.20 ± 0.86
Acetic acid	1.09 ± 0.07	0.64 ± 0.02	0.45 ± 0.05	1.00 ± 0.03	1.02 ± 0.01	0.73 ± 0.1
Butanoic acid	3.22 ± 0.12	1.32 ± 0.08	0.86 ± 0.06	3.40 ± 0.17	2.61 ± 0.06	1.98 ± 0.29
Hexanoic acid	2.20 ± 0.11	0.93 ± 0.03	0.58 ± 0.06	2.77 ± 0.28	2.41 ± 0.06	1.35 ± 0.19
Octanoic acid	0.39 ± 0.03	0.62 ± 0.22	0.32 ± 0.09	0.61 ± 0.08	0.84 ± 0.15	0.28 ± 0.08
Ethyl butanoate	31.11 ± 0.98	33.01 ± 0.56	33.18 ± 1.33	27.65 ± 1.18	28.63 ± 1.06	28.69 ± 3.85
Ethyl hexanoate	9.71 ± 1.1	14.17 ± 2.15	14.26 ± 2.31	5.51 ± 0.55	10.30 ± 1.15	6.31 ± 1.37
Ethyl octanoate	3.11 ± 0.66	3.49 ± 0.94	3.07 ± 0.89	1.10 ± 0.25	3.60 ± 0.72	1.13 ± 0.34

Table D-2: Enrichment factors (mean ± standard error) of flavour compounds at various operating conditions (PDMS Type 2 membrane; standard multicomponent feed).

	Enrichment factor									
Feed temperature	20°C			30°C			35°C	40°C		
Permeate pressure	0.5 kPa	0.9 kPa	1.3 kPa	0.9 kPa	1.3 kPa	2.0 kPa	1.3 kPa	1.3 kPa	2.0 kPa	3.3 kPa
2-Heptanone	16.18 ± 2.03	19.38 ± 1.46	21.15 ± 1.79	12.36 ± 1.43	13.66 ± 0.90	15.59 ± 0.32	12.34 ± 1.21	10.29 ± 0.70	10.17 ± 0.77	15.34 ± 0.44
2-Nonanone	4.65 ± 0.82	6.24 ± 0.93	7.10 ± 2.46	4.92 ± 0.70	3.90 ± 0.06	3.99 ± 0.22	2.98 ± 0.28	3.92 ± 0.35	3.89 ± 0.49	3.64 ± 0.21
Acetic acid	0.52 ± 0.07	0.44 ± 0.03	0.35 ± 0.10	0.50 ± 0.05	0.61 ± 0.06	0.70 ± 0.18	0.60 ± 0.07	0.74 ± 0.11	0.50 ± 0.07	0.59 ± 0.00
Butanoic acid	0.80 ± 0.09	0.67 ± 0.07	0.57 ± 0.01	1.05 ± 0.09	1.08 ± 0.15	1.13 ± 0.19	1.18 ± 0.12	1.43 ± 0.14	1.04 ± 0.14	1.22 ± 0.04
Hexanoic acid	0.78 ± 0.10	0.57 ± 0.02	0.36 ± 0.05	1.42 ± 0.13	1.17 ± 0.17	1.09 ± 0.11	1.36 ± 0.15	1.92 ± 0.19	1.34 ± 0.18	1.39 ± 0.03
Octanoic acid	0.29 ± 0.05	0.23 ± 0.02	0.15 ± 0.02	1.15 ± 0.31	0.36 ± 0.02	0.32 ± 0.04	0.36 ± 0 .02	1.03 ± 0.01	0.86 ± 0.06	0.62 ± 0.09
Ethyl butanoate	9.03 ± 1.07	10.99 ± 0.51	12.89 ± 0.65	6.88 ± 1.16	7.32 ± 0.46	8.48 ± 0.28	6.78 ± 0.71	5.56 ± 0.48	5.43 ± 0.41	8.69 ± 0.18
Ethyl hexanoate	7.84 ± 1.23	10.33 ± 1.28	13.90 ± 4.70	7.01 ± 0.71	5.65 ± 0.33	5.87 ± 0.42	5.22 ± 0.32	5.51 ± 0.54	5.47 ± 0.51	6.56 ± 0.45
Ethyl octanoate	2.95 ± 0.68	4.65 ± 0.58	5.53 ± 2.88	3.83 ± 0.62	2.87 ± 0.81	2.29 ± 0.76	1.56 ± 0.25	2.65 ± 0.35	2.47 ± 0.31	1.98 ± 0.34

Appendix E

Flavour compound enrichment factors at two concentrations

Pervaporation experiments were carried out at one set of operating conditions only, with the standard multicomponent feed, except that each flavour compound was at 50% of its standard concentration. The enrichment factors were not significantly different from those obtained at standard concentrations under the same operating conditions (Table E-1).

Table E-1: Enrichment factors of flavour compounds at two feed concentrations. Operating conditions: 30°C feed temperature, 1.5 kPa permeate pressure, PDMS Type 1 membrane.

Compound	Feed concentration (mg kg^{-1})		Enrichment factor (95% confidence)	
	Standard concentration	50% concentration	Standard concentration	50% concentration
2-Heptanone	9.8	4.9	8.2 ± 0.8	9.7 ± 17.7
2-Nonanone	9.8	4.9	4.2 ± 0.6	7.4 ± 12.5
Ethyl butanoate	101	50.5	9.2 ± 0.9	10.0 ± 13.0
Ethyl hexanoate	100	50	5.5 ± 0.8	8.3 ± 11.9
Ethyl octanoate	10.4	5.2	1.1 ± 0.3	1.7 ± 0.5
Acetic acid	105	52.5	0.51 ± 0.12	0.6 ± 0.4
Butanoic acid	107	53.5	0.78 ± 0.08	0.8 ± 2.0
Hexanoic acid	111	55.5	1.14 ± 0.07	1.3 ± 3.0
Octanoic acid	105	52.5	0.60 ± 0.06	1.0 ± 2.3

Appendix F

Feed partial pressures of diacetyl and water

The partial pressure ($p_{i,f}$) of a compound in the feed is given by Equation (F-1):

$$p_{i,f} = x_{i,f}\gamma_{i,f}p_i^0 \qquad \textbf{(F-1)}$$

where $x_{i,f}$ is the mole fraction of that compound in the feed, $\gamma_{i,f}$ is the activity coefficient of that compound, and p_i^0 is its saturated vapour pressure. Table F-1 shows the values of these parameters at 20°C and 40°C, for diacetyl and water, in starter distillate.

Table F-1: Calculation of feed partial pressures of diacetyl and water in starter distillate.

Compound	Feed temperature (°C)	Mole fraction	Activity coefficient[a]	Saturated vapour pressure[b] (Pa)	Partial pressure (Pa)
Diacetyl	20	4.6×10^{-4}	13	5605	33.5
	40	4.6×10^{-4}	13	15679	93.8
Water	20	1	1	2353	2353
	40	1	1	7428	7428

[a]Diacetyl value from Baudot & Marin (1996); water value assumed to be unity for a dilute solution

[b]Diacetyl values calculated from Antoine constants (Baudot & Marin, 1996); water values from Borgnakke & Sonntag (1997)

The feed partial pressure of diacetyl at 40°C was 2.8 times its value at 20°C, and the partial pressure of water at 40°C was 3.2 times its value at 20°C (Table F-1).

Appendix G

Mass balance for concentration of diacetyl in starter distillate

As diacetyl permeates through the membrane, its concentration in the retentate will decrease over time. Under the experimental conditions in this study, the retentate concentration remained approximately constant, because only a small amount of the starter distillate (2% of the total feed, over a four-hour run) permeated through the membrane. However, if 10% of the total feed was removed as permeate, this approximation would no longer be valid. This means that the calculation of the theoretical permeate concentration, when only the enrichment factor and initial feed concentration are known, is more complex than simply multiplying the initial feed concentration by the enrichment factor.

The mass balance in Figure G-1 applies to the hypothetical case in which 10 L of starter distillate feed (2200 mg L^{-1} diacetyl) is used to produce 1 L of permeate (by increasing the run time and membrane area). The enrichment factor of 6.3 was taken from experimental data at 40°C, and it was assumed that 2% of the total feed would permeate through the membrane every four hours (permeate flow rate of 0.05 L h^{-1}).

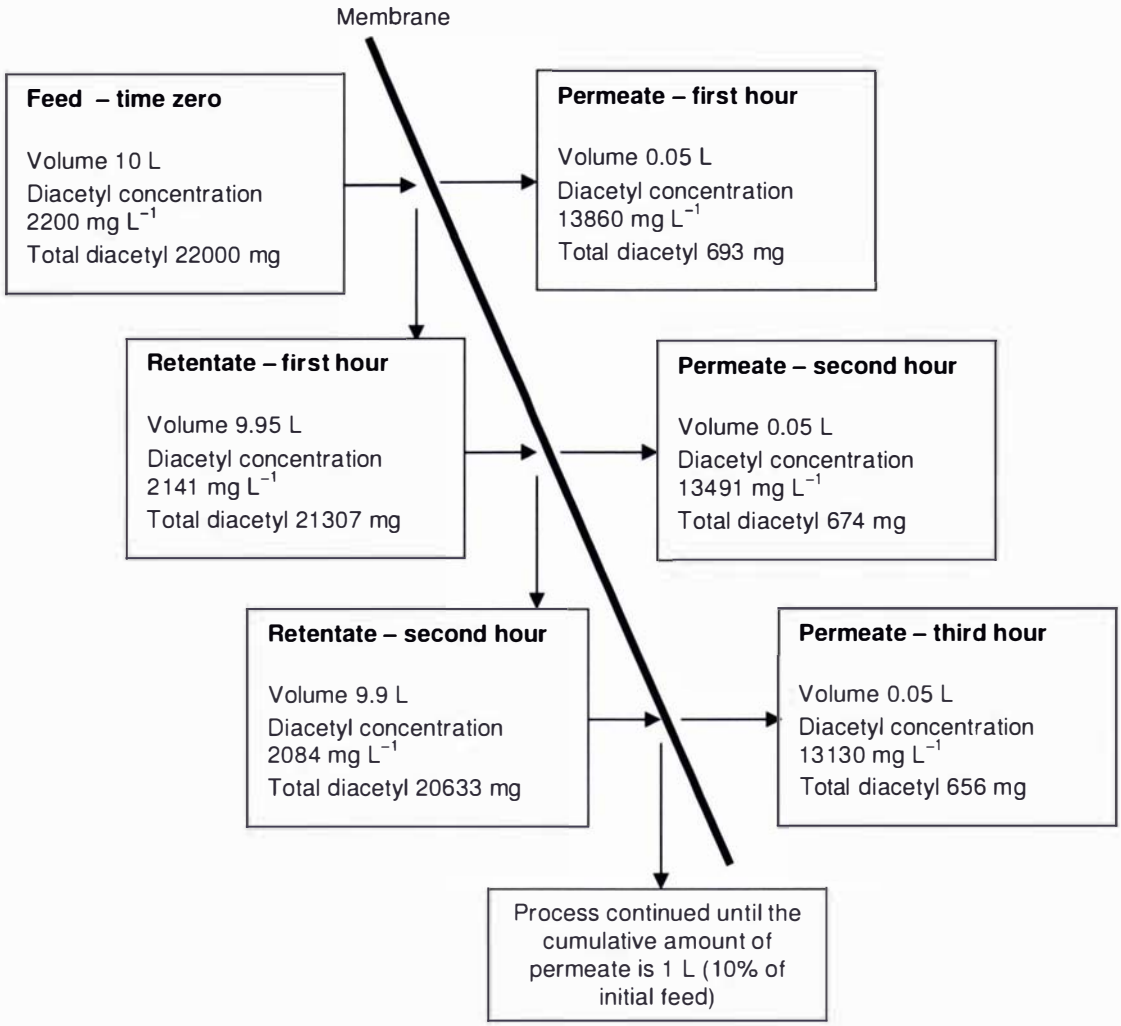

Figure G-1: Mass balance for concentration of diacetyl using pervaporation, with a total permeate flow rate of 0.05 L h^{-1} and an enrichment factor of 6.3 for diacetyl. Example calculations are given on the following page.

Example calculations

First hour: *Permeate*

Volume = 0.5% × 10 L
= 0.05 L

Diacetyl concentration = 6.3 × 2200 mg L^{-1}
= 13 860 mg L^{-1}

Total diacetyl = 13 860 mg L^{-1} × 0.05 L
= 693 mg

Retentate

Volume = 10 L – 0.05 L
= 9.95 L

Total diacetyl = 22 000 mg – 13 860 mg
= 21 307 mg

Diacetyl concentration = 21 307 mg / 9.95 L
= 2141 mg L^{-1}

Second hour: *Permeate*

Volume = 0.5% × 10 L
= 0.05 L
(cumulative volume = 0.05 L + 0.05 L
= 1 L)

Diacetyl concentration = 6.3 × 2141 mg L^{-1}
= 13 491 mg L^{-1}

Total diacetyl = 13 491 mg L^{-1} × 0.05 L
= 674 mg

Retentate

Volume = 9.95 L – 0.05 L
= 9.9 L

Total diacetyl = 21 307 mg – 674 mg
= 20 633 mg

Diacetyl concentration = 20 633 mg / 9.9 L
= 2084 mg L^{-1}

Continuing in the same manner, Figure G-2 shows how the total starter distillate volume distributes between the retentate and cumulative permeate over time, and Figure G-3 shows how the diacetyl distributes between the retentate and cumulative permeate. Hence, the diacetyl concentration in the permeate and retentate changes with time as shown by Figure G-4.

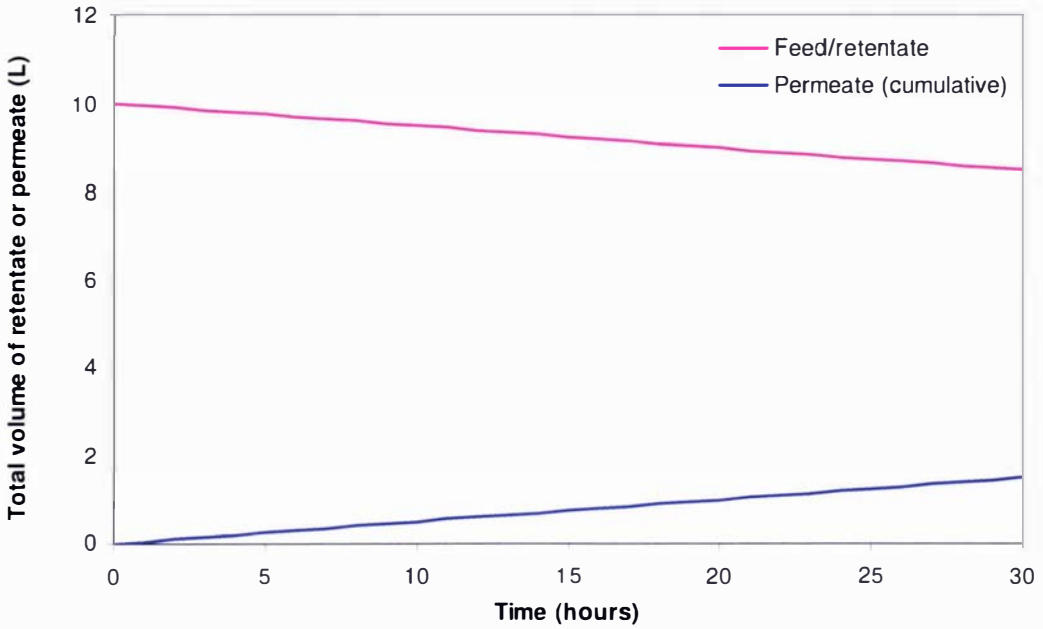

Figure G-2: Calculated change in retentate and cumulative permeate volumes over time (total volume of starter distillate = 10 L).

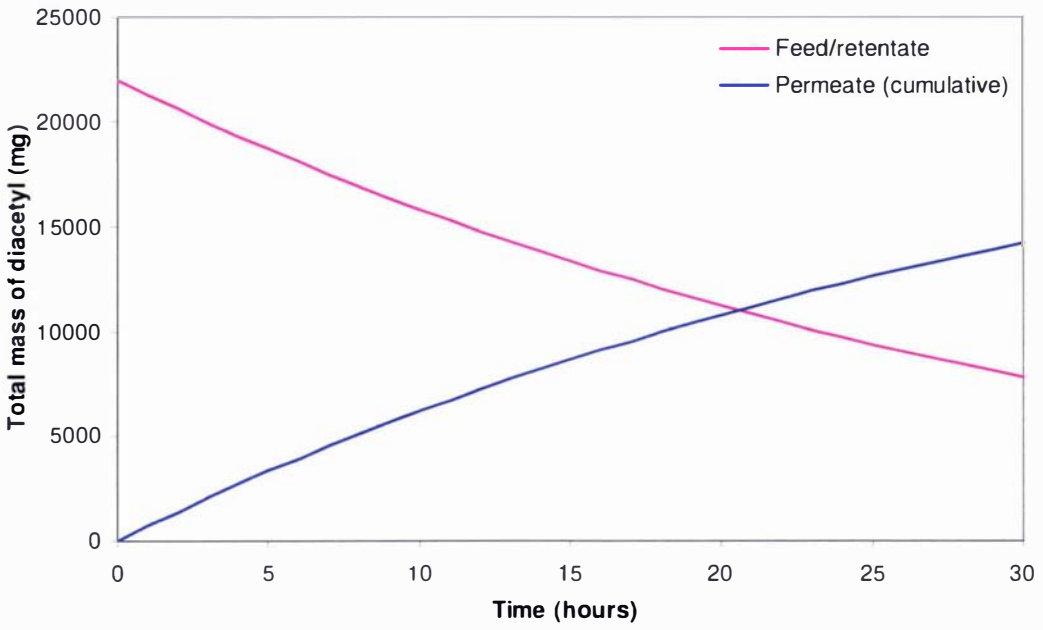

Figure G-3: Calculated mass of diacetyl in retentate and cumulative permeate over time (total mass of diacetyl in system = 22 000 mg).

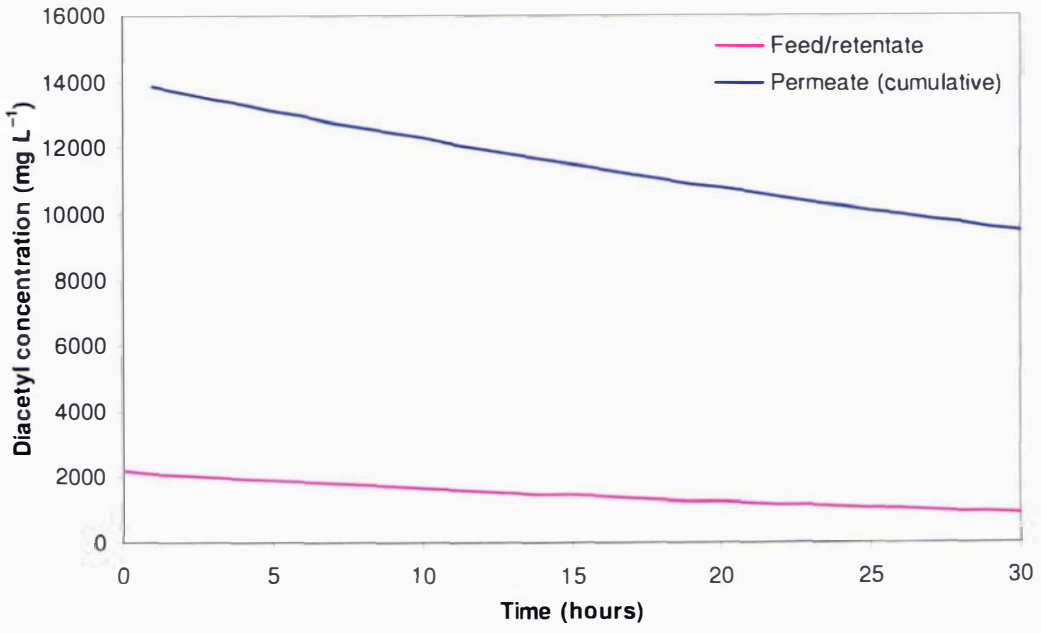

Figure G-4: Calculated change in diacetyl concentration over time, in retentate and cumulative permeate (initial feed concentration = 2200 mg L^{-1}).

After 20 hours, 10% of the total feed volume has permeated through the membrane (Figure G-2). At this point, the calculated diacetyl concentrations in the permeate and retentate are 10 800 mg L^{-1} and 1200 mg L^{-1} respectively (Figure G-4).

Appendix H

Arrhenius plots of mass transfer coefficients

Figures H-1 and H-2 show the relationship between effective mass transfer coefficients and the feed temperature, for the PDMS Type 2 and POMS membranes respectively.

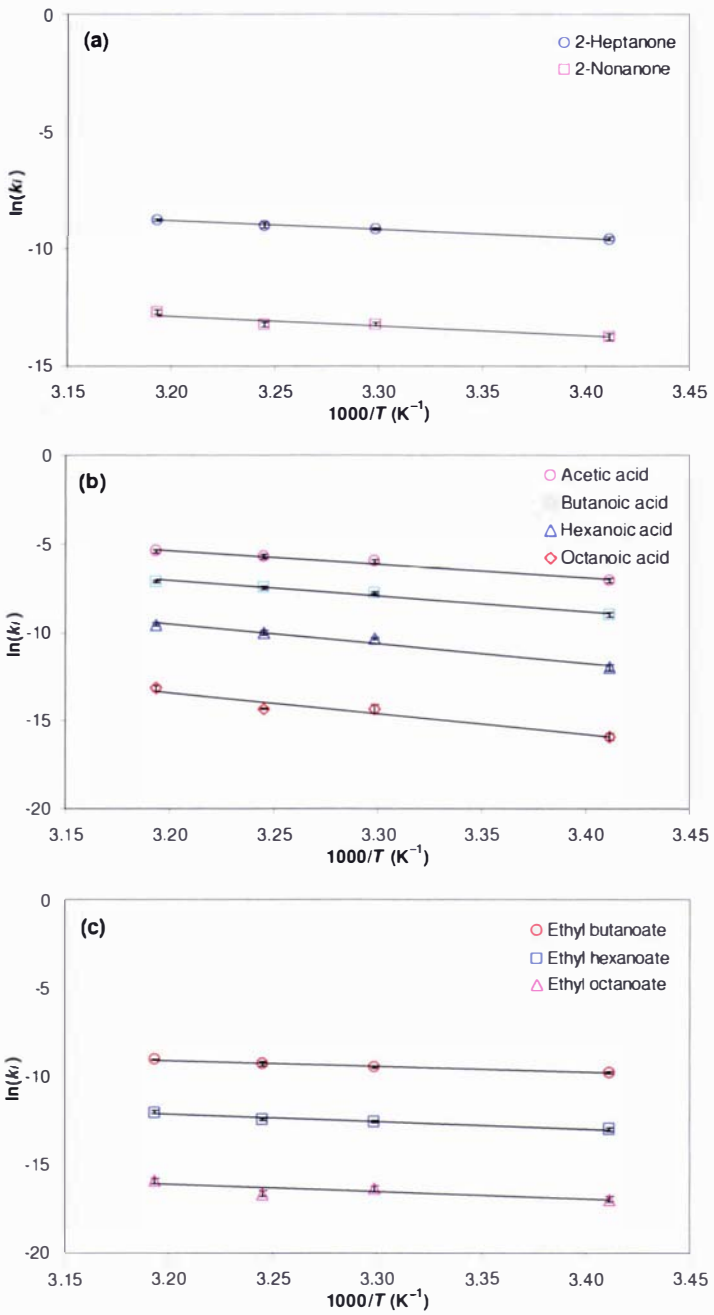

Figure H-1: Arrhenius plots of (a) ketone, (b) acid and (c) ester effective mass transfer coefficients, using the PDMS Type 2 membrane. Data points are means (± standard errors) of 3–12 measurements at each temperature.

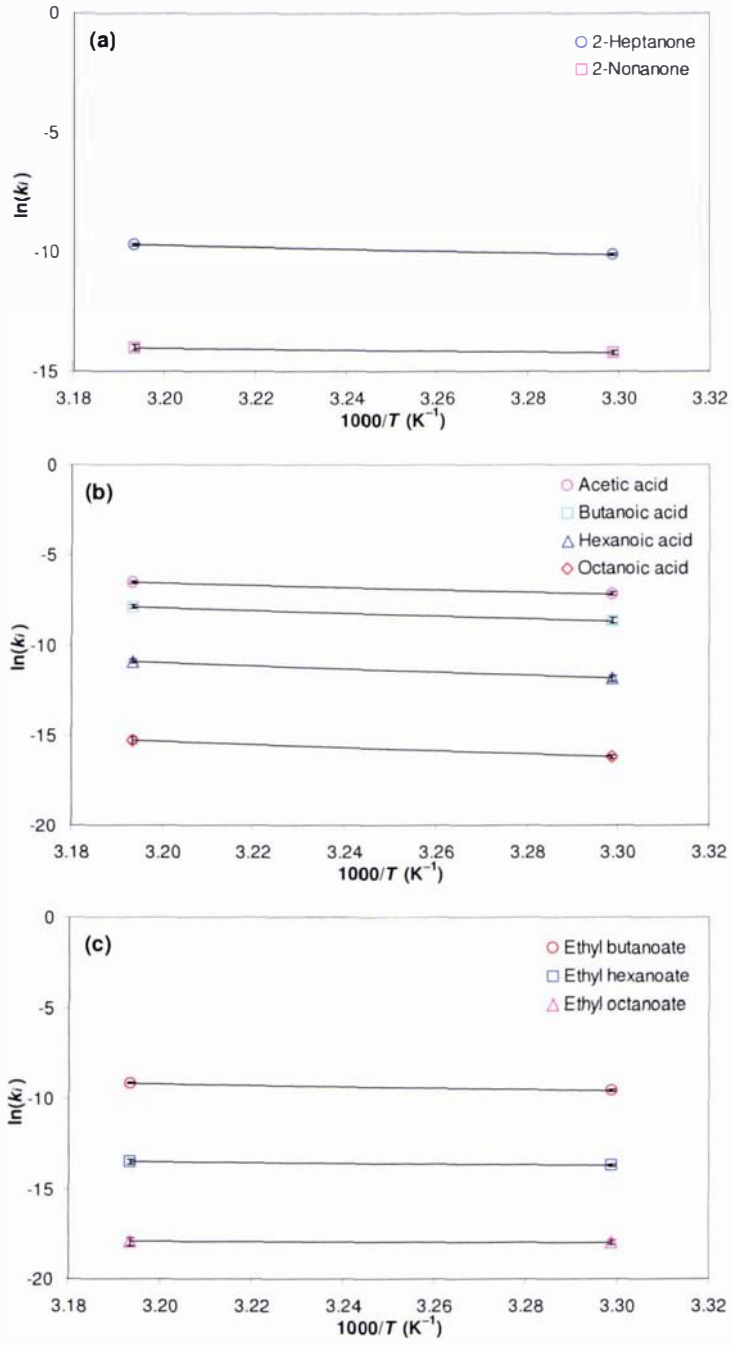

Figure H-2: Arrhenius plots of (a) ketone, (b) acid and (c) ester effective mass transfer coefficients, using the POMS membrane. Data points are means (± standard errors) of 9–18 measurements at each temperature.

Appendix I

Calculation of heat of sorption for diacetyl in PDMS

Vankelecom et al. (1997) reported the sorption of pure diacetyl in PDMS to be approximately 0.025 mL g^{-1} at 57°C. They also reported that its sorption increased by approximately 0.005 mL g^{-1} K^{-1} between 4°C and 57°C, calculated using the following equation (Vankelecom et al., 1997):

$$Temperature\ dependency = \frac{S_{57} - S_4}{S_4 \times \Delta T} \quad \textbf{(I-1)}$$

where S_{57} and S_4 are the sorption capacities at 57°C and 4°C respectively, and ΔT is the temperature difference between 4°C and 57°C.

As Vankelecom et al. (1997) did not report the sorption capacity at 4°C, this was estimated as 0.020 mL g^{-1}, using Equation (I-1). Converting to a molar basis, the sorption capacity was 2.25×10^{-4} mol g^{-1} and 2.85×10^{-4} mol g^{-1} at 4°C and 57°C respectively. These values were substituted in the Arrhenius-type equation:

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \quad \textbf{(I-2)}$$

The resulting equations (one at each temperature) were solved simultaneously for ΔH_S, to obtain a heat of sorption of 3380 J mol^{-1} for diacetyl in PDMS.