Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lipnizki, Frank and Hausmanns, Stephan(2005) 'Hydrophobic Pervaporation of Binary and Ternary Solutions: Evaluation of Fluxes, Selectivities, and Coupling Effects', Separation Science and Technology, 39: 10, 2235 — 2259

To link to this Article: DOI: 10.1081/SS-120039309

URL: http://dx.doi.org/10.1081/SS-120039309

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 10, pp. 2235–2259, 2004

Hydrophobic Pervaporation of Binary and Ternary Solutions: Evaluation of Fluxes, Selectivities, and Coupling Effects

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ABSTRACT

In hydrophobic pervaporation, the evaluation and prediction of coupling effects in multicomponent systems is one of the key requirements to improve its applicability in the biotechnology and food industry. The focus of this study is first on binary aqueous systems with methanol, ethanol, acetone, 1-propanol, 2-propanol 1,3-dioxane, and 1,4-dioxane, and then on ternary aqueous systems with 1-propanol and a second organic/aromatic component. The pervaporation experiments were carried out with polydimethyl siloxane (PDMS)—zeolite Pervap 1070 membranes. From the binary experiments, it was found that for a homologous

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DOI: 10.1081/SS-120039309
0149-6395 (Print); 1520-5754 (Online)

series of alcohols, flux and selectivity are increasing with liquid molar volume and activity coefficients. Dipole moments were identified as additional parameters to consider in the case of isomers. The experiments with ternary aqueous solutions revealed that the effect of coupling increases with the organic concentration. Furthermore, by introducing a coupling factor as a ratio of ternary and binary component permeability, it was found that the effect of coupling increases with decreasing molecular weight and reaches a maximum at the equimolar point of first and second organic components in the feed. This trend was similar for all organic/aromatic components considered in this study and gained further confirmation by using literature values.

Key Words: Pervaporation; Aqueous solutions; Coupling; Solution–diffusion.

INTRODUCTION

Hydrophobic pervaporation is a membrane separation process with high potential in the biotechnology and food industries for the recovery and concentration of products with a high quality. The key advantages of pervaporation in these industries are composed of the following: (1) energy-saving separation of azeotropes without additives; (2) no degradation of temperature-sensitive compounds, due to moderate operating temperatures; and (3) combined with a fermentator, an increased productivity can be achieved by overcoming process inhibitions without an extra heat requirement. Even though separation of a large variety of compounds with relevance to the food and biotechnology industries have been tested successfully with hydrophobic pervaporation, the majority of experimental results published so far are based on binary feed mixtures (water + aromatic/organic compound), while results of multicomponent systems with organic concentrations greater than 1 wt% are rarely reported. For multicomponent systems with an aromatic/organic concentration of only few ppm, it generally is assumed that the effect of coupling can be neglected. However, real systems are commonly multicomponent mixtures with aromatic/organic component concentrations often in the range from a few ppm to several wt%. Hence, this assumption is no longer applicable, and the effect of coupling must be considered.

The focus of this paper is on hydrophobic pervaporation of binary and ternary aqueous solutions with one or two organic/aromatic components. The phenomenological solution–diffusion model will be modified to become suitable for ternary systems by introducing a concentration dependent coupling factor. Data for different binary and ternary systems will be presented and discussed by identifying parameters influencing flux and selectivities. Thus, this paper aims to provide a deeper insight into the separation behavior of pervaporation, as well as a qualitative approach to mass transport phenomena in pervaporation.

THEORY OF SOLUTION–DIFFUSION MODEL INCLUDING COUPLING

The mass transfer in pervaporation across the membrane generally can be divided into three steps: (1) sorption into the membrane on the liquid feed side; (2) diffusion through the membrane; and (3) desorption into the vapor phase on the permeate side. This description of the mass transport through the membrane is perfectly valid for one-component transport (penetrant plus membrane). In the literature, several early approaches to describe the permeation of a single component through a homogenous membrane by using Fick's law with concentration dependent diffusion coefficient showed good agreement between theory and experimental results.[1–4] For hydrophobic pervaporation of binary systems, a linear relationship between flux and organic feed concentration often can be observed for concentrations less than 1 wt%.[5–9] Hence, in these cases, the transport of the individual components is unaffected by the simultaneous transport of other components. This can be related to the relatively low fluxes and the low degree of membrane swelling. Thus, the mass transport for these systems can be simply described by the solution–diffusion model with a concentration independent diffusion coefficient as proposed by Lee.[10] With an increasing number of components, the likelihood that coupling occurs increases, and, for ternary and multicomponent systems, the effect of coupling can commonly no longer be neglected. The relationship between organic concentration vs. flux for these multicomponent mixtures is often far more complex than for binary mixtures. In the following, a modification of the solution–diffusion model is proposed to account for the effect of coupling. In the solution–diffusion model, the flux of a component i, J_i, through a dense membrane can be given as a function of its driving force, the activity difference between feed $a_{i,\mathrm{F}}$ and permeate side, $a_{i,\mathrm{P}}$, combined with the membrane permeability, P_i, and the membrane thickness, l_M, by:

$$J_i = \frac{D_{i,\mathrm{M}}\, c_{i,\mathrm{M}}}{a_{i,\mathrm{M}}} \frac{1}{l_\mathrm{M}} \left(x_{i,\mathrm{F}}\, \gamma_{i,\mathrm{F}} - y_{i,\mathrm{P}}\, \varphi_i\, \frac{p_\mathrm{P}}{p_i^\mathrm{sat}} \right) = \frac{P_i}{l_\mathrm{M}} \left(a_{i,\mathrm{F}} - a_{i,\mathrm{P}} \right) \tag{1}$$

More details on the solution–diffusion model are given in the review paper by Wijmans and Baker.[11] However, this generally applied solution–diffusion model is an ideal solution–diffusion model based on two assumptions: (1) the diffusion coefficient is concentration–independent and (2) sorption as well as desorption coefficient follows Henry's Law. However, for multicomponent systems and high concentrations, these approaches are often not applicable since:

a. The diffusion coefficient becomes concentration dependent.
b. The effect of sorption and desorption does not follow Henry's Law.

Commonly, these two effects are summarized as coupling and are often observed in the case of ternary aqueous feed solutions[12,13–15] and in the case of some binary aqueous feed solutions.[9,16] Since it is difficult to distinguish between these interdependent effects, namely coupled sorption, diffusion, and desorption, it is suggested to describe the overall effect instead of isolating the independent effects (even though this might be desirable, it would lead to an increased complexity without improving understanding at this level). A coupling factor C_i is, therefore, introduced to account for the overall effect. This coupling factor C_i is a concentration dependent function that accounts for the difference between the permeability observed and the reference permeability P_i^0 defined at infinite dilution of the permeant *i*. The following relationship can be used to describe the dependence of the permeability on coupling:

$$P_{i,\mathrm{M}}(x_i) = C_i(x_1, \ldots, x_i)\, P_{i,\mathrm{M}}^0 \tag{2}$$

In the case of dilute binary mixtures without coupling effects, P_i^0 often can be obtained directly from the literature, e.g., Baudot and Marin[17] published an extensive review of experimental results of binary mixtures and membranes relevant for food technology. The coupling factor itself is a function of the component concentration in the mixture. The number of components in a mixture will determine the order of this function. Combing Eqs. (1) and (2) extends the solution–diffusion model to cover the effect of coupling as follows:

$$J_i = \frac{C_i(x) P_{i,\mathrm{M}}^0}{l_\mathrm{M}}\,(a_{i,\mathrm{F}} - a_{i,\mathrm{P}}) \tag{3}$$

The coupling factor $C_i(x_1 x_i)$ can be determined easily from analyzing multicomponent mixtures by decoupling permeabilities using P_i^0 as a reference permeability.

MATERIALS AND METHODS

Feed Solution

In this study, seven different ternary feed solutions were analyzed. The binary solutions, water plus one organic compound, were used as reference systems. The study considered a homologous series of alcohols: methanol, ethanol, and 1-propanol, plus its isomer 2-propanol. Furthermore, the study included the ether isomers 1,3-dioxane and 1,4-dioxane plus acetone as ketone. Distilled water was used in all experiments. The purities of 1-propanol, acetone, and 1,4-dioxane were $>99.5\%$, the purity of methanol was $>98.8\%$ and of 1,3-dioxane about 95%. Some key physical properties of the components in the feed solution are summarized in Table 1.

Pervaporation Membranes

A commercial Pervap 1070 membrane manufactured by Sulzer Chemtech (Neunkirchen-Heintz, Germany) was considered in this study. The selective layer of the Pervap 1070 is a composition of polydimethyl siloxane (PDMS) with 40 wt% (46 vol%), ZMS-5 zeolite supported by a porous asymmetric polyacrylnitrile layer, and a polyether support. The selective layer thickness of the membrane was analyzed by using a scanning electron microscope [JEOL 6310 (JEOL, Tokyo, Japan)], and was estimated to be 30.5 μm.

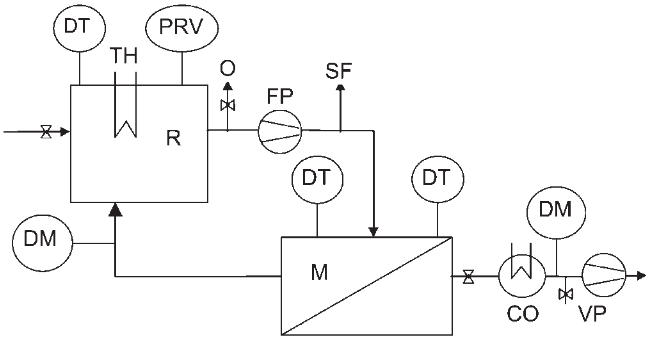
Pervaporation Apparatus

The experiments in this work were carried out with a plate and frame pilot unit supplied by Sulzer Chemtech. The membrane area of the test cell was 178 cm^2 and the volume of the feed tank was 2100 cm^3. On the permeate side of the membrane, the vacuum was maintained by a Saskia MPC 600 T vacuum pump 204 (SASKIA Hochvakuum- und Labortechnik, Ilmenau, Germany) located after a cold trap, with liquid nitrogen to collect and condense the permeate. The permeate side pressure was controlled by using a Saskia Labovac pressure gauge (SASKIA Hochvakuum- und Labortechnik, Ilmenau, Germany). The feed is supplied with a Speck SPV 2071–671 pump (Speckpumpen, Hilpoltstein, Germany). The temperature in the double-wall feed tank was controlled by a thermocouple connected to an external heat unit with integrated pump (ThermoHAAKE, Paramus, NJ, USA). The layout of the experimental setup is shown in Fig. 1.

Table 1. Key physical properties of components in the feed solution.

Feed component	Formula	Molar volume (cm^3/mol)[12]	Molar weight ($kmol/kg$)[a]	Activity coefficient at infinite dilution (80°C) (—)[a]	Dipole moment (Debye)
Water	H_2O	19	18.015	1	1.85
Methanol	CH_4O	118	32.042	2.25	1.70
Ethanol	C_2H_6O	167	46.069	5.73	1.69
Acetone	C_3H_6O	209	58.080	8.09	2.88
1-Propanol	C_3H_8O	219	60.096	15.14	1.68
2-Propanol					1.66
1,3-Dioxane	$C_4H_8O_2$	238	88.107	5.73	1.46
1,4-Dioxane					0.40

[a] Using modified UNIFAC with an organic concentration of 0.001 mol/mol.



O	Outflow	M	Module
DM	Manometer	TH	Thermostat
DT	Thermometer	PRV	Pressure relief valve
FP	Feed Pump	R	Reservoir
CO	Condenser	VP	Vacuum pump
SF	Sampling Feed		

Figure 1. Experimental setup for pervaporation experiments.

Experimental Procedure

The experiments were carried out at a constant temperature of 80°C and a permeate pressure of <6 mbar. To reduce the effect of concentration polarization, the feed pump was adjusted to produce a volumetric flow rate ≥ 6 L/min, which is in the turbulent flow regime (Re $> 20{,}000$). After placing the feed in the feed tank, the membrane was conditioned for a period of at least 2 hr. The reference concentration for all experiments was a 1-propanol concentration of 4.5 wt% in the aqueous feed solution. The experiments with the third component were always started at the lowest concentration of 0.1 mol/L and then increased to 0.5, 1.0, and 1.5 mol/L. The concentrations in the feed were regularly monitored and maintained as constant.

Analysis

The total flux was measured gravimetrically by using a microbalance by weighting the cold trap before and after the experiments with an error of 0.05%. The concentrations of the organic compounds in both feed and permeate were analyzed by using a gas chromatograph Shimadzu 14A

(Shimadzu, Kyoto, Japan) with headspace Shimadzu HSS-2B (Shimadzu Corp., Kyoto, Japan). The gas chromatograph was equipped with a Permabond CW 20M-5 μm column (Macherey-Nagel, Düren, Germany). The injector temperature was 180°C, and the detector temperature was 250°C. The carrier gas was nitrogen at a pressure of $2.5\,\mathrm{kg/cm^2}$.

Estimation of Permeability, Coupling Factor, and Selectivity

To estimate the coupling factor, the permeability as transport flux per unit driving force was determined. Assuming that the influence of both permeate-side and feed-side concentration boundary layer plus permeate side is negligible, the permeability can be determined by:

$$P_i(x_i) = \frac{l_\mathrm{M} J_i(x_i)}{a_{i,\mathrm{F}}(x_i)} = \frac{l_\mathrm{M} J_i(x_i)}{\gamma_{i,\mathrm{F}(x_i)x_i}} \tag{4}$$

The feed-side activity coefficients of the organic compounds required in Eq. (4) were estimated by using the modified universal quasi chemical function group activity coefficients (UNIFAC) method based on a software package (DDBST, Oldenburg, Germany), considering both feed concentration and feed temperature. Based on this, the coupling factor $C_i(x_i)$ was calculated by combining binary and ternary permeabilites of the different compounds:

$$C_i(x_i) = \frac{P_i^\mathrm{ter}(x_i)}{P_i^\mathrm{bin}(x_i)} \tag{5}$$

The selectivity of the separation is expressed in terms of the separation factor α_{ij}:

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} \tag{6}$$

In the following, the trends of fluxes, selectivities, and coupling factors are presented and discussed.

RESULTS AND DISCUSSION

The results are divided into two groups: (1) binary system consisting of water and one organic component and (2) ternary systems consisting of water, 1-propanol, and a second organic component.

Binary Systems: Water and Organic Compound

The fluxes and selectivities of the binary systems (water with 4.5 wt% organic solvent) are presented in Fig. 2.

While the fluxes of the systems with alcohols are independent of the chain length of the alcohols, the selectivity increases with the chain length of the alcohols. The fluxes and selectivities in the case of acetone and 1,3-dioxane are very similar. Comparing the systems with isomers, it can be seen that in case of 1-propanol and 2-propanol, the water flux in the 1-propanol systems was significantly higher, which (despite a slight increase in 1-propanol flux) lead to a lower selectivity compared with 2-propanol. In the case of the 1,3-dioxane and 1,4-dioxane systems, the dioxane fluxes were very similar. However, the water flux in the 1,4-dioxane systems was higher than in the 1,3-dioxane systems, which lead overall to a lower selectivity for the 1,4-dioxane system.

From the binary experiments, the following trends were observed:

- The selectivity increases in the order methanol, ethanol, 1-propanol, and acetone.
- The selectivity of the isomer 1,3-dioxane is increased compared to 1,4-dioxane due to increased water flux.

The trends observed are in agreement with previous works. Watson and Payne[18] showed that for a homologous series of alcohols, the selectivity in silicone rubber increases with increasing chain length. This observation was related to the fact that diffusion coefficient decreases with an increasing chain length/liquid molar volume (see Table 1). The importance of the molecular structure of isomers on the permeability was shown by Böddeker et al.[19] for isomers of butanol through PDMS and (Polyether-Block-Polyamide) membranes. Further, the activity coefficient at infinite dilution in water (see Table 1) can be related to sorption behavior and used as a measure of hydrophobicity.[20,21] Both the influence of liquid molar volume and activity coefficient at infinite dilution in water were identified by Olsson et al.[22] as key parameters determining partial flux of organic compounds and selectivity in hydrophobic pervaporation. It was found that the partial flux of the organic compounds and selectivity increases with molar volume until a critical membrane-specific molar volume, which is determined by intermolecular distance of the polymer chains given by the polymer type and degree of cross-linking, is reached. After this critical molar volume, both selectivity and organic flux are decreasing. Hence, not only the physical properties of the permeating component but also the structure of the membrane are influencing flux and selectivity. Similar results were observed for

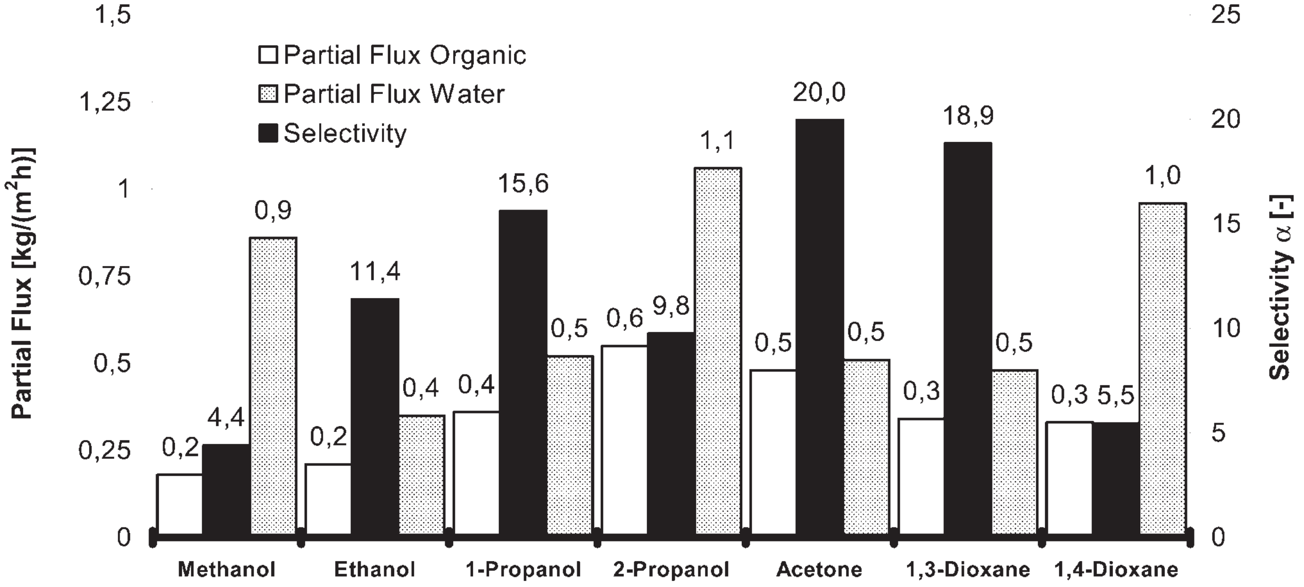


Figure 2. Partial fluxes and selectivities of different binary systems (organic component plus water) through a Pervap 1070.

the binary systems in our study, which show an increase in selectivity with increasing molar volume/weight and reduced fluxes. For the alcohols selected and membrane tested in this study, this critical molar volume was not reached. It also can be seen that these predictions are restricted to the chemical groups, i.e., alcohols. Furthermore, it was observed that the isomers, i.e., 1-propanol and 2-propanol as well as 1,3-dioxane and 1,4-dioxane, have different selectivities and fluxes. The different selectivities are mainly related to the higher partial water fluxes in the case of 2-propanol and 1,4-dioxane. Therefore, we considered dipole moments as additional parameters influencing flux and selectivity. Both 1-propanol and 1,3-dioxane are more polar, therefore, their affinity toward the membrane is more similar to the water affinity than in the case of 2-propanol and 1,4-dioxane. Hence, in the case of 1-propanol and 1,3-dioxane, water flux and organic flux are very similar. The significantly increased water flux in the case of 2-propanol and 1,3-dioxane, which leads to the low selectivities, might be partly related to the swelling of the membrane. The higher affinity of 2-propanol and 1,3-dioxane toward the membrane might lead to an initially higher organic concentration in the membrane combined with an initial swelling of the membrane. This initial swelling allows higher water fluxes, which then result in permanent swelling of the membrane. This effect increases with the dipole moment of the organic compounds and is consequently greater for 1,4-dioxane than for 2-propanol. From the results of this study and previous work, the following can be seen:

- Liquid molar volume, molar weight, and dipole moment are key parameters predicting flux and selectivity in hydrophobic pervaporation. For alcohols, flux and selectivity are increasing with liquid molar volume and activity coefficient.
- The order of flux and selectivity for isomers can be predicted by using solvent dipole moments.
- Both physical properties of permeating components and of the membrane determine flux and selectivity in hydrophobic pervaporation.

Ternary Systems: Water, 1-Propanol, and Second Organic Compound

The results of experiments with 1-propanol and a second component, i.e., methanol, ethanol, acetone, 1,3-dioxane, and 1,4-dioxane with Pervap 1070 membranes are shown in Figs. 3 to 7.

In all cases, it can be observed that the partial flux of 1-propanol approached or went through a minimum. The minimum of the 1-propanol flux depended on the second component and was in the case of ethanol at

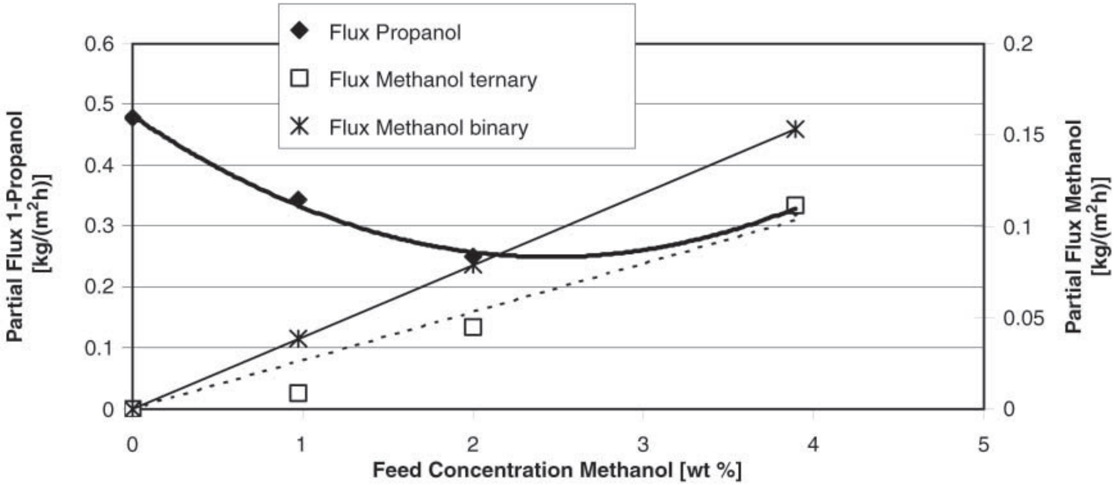


Figure 3. Partial fluxes of 1-propanol and methanol at a constant 1-propanol feed concentration of 4.5 wt% and a changing feed concentration of methanol.

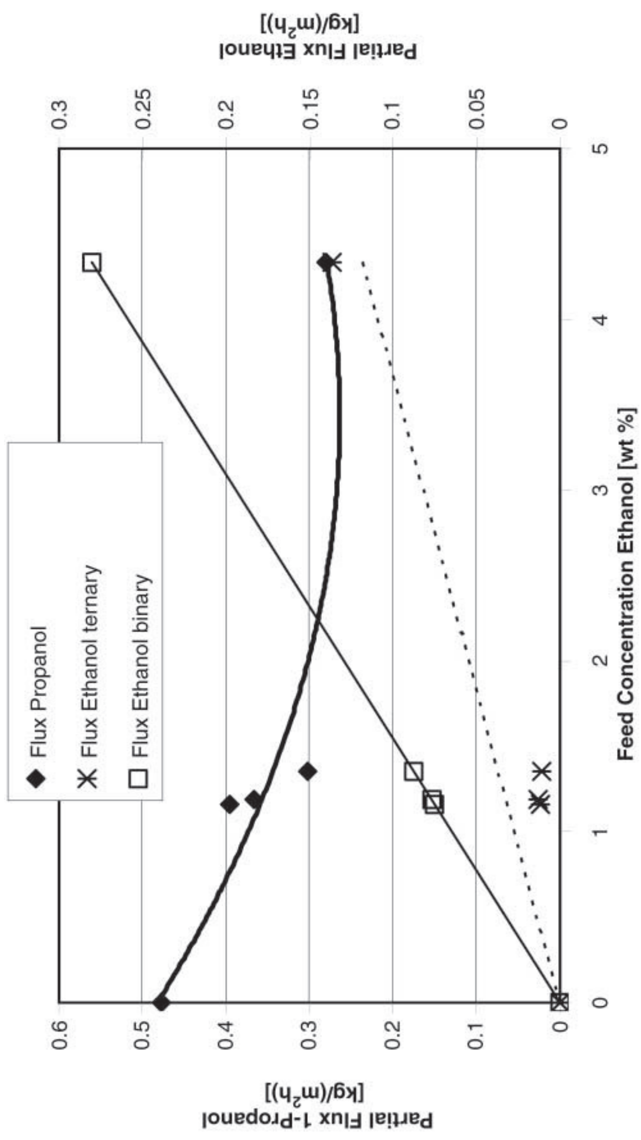


Figure 4. Partial fluxes of 1-propanol and ethanol at a constant 1-propanol feed concentration of 4.5 wt% and a changing feed concentration of ethanol.

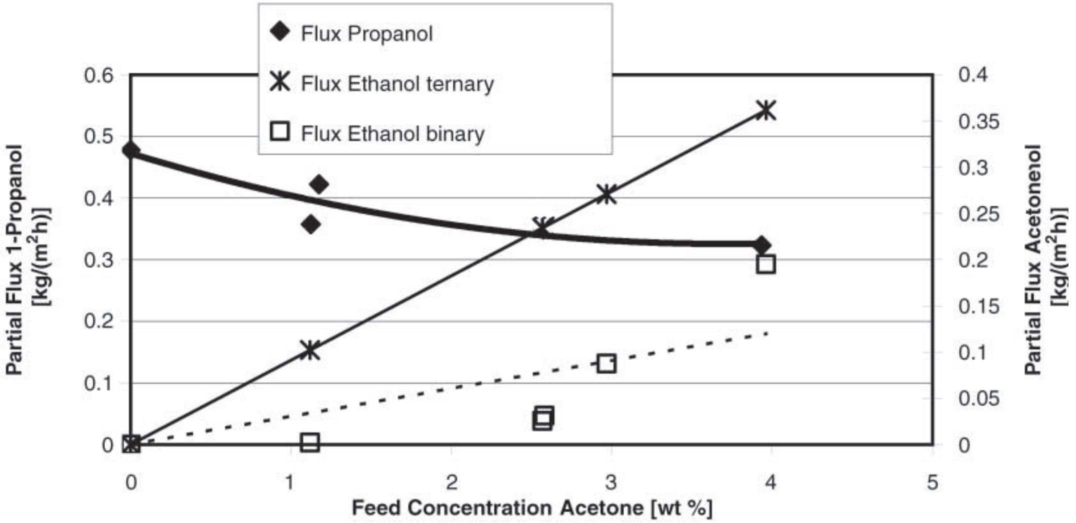


Figure 5. Partial fluxes of 1-propanol and acetone at a constant 1-propanol feed concentration of 4.5 wt% and a changing feed concentration of acetone.

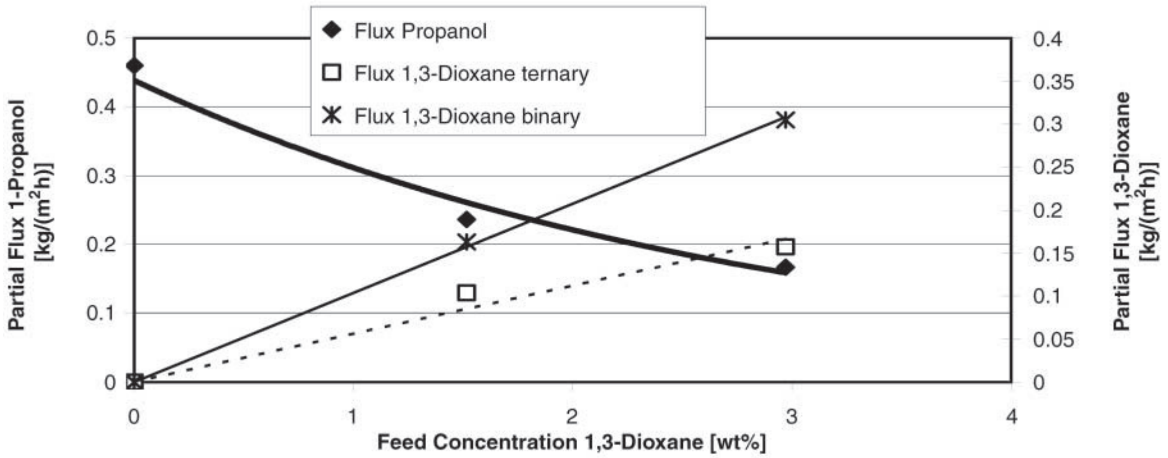


Figure 6. Partial fluxes of 1-propanol and 1,3-dioxane at a constant 1-propanol feed concentration of 4.5 wt% and a changing feed concentration of 1,3-dioxane.

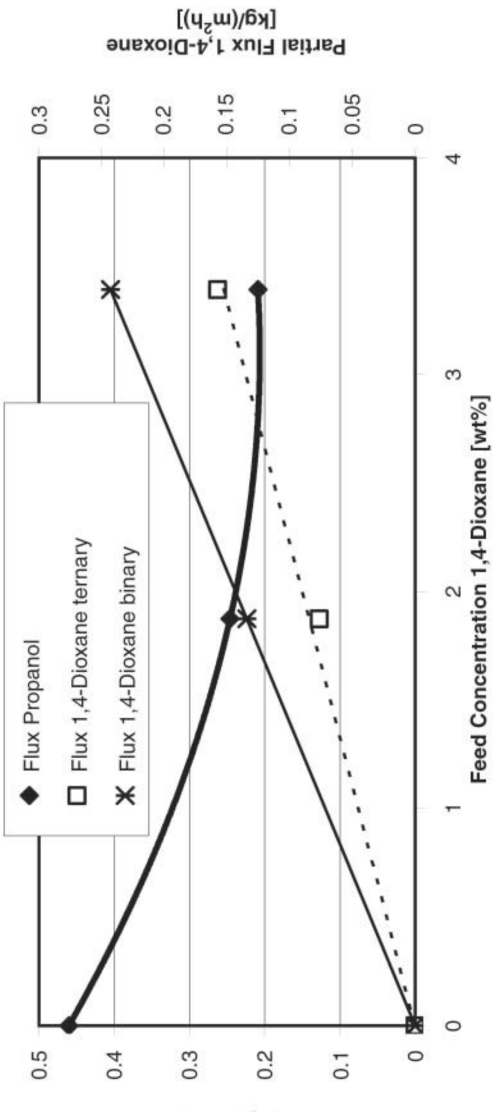


Figure 7. Partial fluxes of 1-propanol and 1,4-dioxane at a constant 1-propanol feed concentration of 4.5 wt% and a changing feed concentration of 1,4-dioxane.

3.0 wt% and of methanol at 4.0 wt%. For acetone, 1,3-dioxane, and 1,4-dioxane, the flux of 1-propanol approached a minimum, which was outside the concentration range considered in this study. From the ternary experiments, the following trends were observed:

- Permeation of one component can significantly influence the permeation of a second component.
- The flux curve of 1-proponal has a parabolic shape, independent of the second component. With increasing feed concentrations of the second component, the flux of 1-propanol decreases to a second component-specific minimum. After the minimum, the flux of 1-propanol increases with increasing feed concentration of the second component.
- In the case of low molecular weight alcohols, the minimum is within the range of investigated feed concentrations of the second component (0–3.5 wt%), while, for the other second components, it is outside the investigated range.
- The minimum has no relationship to the molecular weight or volume of the second organic component.
- The fluxes of the second components increase with an increasing feed concentration of the component.
- Comparing fluxes of the components in the ternary and binary system, it was observed that the fluxes in the ternary system are reduced compared with the binary system.

Overall, the results of pervaporation experiments with the ternary solutions showed that the permeation of the first organic components generally was reduced in the presence of the second organic component by the effect of coupling. Therefore, also, the selectivity toward the first organic component was reduced. The results of this study showed similar trends to the work by Dotremont et al.[7,13] In that work, a reduction of the partial fluxes of the chlorinated hydrocarbon tetrachlormethane and trichloroethene and isopropanol was observed after the addition of 250 ppm chloroform. Favre et al.[23] reported a significant reduction of ethanol flux after the addition of 1-butanol. The concentration range of the solvents was between 7 and 10 wt%. Karlsson and Trgrdh[24] found for the concentrations from 1 to 12 vol% ethanol, a reduction of linalool flux. In all the above studies, the partial flux of water is not influenced by the presence of the second organic component. However, studies with lower concentrations of organic components showed that the second component does not necessarily influence the partial flux of the first component. Ji et al.[8] studied different binary, ternary, and quartary systems of toluene, trichlorethane, methylene chloride, and water. In their study, no coupling of partial organic fluxes was observed for the investigated feed concentrations between 40 and 300 ppm. Similar results have been reported by Jonquières et al.[14] for the ternary system butanol, acetone, and water with changing feed concentrations of acetone of up to 1 wt%. The observation that the partial fluxes of organic components present in the feed at very low concentration do not influence each other is also shared by Karlsson[25] and Olsson,[26] who tested multicomponent mixtures of up to 10 organic compounds, representing the apple aroma at concentrations of 10 ppm each. The results from this and previous work can be summarized in the following rules of thumb for ternary feed mixtures of water with two organic components:

- A total organic concentration in the feed of ≥ 1 wt% will affect the partial organic fluxes. This effect will change with concentration.
- If the total organic concentration in the feed is between 1 wt% and 100 ppm, the partial organic fluxes might be affected.
- A total organic concentration of ≤ 100 ppm will not affect the partial organic fluxes.

For further analysis of the ternary systems, the coupling factor will be used in the following.

Coupling Factor

The function of the coupling factor of 1-propanol in relation to the different organic components is shown in Figs. 8 and 9 by using Eq. (5) and the data presented in the previous two sections.

This trend was similar to the tendencies observed for the ternary systems and depended on the organic component. The coupling factor of 1-propanol approached a minimum, which was determined by the second component. The minima of the studied components were as follows: methanol, 2.5 wt%; 1,4-dioxane, 3.0 wt%; ethanol, 3.5 wt%; and acetone, 4.0 wt%. For 1,3-dioxane, the coupling factor seemed to approach but does not reach a minimum in the investigated concentration range. Plotting the coupling factor of 1-propanol against the concentration of the organic component leads to the following observations:

- The coupling factor of 1-propanol is a function of the second organic component in the feed mixture.
- The plot of the coupling factor of 1-propanol against the organic concentration of the second organic component has a parabolic shape and reaches/approaches a minimum in the investigated concentration range.

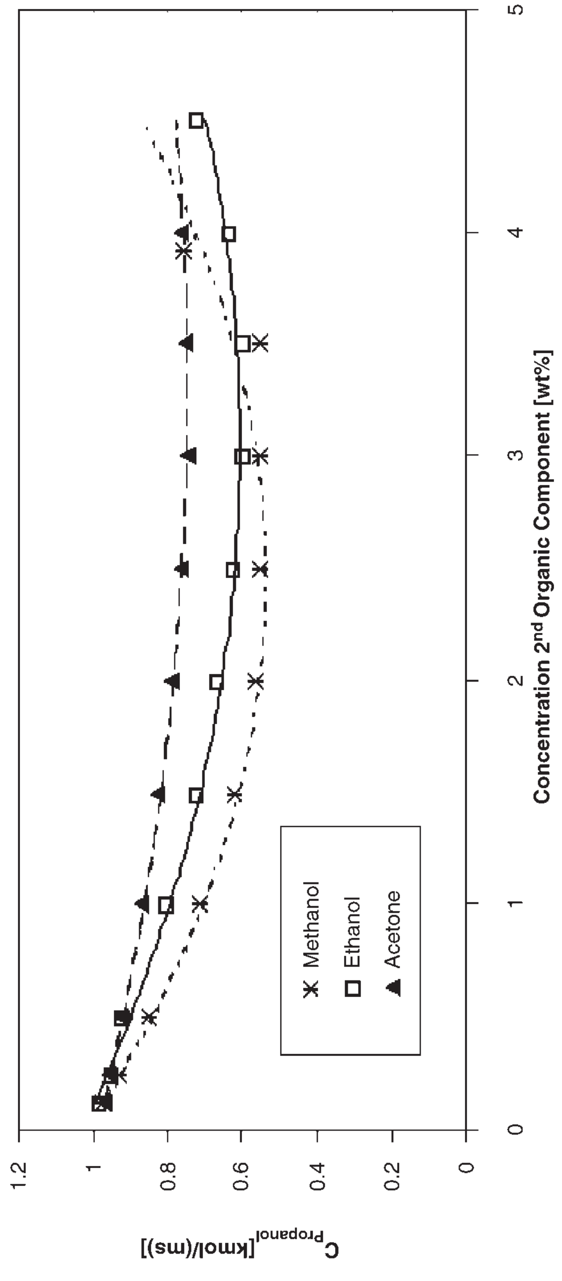


Figure 8. Coupling factor of 1-propanol $C_{1\text{-propanol}}(x)$ as a function of the concentrations of methanol, ethanol, and acetone.

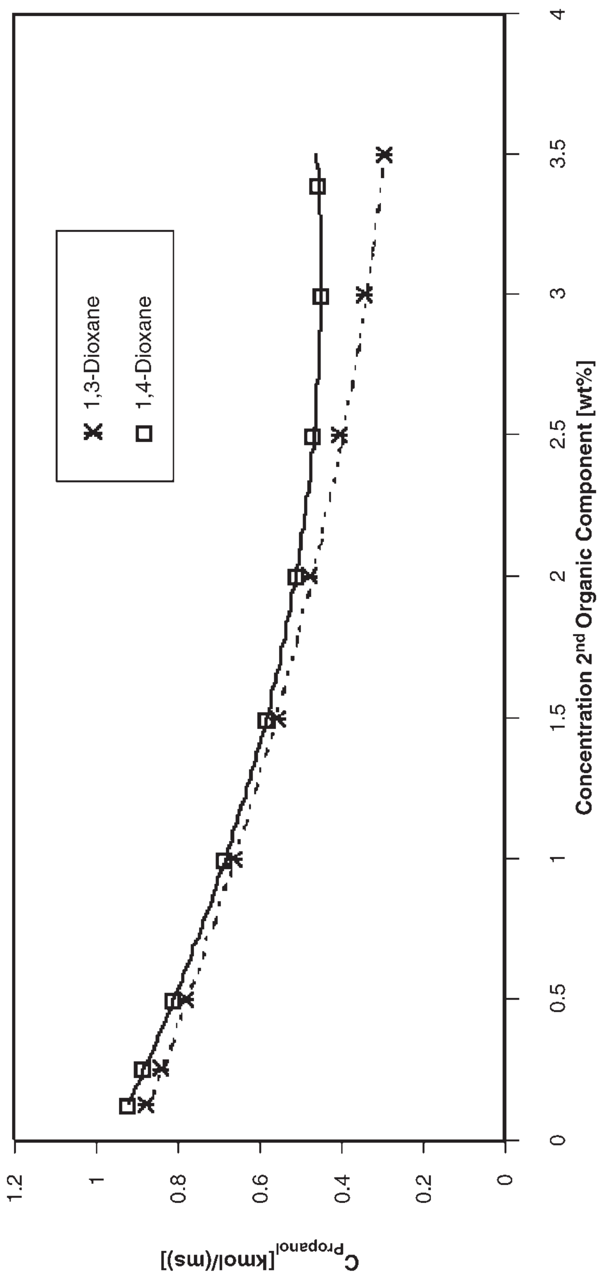


Figure 9. Coupling factor of 1-propanol $C_{1\text{-propanol}}(x)$ as a function of the concentrations of 1,3-dioxane and 1,4-dioxane.

- In case of the low molecular weight alcohols, the concentration of the second organic component required to reach the minimum increases with molecular weight and volume of the component, while the effect of coupling represented by the coupling factor decreases with molecular weight and volume.
- In the case of 1,3- and 1,4-dioxane, the coupling effect of 1,3-dioxane is greater than of 1,4-dioxane.

It should be noted that both coupling factor and fluxes of 1-propanol approached a minimum, but the values of this minima varied. The key difference between the presentation of the coupling factor and the fluxes of 1-propanol was that the coupling factor is independent of the influence of the driving force and corrected with respect to the binary permeability. In contrast to the observations of the fluxes, it was possible to observe a relationship between the minimum of the coupling factor and the physical properties of the second organic components. Therefore, it can be observed from Figs. 8 and 9 that the influence of the organic components on the permeability of 1-propanol was increasing until a minimum was reached. At this minimum, the maximum influence of the second organic component on the permeation of 1-propanol occurred. After the minimum, the influence of the second organic component on the permeation of 1-propanol was decreasing. It was found that the minimum occurred when the concentration of 1-propanol and the second organic component in the feed reached their equimolar point, i.e., the same molar feed concentration. Similar trends also were observed in other studies. Hausmanns[27] observed this trend for PDMS Pervap 1060 membranes (Sulzer Chemtech) and different alcohols. Furthermore, an analysis of the work by Dotrémont,[7] which focused on the permeation of different concentrations of chloroform and trichlorethene in aqueous solution through PDMS-zeolite membranes, revealed a minimum of the coupling factor at the equimolar point of the two components in the feed. From our results, it can be further seen that the effect of the coupling factor increases with the molecular weight and volume. Hence, the effect of coupling increases from methanol to acetone and, therefore, can be related to physical properties of the components. Based on the studied systems, the following trends can be used to predict the effect of coupling by using the coupling factor:

- The effect of coupling can be partly related to physical component properties, i.e., molecular weight and volume. The smaller the molecular weight of the organic component, the greater the effect of coupling.
- The coupling factor approaches a minimum at the equimolar point of the first and second organic component in the feed and, therefore, determines the point where the effect of coupling is most significant.

- Before the equimolar point of the two organic feed components, the effect of coupling is increased to a maximum, and, after the equimolar points, it decreases.

CONCLUSIONS

This study highlights the importance of coupling in the permeation of organic components. The first part of the analysis of the permeation of binary aqueous solutions with different organic/aromatic components through Pervap 1070 membranes revealed that liquid molar volume, activity coefficient at infinite dilution in water, and dipole moments of the different organic/aromatic components can be used to predict the order of flux and selectivity in hydrophobic pervaporation. For alcohols, flux and selectivity generally are increasing with liquid molar volume and activity coefficients. In the case of the isomers, the dipole moments have to be considered as an additional parameter. From the experiments with ternary aqueous solutions consisting of 1-propanol and a second organic/aromatic component, it was found that the flux and selectivity are changed compared with the binary systems. The importance of considering the effect of coupling increases with the organic concentration. To analyze the effect of coupling in further detail, a coupling factor was introduced and calculated. This coupling factor, the ratio of binary and ternary permeability, eliminates the influence of driving force, i.e., the activity difference between feed and permeate side. By using this factor as a measure of coupling, it was found the effect of coupling increases with a decreasing molecular weight and reaches a maximum at the equimolar point of the first and second organic component in the feed. After this point, the effect of coupling decreases again. This effect is similar for all organic/aromatic components considered in this study and was further confirmed by using literature values. Overall, this study gives new insight to improve the understanding and predictability of fluxes, selectivity, and coupling.

NOMENCLATURE

a	activity (—)
C	coupling factor (—)
c	mass concentration (kg/m^3)
D	diffusion coefficient (m^2/s)
l	thickness (m)
J	solute flux (kmol/m^2 sec)
P	phenomenological permeability parameter (kmol/m sec)

p	pressure (Pa, bar)
x	mole fraction in liquid phase (mol/mol)
y	mole fraction in vapor phase (mol/mol)

Greek Letters

γ	activity coefficient (—)
φ	fugacity coefficient (—)

Subscripts

F	feed
i	refers to component i
M	membrane
P	permeate

Superscripts

0	standard, reference
bin	refers to binary system
sat	saturated
ter	refers to ternary system

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