Separation of Azeotropic Organic Liquid Mixtures by Pervaporation

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We have shown that ionomeric membranes of perfluorosulfonic acid (PFSA) polymer allow selective pervaporation of polar organic compounds from their azeotropic mixtures with less polar compounds. A composite membrane of a thin PFSA polymer film, cast on a porous Teflon support, provided desirable permeant fluxes with good selectivity. Model binary azeotropes, composed of alcohols and hydrocarbons, were separated with total pervaporation fluxes of up to 9.5 $kg/h \cdot m^2$ using a stirred membrane permeation cell, the product side of which was exposed to vacuum. Fluxes increased with increasing alcohol content of the feed and with temperature. But the selectivity of the more permeating component remained reasonably constant around the azeotropic point and also over the range of temperature used in the study (25–55°C). Total pervaporation fluxes depended little on downstream pressure up to 6.66 kPa (50 torr). These separation data were explained by a mathematical model based on a solution-diffusion mechanism.

Introduction

Pervaporation, a promising separation method, is an energy-efficient way of separating liquid mixtures that are difficult to separate by conventional means (Mehta, 1982; Rautenbach and Albrecht, 1985). It is difficult to separate components from azeotropic mixtures or from mixtures, in which relative volatilities of the components are low. So is the recovery of a volatile component from a dilute solution. These are examples where pervaporation may find applications. In distillation, relative volatilities are indicators of the ease of separation. In pervaporation, by contrast, the flux and selectivity of permeating species depend on the membrane-sorption and membrane-diffusion properties of the species. Sorption properties can be controlled by choosing the membrane material. Since diffusion through the membrane often is rate-limiting, transport rate can be controlled by properly choosing the membrane thickness.

Work reported in the published literature on pervaporation is dominated by attempts to separate alcohol-water mixtures (Nagy et al., 1983; Hennepe et al., 1987; Sanders and Soukup, 1988; Pkamoto et al., 1987; Changluo et al., 1987; Neimoller et al., 1988; Wenzlaff et al., 1985; Hoover and Hwang, 1982; Hirotsu and Isayama, 1989; Mulder and Smolders, 1984). Removal of trace organics from aqueous solutions (Lee et al., 1989a,b; Psaume et al., 1988) and dehydration of organic compounds (Reddy and Reineke, 1988) have also been reported. The first application of pervaporation to organic liquid mixtures was reported by Aptel et al. (1976). They separated a number of azeotropic organic liquid mixtures by a Teflon film grafted with *N*-vinylpyrrolidone, a Lewis base. Later, Mulder et al. (1982) applied pervaporation to the separation of isomeric xylenes by thin films of cellulose esters. Recently, Ghosh et al. (1988) reported separating mixtures of methanol and ethylene glycol by cellophane membranes.

This work focuses on membranes made of perfluorosulfonic acid (PFSA) polymer for the separation of generic mixtures containing polar and nonpolar organic compounds that form close-boiling or azeotropic mixtures. Ion exchange membranes were applied previously by Cabasso (1983), Cabasso and Liu (1985), and Cabasso et al. (1986) to liquid hydrocarbon mixtures, such as benzene-cyclohexane and styrene-ethylbenzene, and to alcohol-hydrocarbon mixtures such as methanol-cyclohexane. The flux and selectivity they reported were promising for only the alcohol-hydrocarbon mixtures. Our work was motivated by two factors:

1. We prepared a composite PFSA-polymer membrane that provided high fluxes of amino acids from aqueous solutions (Dutta et al., 1990; Dutta and Sikdar, 1990). This membrane

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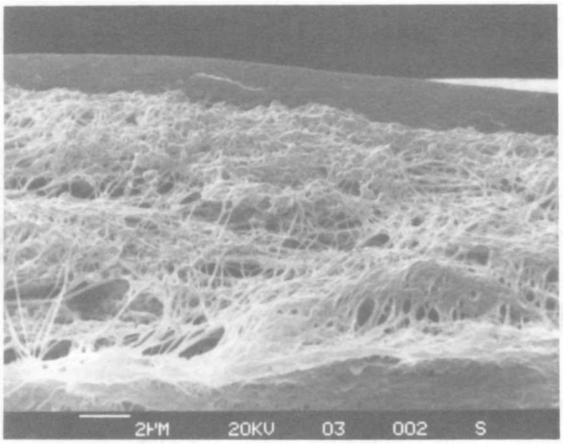


Figure 1. SEM picture of composite membrane.

became a good candidate for high-flux pervaporation because PFSA polymer undergoes swelling in the presence of polar solvents such as water and alcohols.

2. We wanted to explore the potential of PFSA-based membranes for separating a large number of mixtures composed of polar and nonpolar organic compounds.

Both the commercially available PFSA-polymer membranes and this composite membrane underwent considerable swelling in polar solvents like water and alcohols, and were expected to be selectively permeable to these compounds in contrast to compounds like hydrocarbons, which do not swell the material measurably. In this work we provide such separation and flux data, and present a mathematical model to describe pervaporation. A notable component of this model is that it accounts for the variation of membrane swelling along the membrane thickness.

Materials

Two types of PFSA-polymer membrane were used. The first type was a commercially available PFSA membrane (DuPont's Nafion membrane, Type 117, H-form, 170 μm dry thickness). For use in the pervaporation experiments, this membrane was treated with 2M H_2SO_4 at 60°C for 2 h, washed repeatedly with water to remove the last trace of the acid, and dried in vacuum overnight. The second type consisted of a thin layer of PFSA polymer (10-μm) on a 30-μm-thick Teflon backing with 60% porosity (Tetratek).

The composite membrane was prepared in the laboratory using a commercially available 5% solution of the PFSA polymer (equivalent weight 1,100) in lower alcohols and water (Solution Technology, Inc.). An SEM picture of the membrane is given in Figure 1. Details of the casting procedure for the composite membrane were reported elsewhere (Dutta et al., 1990). Organic liquids used in the experiments were all reagent grade.

Experimental Procedure

Pervaporation experiments were carried out in a batch stirred cell (Figure 2) operated under vacuum. The cell had two flanged compartments. The upper compartment contained the feed liquid and was surrounded by a water jacket for temperature

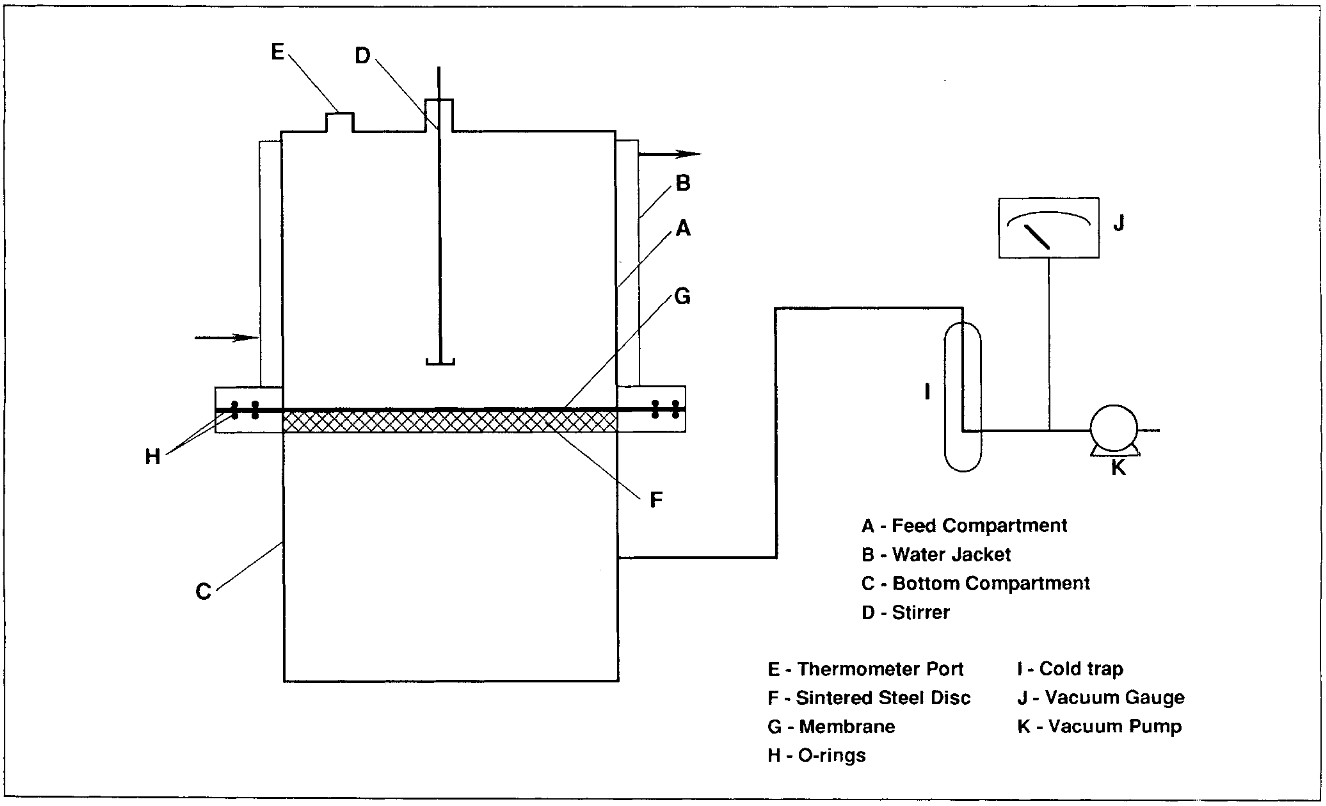


Figure 2. Experimental setup.

control. The membrane was supported on a sintered steel disk (average pore diameter = 5 μm) welded to the top of the lower compartment. Two pairs of O-rings between the flanges provided the vacuum seal.

Before starting an experiment, the membrane was allowed to equilibrate for 30 minutes in a liquid mixture of the same composition as that of the feed liquid. The swollen membrane was then placed between the flanges, and the feed liquid was charged to the upper compartment. The feed liquid mixture was brought to the desired temperature by circulating water in the jacket from a thermostatic bath. Vacuum was applied to the lower compartment and the permeate was collected in a liquid nitrogen trap. Permeate samples were collected beginning about 15 minutes after the start of vacuum. To collect a sufficient amount of permeate for the analysis of product composition, duration of an experiment varied between 10 minutes and 1 hour, depending on such factors as feed composition, temperature, and membrane type. Samples of the feed liquid were collected at the beginning and at the end of a run. Feed and permeate samples were analyzed by a refractometer (AO Scientific Abbe Mark III) or by a gas chromatograph (Hewlett Packard 5890a). Calibration curves were prepared over the concentration range by using the standard mixtures of components involved. Error in analysis remained with 2%. Fluxes were calculated from the amount of permeate collected in the trap. Feed concentration used in calculating selectivity was the average between the beginning and end of an experiment. The change in feed concentration during an experiment did not exceed 2% of the initial concentration.

The commercial and thin composite PFSA-polymer membranes that were used in pervaporation experiments were in both H- and Na-forms. For preparing the Na-form, a piece of a membrane in the H-form was kept in 1M NaOH solution overnight. Pervaporation experiments were conducted over the temperature range 25-55°C. Absolute pressure in the lower compartment of the cell was measured by a digital pressure gauge with an accuracy of 1.3 Pa (0.1 torr).

Sorption Studies

For measuring equilibrium swelling of membranes, a piece of the membrane was dried in vacuum overnight. It was then placed in a stoppered bottle containing 200 mL of a solution. The bottle was placed in a thermostat for 20 hours for the membrane and the solution to come to equilibrium. The piece of membrane was then removed from the bottle, quickly wiped with a tissue to remove the surface liquid, and then put into a flask connected to a vacuum pump through a liquid nitrogen trap. During this operation, the membrane lost the sorbed liquid, which condensed in the trap. The condensate was analyzed for its composition. The thickness of the swollen membrane and its total sorption were also measured. The latter was determined by weighing the equilibrated membrane in a stoppered bottle after removing the surface liquid.

Experimental Results

We chose several model organic mixtures to test the pervaporation efficacy of the commercial and composite PFSA-polymer membranes. These systems were: isopropanol-cyclohexane, ethanol-cyclohexane, ethanol-benzene, methanol-carbon tetrachloride, ethyl acetate-carbon tetrachloride, acetonitrile-carbon tetrachloride, ethyl acetate-cyclohexane, and methanol-benzene. The polar components were chosen to represent a wide range of polarity. Each of these mixtures forms a binary azeotrope. For some of the mixtures, data were collected over a composition range that included the azeotropic point, and for the rest a composition at or near the azeotropic point was selected.

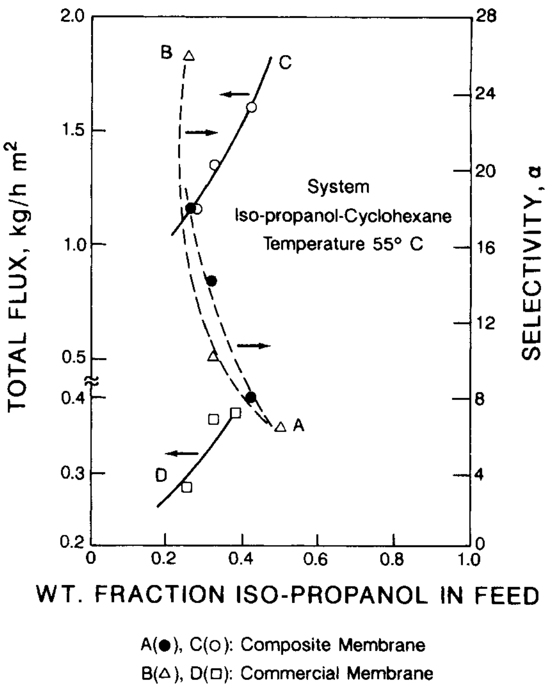


Figure 3. Flux vs. selectivity for commercial and composite membranes.

Representative total flux and selectivity data for the commercial and composite membranes are presented in Figure 3 for the isopropanol-cyclohexane system at 55°C. Selectivity of component 1 (isopropanol) over 2 is defined as:

$$\alpha = \frac{[y_p/x_p]}{[y_f/x_f]}$$

where y and x denote the weight fractions of the more permeating and the less permeating components, respectively, and the suffixes p and f denote pervaporate and feed, respectively. We found that while the composite membrane provided about 5 times more total flux than the commercial membrane, the loss in selectivity was only marginal. Similar results were obtained for the other systems also.

We found that downstream pressure, in the range 0.27-6.67 kPa (2 to 50 torr), did not affect total flux and product composition significantly for ethanol-benzene and ethanol-cyclohexane systems. These results are shown in Figures 4 and 5. These results suggest that pervaporation can be conducted at moderate vacuum. Maintaining a high vacuum in pervaporation contributes substantially toward the operating cost. For a great majority of membranes, a low downstream pressure has to be maintained to achieve desirable fluxes (Sanders and Soukup, 1988; Changluo et al., 1989). Our observation of the near-independence of flux and composition from downstream pressure, however, is at odds with previous findings. Other

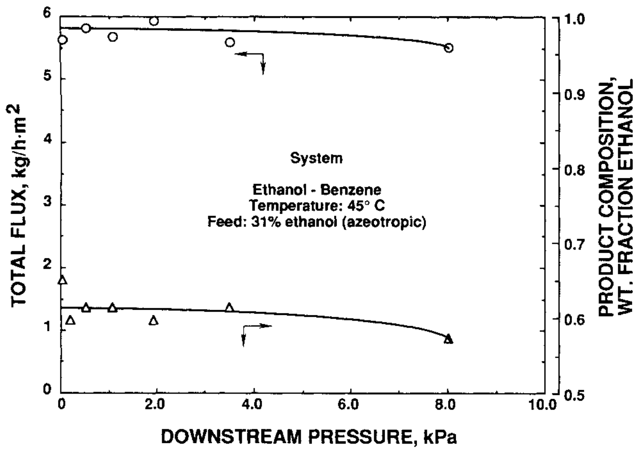


Figure 4. Effect of downstream pressure on flux and product composition: composite membrane, H-form.

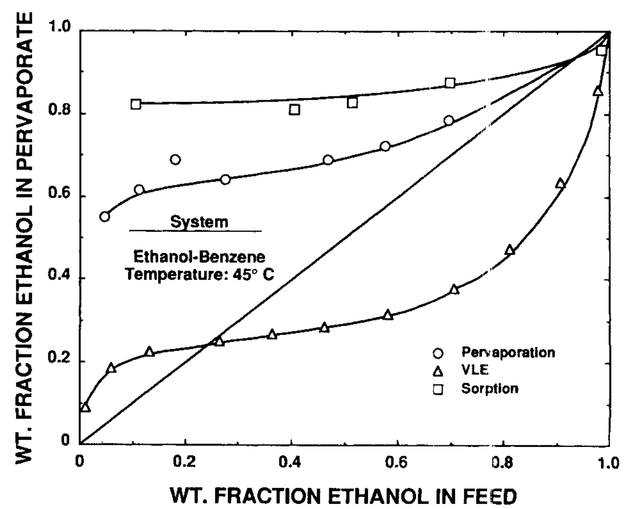


Figure 6. Pervaporation, sorption and VLE data: commercial membrane, H-form.

researchers (Nguyen, 1987; Neel et al., 1986) showed important effects of downstream pressure on pervaporation fluxes. For example, Neel et al. (1986) reported 70% reduction in total flux when downstream pressure was increased from about 0.133 to 3.07 kPa (1 to 23 torr) in experiments on water-tetrahydrofuran mixtures through a regenerated cellulose acetate membrane. The probable cause of our results is very low equilibrium concentration of solutes at the downstream face of the membrane over a range of downstream pressure. In other words, the membrane remained nearly "dry" in contact with solute vapor. This is perhaps an extreme situation, but we will make use of this observation in modeling pervaporation.

Equilibrium solubility of the components in the membrane phase is compared with vapor-liquid equilibrium (VLE) data in Figure 6 for the ethanol-benzene system. To qualitatively show the ability of the membrane to separate azeotropic mixtures, in Figure 6 we compared solubilities of the components in the membrane with their VLE data (Hirata et al., 1975). Pervaporate compositions are also plotted in the same figure. The pervaporate composition curve was nearly flat around the azeotropic point, indicating that the selectivity also remained reasonably constant around this point. In the sorption experiments, the concentration of the more polar component was higher than that of the pervaporate. Pervaporation is governed by diffusion of the components through the membrane. A sorption or swelling gradient existed in the membrane during diffusion, as a result of which the entire diffusional distance of the membrane was not at equilibrium with the upstream liquid.

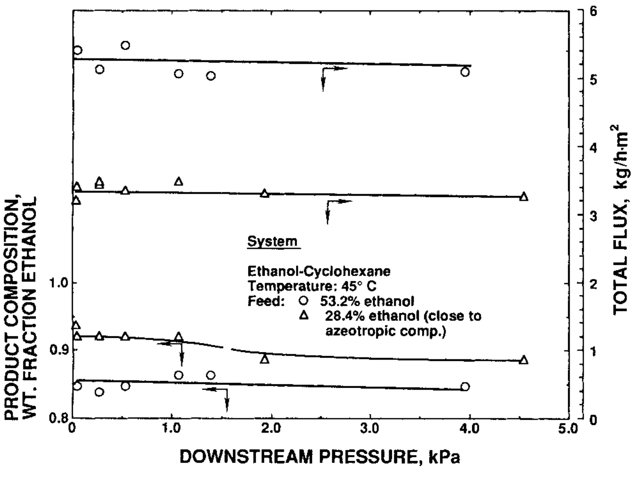


Figure 5. Effect of downstream pressure on flux and product composition: composite membrane, H-form.

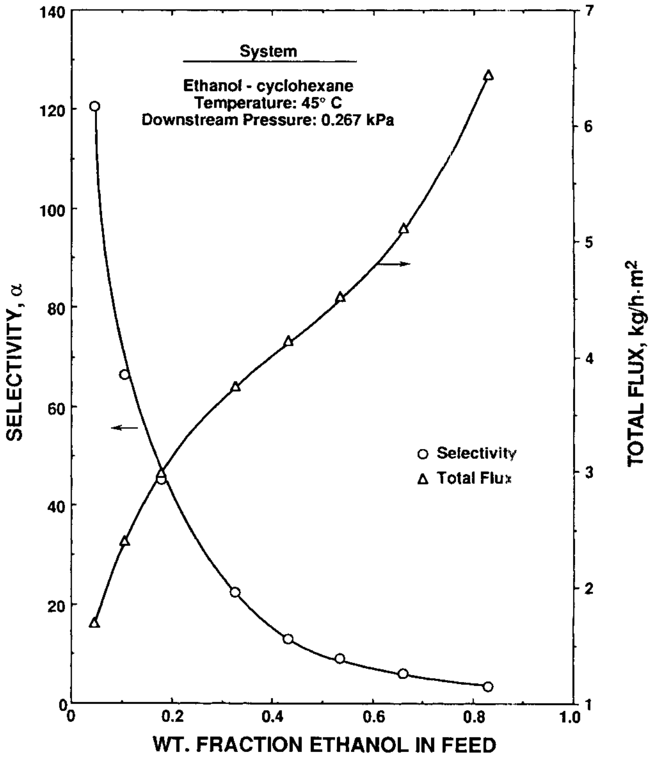


Figure 7. Effect of feed composition on pervaporation flux and selectivity: H-form of composite membrane.

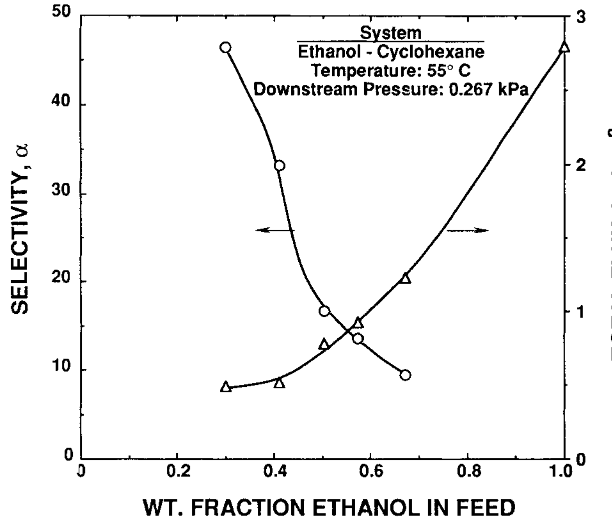


Figure 8. Effect of feed composition on pervaporation flux and selectivity: Na-form of composite membrane.

Effects of feed composition on pervaporation flux and selectivity for ethanol-cyclohexane system are shown in Figure 7 (for the H-form of the composite membrane) and in Figure 8 (for the Na-form of the composite membrane). The selectivity in the latter case was much higher but the flux was lower. The Na-form of PFSA swelled less than the H-form. For any particular form, the flux increased at higher alcohol concentration, at the cost of selectivity. The total flux also increased with temperature. An Arrhenius-type dependence on temperature (Figure 9) was observed with an activation energy of 23.44 kJ/mol (5.6 kcal/mol), which corresponds to diffusive transport through membranes.

Flux and selectivity data for several mixtures are given in Table 1, again showing that the high fluxes were attained by the composite membrane for mixtures of polar and nonpolar compounds. Excellent fluxes were exhibited by a small polar molecule like methanol. But, the membrane did not work well when both of the components were comparably nonpolar.

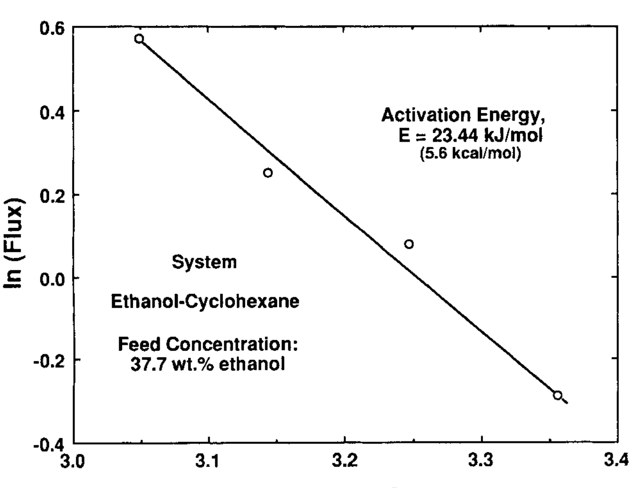


Figure 9. Temperature dependence of flux.

Table 1. Flux and Selectivity for Pervaporation of Some Organic Mixtures*

System	Feed wt, % Comp. 1	Flux, kg/h·m²	Selectivity Comp. 1
Methanol (1)-Carbon Tetrachloride (2)	15.4	6.06	14.6
Ethylacetate (1)-Carbon Tetrachloride (2)	44	0.653	1.29
Acetonitrile (1)-Carbon Tetrachloride (2)	15.5	0.885	2.35
Ethylacetate (1)-Cyclohexane (2)	54	0.483	1.73
Methanol (1)-Benzene (2)	32.5	10.280	9.56

*Temperature = 45°C; membrane, composite, H-form

Mathematical Model

Known mathematical models of pervaporation are based generally on the solution-diffusion transport mechanism with concentration-dependent diffusivities of the permeating components. In model calculations, an assumption has usually been made that the diffusivities vary linearly or exponentially with local concentrations (Rautenbach and Albrecht, 1985; Brun et al., 1985). Dry thickness of the membrane has also been used for simplicity. In reality, for highly swelling membranes, however, swelling varies considerably through the membrane depending on the local concentration of the liquid. We measured the thicknesses of swollen membranes that were equilibrated with solutions of varying alcohol concentration and found that membrane thickness increased linearly with sorbed alcohol concentration (Figure 10). Taking local swelling into account represents a major difference between our modeling and previous work. Here are the other assumptions made to build our model.

- Interfacial equilibrium existed between the membrane and the feed liquid.
- Diffusional resistances outside the membrane were low.

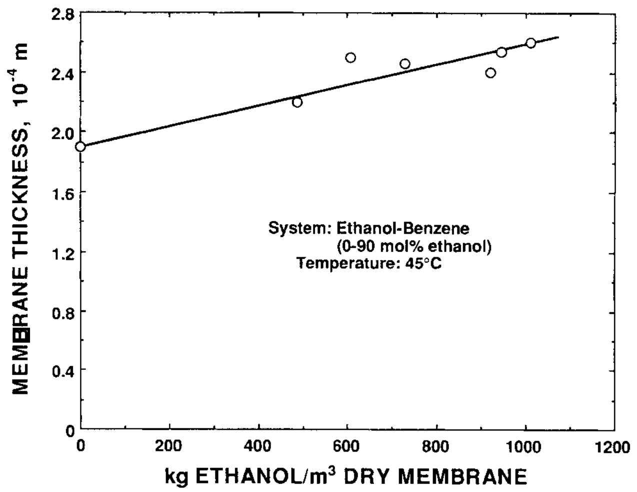


Figure 10. Swollen membrane thickness vs. ethanol concentration: commercial membrane, H-form.

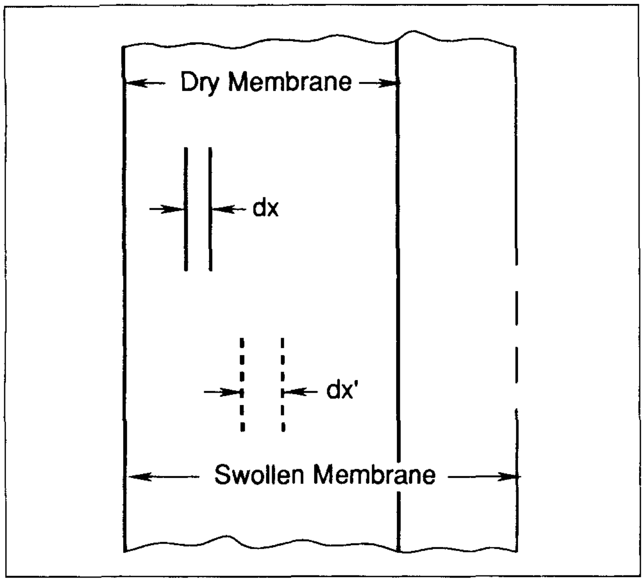


Figure 11. Dry and swollen membrane under pervaporation condition.

This assumption is based on our observation that the stirrer speed did not have any measurable effect on pervaporation flux.

- At low downstream pressures, the concentrations of the solutes at the downstream face of the membrane were negligible, i.e., this face of the membrane was essentially dry. We observed that the experimental flux remained fairly constant over the range of downstream pressure of this study. This can happen if the downstream side of the membrane remains essentially dry. However, we do not have direct experimental evidence in favor of this assumption. To improve upon this first approximation, equilibrium sorption data at low pressures of the applied vacuum must be experimentally obtained. Such data do not exist now.
- Any temperature drop across the membrane was negligible. We estimated that the maximum temperature drop across the membrane was about 1 °C.
- Diffusion through the membrane was governed by Fick's Law with the diffusivities dependent on alcohol concentrations only, since alcohols were the primary permeant. In the alcohol-hydrocarbon systems, hydrocarbon was the minor component.
- Conditions of steady-state transport were attained.

If ϕ_1 and ϕ_2 are the local concentrations of components 1 and 2 in the membrane, the respective fluxes are:

$$J_1 = -D_1 \frac{d\phi_1}{dx'} \tag{1a}$$

$$J_2 = -D_2 \frac{d\phi_2}{dx'} \tag{1b}$$

where x' refers to the position in the swollen membrane, the origin being at the feed side of the membrane surface.

If the thickness of the dry membrane is l_d and that of the swollen membrane is l_s when equilibrated with a solution such that the concentrations in the membrane phase are ϕ_1 and ϕ_2, then the differential thickness in the respective membranes are related as (Figure 11):

$$dx' = (l_s/l_d)\,dx. \tag{2}$$

But

$$l_s/l_d = 1 + \beta(\phi_1, \phi_2) \tag{3}$$

where β is a suitable function that relates the dry and equilibrated membrane thickness.

The concentration dependence of the diffusivities may be expressed as:

$$D_1 = D_{10} f_1(\phi_1, \phi_2) \tag{4}$$

$$D_2 = D_{20} f_2(\phi_1, \phi_2) \tag{5}$$

Combining Eqs. 1 through 5, the transport equations become

$$J_1 = -\frac{D_{10} f_1(\phi_1, \phi_2)}{1 + \beta(\phi_1, \phi_2)} \frac{d\phi_1}{dx} \tag{6}$$

$$J_2 = -\frac{D_{20} f_2(\phi_1, \phi_2)}{1 + \beta(\phi_1, \phi_2)} \frac{d\phi_2}{dx} \tag{7}$$

The following functional forms of f_1, f_2 and β are assumed:

$$f_1(\phi_1, \phi_2) = 1 + \alpha_1 \phi_1, \tag{8}$$

$$f_2(\phi_1, \phi_2) = 1 + \alpha_2 \phi_1, \tag{9}$$

and

$$\beta(\phi_1, \phi_2) = 1 + \beta_1 \phi_1. \tag{10}$$

The assumptions of these functional forms are based on the observation that the concentration of alcohol (the more permeating component) is much larger than that of the hydrocarbon, and it mainly contributes toward swelling.

The following boundary conditions apply:
when $x = 0$,

$$\phi_1 = \phi_{10}, \quad \phi_2 = \phi_{20}; \tag{11}$$

when $x = l_d$,

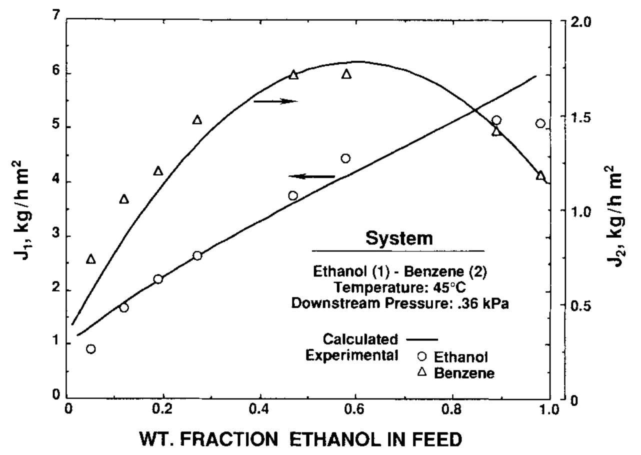
$$\phi_1 = \phi_2 = 0. \tag{12}$$

Solutions of Eqs. 6 and 7, subject to the boundary conditions (Eqs. 11 and 12) and the simplifications (Eqs. 8-10), are given by

$$J_1 = \frac{D_{10}}{\beta_1} \left[\left(1 - \frac{\alpha_1}{\beta_1}\right) \ln(1 + \beta_1 \phi_{10}) + \alpha_1 \phi_{10} \right] \tag{13}$$

$$J_2 = \frac{J_1 \phi_{20}}{\left(1 - \frac{\alpha_1}{\alpha_2}\right) \ln(1 + \alpha_2 \phi_{10}) + \alpha_1 \phi_{10}} \cdot \frac{\alpha_2 D_{20}}{D_{10}} \tag{14}$$

Validity of the proposed model was tested by membrane swelling and pervaporation data on a commercial PFSA-polymer membrane (H-form) for the system ethanol-benzene. The local swelling parameter, β_1, was estimated by linear least-square fitting of the swollen membrane thickness and corresponding ethanol concentration. The diffusion and plasticization parameters (D_{10}, D_{20}, and α_1 and α_2) were obtained by the nonlinear least-square fitting of experimental flux data (J_1 and J_2) by the model (Eqs. 13 and 14) using Levenberg-Marquardt technique (Draper and Smith, 1981). The estimated diffusivities compare well in magnitude with diffusivities reported for other pervaporation systems (e.g., Mulder and Smolders, 1984). The computed parameter values were used to determine the theoretical flux of both the components. The calculated results are presented in Figure 12 along with the experimental data, which show that the proposed model satisfactorily predicted the pervaporation data for a typical alcohol-hydrocarbon system. Standard error estimates of J_1 and J_2 were 0.432 and 0.138 kg/m²·h, respectively. The 95% confidence intervals of the estimated parameters are given in Figure 12.



$\beta_1 = (3.36 \pm 0.6) \times 10^{-4}$ m³/kg

$D_{10} = (4.92 \pm 0.57) \times 10^{-9}$ m²/h $\alpha_1 = 0.047 \pm 0.007$ m³/kg

$D_{20} = (6.45 \pm 0.8) \times 10^{-8}$ m²/h $\alpha_2 = 0.005 \pm 0.001$ m³/kg

Figure 12. Experimental vs. calculated flux values: ethanol (○)-benzene (△) system.

Concluding Remarks

We have demonstrated in this work that the PFSA polymer composite membrane we prepared in the laboratory separated organic liquid mixtures containing polar and nonpolar components. The composite membrane offered 4 to 5 times larger flux than the commercial membrane without appreciable loss in selectivity. Downstream pressure, up to 6.67 kPa (50 mm Hg), had little effect on the total flux and product composition. Temperature effect on flux corresponded to the diffusional regime of transport. PFSA polymer membranes, however, did not work well for mixtures of nonpolar or slightly polar organic compounds. The flux and selectivity data could be interpreted by a mathematical model that is based on Fick's Law with concentration-dependent diffusion coefficients and that also took into account the distribution of swelling of the membrane across its thickness.

Acknowledgment

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Notation

D_1, D_2 = diffusivities of components 1 and 2 in the membrane
D_{10}, D_{20} = limiting values of D_1 and D_2 at very low concentrations
J_1, J_2 = fluxes of components 1 and 2
l_d = thickness of the dry membrane
l_s = thickness of the swollen membrane
x = local position in the dry membrane
x' = local position in the swollen membrane

Greek letters

α_1, α_2, β_1 = constants in Eqs. 8, 9 and 10
ϕ_1, ϕ_2 = local concentrations of components 1 and 2 in the membrane

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