The Separation of Water–Ethanol Mixtures by Pervaporation through Hydrophilic–Hydrophobic Composite Membranes

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Synopsis

A new kind of polymer composite membrane, which we refer as hydrophilic–hydrophobic composite membrane, is prepared by the concentrated emulsion polymerization method[6,7] and employed to separate permselectively ethanol–water mixtures. This composite contains polyacrylamide as the dispersed phase and crosslinked polystyrene as the continuous phase. The swelling in water of this composite membrane is around 4 g water/g polymer and its swelling in ethanol is negligible. The permeation of the composite membrane by pervaporation decreases with increasing ethanol concentration in the feed and increases with increasing polyacrylamide fraction in the composite. The rate of permeation is in the range of 30–10^3 g/m^2 h. The selectivity of the membrane ranges between 2 and 50 and increases with increasing ethanol concentration in the feed and increasing polyacrylamide fraction in the composite. The permeation increases and the selectivity decreases with increasing feed temperature. The activation energy of permeation varies between 1.8 and 4.9 kcal/mol, depending upon the compositions of the feed and membrane.

INTRODUCTION

The separation of alcohol–water mixtures by pervaporation through membranes has been investigated by various groups.[1–5] Earlier studies have used cellophane[1] and cellulose acetate[2] as membranes. Later, membranes of polytetrafluoroethylene (PTFE) grafted with *N*-vinyl pyrrolidone[3] and PTFE grafted with styrene and then sulfonated[4] were prepared. More recently, plasma-grafted copolymer membranes of acrylic acid and acrylamide were reported.[5]

A new kind of polymer composite, the hydrophilic–hydrophobic composite,[6] was prepared recently in our laboratory by the concentrated emulsion polymerization method.[7] The concentrated emulsion is a gel-like emulsion in which the volume fraction of the dispersed phase is greater than 0.74 (which is the volume fraction of the most compact arrangement of spheres of equal size) and can be as large as 0.995. In this type of emulsion, the dispersed phase is composed of polyhedral cells separated by thin films of the continuous phase. The morphology of the concentrated emulsion remains relatively unchanged during polymerization and the polymer composites obtained by the concentrated emulsion polymerization contain hydrophilic (hydrophobic) cells, in the range of submicrometer, separated by thin hydrophobic (hydrophilic) polymer films.[6] A hydrophilic–hydrophobic polymer composite membrane whose dispersed phase was polystyrene and continuous phase was polyacrylamide, exhibited high permselectivity to toluene from a mixture of toluene and cyclohexane.[8] A hy-

drophilic–hydrophobic polymer composite synthesized by using a concentrated emulsion of acrylamide dispersed in a continuous phase of a mixture of styrene and divinyl benzene as precursor is expected to be highly permeable to water because of the high hydrophilicity of polyacrylamide.

This paper reports the results obtained regarding the pervaporation of ethanol–water mixtures through such a hydrophilic–hydrophobic polymer composite. It will be shown that this membrane is permselective to water over a wide range of ethanol concentrations in the feed.

EXPERIMENTAL

Preparation of the Concentrated Emulsion

The materials used as well as the preparation of a concentrated emulsion (gel) were described in a previous paper.[6] Since there are slight differences in the preparation conditions, some details are included in what follows.

A small amount of a mixture of styrene (Aldrich) and divinyl benzene (Polysciences) (8/2 by weight) containing sorbitan monooleate (Fluka) as dispersant and AIBN (Alfa) as initiator was placed in a three-neck flask (250 mL capacity) equipped with a mechanical stirrer and an addition funnel. An aqueous solution of acrylamide (Polysciences) was placed in the addition funnel, and a potassium persulfate (Aldrich) solution in water was added as initiator. The concentrated emulsion was prepared at room temperature by dropwise addition of an aqueous solution of acrylamide to the stirred mixture of styrene and divinyl benzene. Four sets of amounts (M_1–M_4) of the components involved, which are listed in Table I, have been employed.

Preparation of the Membrane

Two glass plates (10 × 15 cm) were cleaned with detergent and dried at 140°C for 4 h. A small amount of glycerol was placed on the surfaces of the glass plates as lubricant. The concentrated emulsion was set between the two glass plates and squeezed slowly to avoid trapping of air bubbles. For polymerization to occur, the glass plates containing gel between them were placed in a temperature controlled oven at 50°C for 24 h. After its preparation, the

TABLE I
Amounts of Components Used in the Preparation of the Polymer Composites

	M_1	M_2	M_3	M_4
The continuous phase				
Styrene (g)	0.8	0.8	4.0	4.0
Divinyl benzene (g)	0.2	0.2	1.0	1.0
Initiator (AIBN)	2.0×10^{-4} g/g monomers for all four systems			
The dispersed phase				
Acrylamide (g)	4.0	2.0	2.0	0
Water (mL)	28	28	28	28
Initiator (potassium persulfate)	1.7×10^{-4} g/g acrylamide for all four systems			
Surfactant (sorbitane monooleate)	1 mL for all four systems			

membrane was dried at 70°C in a circulating oven for 24 h. The thickness of the membranes was around 150 μm.

The Swelling Test

The change in the weight of the membrane produced by swelling was determined as follows. Dried membrane strips were placed in a flask that was filled with various mixtures of ethanol and water. The strips were allowed to equilibrate for a long time (a week) and the weight changes measured.

The swelling of the membrane is defined as

$$S = \frac{W_s - W_0}{W_0} \times 100 = \frac{\Delta W}{W_0} \times 100$$

where W_0 and W_s represent the weights of the dry and swollen membranes, respectively.

Permeation Experiments

Permeation studies of water–ethanol mixtures were carried out by employing the apparatus used in a previous paper.[8] The membranes, swelled for 30 min in the feed mixtures, were introduced into the pervaporation cell. In the upstream compartment the permeant mixture was under stirring, while the downstream compartment was evacuated to 30 ± 5 torr. The vapors thus produced were collected in three cold traps which were immersed in a cold bath (below $-60°C$). The pervaporation cell was thermostatically controlled.

Analysis of the Permeate

The permeate compositions were analyzed by using a gas chromatograph (Varian 3700) which had a thermal conductivity detector. The separation was carried out at a column temperature of 150°C, with a Porapak Q column using helium as the carrier gas.

The selectivity $\alpha_{w,E}$ is defined as

$$\alpha_{w,E} = \frac{X_w^P X_E^F}{X_w^F X_E^P}$$

where X_w^F, X_E^F, X_w^P, and X_E^P denote the weight fractions of the components water and ethanol, in the feed and permeate, respectively.

RESULTS AND DISCUSSION

The Swelling Test

The swelling of the hydrophilic–hydrophobic membrane is plotted in Figure 1 as a function of composition. It increases with the amount of polyacrylamide in the composite membrane and decreases with the amount of ethanol in the solution. Negligible swelling was observed in pure ethanol. Membrane M_3 exhibited a lower degree of swelling than membranes M_1 and M_2 for low ethanol
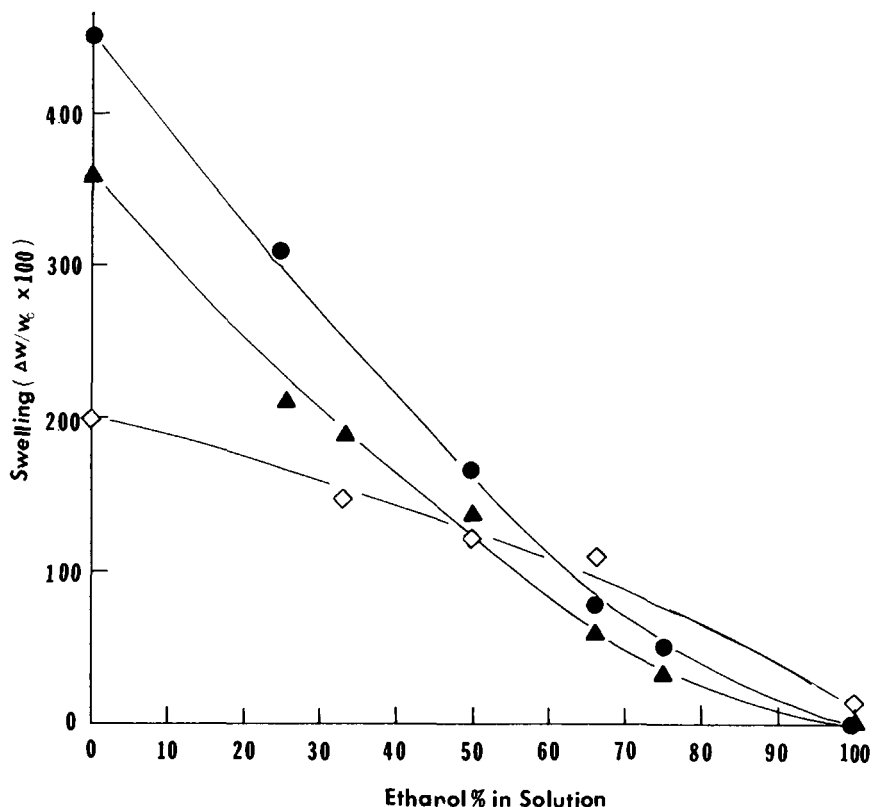
Fig. 1.   Swelling of hydrophilic–hydrophobic composite membranes against ethanol concentration in the feed. The symbols ●, ▲, and ◇ correspond to membranes M_1, M_2, and M_3, respectively.

concentrations, and a higher one for high concentrations. The swelling of membrane M_3 in ethanol was of about 8%. The latter swelling can be explained as follows: The composite membranes M_1 and M_2 shrunk after drying because of the loss of water from the cells of the dispersed phase. In contrast, membrane M_3 exhibited no change in size after the water loss. The larger amount of crosslinked polystyrene in the continuous phase of this membrane probably increases the rigidity of the films between the cells. The micropores, formed between the shrunk cells and the more rigid films, are probably responsible for the absorption of ethanol in membrane M_3. Like membrane M_3, membrane M_4 exhibited no change in size after the water loss. The microstructure of the dried membrane M_4 is presented in the scanning electron micrograph of Figure 2.

Permeation Experiments

The water–ethanol separation through the hydrophilic–hydrophobic polymer composite membrane was evaluated by pervaporation. Figure 3 presents the dependence of the permeate flux on the ratio of polyacrylamide to polystyrene in the membrane and on the ethanol concentration in the feed. The flux through the membranes M_1 and M_2 decreases as the ethanol concentration in the feed
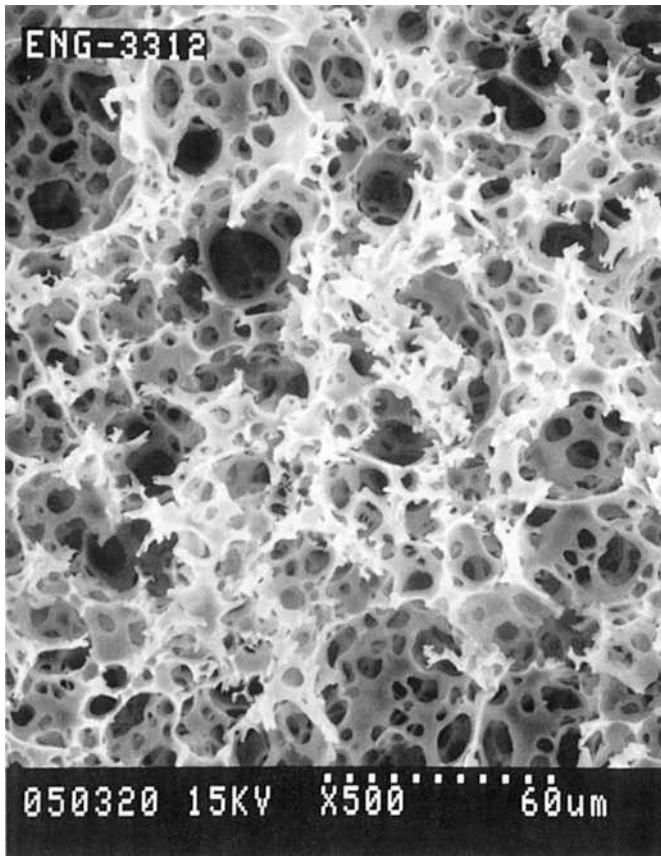
Fig. 2. Scanning electron micrograph (SEM) of membrane M_4.

increases from 0 to 75%. This constitutes a common characteristic of the water perselective membranes.[4,5] Membrane M_1 exhibits a higher flux than membrane M_2; this observation is consistent with the swelling results. Membrane M_3 exhibits a decrease in flow rate with increasing ethanol concentration, in the low concentration range of ethanol. However, the flux increases with ethanol concentration when the latter is sufficiently large.

The permselectivity of the membranes to water was found to depend on the composition of the membranes. Figure 4 shows the dependence of the selectivity for water on the ethanol concentration, for various ratios of polyacrylamide and polystyrene in the composites. The selectivity of the membrane M_1 is greater than that of membrane M_2. As the concentration of ethanol in feed increases, the selectivities of these membranes increase. However, the selectivity of membrane M_3 decreases with increasing ethanol concentrations in the feed probably because of the presence of the micropores.

From the experimental results regarding membranes M_1 and M_2, one can conclude that the flux and selectivity of the membrane are highly influenced by the ethanol concentration in the feed. This is a direct consequence of the membrane's absorption behavior.
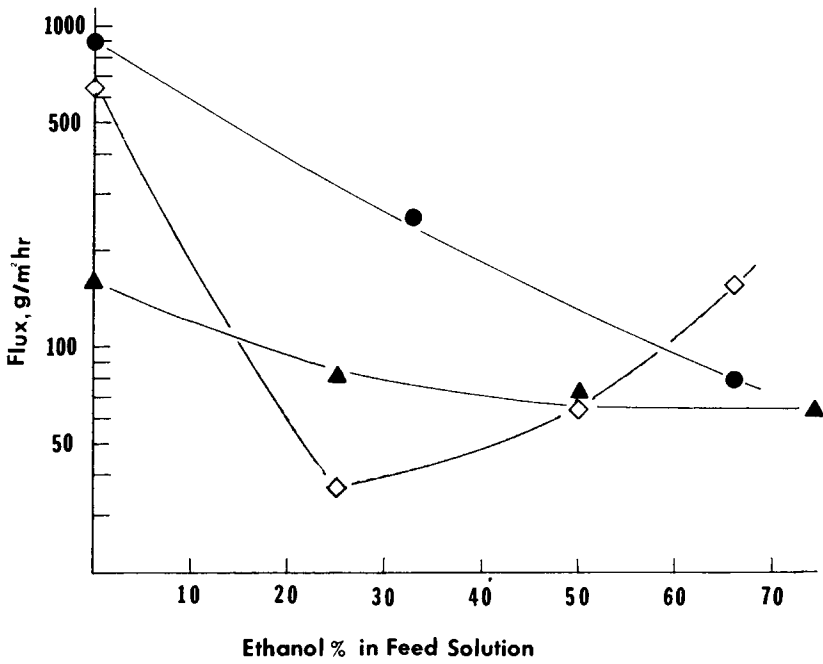
Fig. 3.   Flux through the membrane against ethanol concentration in the feed. The symbols are as in Fig. 1.
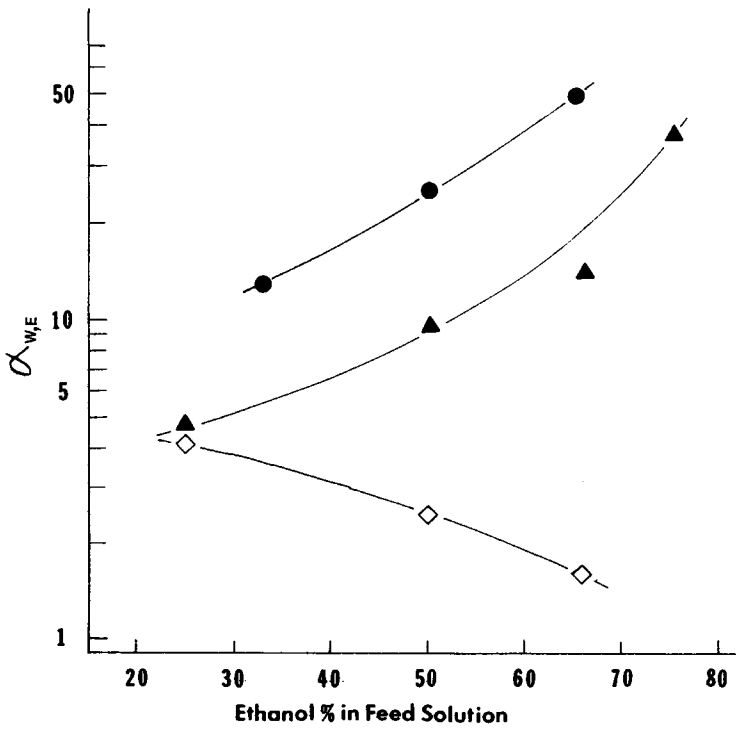

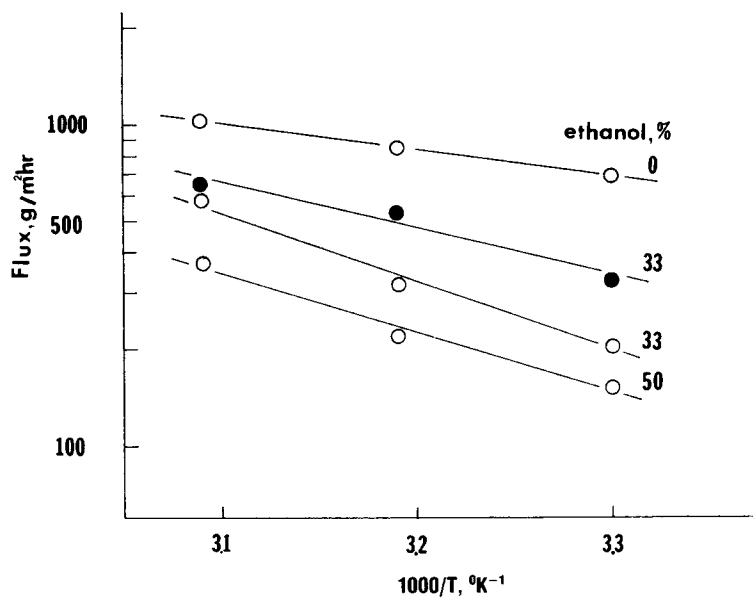Fig. 4.   Selectivity through the membrane against ethanol concentration in the feed. The symbols are as in Fig. 1.

Fig. 5.   Arrhenius plots of the flux through the membrane. The symbols ● and ○ correspond to membranes M_1 and M_2, respectively.
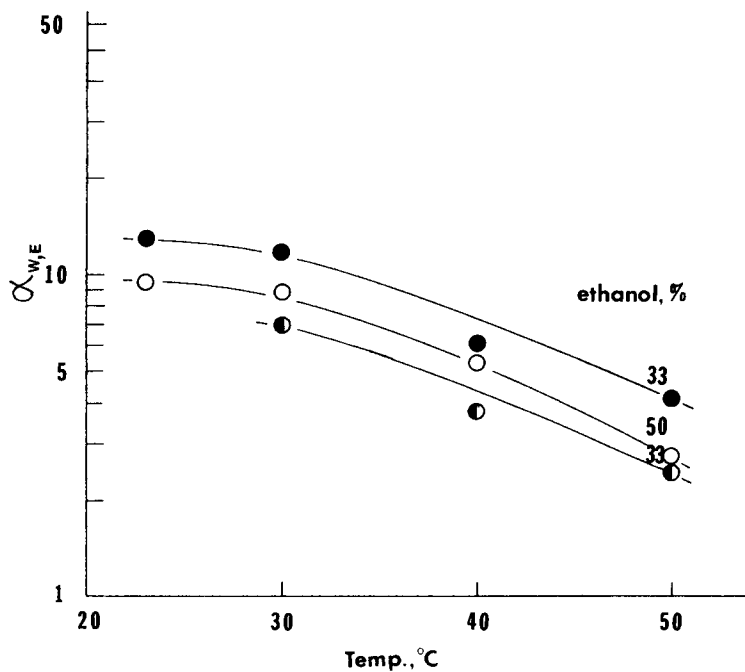

Fig. 6.   Temperature dependence of the selectivity of the membranes. The symbols ●, ○, and ◐ correspond to the membranes M_1, M_2, and M_2, respectively. The ethanol concentration in the feeds for ●, ○, and ◐ is 33, 50, and 33%, respectively.

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TABLE II
Activation Energy of the Flux of Water–Alcohol Mixtures through
the Hydrophilic–Hydrophobic Composite Membrane

		Activation energy (kcal/mol)		
Membrane	Ethanol concn (%): 0		33	50
M_1			3.34	
M_2	1.82		4.86	4.13

The temperature dependence of pervaporation in the temperature range of 22–50°C was also investigated for both the flux (Fig. 5) and selectivity (Fig. 6). The flux increases with the temperature of the feed. Arrehnius plots are presented in Figure 5 for membranes M_1 and M_2 and for 0, 33, and 50% ethanol. The activation energies are summarized in Table II. They are in the range of 1.8–4.9 kcal/mol and depend on the ethanol concentration in the feed as well as on the type of membrane.

The trend of the curves in Figure 4 appears to indicate that the selectivity in the azeotropic range can be high. However, the permeability of these membranes in the same range is very low. Attempts to prepare suitable membranes for this range are under way.

CONCLUSION

Hydrophilic–hydrophobic composite membranes, prepared by the concentrated emulsion polymerization method, and containing polyacrylamide as the dispersed phase and crosslinked polystyrene as the continuous phase, show high permselectivity to water because of the presence of the hydrophilic polyacrylamide cells in the composite.

The flux and selectivity of the membrane, which can be as high as $10^3 \mathrm{g}/\mathrm{m}^2$ h and 50, respectively, are strongly dependent upon the ethanol concentration and temperature of the feed.

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8. J. S. Park and E. Ruckenstein, *J. Appl. Polym. Sci.*, **38**, 453–461 (1989) (PC1 and PC2 should be interchanged in the caption of Figure 8 of Ref. 8).