Separation of Water–Alcohol Mixtures by Pervaporation Through Asymmetric Nylon 4 Membrane

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SYNOPSIS

The dehydration of aqueous alcohol solutions through asymmetric nylon 4 membranes were investigated using pervaporation processes. The formation of asymmetric pervaporation membranes are discussed in terms of the content of the nonsolvent in the casting solution, polymer concentration, and compositions of the coagulation medium. The effects of the feed composition, feed temperature, and molar volume of the alcohols on the pervaporation performances of the asymmetric membranes are discussed. A separation factor of 4.72 and a permeation rate of 0.78 kg/m² h for the asymmetric membrane were obtained. Compared to the conventional homogeneous nylon 4 membrane, the asymmetric membrane can effectively overcome the pervaporation performances of the nylon 4 membrane for separation of water–alcohol mixtures. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is an attractive separation process for the close boiling-point mixtures, heat-sensitive mixtures, azeotropic and isomeric mixtures, the removal of water from organic liquids, and the removal of organic contaminants from waste water.[1–3] Recently, the separation of alcohol/water mixtures by a pervaporation technique using a dense homogeneous membrane has been given much attention. In a previous article, we investigated various ways such as plasma deposition,[4] homografting and heterografting of [60]Co γ-ray irradiation,[5,6] and chemical grafting[7] to improve the membrane morphology and pervaporation performances of a dense homogeneous nylon 4 membrane. One of the disadvantages of the dense homogeneous membrane for pervaporation is the low permeation rate, especially with highly selective membrane materials. Thus, we attempted to prepare an asymmetric nylon 4 membrane via a wet phase inversion method to increase the permeation rate for pervaporation of aqueous alcohol solutions, while the selectivity remains the same or decreases slightly. Wet phase inversion is the most widely used technique for preparing asymmetric membrane: A polymer solution is cast onto a suitable support and immersed in a coagulation medium. The asymmetric membrane is formed by exchange of the solvent and coagulation medium.[8–11] Loeb and Sourirajan[12] were the first to prepare asymmetric hyperfiltration membranes. Mulder et al.[13] made integrally skinned asymmetric pervaporation membranes from cellulose acetate.

The objective of this article was concerned with the preparation of asymmetric membranes via a wet phase inversion method. The effects of the feed composition, swelling degree, and molar volume of the alcohols on the pervaporation performances for the asymmetric nylon 4 membranes were studied.

EXPERIMENTAL

Materials

The nylon 4 synthesis procedure was described previously.[14] The molecular weight of the samples, measured by a Cannon Fenske viscometer with m-cresol as solvent at 25°C, was 20,000–22,000. All reagent-grade chemicals were used directly without further purification. Water was deionized.

Membrane Preparation

The homogeneous nylon 4 membranes were prepared by dissolving the polymer in formic acid. The membrane was formed by casting the polymer solution onto a glass plate. After casting, the membrane was heat-treated at 70°C for 40 min to evaporate the solvent. The membrane thickness was in the range of 40–50 μm.

Asymmetric Membranes

The asymmetric membranes were prepared from a casting solution with varying compositions as shown in Table I. The polymer solution was cast onto a glass plate, then evaporated for a period of time, and after immersion in a coagulation medium for 20 min at room temperature, the membrane was obtained. The membrane thickness was in the range of 40–50 μm.

Apparatus and Measurements

The traditional pervaporation process was used.[15] The effective membrane area was 10.2 cm^2. The feed temperature was studied in the range of 25–45°C. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions and permeates were measured by gas chromatography (GC, China Chromatography 8700T). The separation factor, $\alpha_{H_2O/alc}$, was calculated from the following equation:

$$\alpha_{H_2O/alc} = (Y_{H_2O}/Y_{alc})/(X_{H_2O}/X_{alc})$$

where X_{H_2O}, X_{alc} and Y_{H_2O}, Y_{alc} are the weight fractions of water and alcohol in the feed and permeate, respectively.

The degree of swelling of the membrane was defined by the following equation:

$$DS = \frac{W_w - W_d}{W_d} \times 100\%$$

where W_d and W_w denote the weight of dry and swollen membranes, respectively.

Preferential Sorption Measurements

Membranes were immersed in ethanol–water mixtures for 24 h. They were subsequently blotted between tissue paper to remove adherent solvent and placed in the left half of a twin tube setup. The system was evacuated while the left tube was heated

Table I   Effect of Polymer Concentration on the Pervaporation Performances[a] for the System of $C_2H_5OC_2H_5$/HCOOH/Nylon 4

Polymer Concentration (Wt %)	H$_2$O in Permeate (Wt %)	Permeation Rate (kg/m^2 h)	Separation Factor
10	35.03	0.78	4.72
15	36.64	0.59	5.13
18	38.04	0.51	5.75
20	39.25	0.44	6.40

[a] Feed composition: 90 wt % aqueous ethanol solution. Operation temperature: 25°C.

with hot water and the right one was cooled in liquid N$_2$. The composition of the condensed liquid in the right tube was determined by GC.[4] The separation factor of sorption, α_{sorp}, was calculated from the following equation:

$$\alpha_{sorp} = (Ye/Yw)/(Xe/Xw)$$

where Xe, Xw and Ye, Yw are the weight fractions of ethanol and water in the feed and membranes, respectively.

RESULTS AND DISCUSSION

Effect of Nylon 4 Concentration on the Pervaporation Performances

The effect of nylon 4 concentration on the pervaporation performances for the system of $C_2H_5OC_2H_5$/HCOOH/nylon 4 are shown in Table I. As shown, the separation factor increases and the permeation rate decreases with increasing nylon 4 concentration of the casting solution from 10 to 20 wt %. These results might be due to the fact that an increasing initial polymer concentration in the casting solution leads to a much higher polymer concentration at the surface. A solution with a relatively high polymer concentration is thought to be closer to the incipient point of precipitation than demixing with a nonsolvent spontaneously. But for a high polymer concentration with higher viscosity, the precipitation rate is low. Once the wet nascent membrane is immersed in the gelation bath, the rate of membrane shrinkage will be decreased, resulting in an increase in the top-layer thickness of asymmetric membrane. Meanwhile, this implies that the volume fraction of the polymer increases and, consequently, a lower
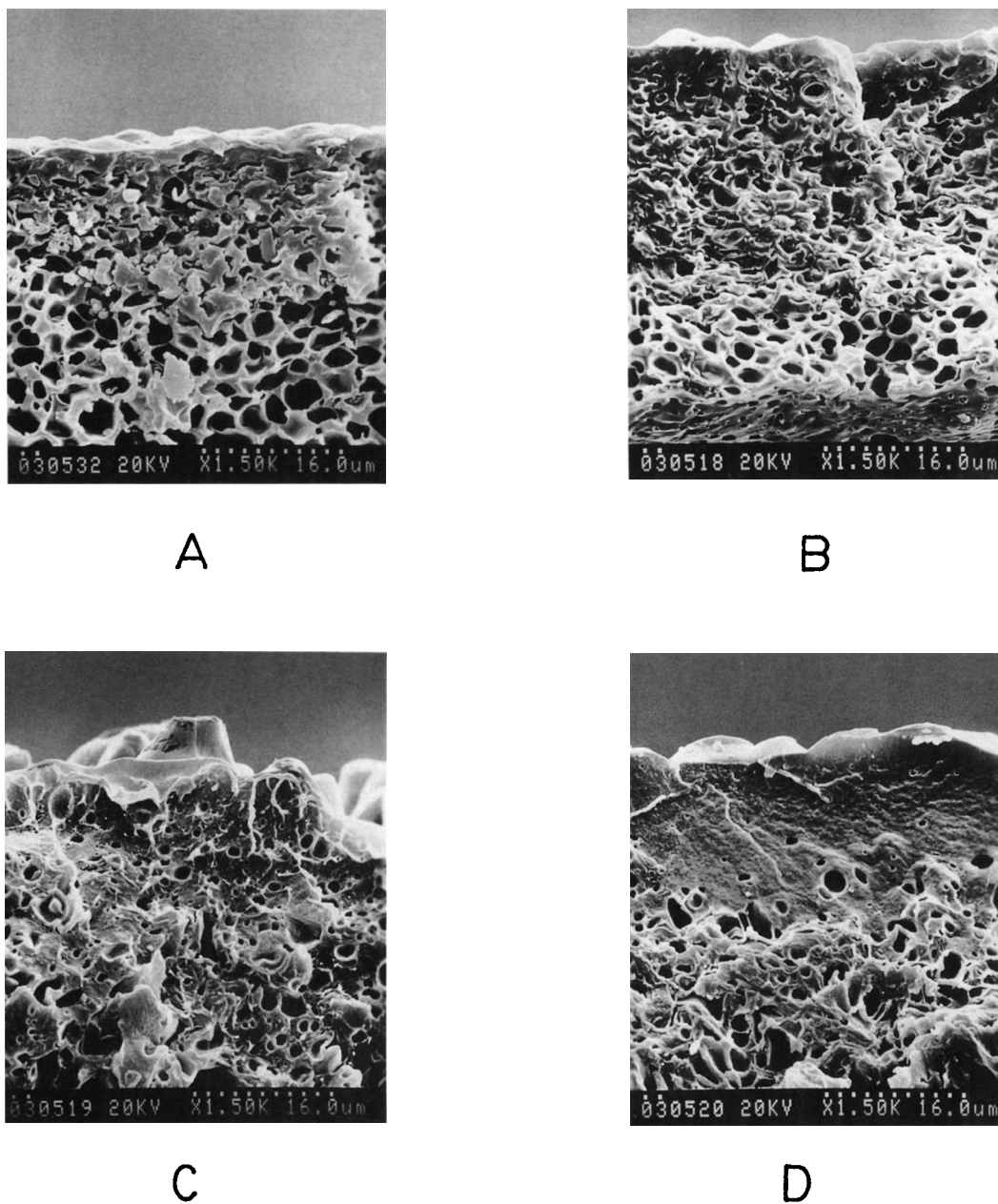
A

B

C

D

Figure 1 Cross-section view of SEM for the membranes prepared from the $C_2H_5OC_2H_5/$ HCOOH/nylon 4 system with different polymer concentrations: (A) 10 wt %; (B) 15 wt %; (C) 18 wt %; (D) 20 wt %.

porosity is obtained. Furthermore, compared to the dense homogeneous nylon 4 membrane that possesses a separation factor of 4 and a permeation rate of 0.35 kg/m² h, the asymmetric membrane can effectively overcome the pervaporation performances of the nylon 4 membrane for separation of water–alcohol mixtures. While attempting to investigate the structure of the asymmetric membranes, the cross-section views of the membrane were studied with a Hitachi S-570 scanning electron microscope (SEM). The SEM photographs are presented in Figure 1, which shows that the thickness of the membranes' top layer increases and the porosity of sublayer decreases with increasing the polymer concentration. This clearly supports the hypothesis that two different types of phase separation are respon-
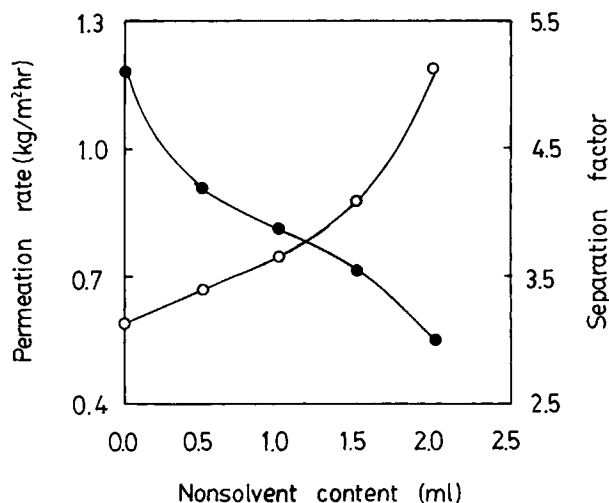
Figure 2 Effect of nonsolvent content in the casting solution on the pervaporation performances for the system of $C_2H_5OC_2H_5$/HCOOH/nylon 4; polymer concentration 15 wt %: (O) permeation rate; (●) separation factor.

sible for the formation of asymmetric membranes: gelation for the formation of the top layer and liquid–liquid phase separation followed by gelation of the concentrated polymer phase for the formation of the porous sublayer. Similar results were obtained by Mulder et al.[13].

Effect of Nonsolvent in Casting Solution on Pervaporation Performance

To further improve the pervaporation performances, the effect of nonsolvent content in the casting solution for the $C_2H_5OC_2H_5$/HCOOH/nylon 4 system with 15 wt % polymer concentration (2 g nylon 4/ 9.3 mL HCOOH) were made. Figure 2 shows the influence of nonsolvent (methanol) content in the casting solution on pervaporation performance. The permeation rate sharply increases and the separation factor decreases with an increase in the nonsolvent content in the casting solution. These phenomena might be due to the fact that defects are evidently present in the membrane surface at the higher non-solvent content in the casting solution, as shown in Figure 3. In addition, the ternary phase diagram can be used to further explain the above phenomena. As the nonsolvent content in the casting solution increases, the initial compostion profile shifts toward the binodal curve, i.e., the rate of liquid–liquid demixing increases with increasing nonsolvent content in the casting solution. Thus, the thickness of the dense top layer decreases and the pore size of the

membrane sublayer increases with increasing non-solvent content, resulting in the permeation rate increases.[11]

Effect of Binary Mixtures as Coagulation Medium on Pervaporation Performance

With the point of view of Renuers et al.,[9] the liquid–liquid demixing process in polymer solutions during membrane formation may proceed in two different ways, denoted as delayed demixing and instantaneous demixing. The membrane structure of the former is denser than that of the latter. Meanwhile, owing to the slow exchange between CH_3OH (nonsolvent) and HCOOH (solvent), a delayed demixing was obtained. Therefore, it is expected that the addition of methanol in the coagulation medium, $C_2H_5OC_2H_5$, could delay the liquid–liquid demixing and result in the membrane with a dense and thick top layer. However, in this study, we observed the opposite phenomena, with the permeation rate increasing with increase in the concentration of CH_3OH up to 20 wt %; beyond this concentration, poor membrane formation was observed. The effect of CH_3OH concentration in the $C_2H_5OC_2H_5$ coagulation medium on the pervaporation performances of the membranes is revealed in Table II. These phenomena could be explained as that CH_3OH plays a stronger swelling effect on the nylon 4 membrane than does $C_2H_5OC_2H_5$. This would reduce the polymer concentration in the film at the interface; therefore, the exchange rate of solvent and nonsolvent could be improved, and an instantaneous liquid–liquid demixing process may occur during membrane formation. Moreover, to further investigate the membrane morphology, the SEM micrographs of the cross-section and surface of the membranes were taken as shown in Figure 4. The figure

Table II Effect of CH_3OH Concentration of the Coagulation Medium on the Pervaporation Performances[a] for the System of $C_2H_5OC_2H_5$/HCOOH/Nylon 4

CH_3OH Concentration (Wt %)	H_2O in Permeate (Wt %)	Permeation Rate (kg/m² h)	Separation Factor
0	36.64	0.54	5.13
10	35.02	0.76	4.56
20	31.17	0.92	3.68

[a] Feed composition: 90 wt % aqueous ethanol solution. Operation temperature: 25°C.
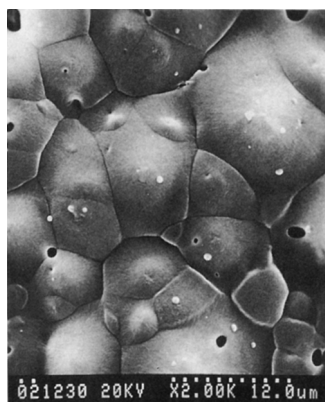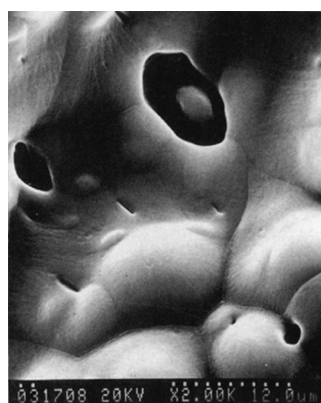
Surface

A

B

C

D

E

Figure 3   Surface views of SEM for the membranes prepared from the $C_2H_5OC_2H_5/$ HCOOH/nylon 4 system with various nonsolvent contents in the casting solution; polymer concentration 15 wt %: (A) without additive; (B) 0.5 mL; (C) 1.0 mL; (D) 1.5 mL; (E) 2.0 mL.
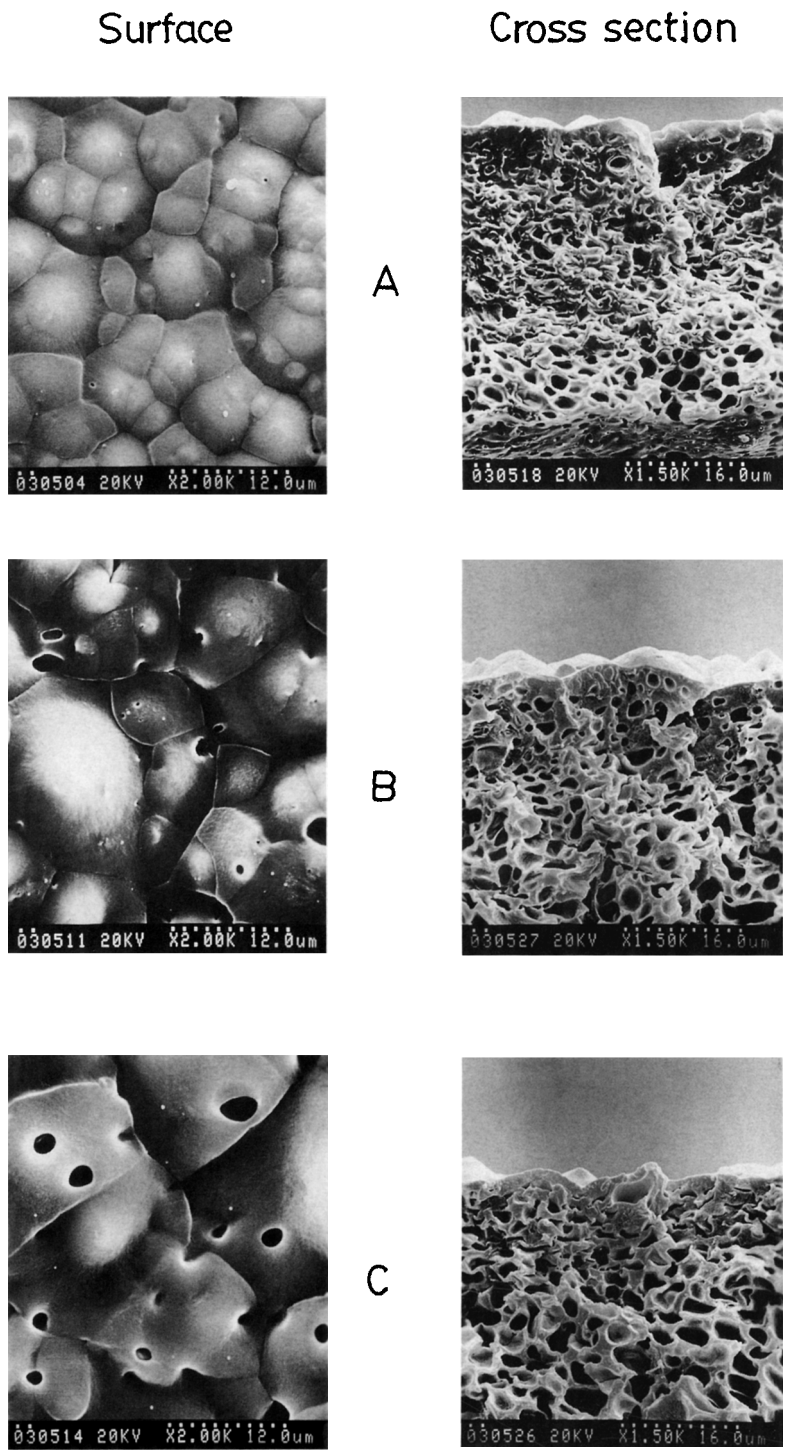
Surface   Cross section

A

B

C

Figure 4   Surface and cross-section views of SEM for the membranes prepared from the C$_2$H$_5$OC$_2$H$_5$/HCOOH/nylon 4 system with various CH$_3$OH concentrations in the coagulation medium: (A) 10 wt %; (B) 20 wt %; (C) 30 wt %.

shows that the pore size of the membrane surface gradually increases, and the thickness of the membrane top layer slightly decreased, resulting in the permeation rate increases with increasing CH$_3$OH concentration of the coagulation bath. This observation agrees with the result indicated in Table II.
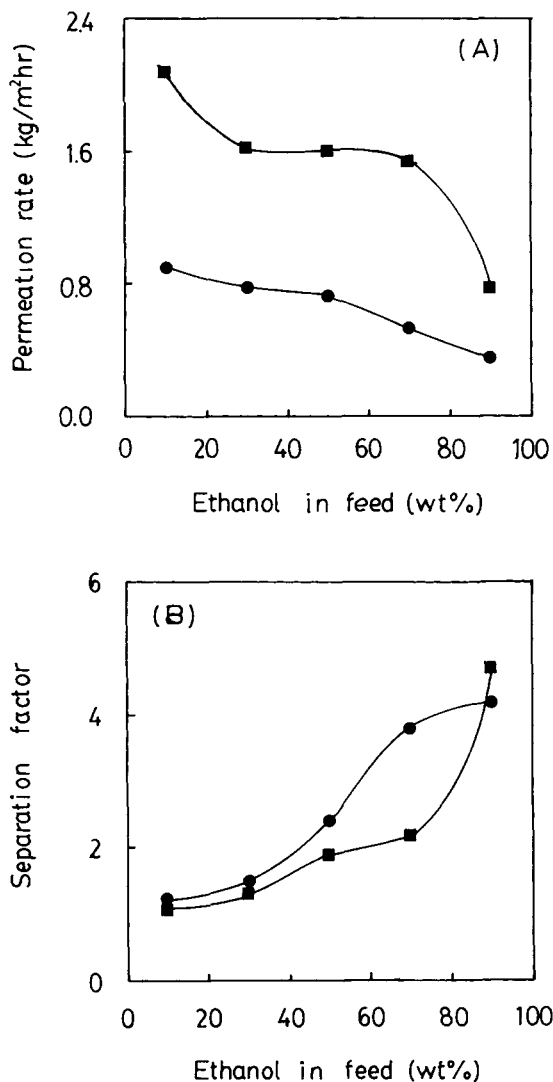
Figure 5 Effect of feed compositions on pervaporation performances: (A) permeation rate; (B) separation factor: (●) homogeneous membrane; (■) asymmetric membrane.

Comparison of Pervaporation Performance of Homogeneous and Asymmetric Membranes

To improve the permeability without loss in selectivity, the objective of the investigations was to develop asymmetric pervaporation membranes. The effects of the feed compositions on the pervaporation performances of homogeneous and asymmetric nylon 4 membranes are given in Figure 5. The separation factor increases and the permeation rate decreases with an increase of the feed concentration of ethanol for both nylon 4 membranes. These phenomena might be due to the fact that the interaction between the nylon 4 membrane and the water mol-

ecules of the feed solution increases with increasing water concentration in the feed solution. Hence, the polymer chains become more flexible, resulting in the permeation rate increasing with increasing water concentration in the feed solution.

Figure 6 shows that the degree of swelling decreases as the feed ethanol concentration increases for both homogeneous and asymmetric nylon 4 membranes. These results correspond well with the results of the pervaporation performance study, as indicated in Figure 5. Furthermore, from the Figure 5(A), compared with the pervaporation separation performances of homogeneous membranes, the asymmetric membrane effectively increases the permeation rate for the aqueous alcohol solution. The transport mechanism of pervaporation is the solution–diffusion model,[16] which could be used to clearly explain the above phenomena.

The SEM photographs (Fig. 7) reveal the structures of the homogeneous and asymmetric membranes. The porous sublayer of the asymmetric membrane decreased the diffuse resistance through the membrane and the porous surface of the downstream side could let the vapor leave the phase boundaries unhindered. Hence, the asymmetric membrane possesses higher permeation rate than that of the homogeneous membrane. Additionally, there is a specific phenomenon in Figure 5(B): The separation factor of the asymmetric membrane is lower than that of the homogeneous membrane for the feed aqueous ethanol solution in the range of
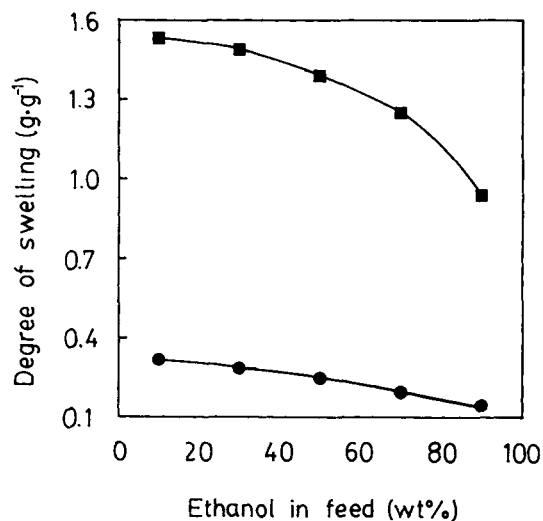

Figure 6 Effect of feed compositions on the degree of swelling: (●) homogeneous membrane; (■) asymmetric membrane.
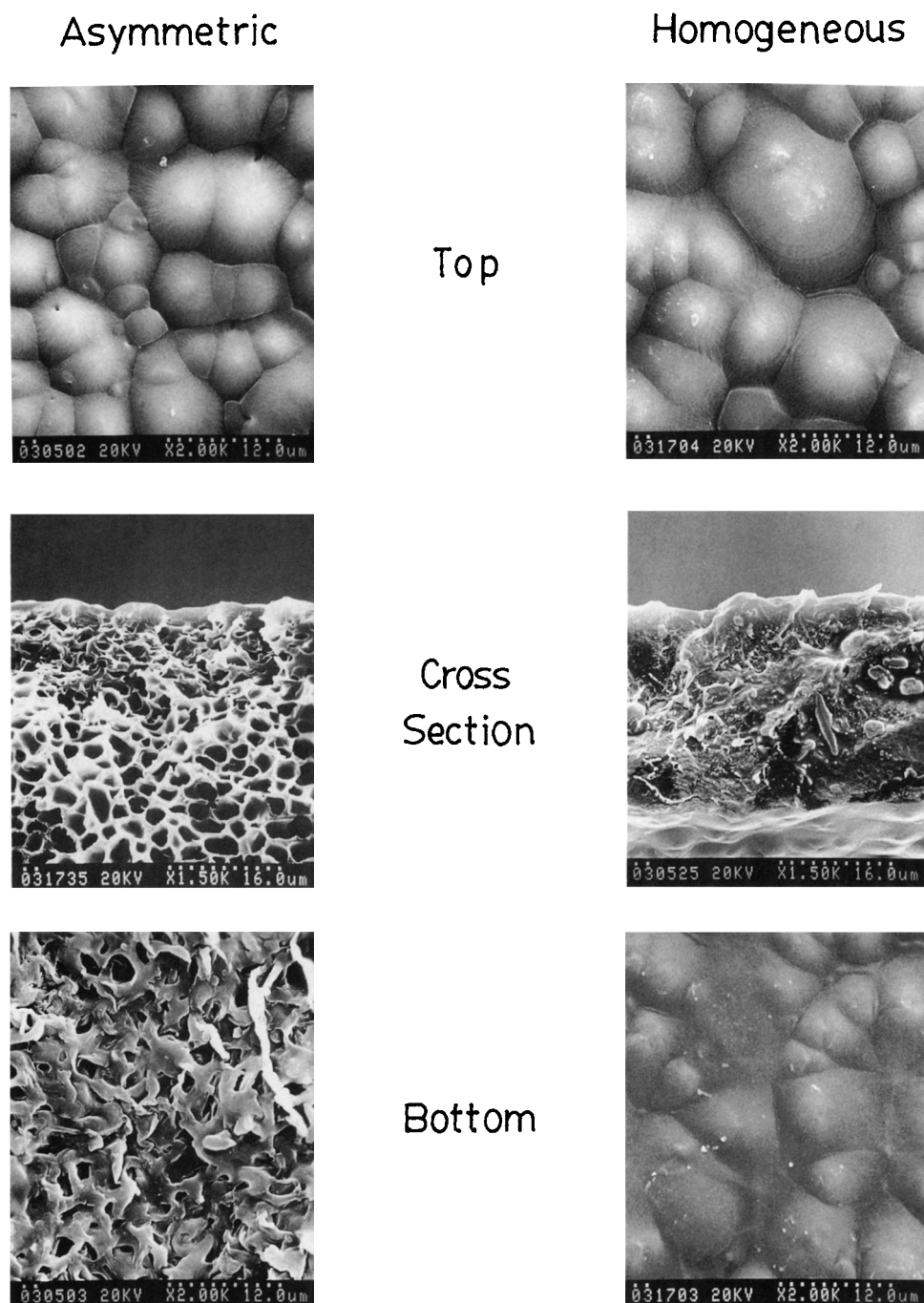
Asymmetric   Homogeneous

Top

Cross
Section

Bottom

Figure 7 Top-layer, bottom-layer, and cross-section views of SEM for the homogeneous and asymmetric membranes.

10–70 wt % and the separation factor of the former increases abruptly in the 90 wt % feed aqueous ethanol solution. The results might be due to the fact that the skin layer of the asymmetric membrane is the active layer that is the selective region.

As shown in Figure 7, the skin layer of the asym-

metric membrane is very thin. At a high concentration of water in the feed solution (below 70 wt % of the ethanol concentration), the membrane is swollen remarkably, namely, the skin layer would lose its density and the swollen membrane introduced a reduction of the separation capability. Nevertheless,
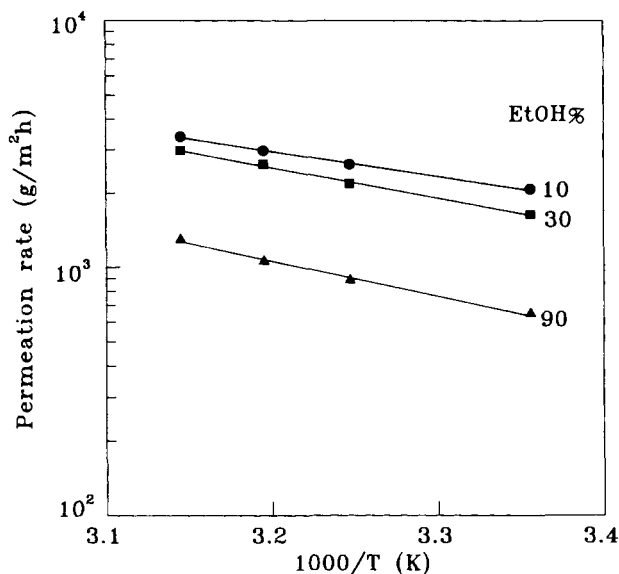
Figure 8 Effect of temperature on permeation rate of asymmetric membrane for different ethanol concentrations: (●) 10 wt %; (■) 30 wt %; (▲) 90 wt %.

at a low concentration of water, the separation factor increased because the membrane was not swollen so much; on the contrary, the membrane was shrunk by ethanol.

Temperature Effect

The effects of temperature and feed composition on the total permeation rate is shown in Figure 8. The total permeation rate increases with increasing temperature and with decreasing ethanol concentration of the feed solution. According to the free-volume theory,[17] the thermal motion of the polymer chains in the amorphous regions randomly produces the free volume. As temperature increases, the frequency and amplitude of the chain jumping increase and the resulting free volume become large, and the activity of permeating molecules increases at the same time. Thus, the permeation of individual molecules and associated molecules through the asymmetric membrane becomes easier, resulting in an increased total permeation rate.

In other words, the plasticizing effects of the permeants and the interaction between permeant and polymer can be used to further explain the above phenomena. As the temperature increases, the interaction become weaker, so that the plasticizing effect can be recovered. However, strong interactions can be formed at low temperature that reduce the plasticizing effect.[18] Moreover, the degree of swelling

Table III Activation Energy of Permeation of Water–Ethanol Mixture Solution Through the Homogeneous and Asymmetric Membranes

Membrane Morphology	Activation Energy (kcal/mol)		
	10%[a]	30%[a]	90%[a]
Homogeneous	6.2	6.9	7.6
Asymmetric	2.3	2.8	3.0

Ethanol wt % in the feed. Operation temperature 25°C.

decreases as the feed ethanol concentration increases for the asymmetric membrane, as shown in Figure 6. The result corresponds well with the result mentioned above regardless of the temperature, as indicated in Figure 8. Meanwhile, in the 90 wt % ethanol concentration of the feed solution, the membrane is shrunk by ethanol, which inhibits the plasticizing effect.

Table III shows the activation energies of the aqueous alcohol solution through the homogeneous and asymmetric membranes. Because the variation of the permeation rate for a given feed concentration as a function of the reciprocal of the absolute temperature is generally linear, an apparent activation energy can be drawn from the slope of the plots. Table III indicates that the activation energy of the asymmetric membrane became generally smaller than that of the homogeneous membrane. The activation energy of the homogeneous membrane and the asymmetric membrane lies in the range of 6.2–
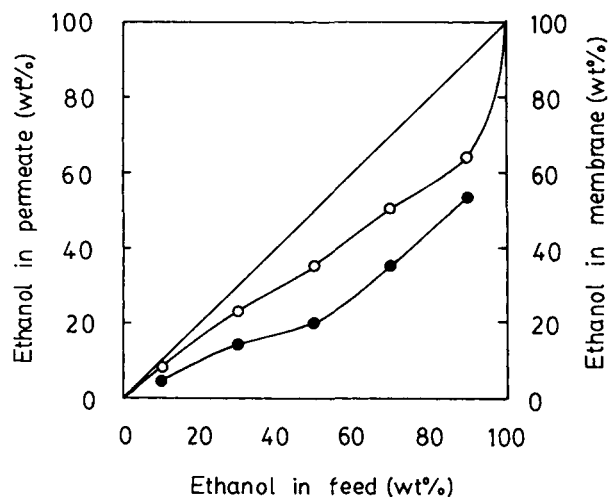

Figure 9 Effect of feed ethanol concentration on the compositions of the solution adsorbed and permeated with the asymmetric membrane: (○) permeated; (●) adsorbed.

Table IV Pervaporation and Sorption Properties of the Asymmetric Membrane for Alcohol–Water Mixtures[a]

| Alcohol | Total Sorption $(g\ g^{-1})$ | Water Sorption $(g\ g^{-1})$ | Alcohol Sorption $(g\ g^{-1})$ | Separation Factor | | Permeation Rate $(kg/m^2\ h)$ |
				A[b]	B[c]	B
Methanol	0.96	0.43	0.54	7.16	1.59	1.26
Ethanol	0.94	0.43	0.51	7.59	4.72	0.78
n-Propanol	0.83	0.44	0.39	10.15	9.56	0.27
t-Butanol	0.72	0.54	0.18	27.80	16.84	0.16

[a] 90 wt % aqueous alcohol solution.
[b] A: sorption.
[c] B: pervaporation.

7.6 and 2.3–3.0 kcal/mol, respectively. The lower activation energy of the asymmetric membrane for the ethanol–water feed solution could be explained by that the diffuse resistance of asymmetric membrane is lower than that of homogeneous membrane.

Sorption of Binary Liquid Mixture

According to the solution–diffusion model, the effects of solubility and diffusivity play an important role in the membrane permselectivity. Thus, sorption experiments for the asymmetric membrane in the ethanol feed concentrations varying from 10 to 90 wt % were made. Figure 9 shows the influence of the feed ethanol concentration on the ethanol concentration in the permeate and in the membrane for the asymmetric membrane. The ethanol concentration in the membrane is lower than that in the permeate for the ethanol feed concentrations in the range of 10–90 wt %. The permeate and sorption composition curves lie under the diagonal line, indicating that the water molecules are selectively dissolved into the asymmetric membrane, which contains an amide group, and are also predominantly diffused through the membrane. The separation factor of sorption is higher than that of the pervaporation. For example, the separation factors for pervaporation and sorption of 90 wt % aqueous ethanol feed solution through an asymmetric membrane are 4.72 and 7.59, respectively.

In addition, the pervaporation and sorption properties of the asymmetric membrane for alcohol–water mixtures are shown in Table IV. The data show that an increase in the molar volume of the alcohols results in an increase in the separation factor of pervaporation and sorption, but gives a decrease in permeation rate of pervaporation and total sorption. These phenomena can be explained by the molecular size and shape of the alcohol. The molec-

ular length, L (Å), of methanol, ethanol, and n-propanol are 2.9, 4.2, and 5.4, respectively.[19] The separation factor was found to depend on the molecular length for this linear alcohol system, and it was also found that the permeation rate increased as the molecular length decreased. The permeation rate of tert-butanol is lower than that of n-propanol, which may be due to the steric hindrance of the former being higher than that of the latter. Besides, Table IV also reveals that the sorption of water increases a little in going from methanol to tert-butanol, but that the sorption of the alcohol decreases drastically, resulting in an increase in sorption selectivity. Comparison of the preferential sorption and the pervaporation shows that it is apparent that the water is adsorbed and permeated preferentially.

CONCLUSION

The rate of liquid–liquid demixing increases with the presence of nonsolvents in the casting solution, and with the addition of methanol in the coagulation medium, the membranes with a loose surface structure can be prepared. The pervaporation performances of the nylon 4 membrane are evidently improved using wet phase inversion. Water molecules are preferentially incorporated into asymmetric membranes and also are predominantly diffused through the asymmetric membranes.

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