

NOTE

Pervaporation Performance of Asymmetrically Crosslinked PVA Membranes

INTRODUCTION

Pervaporation is a hopeful membrane-separation process for liquid mixtures.¹ A large number of highly selective pervaporation membranes have been presented so far, especially for dehydration of alcohol/water mixtures. Although most of the commercialized pervaporation membranes such as GFTs² have a composite structure, research studies on pervaporation have been done mainly on homogeneous membranes, paying attention only to the chemical aspect of membrane materials.³ This trend is in contrast with other membrane separation processes such as reverse osmosis and gas separation, where the effect of membrane structure (morphology) on performance has been intensively studied.^{4,5}

Poly(vinyl alcohol) (PVA) shows an excellent water selectivity for dehydration of alcohol/water mixtures.^{6,7} However, water selectivity was often reduced because of swelling, especially for a low alcohol concentration range of the feed composition. Crosslinking is a way to prevent excess swelling of the membrane. An active layer of the GFT membrane (PVA) is crosslinked with maleic acid to prevent excess swelling and to accomplish a higher selectivity. Crosslinking, on the other hand, decreases the permeation flux, so that the total product rate will be decreased. Yamada et al.⁸ studied the effect of crosslinking density of PVA membranes on pervaporation performance. They reported that with increase in the crosslinking density water selectivity increased while its flux decreased. These results were on homogeneously crosslinked membranes. However, it is not necessary to crosslink the whole membrane because only one part of the membrane should contribute to the selectivity (such as the skin layer of integrally skinned asymmetric membranes), and the permeation resistance of the other part should be minimized to obtain a higher productivity (such as the porous part of asymmetric membranes). In this study, we prepared asymmetrically crosslinked membranes by a method described in the following section and studied the effect of the asymmetry of the crosslinking density on pervaporation performance.

EXPERIMENTAL

Materials and Membrane Preparation

PVA was kindly supplied by Kuraray Co. (No. 117 H), of which the degree of polymerization is 1700 and that of the acetylation is more than 99%. Glutaraldehyde (Wako Chemical Co.) was used as the crosslinking reagent. Sulfuric acid was used as the catalyst for the crosslinking reaction. The solution that comprised 10% PVA and 90% water was cast onto a glass plate and dried in a desiccator for a few days. The thickness of the dry membrane was 100 μm . The membrane was mounted between two cells. The crosslinking solution of glutaraldehyde (0.05%) and sulfuric acid (1%) (crosslinking solution) balanced with water was poured into only one cell. The crosslinking solution diffused from one side of the membrane toward the other side, and the crosslinking reaction took place at the same time. The crosslinking solution in the cell was stirred vigorously to avoid concentration polarization. During the reaction, the other cell was kept empty. After a given time, the membrane was taken out and washed thoroughly with distilled water to prevent further reaction. The reaction temperature was kept 25°C by a constant temperature bath.

Pervaporation Experiment

The membrane was settled in a permeation cell of which the temperature was kept 35°C with a constant temperature bath. The feed liquid was circulated between the cell and the feed tank by a liquid pump. The permeate side was kept at the pressure of 0.1 Torr, and the permeate was collected in a trap cooled by liquid nitrogen. The permeation flux was calculated from the weight change of the trap. The composition of the permeate was analyzed by gas chromatography.

The pervaporation experiment was carried out in two ways: namely, UP and DOWN runs. For the UP runs, feed liquid was put in contact with the side of the membrane that had been directly in contact with the crosslinking reagent during the crosslinking. For the DOWN runs, the feed liquid was in contact with the other side of the membrane. To get rid of the effect of the membrane

* To whom correspondence should be addressed.

morphology change which may be caused by the feed liquid or application of vacuum during the pervaporation experiment, different coupons of the membranes were used for the UP and DOWN experiments. The measurements in each condition were carried out at least three times. The deviation of the results for each condition were within 0.1% (absolute) for the composition measurements and 0.01 kg/m²/h for the total flux measurements.

RESULTS AND DISCUSSION

Pervaporation of Pure Water

Figure 1 shows the permeation flux of water as a function of crosslinking time. The water flux decreased with increase in the crosslinking time. For a given crosslinking time, the water flux for the DOWN run was larger than the that for the UP run at a smaller crosslinking time range. The difference in the flux between the UP run and the DOWN run decreased with increase in the crosslinking time, and for the 60 min crosslinked membrane, the difference became almost negligible. This result indicates that the asymmetry of the crosslinking density decreases with increase in the crosslinking time and the 60 min crosslinked membrane has a uniform distribution of the crosslinking density (homogeneously crosslinked).

The difference in the flux between the UP and DOWN runs for the asymmetrically crosslinked membranes can be explained in terms of the sorption-diffusion theory. According to the theory, pervaporation transport takes place by three steps⁹: (1) Dissolution of the feed liquid into the membrane (sorption). (2) Transport through the membrane due to the chemical potential gradient across the membrane (diffusion). (3) Desorption of the permeates at the downstream side of the membrane (desorption). Steps 1 and 3 are considered to be very fast, so that sorption equilibria in both sides of the membrane is usually assumed. Step 2 is the rate-determining step, and Fick's law is applied to express the transport equation.

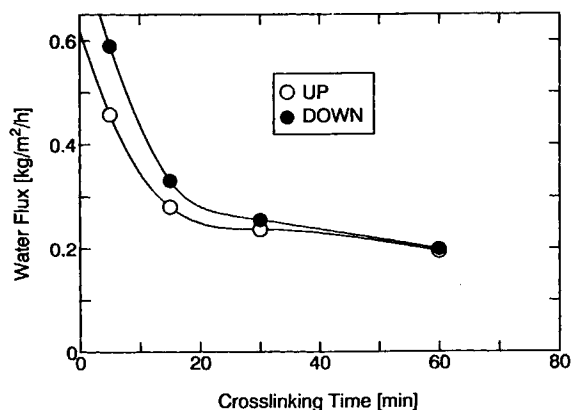


Figure 1 Effect of crosslinking time on water flux (pure water permeation).

We assume here that distribution of the crosslinking density of the membrane can be represented by a lamination model. Let the crosslinking density profile of the membrane be composed of two parts: one is the highly crosslinked region (region 1 hereafter), and the other is the less crosslinked region (region 2 hereafter). We also assume that the crosslinking density is uniform in each region. Region 1 is the part of the membrane that is close to the side contacted with the crosslinking reagent. Let the thickness of the region 1 be L_1 and that of the region 2, L_2 . In addition, we assumed that the concentration profile along the membrane in each region is linear. This assumption is equivalent to the one in which the diffusion coefficient in each region is constant. Let the concentration of water in the membrane of the feed side be S_1 (for the UP run) and S_2 (for the DOWN run) and the equilibrium concentration of the boundary of the two regions be S_u (for the UP run) and S_d (for the DOWN run). The concentrations in the permeate side can be assumed to be zero because the downstream pressure is much smaller than is the saturation vapor pressure, so that the amount of sorption on the permeate side is negligibly small. The steady-state permeation flux can be expressed by eqs. (1) and (2) as follows based on Fick's law:

$$J_u = D_1(S_1 - S_u)/L_1 = D_2(S_u - 0)/L_2 \quad (\text{UP}) \quad (1)$$

$$J_d = D_2(S_2 - S_d)/L_2 = D_1(S_d - 0)/L_1 \quad (\text{DOWN}) \quad (2)$$

where J_u and J_d are the permeation fluxes for the UP and DOWN runs, respectively. D_1 and D_2 are diffusion coefficients through regions 1 and 2, respectively. By eliminating S_u and S_d from eqs. (1) and (2), we obtain the following equations:

$$J_u = S_1(D_1D_2)/(L_1D_2 + L_2D_1) \quad (3)$$

$$J_d = S_2(D_1D_2)/(L_1D_2 + L_2D_1) \quad (4)$$

From eqs. (3) and (4), the ratio of the flux for the UP run to that for the DOWN run (J_u/J_d) depends solely on the ratio of the solubility in the feed side (S_1/S_2):

$$J_u/J_d = S_1/S_2 \quad (5)$$

With increase in the crosslinking density, the solubility should decrease, i.e.⁸:

$$S_1 < S_2 \quad (6)$$

Thus, the permeation rate for the DOWN run (J_d) should be always larger than that for the UP run (J_u).

Pervaporation of Ethanol/Water Mixture

Figure 2 shows the separation diagram of the pervaporation for the ethanol/water mixture through 5 min cross-

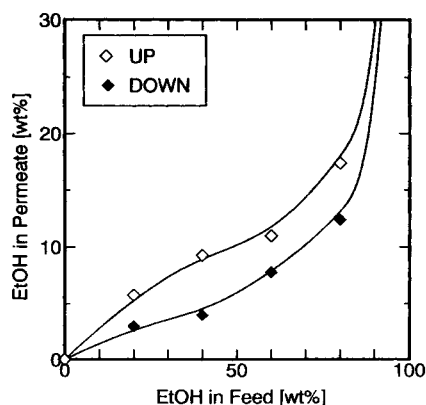


Figure 2 Separation diagram for 5 min crosslinked membranes.

linked membranes. Over the whole range of the feed composition, ethanol concentration in the permeate for the UP run is larger than that for the DOWN run. In other words, the overall water selectivity is higher when the less crosslinked side is contacted with the feed. Permeation fluxes are shown in Figure 3. The water flux in the mixture was larger for the DOWN run than that for the UP run for a given feed composition. On the other hand, the ethanol flux for the DOWN run was always smaller than that for the UP run.

Figures 4 and 5 show the results for 15 min crosslinked membranes. Although the differences in the results between the UP and DOWN runs were smaller than those for 5 min crosslinked membranes, similar trends were observed for 15 min crosslinked membranes. Figure 6 shows the results for 60 min crosslinked (homogeneously crosslinked) membranes. As expected from the results of the pure water permeation, the results the UP and DOWN runs are very close; no effect of asymmetry was observed. Note the absolute values of the water selectivity increased while the fluxes decreased with an increasing crosslinking time.

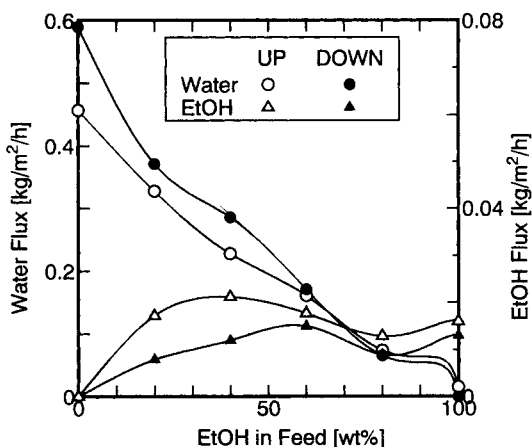


Figure 3 Permeation fluxes for 5 min crosslinked membranes.

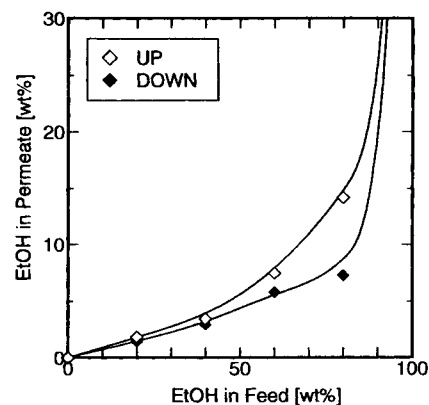


Figure 4 Separation diagram for 15 min crosslinked membranes.

From the above results, the asymmetry of the crosslinking density affects both the permeation rate and selectivity. Also, surprisingly, the DOWN runs, where the feed liquid was contacted with the less crosslinked side, always show higher water selectivity and higher water flux at the same time. This is in contrast to the fact that composite membranes or asymmetric membranes are always used with the feed liquid in contact with the dense side (UP runs).^{10,11}

The difference in the water flux for the mixture between the UP and DOWN runs can be explained in the same way for pure water permeation. If we neglect the coupling on the diffusion coefficient, eqs. (3)–(6) still hold for the mixture system. For ethanol, however, the effect of crosslinking on the solubility will not be so large as that for water¹² or crosslinking may even increase the solubility. Thus, the difference in the ethanol fluxes between the UP and DOWN runs should be small.

Let us discuss the higher overall pervaporation selectivity. The water selectivity should increase with an increase in the crosslinking density, because the 60 min crosslinked membrane (with the highest crosslinking

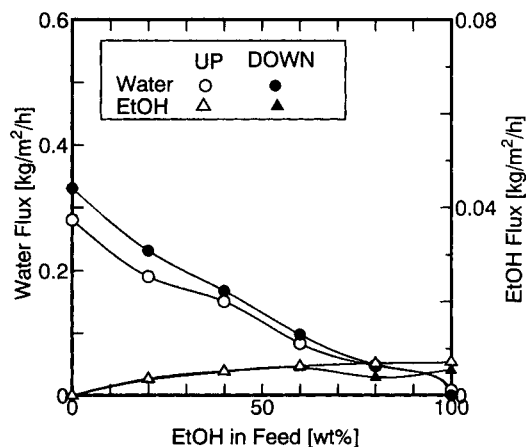


Figure 5 Permeation fluxes for 15 min crosslinked membranes.

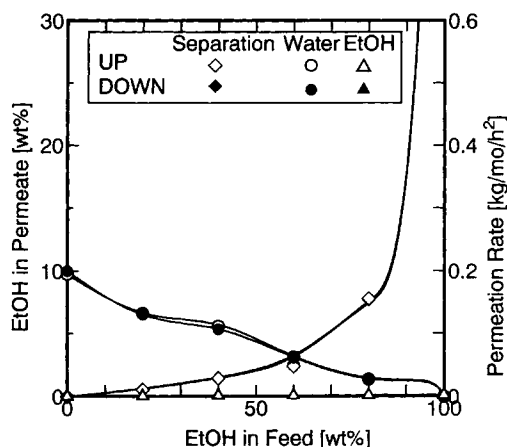


Figure 6 Separation performances for 60 min cross-linked membranes.

density) showed the highest selectivity among the membrane studied. Therefore, the highly crosslinked region (region 1) in the asymmetrically crosslinked membranes should show higher water selectivity than does the less crosslinked region (region 2). If the water selectivity is determined mainly by the behavior of the feed side, the selectivity of the UP run should be higher than that for the DOWN run. It was not the case for the present system. Therefore, the overall selectivity should be determined not by the behavior of the feed side, but by that of the permeate side. The overall water selectivity is larger when region 1 is in contact with the permeate side, because region 1 is more water-selective than is region 2. Similar effects have been reported by Mochizuki et al.¹³ and Deng et al.¹⁴ on the pervaporation of the laminated membranes. They used laminated membranes of different selectivities; one (membrane 1) is selective for one component (A) of the mixture and the other (membrane 2) is selective for the other component (B). They both found that when the feed side was in contact with the A-selective membrane (membrane 1) the selectivity of component A in the laminated membrane was smaller than in the other case, i.e., the B-selective membrane (membrane 2) is in contact with the feed liquid. These results support that the overall selectivity is governed mainly by the behavior of the permeate side. It should be noted that, however, no simultaneous increase in selectivity and permeation rate was reported for the laminated membranes. This should be an advantage of the asymmetrically crosslinked membranes.

CONCLUSION

Asymmetrically crosslinked PVA membranes which have distribution of crosslinking density along the membrane cross section were prepared and their pervaporation performances were studied. Both the water flux and the water

selectivity were larger when the feed liquid was in contact with the less crosslinked side (DOWN), compared with the case of the membrane being upside down (UP). The differences in the performance between DOWN and UP were larger when the asymmetry was larger. These results suggested that the selectivity is determined mainly by the behavior of the permeate side.

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AKIHIRO YAMASAKI*
T. IWATSUBO
T. MASUOKA
K. MIZOGUCHI

National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba 305, Japan

* To whom correspondence should be addressed.

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