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Effect of Evaporation Time on the Pervaporation Characteristics through Homogeneous Aromatic Polyamide Membranes. II. Pervaporation Performances for Ethanol/Water Mixture*

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SYNOPSIS

Pervaporation of ethanol/water mixtures through symmetric dense aromatic polyamide membranes was investigated. The membrane structure was controlled by varying the solvent evaporation time before gelation. The membranes were water-selective and the selectivity increased with an increase in the solvent evaporation time. On the other hand, the water flux as well as the ethanol flux decreased with an increase in the evaporation time. These results were consistent with the morphology change of the membrane which takes place with solvent evaporation: the decrease in the channel size. The effects of the downstream pressure on the pervaporation performances were also studied for membranes with different solvent evaporation times. The ethanol concentration in the permeate side increased with an increase in the downstream pressure to certain point, showed a maximum there, then decreased thereafter. The water flux decreased with an increase in the downstream pressure for all membranes studied; the dependence was expressed by a parabolic curve in the lower pressure range. The ethanol flux also decreased with an increase in the downstream pressure for the membrane with shorter evaporation time, while this flux was slightly affected by the downstream pressure for the membrane with longer evaporation time. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation has been recognized nowadays as one of the most versatile membrane separation processes for liquid mixtures.¹ A number of new polymeric materials have been synthesized and tested for pervaporation performance. A thin dense film is usually used for studies of the pervaporation characteristics. The effect of the preparation method on the performance has been mostly ignored because it was thought that the intrinsic permeation properties of polymeric membranes are not affected by the preparation method as far as the membrane is homo-

geneous. The previous paper,² however, showed that the pervaporation performances for pure water through homogeneous aromatic polyamide membranes depended on the solvent evaporation time before gelation; the pure water flux decreased with an increase in the evaporation time. The membranes were characterized by sorption measurement for liquid and vapor of water; the liquid sorption amount decreased with an increase in the evaporation time while the surface area for vapor sorption increased. This apparently contradictory result could be explained in terms of the size and number of the channels in the membranes; the channel size decreased and the number increased with increased evaporation time. Moreover, the change in the pervaporation performance for pure water could be correlated with the change in the size of the channels, which was calculated from the sorption experiment results. In

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this paper, the pervaporation performances for ethanol/water mixtures have been reported for the homogeneous aromatic polyamide membranes with different solvent evaporation times. Naturally, it is expected that the selectivity as well as the pervaporation flux will be affected by the morphology change that results from the solvent evaporation.

EXPERIMENT

Materials and Membrane Preparation

The polymer used in this study was poly-*m*-phenylene-iso(70)-*co*-terephthal(30)-phthalamide, which was synthesized in our laboratory according to the method reported elsewhere.³ The membrane preparation method was the same as that reported in the previous paper.² Briefly, membranes were cast from the solution of 10.3 wt % polymer, 3.8 wt % LiCl, and 85.9 wt % dimethylacetamide (DMAc) with a fixed thickness of 2 mils (50.4 μm). The evaporation of the solvent was carried out at 95°C in an air atmosphere for 5 to 240 min. The membranes were dense and homogeneous, with a thickness of 5 $\mu\text{m} \pm 0.5 \mu\text{m}$, and no visible pores were observed under a scanning electron microscope (SEM).

Pervaporation

Pervaporation experiments were carried out at 25°C with the same apparatus previously described.² The steady-state performances for different downstream pressures were obtained for different feed compositions. The downstream pressure was controlled by a needle valve and monitored by a pressure transducer.

RESULTS AND DISCUSSIONS

Effect of Solvent Evaporation Time on Pervaporation Characteristics

Figure 1 shows the separation diagram for the membranes with different evaporation periods. The downstream pressure was fixed at about 3 Torr to eliminate the effect of downstream pressure. The membrane with 15 min evaporation time showed very low water selectivity over the whole range of the ethanol concentration in the feed. All other membranes with longer evaporation times were more water-selective. With an increase in the solvent evaporation time, the water selectivity increased. The selectivity for the membrane with 120 min

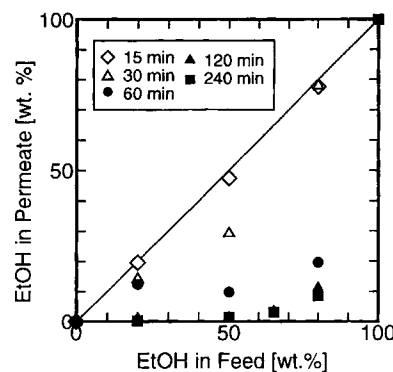


Figure 1 Separation diagrams for the polyamide membranes with different evaporation times.

evaporation time was very close to that with 240 min evaporation. These results imply that the water selectivity increased with a decrease in the size of channels in the membrane, since the channel size decreased monotonously with an increase in the evaporation time.² There was a gap between the membrane with 30 min evaporation time and the one with 60 min evaporation time. This should correspond to an observation in the previous paper that the morphology changes in different manners before and after 30 min of evaporation time.

Figure 2 shows the effect of feed composition on the water flux through the membranes. For the membranes with evaporation times shorter than 60 min, the water flux decreased with an increase in the ethanol content in the feed. For the membranes with 120 and 240 min evaporation, the water flux showed a minimum at 20% ethanol concentration in the feed. For a given ethanol concentration, the water flux decreased with an increase in the evaporation time. Figure 3 shows the results for the ethanol flux. Contrary to the water flux, the ethanol flux increased with increasing ethanol content in the feed mixture for a given evaporation time. The ethanol flux decreased monotonously with an increase in the evaporation time for a given feed composition.

Based on the pore-flow model of pervaporation, the transport through the membranes can be divided into two parts: nonselective liquid phase flow and selective vapor phase flow.⁴ The vapor phase flow is supposed to be the surface flow that takes place in the wall of the channels. The Knudsen flow rate is proportional to the cube of the channel size, whereas the surface flow rate is proportional to the square of the channel size.⁵ Therefore, when the channel size becomes large, the contribution from the Knudsen flow cannot be neglected and may even domi-

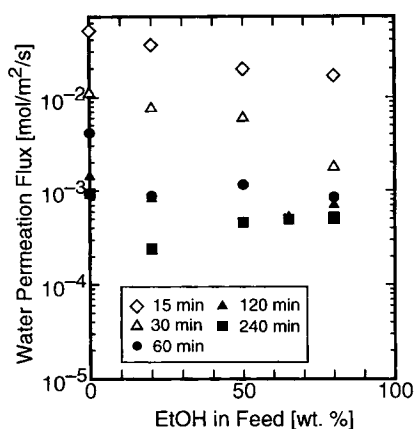


Figure 2 Permeation flux of water.

nate, and total flow rate increases. On the other hand, since the Knudsen flow rate is inversely proportional to the square root of molecular weight,⁵ it is less selective than the surface flow. The surface flow should be more selective than the Knudsen flow because it reflects the interaction between polymer wall and the diffusing species.⁶ Therefore, the selectivity increased with a decrease in the channel size, which was caused by the solvent evaporation.

Effect of Downstream Pressure

20% Ethanol/80% Water Mixture

Figure 4 demonstrates the effect of downstream pressure on the ethanol concentration in the permeate side (membrane selectivity). The results for the membrane with 15, 30, and 240 min evaporation time are shown in the figure. The downstream pressure dependence was almost similar for the membranes with 15 and 30 min of evaporation time; with an increase in the downstream pressure, the ethanol concentration in the permeate side increased, and it showed a maximum at about 35 Torr. When the downstream pressure was higher than 35 Torr, the ethanol content in the permeate side decreased with an increase in the downstream pressure to reach the concentration in the feed side (no separation). The ethanol concentration in the permeate side for the membrane with 240 min evaporation started from a lower region. However, a rapid increase in the ethanol concentration was observed above 20 Torr of downstream pressure, which is almost equal to the saturation water vapor pressure at 25°C. These results imply that the highly water-selective membrane at lower downstream pressure becomes ethanol-selective at higher downstream pressure ranges.

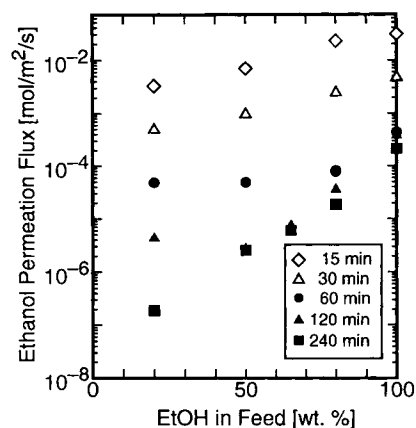


Figure 3 Permeation flux of ethanol.

The downstream pressure dependence on the water selectivity should be attributed to that of the surface flow because the selectivity due to the Knudsen flow is independent of the downstream pressure.⁵ The surface flow is caused by adsorbed molecules in the channel walls. With increasing downstream pressure, the adsorption amount should increase. The increase in adsorption amount leads to the decrease in selectivity through adsorption because the interaction between ethanol and water should increase the adsorption amount of ethanol. Furthermore, the increase in the interaction of the adsorbed molecules due to the increase in the adsorption amount should result in an increase in the surface diffusion coefficient of ethanol. Both effects should increase the ethanol concentration in the permeate side with an increase in the downstream pressure. The increasing rate is more rapid for the membranes with smaller channels (240 min of evaporation time) because the contribution of surface flow to the total flow rate is much larger. The con-

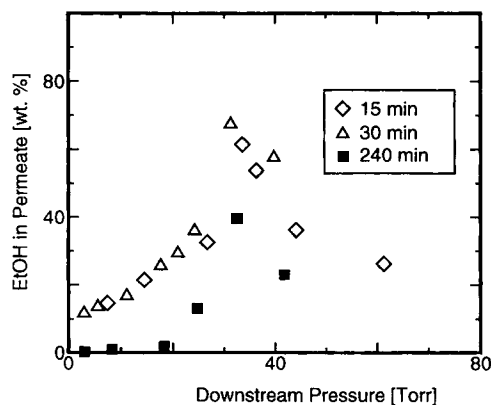


Figure 4 Effect of downstream pressure on the selectivity (feed: ethanol 20%/water 80%).

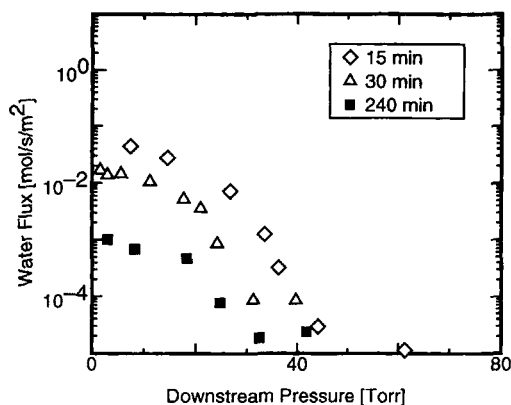


Figure 5 Effect of downstream pressure on the flux of water (feed: ethanol 20%/water 80%).

tribution of surface flow to the total flux should end when the downstream pressure reaches the saturation vapor pressure. At higher pressure ranges, only liquid transport takes place with almost no selectivity.

Figure 5 shows the effect of the downstream pressure on water flux. A parabolic part and a linear part were observed for each membrane. For a given pressure, the water flux decreased with an increase in the evaporation time. The parabolic part reached about 35–40 Torr while it ended at about 20 Torr for pure water pervaporation.² This result reflects that the saturation vapor pressure is higher for the mixture than for pure water; liquid transport starts from a higher pressure range. The surface flow rate is in proportion with the gradient of adsorption amount through the membrane. The Knudsen flow rate is in proportion with the pressure gradient through the membrane. The gradient of adsorption amount decreases with an increase in the downstream pressure due to an increase in the adsorption amount in the permeate side. The decrease in the water flux can be explained by the decrease in the gradient of adsorption amount for surface flow and the decrease in the pressure gradient through the membrane for Knudsen flow. Figure 6 shows the effect of the downstream pressure on the ethanol flux. For the membranes with 15 and 30 min evaporation times, a parabolic part was observed; whereas no parabolic part was observed for the membrane with 240 min evaporation. The latter result suggests that the surface flow rate increased with an increase in the downstream pressure because of an increase in the surface mobility of ethanol.

Pervaporation for 50% Ethanol Mixture

Figure 7 shows the effect of the downstream pressure on the ethanol concentration in the permeate side;

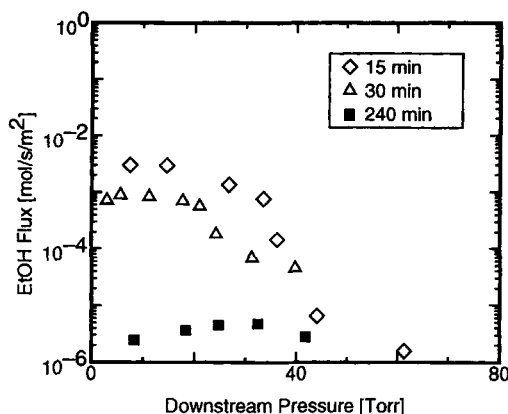


Figure 6 Effect of downstream pressure on the flux of ethanol (feed: ethanol 20%/water 80%).

the feed concentration of ethanol was 50%. Similar results to the 20% feed concentration were obtained for the 50% feed concentration; with an increase in the downstream pressure, ethanol concentration in the permeate side increased, showed a maximum, and then decreased. The pressure that gives the maximum was about 40 Torr, which is higher than that for the 20% feed. The effect of the downstream pressure on the water flux is shown in Figure 8. A parabolic curve was observed for each membrane, as for the 20% feed. The parabolic part reached pressure range of more than 40 Torr. Ethanol flux is shown in Figure 9. A dependence expressed by a parabolic curve was observed for the membrane with 15 and 30 min of evaporation, although the curvature is much smaller than that for 20% ethanol in feed. For the membrane with 240 min evaporation time, the ethanol flux increased slightly with an increase in the downstream pressure. The similar explanation in terms of surface flow and Knudsen flow can be

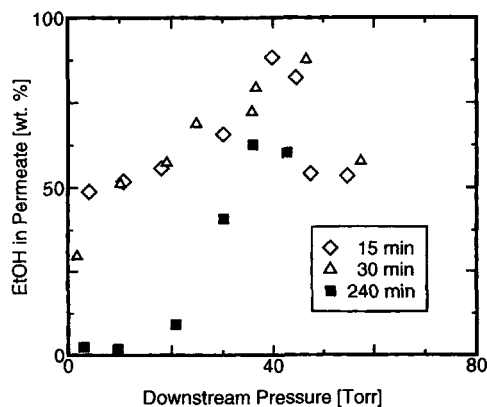


Figure 7 Effect of downstream pressure on the selectivity (feed: ethanol 50%/water 50%).

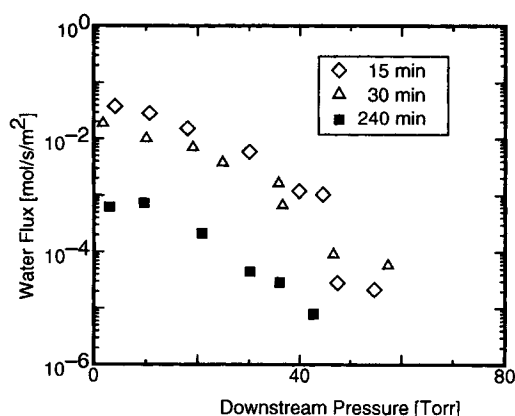


Figure 8 Effect of downstream pressure on the flux of water (feed: ethanol 50%/water 50%).

applied to the system with 50% ethanol in the feed. The observation that the parabolic part for the downstream pressure dependence of fluxes reach above 40 Torr should reflect the higher saturation vapor pressure for the 50% ethanol/50% water mixture.

Pervaporation for 80% Ethanol Mixture

Figure 10 shows the effect of the downstream pressure on the ethanol concentration in the permeate side. The ethanol concentration for the membrane with 15 and 30 min evaporation was almost independent of the downstream pressure. On the other hand, the ethanol concentration in the permeate side increased rapidly with an increase in the downstream pressure for the membrane with 240 min of evaporation time and it leveled off above 35 Torr, where it was almost equal to the one for the membranes with 15 and 30 min evaporation. Ethanol

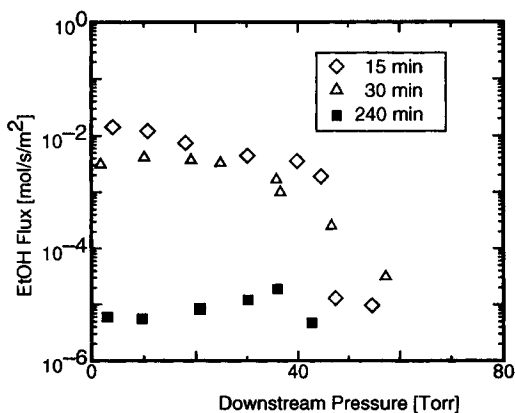


Figure 9 Effect of downstream pressure on the flux of ethanol (feed: ethanol 50%/water 50%).

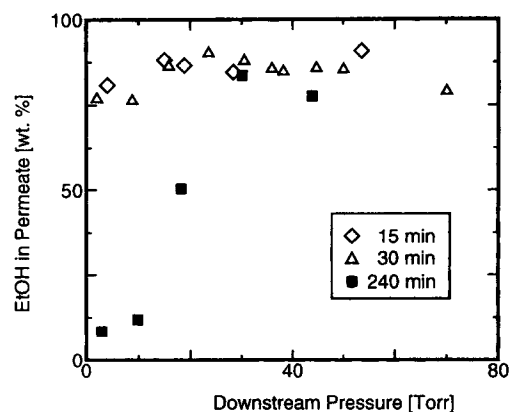


Figure 10 Effect of downstream pressure on the selectivity (feed: ethanol 80%/water 20%).

concentration in the permeate side did not exceed 95%.

Figure 11 shows the effect of the downstream pressure on the water flux. A parabolic curve was observed for the membrane with 240 min evaporation, while the water flux decreased slightly with an increase in the downstream pressure for the membranes with 15 and 30 min evaporation. Figure 12 shows the ethanol flux. Ethanol flux was slightly decreased with an increase in the downstream pressure for all membranes.

CONCLUSIONS

From the results of the pervaporation experiments described above, the following conclusions can be drawn:

1. With an increase in the solvent evaporation

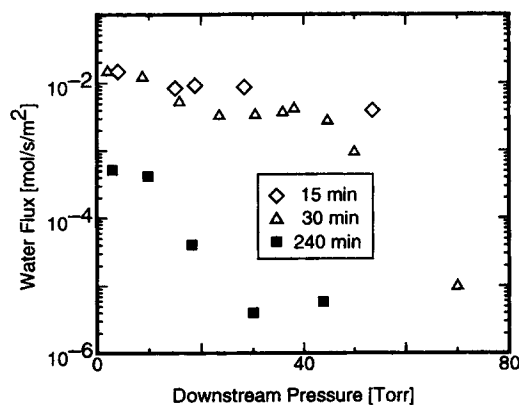


Figure 11 Effect of downstream pressure on the flux of water (feed: ethanol 80%/water 20%).

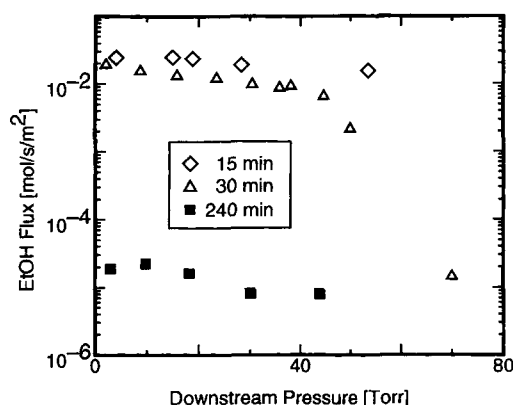


Figure 12 Effect of downstream pressure on the flux of ethanol (feed: ethanol 80%/water 20%).

time, the water selectivity increased but the water permeability decreased. This result was consistent with the morphology change of the homogeneous membrane; the decrease in the channel size.

2. With an increase in the downstream pressure, the ethanol concentration in the permeate side increased and water selectivity de-

creased. The ethanol concentration in the permeate side showed a maximum at 35–40 Torr and then decreased to reach the feed-side concentration. Similar dependence was observed regardless of the solvent evaporation times of the membranes.

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