

# Preparation of Crosslinked Alginate Composite Membrane for Dehydration of Ethanol–Water Mixtures

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**ABSTRACT:** The purpose of this article was to develop new membranes with a high selectivity and permeation rate for separation of an alcohol/water system. Crosslinked alginate composite membranes were prepared by casting an aqueous solution of alginate and 1,6-hexanediamine (HDM) onto a hydrolyzed microporous polyacrylonitrile (PAN) membrane. The influence of hydrolysis of the support membrane and crosslinking agent content in a dense layer on the selectivity and flux was studied and it was shown that both could improve the separation performance of the composite membrane greatly. The counteraction of alginate coatings as a dense separating layer also influenced the separation properties of the membrane, which was better for  $K^+$  than for  $Na^+$ . This novel composite membrane with  $K^+$  as a counterion has a high separation factor of 891 and a good permeation rate of  $591 \text{ g m}^{-2} \text{ h}^{-1}$  for pervaporation of a 90 wt % ethanol aqueous solution at  $70^\circ\text{C}$ . At the same time, SEM micrographs showed that the pore structure of the PAN microporous membrane is changed by hydrolysis. The reason for the influence of the preparation conditions on the separation performance of the novel membrane is discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3054–3061, 2000

**Key words:** pervaporation; dehydration; alginate; alcohol–water mixture; composite membrane

## INTRODUCTION

In a pervaporation process, it is desirable to use a polymeric membrane with the combined characteristics of a high permeation rate and good selectivity. Since the efficiency of pervaporation depends to a great extent upon the membrane employed, the development of the best membrane is critical.

According to solution–diffusion theory, many hydrophilic polymer membranes have been investigated for the dehydration of a water/alcohol mixture.<sup>1,2</sup> Among the hydrophilic membranes,

alginate membranes<sup>3,4</sup> are reported to present the most outstanding separation performance by pervaporation for the dehydration of organic/water mixtures. However, alginate is water-soluble and excess hydrophilicity of the membrane material is not necessarily suitable for the dehydration process, because an alginate membrane lacks dimensional stability in organic aqueous mixtures. It was reported<sup>5</sup> that a serious decline took place with the operating time during pervaporation separation of an ethanol–water mixture through sodium alginate membranes, which influences its commercial utilization in the separation of an organic aqueous mixture. Usually, when a highly permeable polymer material is selected, selectivity and membrane stability can be enhanced by chemical modification or crosslinking, with a corresponding sacrifice of flux. Therefore, the mem-

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brane material should be modified to have the optimal combination of flux and membrane stability or selectivity.

To obtain a high-separation performance membrane, a novel composite membrane with a three-layer structure was designed and prepared by using a hydrolyzed microporous polyacrylonitrile (PAN) membrane as a support in our previous articles.<sup>6–8</sup> At the same time, it was found that hydrolysis of the PAN sublayer, to a moderate extent, is favorable for improving the separation performance of the composite membrane.

In this work, we prepared a novel composite membrane consisting of a hydrolyzed PAN microporous membrane as a sublayer and an alginate crosslinked with 1,6-hexanediamine (HDM) as a dense layer to investigate its application in pervaporation for separation of ethanol–water mixtures. At the same time, the influence of the sublayer on the separation properties of the composite membrane is also discussed.

## EXPERIMENTAL

### Membrane Materials

Sodium alginate (SA) (viscosity  $\geq 0.02$  Pa s in 1% aqueous solution at 20°C), HDM (C.P.) were obtained from Shanghai Chemical Reagent Co. (Shanghai, China). Potassium alginate (PA) was obtained by the neutralization of alginic acid (prepared from an SA aqueous solution by adding 0.6N hydrochloric acid) with potassium hydroxide. The support layer was a PAN ultrafiltration membrane provided by the Development Center of Water Treatment (Hangzhou, China).

### Characterization

A differential scanning calorimeter (Perkin–Elmer Delta Series DSC-7) and a thermogravimetric analyzer (Perkin–Elmer Delta Series TGA-7) were used for the structural determination.

### Membrane Preparation

PAN microporous membranes were hydrolyzed by immersing them in a 5% NaOH aqueous solution at 50°C for a given time and then washed thoroughly with deionized water until neutral. The novel composite membrane was prepared by casting the solution, which was made from a mixture of a 1% aqueous solution of alginate and 0.25%

HDM, onto the hydrolyzed PAN microporous membrane and dried at 55°C for 4 h. The dry composite membrane was immersed at room temperature for 24 h in a 75% ethanol aqueous solution containing 3% acetic acid, subjected to heat treatment at 80°C for 1 h to effect the crosslinking structure, then immersed in an 80% ethanol aqueous solution containing 1% NaOH or KOH for 1 h at room temperature. The membrane was immersed in an 80% ethanol aqueous solution for 1 h to eliminate any possible residual HDM and then dried at room temperature. The thickness of the top layer of the composite membrane was about 5  $\mu\text{m}$ .

The homogeneous membrane was prepared by casting the solution onto a glass plate. The conditions and the procedures of membrane preparation are the same as those of the composite membrane.

### Swelling Characteristics and Evaluation of Solubility Selectivity

A homogeneous crosslinked membrane sample was immersed in an 85% ethanol aqueous solution at 15°C for 72 h. After the sorption, equilibrium was reached, and the membrane was rapidly taken out from the immersing solution, wiped with tissue paper to remove any adherent solvent, and weighed immediately. The swelling degree ( $S$ ) was determined by

$$S = (W_s - W_d)/W_d$$

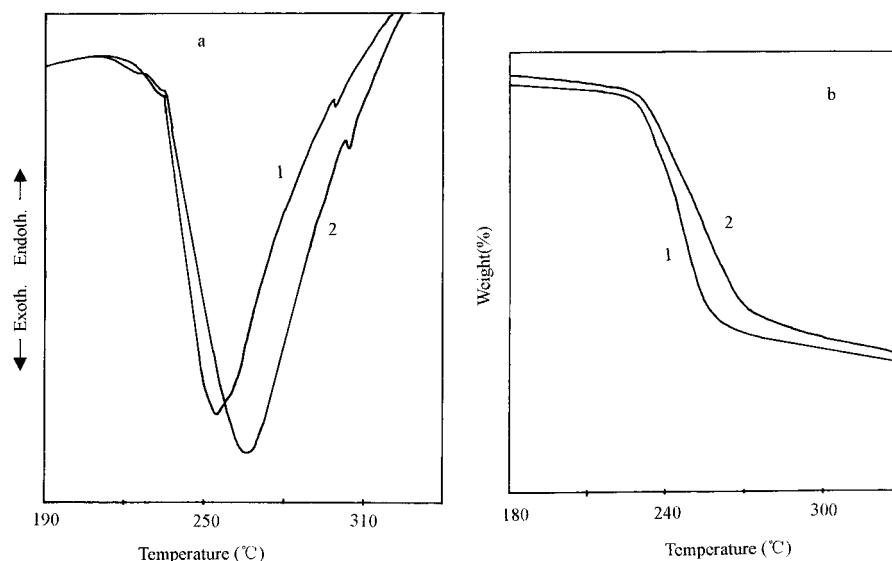
where  $W_d$  and  $W_s$  are the weight of the dry and swollen membranes, respectively.

The solvent in the swollen membrane was allowed to evaporate under reduced pressure and then collected in a liquid nitrogen trap. The composition of the solvent was determined by a gas chromatograph.

### Pervaporation

A detailed procedure for performing the pervaporation experiment can be found in our previous article.<sup>6</sup> A pervaporation experiment was carried out by maintaining the permeate side at a reduced pressure at 2 mmHg (266 Pa). The permeate vapor was collected in a dry ice/acetone mixture (–77°C) trap. The composition of the permeate was determined by a gas chromatograph.

The separation factor ( $\alpha_{w/e}$ ) is defined as follows:



**Figure 1** (a) DSC curves and (b) TG curves of homogeneous SA membrane and one crosslinked with HDM: (1) homogeneous SA membrane; (2) homogeneous SA membrane crosslinked with HDM 1.25 mg/g SA.

$$\alpha_{w/e} = \frac{Y_w/Y_e}{X_w/X_e}$$

where  $X_w$  and  $X_e$  are the water and ethanol contents (%) in the feed, respectively, and  $Y_w$  and  $Y_e$  are the water and ethanol contents (%) in the permeate, respectively.

## RESULTS AND DISCUSSION

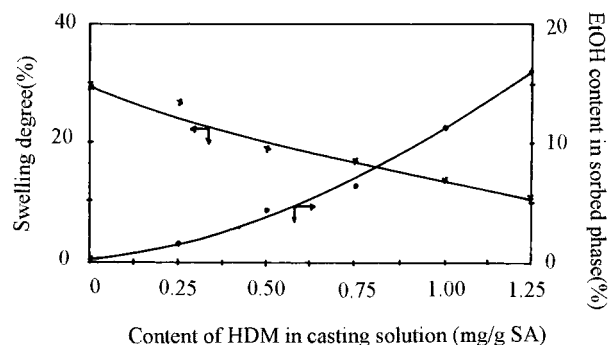
### Thermal Analysis of Homogeneous Alginate Membrane Crosslinked with HDM

Figure 1 illustrate the DSC curves and the TG curves of the homogeneous alginate membranes crosslinked with HDM. The results show that the thermal stability of the homogeneous SA membrane is improved greatly by adding HDM as a crosslinking agent. In addition, the crosslinked homogeneous SA membrane with HDM did not dissolve in water, while SA is water-soluble. It is verified that the crosslinking reaction does take place under the experimental conditions.

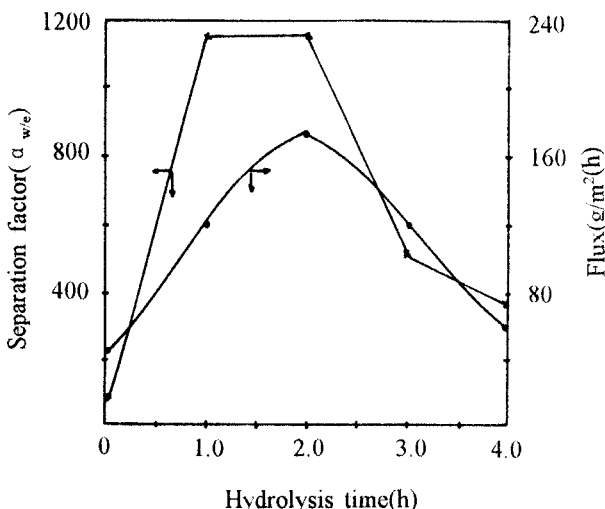
### Swelling Measurement of Homogeneous Membrane

When the HDM content was lower in the reaction solution, a crosslinking reaction might occur insufficiently due to lack of a crosslinking agent in

the solution, so that the resulting membrane could not be stable enough in water. Swelling measurements of the crosslinked membranes were conducted in an 85 wt % ethanol aqueous solution. Figure 2 exhibits the plot of the swelling degree of the crosslinked membrane versus the HDM content in the reaction. With increasing the HDM content, the swelling degree of the crosslinked membrane decreased. This may be attributed to a decline in hydrophilicity of the SA membrane crosslinked with HDM. From this fact, it could be postulated that the crosslinked SA membranes would have less affinity to water (i.e.,



**Figure 2** Swelling degree and composition of the liquid mixture inside the swollen SA membranes crosslinked at various HDM contents in the reaction solution measured in an 85 wt % ethanol aqueous solution at 15°C.



**Figure 3** Effects of hydrolyzing time of the sublayer on pervaporation performance of crosslinked SA composite membrane for 90 wt % ethanol aqueous solution at 70°C. Crosslinking agent content: 0.5 mg/g SA.

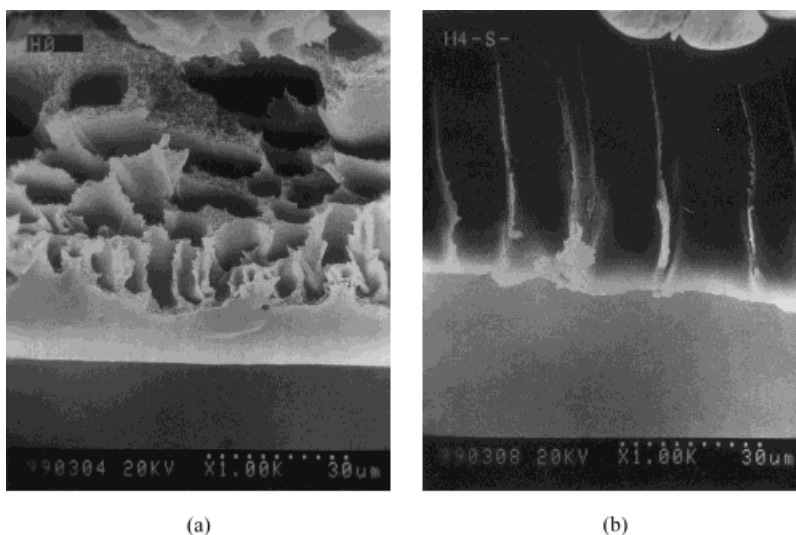
less preferential sorption of water). This was verified by the data as shown in Figure 2.

#### Influence of the Support Membranes

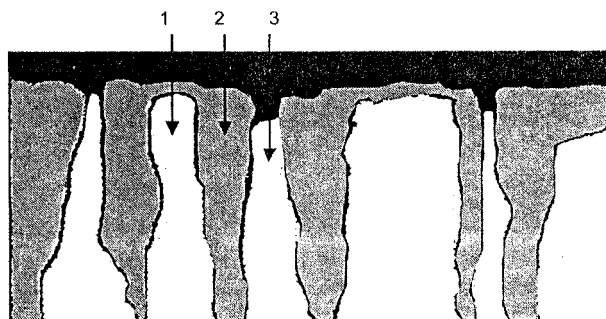
The effect of the hydrolysis time of the PAN microporous membrane on the permselectivity of the crosslinked SA composite membrane for pervaporation separation of a 90% ethanol aqueous solution is shown in Figure 3. It indicates that the

permeation rate and the separation factor increase with increasing hydrolyzing time of the support membrane from 0 to 2 h, while both will exhibit the opposite trend with a hydrolysis time over 2 h. The curves have maximum points in about 2 h and a flux of  $170 \text{ g m}^{-2} \text{ h}^{-1}$  and a separation factor of 1116, respectively. This separation behavior of the membrane with the hydrolysis time of the sublayer may be attributed to the changes in the chemical structure and morphology of the support layer, since the support layer does contribute to the separation properties of the composite membrane.<sup>9</sup> The number of  $-\text{COOH}$  on the PAN support membrane increase with increasing hydrolysis time,<sup>8</sup> which results in increasing the affinity toward water; thus, both the permeation rate and the separation factor were improved as shown in Figure 3 with a hydrolyzing time from 0 to 2 h.

On the other hand, as hydrolysis converts some PAN molecules into poly(acrylic acid) dissolved in water, the pore diameter of the microporous PAN membrane becomes larger with increasing hydrolysis time. This is verified by SEM micrographs of the cross sections of the hydrolyzed support layers as shown in Figure 4. When the hydrolysis time is in excess of 2 h, the surface porosity of the sublayer may be high enough to play a big part in the separation performance of the composite membrane. Koops et al.<sup>9</sup> reported that ideal support layers for a composite membrane must have a relatively high surface porosity and the separa-



**Figure 4** SEM micrographs of the cross sections of (a) PAN microporous membrane and (b) PAN microporous membrane hydrolyzed for 4 h.



**Figure 5** Schematic representation of a composite membrane showing three different permeating regions.

tion properties of these composite membranes will be determined mainly by the top layer, but if the pore diameter is large enough, the top layer material penetrates into the pores of the sublayer to a depth which results in a much higher resistance, while the permeants diffuse through path 3 compared to path 1 (see Fig. 5). Thus, lower flux occurs. At the same time, problems might occur in achieving a thin, defect-free coating (top layer) which may result in a decline of the separation factor if the pore diameters are too large. Therefore, the reason why the separation factor and flux decrease with a hydrolyzing time over 2 h may be explained by the increase in the pore diameters of the sublayer (as shown in Fig. 3).

#### Effects of Counterion of Alginate

The effects of the counterion of alginate on the separation performance of the composite membrane for a 90 wt % ethanol aqueous solution are shown in Table I. The results indicate that the pervaporation performance of the composite

membrane with the  $K^+$  counterion is higher than that of the one with  $Na^+$ . The cause can be well explained by the conformation change, mobility of the alginate molecules, water mobility within the alginate membrane, and crystallinity of the membrane, as Mochizuki et al. did for a homogeneous membrane.<sup>3</sup> The pervaporation properties of the membranes prepared with a sublayer having a different degree of hydrolysis were also studied. For the support layer being hydrolyzed for 2 h, the difference in flux and selectivity through the membrane with the counterion  $Na^+$  or  $K^+$  is small. However, when the PAN microporous membrane is hydrolyzed for 4 h, the separation properties of the composite membrane was improved significantly by using the counterion  $K^+$  instead of  $Na^+$  (as shown in Table I). Compared with the data of Figure 3, the effects of the hydrolysis degree of the sublayer on the pervaporation performance were different due to the counterion of alginate. It is very obvious that the hydrolysis degree of the sublayer has only a little influence on pervaporation performance of the composite membrane using PA as the active layer.

#### Effects of Crosslinking Agent Content in the Reaction Solution

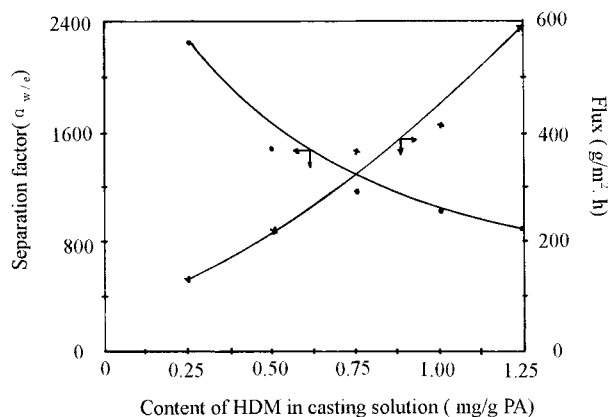
Figure 6 shows that the effects of the content of HDM in top layer on the pervaporation properties of the novel composite membrane. The separation factor decreases and the permeation rate increases with increase of the crosslinking agent. When the content of HDM is 1.25 mg/g PA, the separation factor and the flux of the composite membrane are 891 and  $590 \text{ g m}^{-2} \text{ h}^{-1}$ , respectively. This result is identical to that of the homo-

**Table I** Pervaporation Performance Versus Operating Temperature for the Alginate Composite Membrane with Different Counterions

Operating Temperature (°C)	Sublayer Hydrolyzed for 2 h				Sublayer Hydrolyzed for 4 h			
	$Na^+$		$K^+$		$Na^+$		$K^+$	
	Flux <sup>a</sup>	$\alpha_{w/e}$	Flux <sup>a</sup>	$\alpha_{w/e}$	Flux <sup>a</sup>	$\alpha_{w/e}$	Flux <sup>a</sup>	$\alpha_{w/e}$
40	115	591	93	634	17	96	80	441
50	131	809	150	891	23	121	109	520
60	148	991	188	1116	37	228	172	991
70	170	1116	221	1491	59	382	202	991

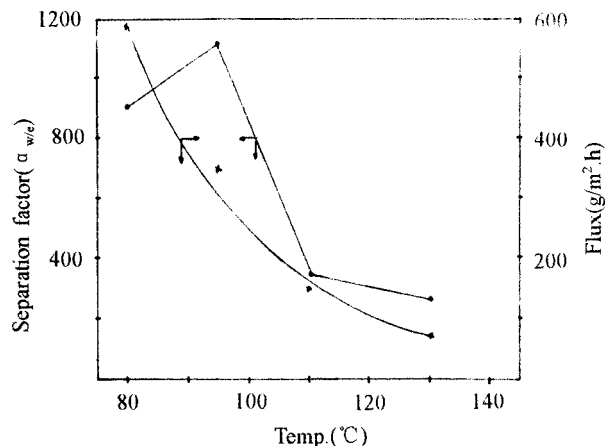
Feed concentration: 90 wt % ethanol.

<sup>a</sup> Flux:  $\text{g m}^{-2} \text{ h}^{-1}$ . Crosslinking agent: 0.5 mg/g alginate.



**Figure 6** Effects of crosslinking agent content on pervaporation properties of the PA composite membrane for 90 wt % ethanol aqueous solution at 70°C. Hydrolysis time of support membrane: 2 h.

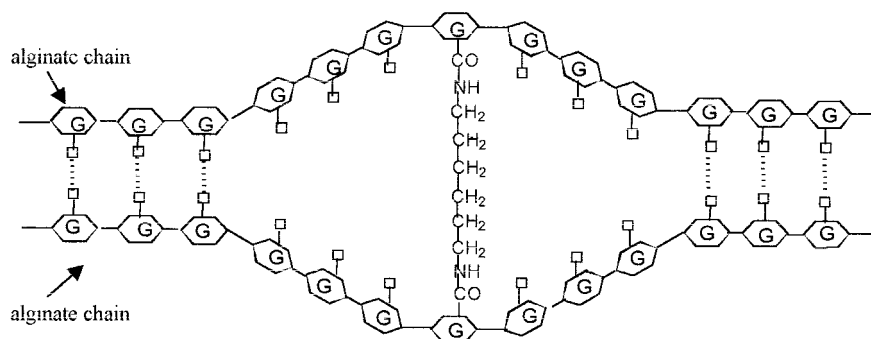
geneous crosslinking chitosan membrane<sup>10</sup> and can be explained by the structure of crosslinking membrane, that is, as the membrane-separation process is conducted mainly in the amorphous region of the membrane according to the conventional solution-diffusion mechanism, the presence of crosslinking causes a more amorphous region to occur. Meanwhile, as the rate of the crosslinking reaction increases with increasing of the crosslinking agent, the structure of the crosslinking active layer becomes looser (as shown in Fig. 7), which results in a decrease of the diffusion selectivity and increase of the flux. At the same time, the distribution selectivity of the SA membrane crosslinked with HDM to water is much lower than that of the SA membrane (shown in Fig. 2). As the separation factor can be divided into distribution selectivity and diffusion selectivity,<sup>4</sup> the selectivity decreases with increasing crosslinking agent content.



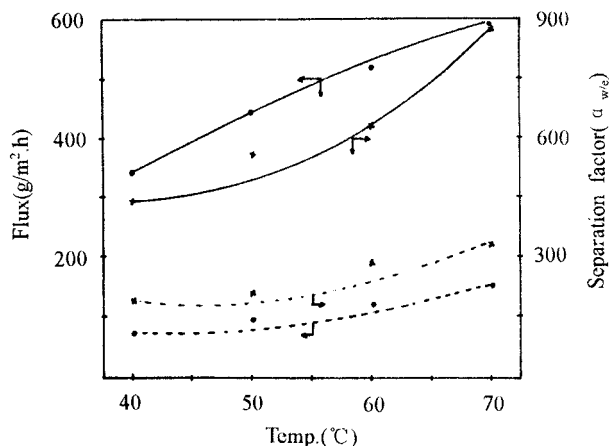
**Figure 8** Effects of heat-treating temperature on pervaporation performance for 90% ethanol aqueous solution at 70°C with K<sup>+</sup> counterion with the heat-curing period fixed at 1 h. Crosslinking agent content: 1.25 mg/g PA. Hydrolysis time of PAN support membrane: 2 h.

**Effects of Heat-treating Temperature**

Figure 8 shows the effect of the heat-treating temperature on both the separation factor and permeation rate of the composite membrane for a 90 wt % ethanol aqueous solution at 70°C. The results indicate that the heat-treating temperature has a strong influence on the pervaporation performance of the alginate composite membrane crosslinked with HDM. At a low temperature of 80–95°C, a much larger flux and separation factor were obtained. With increasing temperature, the separation factor increased and flux decreased markedly. At 95°C, the separation factor had a maximum value, and at a higher temperature than 95°C, the separation factor decreased sharply. It is not clear, however, why the heat-



**Figure 7** Schematic drawing of reactions of alginate with 1,6-hexanediamine (HDM). (⊗) glucosamine unit; (□) hydrophilic groups; (· · ·) hydrogen bond.

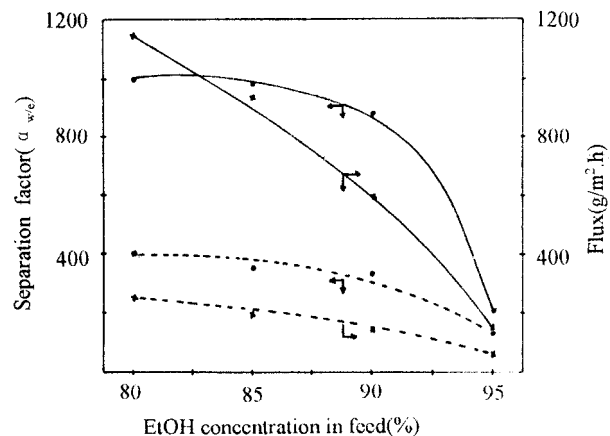


**Figure 9** Effects of operating temperature on pervaporation performance of the composite membrane with different heat-treating temperatures for 90 wt % ethanol aqueous solution. Hydrolysis time: 2 h; crosslinking agent content: 1.25 mg/g PA; (—) heat-treating temperature at 80°C; (---) heat-treating temperature at 80°C; (···) heat-treating temperature at 110°C.

treating temperature greatly influences the separation properties of the composite membrane. The reason seems to be that the hydrophilicity of the membrane was decreased immoderately by the excess crosslinking reaction. In addition, when the heat-treating temperature is higher than the glass transition temperature of the support membrane material, the pore structure of the sublayers change,<sup>11</sup> which may be another reason for a decline in the pervaporation performance of the composite membrane.

Figure 9 shows the dependence of the separation factor and permeation rate of the composite membranes with different heat-treating temperatures on the operating temperature for a 90% ethanol aqueous solution. The results indicate that both the selectivity and permeability increase with the increase in the feed temperature. This behavior is attributed mainly to the extraordinary permselectivity of alginate to water in the sorption step as reported by Yeom et al.<sup>5</sup> and the rigid chain structure of alginate. At the same time, the distribution selectivity of the alginate membrane increases markedly with the temperature and is so high that its diffusion selectivity can be neglected, namely, diffusion selectivity has little contribution on the permselectivity.<sup>4</sup>

The effects of ethanol concentration on the pervaporation performance of two different membranes are shown in Figure 10. The flux with the feed composition shows a normal trend as in the



**Figure 10** Effects of ethanol concentration on pervaporation performance of the composite membrane with different heat-treating temperatures at 70°C. Hydrolysis time: 2 h; crosslinking agent content, 1.25 mg/g PA; (—) heat-treating temperature at 80°C; (---) heat-treating temperature at 110°C.

permeation of aqueous ethanol through a hydrophilic membrane: smaller flux at a higher ethanol content in the feed. However, it is interesting to note the change in the separation factor with the feed composition: The separation factor decreased with increasing ethanol content in the feed. The results from Figures 9 and 10 also show that the variation of the permeation rate and selectivity through the membrane heat-treated at 110°C with the operating temperature or feed concentration is smaller than that through one heat-treated at 80°C. A possible explanation is that the hydrophilicity of the membrane decreases due to the excess crosslinking at a higher heat-treatment temperature, which results in a decrease of distribution selectivity and swelling degree.

## CONCLUSIONS

For the pervaporation separation of ethanol-water mixtures, crosslinked alginate composite membranes with HDM were prepared by casting an aqueous solution of alginate and HDM on a hydrolyzed microporous PAN membrane. The counterion of alginate, the crosslinking agent content, the hydrolysis degree of the support layer, and the heat treatment temperature all have great influence on the separation properties of the membrane. The composite membrane with an active layer of crosslinked PA has a better pervaporation performance with a separation factor of

891 and  $591 \text{ g m}^{-2} \text{ h}^{-1}$  flux for a 90 wt % ethanol aqueous solution at  $70^\circ\text{C}$ . At the same time, it can be concluded from the results that the chemical structure and pore structure of the sublayer, being changed by hydrolysis, influence the separation properties of the composite membrane.

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