

# Pervaporation Separation of Water/Ethanol Mixture Using Asymmetric Ion-Exchange Membranes Containing Aluminum Ions

Shih-Hsiung Chen,<sup>1</sup> Rey-May Liou,<sup>1</sup> Chi-Yu Shih,<sup>2</sup> Cheng-Lee Lai,<sup>1</sup> Juin-Yih Lai<sup>3</sup>

<sup>1</sup>Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan

<sup>2</sup>Department of Chemical Engineering, Cheng Shiu University, Kaohsiung 83305, Taiwan

<sup>3</sup>Research and Development Center for membrane technology, Chung Yuan University, Chung Li 320, Taiwan

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**ABSTRACT:** The asymmetric aluminum ion exchange polysulfone membranes have successfully been prepared for the dehydration of ethanol-water mixture. The relationship between the membrane morphology, separation performance, and the ion content of membranes were discussed in this study. The experimental results showed that the separation performance of those membranes was increased upon increasing the degree of aluminum ion exchange in polysulfone membranes. Both permeation rate and separation factors of those membranes increased with increasing the degree of ion exchange. The increase in separation performance of aluminum ion exchange membranes was mainly attributed to ion crosslinking in poly-

mer network and the hydration effects of exchanged ion in membranes. On the other hand, the operating temperature in the PV process showed a significant influence on the dehydration of water molecules in the permeate. An increase in temperature increased the permeation flux of permeate but slightly decreased its selectivity. The aluminum asymmetric ions in membranes showed a strong influence on permselectivity of asymmetric ion exchange membranes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1412–1420, 2007

**Key words:** asymmetric; ion exchange; polysulfone; pervaporation; membrane

## INTRODUCTION

Dehydration of organic mixture by pervaporation process is an important topic in the field of membrane technology. Previous studies<sup>1–3</sup> showed that the hydration of water and hydrophilic groups of organic compounds play important roles in the dehydration process of organic mixtures. The balance between hydrophilic and hydrophobic moieties in membrane materials is a key factor in preparing a high-performance pervaporation membrane.<sup>4–5</sup> Previous studies have demonstrated the use of hydrophilic polymers such as PAA, PVA, and chitosan, for preparing pervaporation membranes.<sup>6–7</sup> However, the content of hydrophilic moiety in the membrane

usually induced an excessive swelling during the pervaporation process and loss their permselectivity. Therefore, the grafting technology or composite hydrophilic membranes were used to modify polymeric membrane for avoiding the excessive swelling during the pervaporation process. But grafting and composite methods decreased the permeation rate of modified membranes because of the increase in permeation barrier.

Therefore, the application for the dehydration of an organic azeotropic mixture by using ion electrolyte membranes is a new approach to achieve high separation performance in pervaporation. Many previous investigations have focused on the development of a new polyelectrolyte material using hydrophilic composite membranes to enhance the dehydration performance of pervaporation.<sup>8–11</sup> Recently, Nafion and Alginate membranes showed a good potential to achieve a high separation performance for pervaporation. Because of the strong interaction between water and the ionic group of membrane, they presented rich hydrophilic properties and then enhanced the permselectivity of membranes in the separation process. However, the permselectivity of water and permeate permeation rate of those membranes were still too low for the pervaporation

Correspondence to: S.-H. Chen (mshchen@mail.chna.edu.tw).

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application.<sup>8,12</sup> On the other hand, highly hydrophilic alginate materials were also prepared for dehydration application. Many modified and composite alginate membranes were reported in the literature.<sup>13–17</sup> Their pervaporation experiments showed that the permeation behavior of alginate membranes were the same as that of Nafion membranes. The dominant factor of those membranes was almost contributed by the counter ion hydration effect in membranes. But the solvation effect usually swells the polymer matrix and reduced the permselectivity. Those membranes still cannot balance the swelling properties and the hydration effect on the permeate transport during the pervaporation process. Therefore, developing a new type of ionic polymer for pervaporation is still a challenge for membrane research.

The purpose of this study is to prepare asymmetric ion exchange polysulfone membranes with hydrophilic counter ion distributed in the polymer matrix for dehydration of water/ethanol mixture. To clarify the influences of hydration effect of counter ion on the separation performance of membranes, the corresponding influencing parameters on the membrane formation of asymmetric ion exchange polysulfone membranes were studied. We measured the degrees of swelling with different degrees of ion content in membranes and analyzed the sorption content of permeate in those membranes to clarify the permselectivity and diffusion properties of modified membranes. Therefore, the permeation rate and degree of swelling of ion exchange membranes were measured independently to make sure the permeation and diffusion properties of ion containing membranes. The influence of counter ion on the morphology of asymmetric membrane and polymer packing density of those membranes was investigated by DSC and SEM measurements. The influence of aluminum ion content in casting solution on the membrane formation behavior will also investigate by the light transmittance measurement.

## EXPERIMENTAL AND METHODS

### Material

Udel<sup>®</sup> Polysulfone P-3500 was obtained from Amoco Performance Products. *N*-Methyl-2-pyrrolidone (NMP) was used as casting solvent. Chlorosulfonic acid was used as the sulfonation agent in chloroform solution. Butanol was used as cosolvent additive in casting solution. Those solvents were chemical grade and supplied from Merck Chemical Co which were used in this investigation without further purification. The deionized water was used as coagulant in wet phase inversion process.

### Membrane preparation

The sulfonated polysulfone were prepared from direct sulfonation method by adding chlorosulfonic acid.<sup>18</sup> The sulfonation method of polysulfone was obtained by means of chlorosulfonic acid at 0°C.

The aluminum ion exchanged polysulfone was prepared by ion exchanged method with the sulfonated polysulfone<sup>19,20</sup> in 0.1N AlCl<sub>3</sub> ethanol solution over 12 h and precipitation in methanol and then dried in vacuum oven for 24 h. The asymmetric aluminum exchange polysulfone membranes were prepared from a casting solution in NMP and *n*-butanol was added as cosolvents. Then those membranes were prepared by wet phase inversion method in a water coagulation bath. The casting solution contained 20 wt % aluminum ion exchanged polysulfone in NMP. With various amount of cosolvent (*n*-butanol) adding, the polymer solution was casted onto a glass plate to a predetermined thickness of 400 μm using a Gardner Knife. Then the casting films were immersed into de-ionized water bath at 25°C. The asymmetric membranes was formed after 30 min and then peeled off, and finally put into vacuum oven for 24 h before sorption and pervaporation measurements. The dense ion exchanged membranes were prepared from the chloroform solution for at room temperature. The polymer solution was casted onto a glass plate to a predetermined thickness of 400 μm using a Gardner Knife at room temperature.

### Pervaporation experiment

A traditional pervaporation process was used.<sup>21</sup> In pervaporation, the feed solution of 90 wt % ethanol solution was in direct contact with the membrane and kept at 25°C. The effective membrane area was 10.2 cm<sup>2</sup>. The down stream pressure was maintained at about 5–8 Torr. The permeation rate was determined by measuring the weights of permeate. The compositions of the feed solution permeate and solution adsorbed in the membranes was measured by gas chromatography (GC model 8990, China Chromatography). The separation factor,  $\alpha_{A/B}$ , was calculated by the formula:

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where,  $X_A$ ,  $X_B$  and  $Y_A$ ,  $Y_B$  are the weight fractions of *A* and *B* in the feed and permeate, respectively (*A* being the more permeative species).

### Swelling measurement

The degrees of swelling of ion exchanged membranes were determined in distilled water and in

aqueous ethanol solution at 25°C. The weight of dry membrane ( $W_{\text{dry}}$ ) was first determined. After equilibrium with water or ethanol solution, the fully swollen membrane was wiped with tissue paper and weighted. Since the ethanol evaporated very fast, it is difficult to read the real weight directly. The weight of the membrane was measured every 5 s and plotted as a function of time for 30 s after wiping dry. The weight at time zero could be extrapolated and was taken as swollen weight ( $W_{\text{wet}}$ ) of the membrane. The degree of swelling was calculated by following equation:

$$\text{Degree of swelling (\%)} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100 \%$$

### Sorption measurements

The dense membrane was immersed in the ethanol-water mixture for 24 h at 25°C, then blotted between tissue paper to remove excess solvent and placed in the left half of a twin tube set-up. The system was evacuated to  $10^{-3}$  torr after immersing the left tube in liquid for 30 min. Then the tube was heated with hot water for 30 min and the right tube was cooling in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by gas chromatography. The separation factor of sorption was calculated by:

$$\text{Sorption Selectivity} = (Y_w / Y_e) / (X_w / X_e)$$

where  $X_e$ ,  $X_w$ , and  $Y_e$ ,  $Y_w$  are the weight fraction of ethanol and water in the feed and membranes, respectively.

### Scanning electron microscope

Hitachi S4100 SEM observed the surface and cross-section structures of asymmetric membrane. In SEM studies membranes samples were immersed in liquid nitrogen and then fractured membranes for preparing samples. The SEM samples were then deposited with gold using a sputter coater.

### Light scattering

Light transmission experiments have been performed to measure the time of onset of liquid-liquid demixing in phase inversion. For the detail experimental setup and procedures, one can refer to the work of Mulder and Hideto et al.<sup>22,23</sup>

### Contact angle measurement

Water contact angle was used to measure the hydrophobicity of a polymer surface. A contact angle mea-

surement of water drop was based on a setup as description in literature.<sup>24</sup>

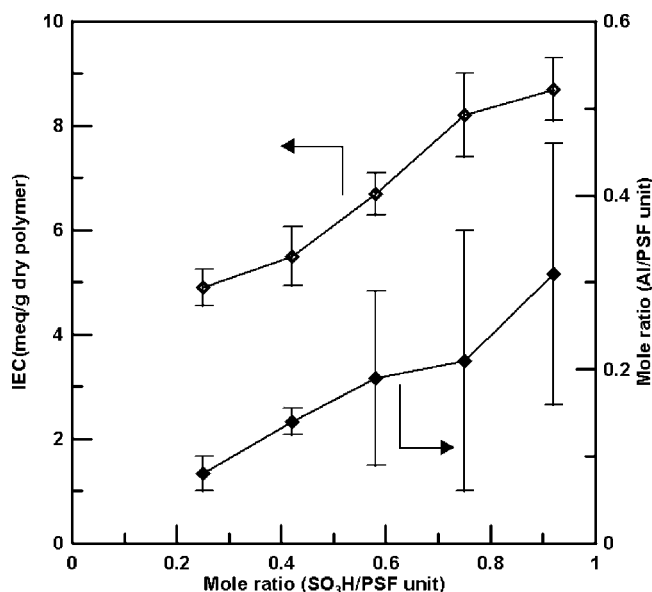
## RESULTS AND DISCUSSION

### Degree of aluminum substitution by polysulfone membrane

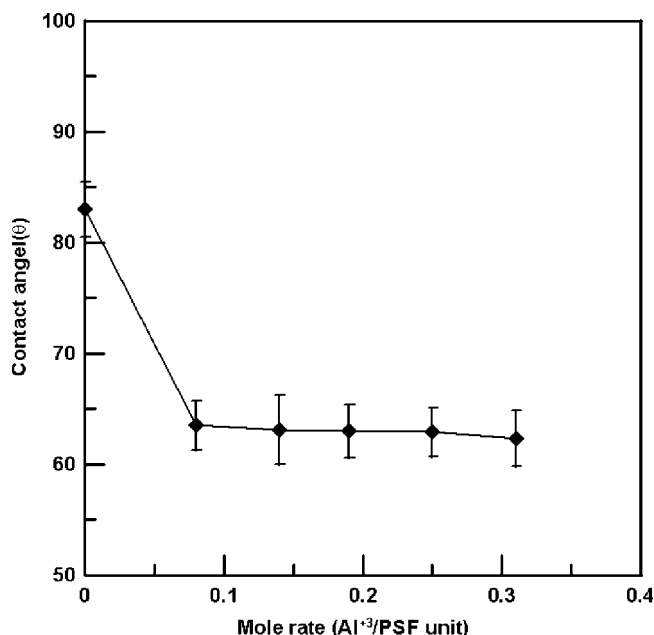
The aluminum containing polysulfone was prepared by ion exchange method with sulfonated polysulfone. Elementary analysis, XDS, and atomic adsorption spectrum were used to identify the degree of aluminum substitution. Figure 1 shows the effect of the degree of sulfonation of polysulfone on aluminum content and their ion exchange capacity (IEC). It can be seen that both the aluminum content and IEC of modified membranes increased with increasing the degree of sulfonation of polysulfone. It is indicated that the IEC value is almost proportional to the degree of aluminum ion substitution in membranes. Therefore, it can be concluded that the ion exchange occurred almost completely in those membranes. It is suggested that the degree of sulfonation of polysulfone dominated the ion content in the ion exchange membranes.

### Contact angle measurements

Figure 2 shows the experimental values of the water contact angles as a function of aluminum ion content in ion exchange membranes. The contact angles of the ion exchange membrane rapidly decreased with an increase in the molar ratio of aluminum in the polysulfone unit. The contact angles of asymmetric



**Figure 1** Effect of degree of substitution of polysulfone on the degree of aluminum substituted and asymmetric ion exchange capacity (IEC) of modified polysulfone.



**Figure 2** Water contact angles of aluminum ion exchange membranes.

ion exchange membranes decreased upon increasing the Al ion content and then level off with increasing the mole ratio of Al/PSF up to 0.31. As expected, inducing aluminum ion in the polymer unit increased the hydrophilicity of ion exchange membranes because of the ion hydration effect. This result showed that the presence of Al ion on the membrane surface enhanced the hydrophilic nature. On the other hand, it was found that the high degree of Al substitution on membranes could not further improve the hydrophilic properties. It was proposed that the hydration water molecules saturated on the membrane surface at high degree of Al ion exchange and then the contact level off after ion ratio becomes higher than 0.1 (molar ratio). It was implied that the hydration of water molecules occurred on the membrane surface and then the hydrophilic property of exchanged membranes became slightly different with further increasing of Al content in membranes. Therefore, the swelling properties in aqueous solution would also be affected by the hydration of water molecules. However, based on the viewpoint of solution-diffusion mechanism, the permeate was transported through the membrane not only because of the sorption but also due to the diffusion mechanism. The hydrophilic properties affected the permeate sorption in membranes, and, on the other hand, the diffusion of permeate as a result of free volume in the membranes were also important in the permeate transport. The membrane swelling induced an increase in free volume of the exchanged membranes and also enlarged the permeation flux. Therefore, the increase in free volume of membranes lead to

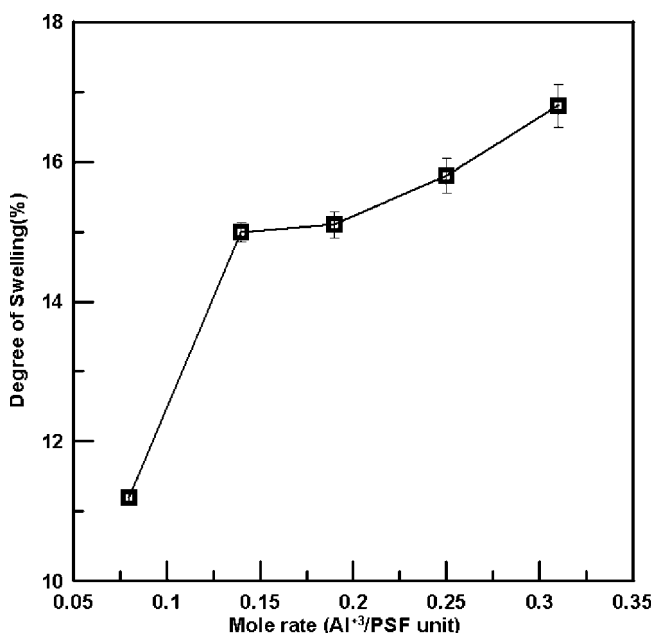
high diffusion rate of permeates and low diffusion selectivity. Therefore, the swelling property of those membranes is an important factor to determine the selectivity of asymmetric ion exchanged membrane.

#### Effect of the degree of substitution on the swelling property of membranes

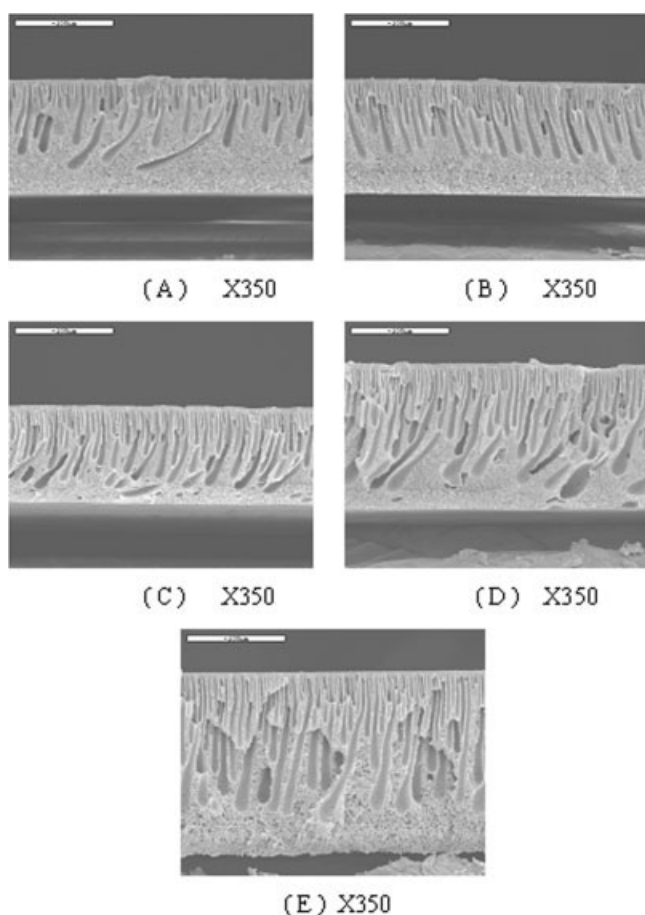
Figure 3 shows the effect of degree of Al substitution on the swelling property of asymmetric ion exchange membranes in 90-wt % ethanol solution. It can be seen that the degree of swelling slightly increased upon increasing the degree of Al substitution. Therefore, it can be expected that the asymmetric ion exchange membranes present a low permselectivity of water to ethanol because of the increase in swelling in those asymmetric ion exchange membranes.

#### Effect of Al substitution on the membranes' structure

The skin layers formation of asymmetric membranes is mostly dominated by the demixing rate of casting solution in the coagulation solvent during the phase inversion process.<sup>23</sup> Generally, the rapid liquid-liquid demixing of casting solution in coagulation bath formed a porous sublayer structure and defective surface. In this investigation we induced 8 wt % butanol in the casting solution to delay the demixing rate of casting solution in the coagulation bath. If the delay demixing can be achieved in this way, it can be expected that the weak solvent-coagulant interaction lead to a delay demixing and a dense surface



**Figure 3** Effect of degree of Al substitution in polysulfone on the swelling property of ion exchange membranes for 90-wt % ethanol solution in feed.



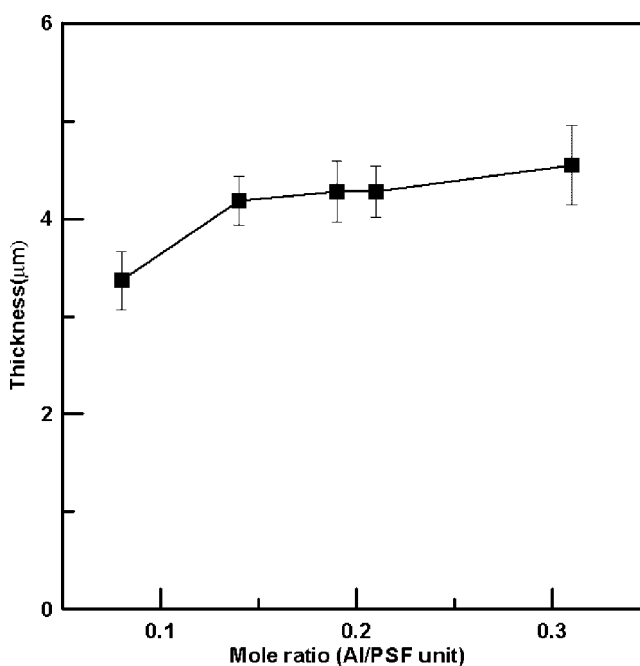
**Figure 4** Cross section structure of asymmetric ion exchange membranes. Degree of substitution with aluminum: (A) 0.08, (B) 0.14, (C) 0.19, (D) 0.25, and (E) 0.31.

layer on the porous support in this wet phase inversion process. On the other hand, the interaction between polymer and coagulant usually plays another important role in affecting the demixing process. Upon increasing the aluminum ion substitution on polymer, it can be expected that the hydration of aluminum ion will enhance the interaction between polymer and coagulant (water).

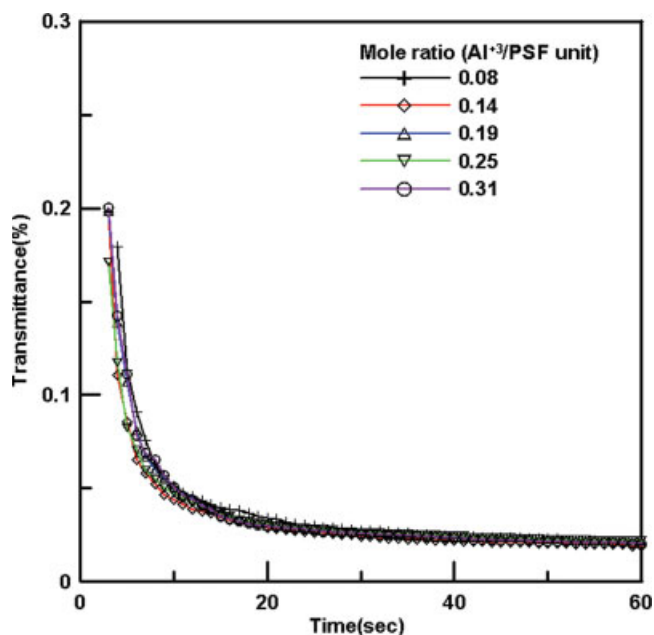
The effects of aluminum substitution on membrane morphology were observed by SEM. Figure 4 shows the degree of aluminum substitution on the cross-sectional structure of asymmetric membranes. As shown in Figure 4, dense skin layers and finger-like porous sublayer were found in all membranes with 8 vol % butanol additive in the casting solution. The support sublayer of asymmetric membranes showed a finger type structure and the bottom of membranes presents a sponge layer. It can be seen that similar skin layer structure were formed in non-ion exchanged asymmetric membranes. It was found that no detectable defects were observed in SEM images. In Figure 4, with increasing the molar ratio of Al ion to polymer unit, the sub layer thickness of

bottom sponge structure was inhibited. It was indicated that the Al ion in polymer present a remarkable influence on the membrane sub layer structure. As far as the permeate separation by asymmetric membranes are concerned, the skin layer structure plays a more important role than the sub layer structure to determine the permselectivity of membranes. The skin layer structures of asymmetric membranes is dominated by the demixing rate of casting solution during the phase inversion process, which can be changed by the interaction between polymer and coagulant.<sup>20</sup> Thus the relationship between the degree of Al ion substitution and the thickness of skin layer should be clarified for further understanding the membrane formation in the wet phase inversion process.

Figure 5 shows the effect of the molar ratio of Al/PSF unit on the skin layer thickness of prepared membranes. It can be seen that the thickness of skin layer was only slightly increased with increasing the molar ratio. It was found that the difference in interaction between Al substituted polymer and water (coagulant) in casting solution did not significantly affect the skin layer thickness. On the basis of the liquid-liquid demixing view point, the ion exchanged membranes own the similar skin layer which can be proposed that the similar demixing rate of the casting solutions with various degree of Al substitution should be found in coagulant bath. The skin layer of asymmetric membrane was dominated by the precipitation rate during the phase inversion process. Usually, the light transmittance



**Figure 5** Effect of different mole ratio of Al/PSF unit on the skin layer thickness of ion exchange membranes.



**Figure 6** Plots of the transmittance curve of different mole ratio of Al/PSF casting solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

measurement was used to determine the rate of phase separation.<sup>20</sup>

#### Light transmission measurement

The delay demixing phenomena can be observed by measuring the light transmittance measurement through the casting solution. The transmittance curves with water as the coagulant are presented in Figure 6. It can be seen that various Al substitutions in polysulfone only show a slight influence on the light transmittance of casting solution. It was indicated that the demixing rate of those casting solutions nearly followed a similar behavior and the different Al substitution form similar skin layer structures. The light transmittance measurements evidenced the expectation of liquid–liquid demixing behavior of ion exchange polymer solution in the coagulation bath.

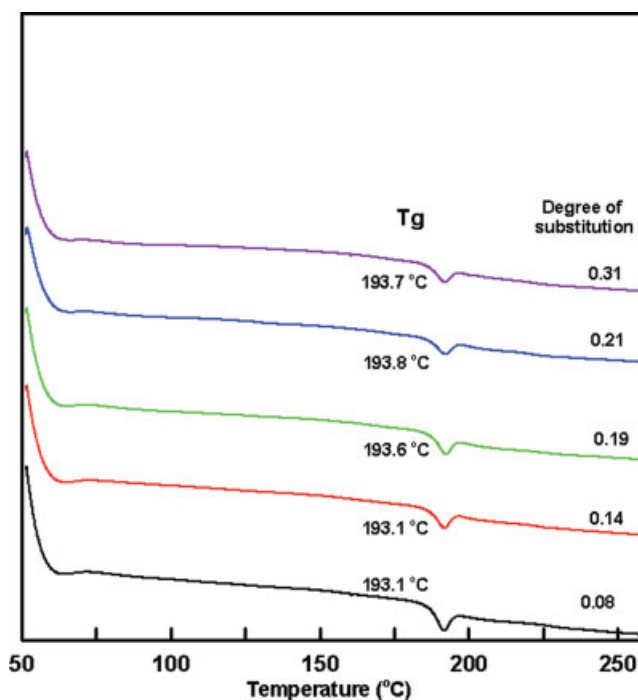
#### Glassy transition temperature measurement

The effect of the degree of substitution on glassy transition temperature ( $T_g$ ) of the Al ion exchange polysulfone membrane is shown in Figure 7. The glassy transition temperature of the aluminum substituted membrane slightly increased with increasing the degree of Al substitution. The glass transition temperature of polysulfone is 189°C. This result indicates that the polymer packing density of Al substituted membrane will be slightly increased with

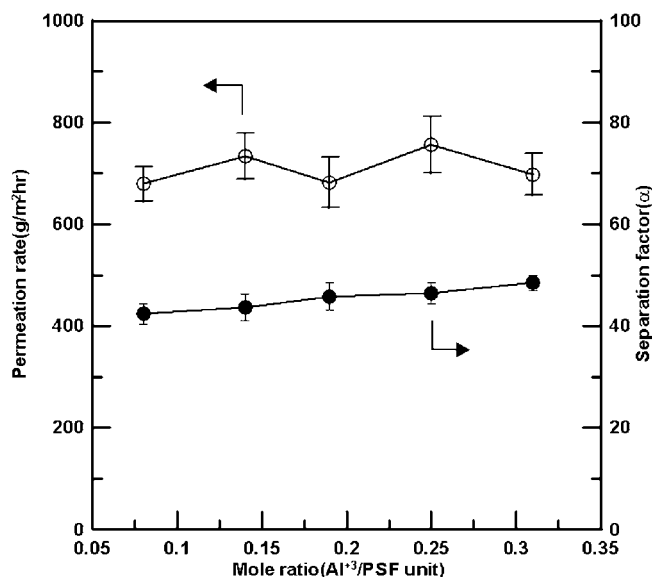
increasing the degree of substitution. Therefore, it can be expected that the polymer packing in those substituted membranes own a more dense structure than those with less substitution. Because of the dense packing of polymer chain in ion exchange membranes, an increase in polymer packing density leads to a decrease in permeation flux and an increase in selectivity. Thus, the ion substituted membranes may increase in permselectivity and decrease the permeation rate with increasing the Al ion substitution.

#### Pervaporation properties of aluminum substituted polysulfone membranes

The pervaporation performance of Al substituted membranes as a function of degree of substitution for the 90-wt % ethanol solution is shown in Figure 8. It can be seen that the permeation flux almost keep constant but the separation factor significantly increased upon increasing the degree of substitution. On the basis of the result of  $T_g$  measurement, it was implied that the ion exchange membranes should be presented with a higher selectivity and lower permeation rate. But the result was contradictory as shown in Figure 8. The constant permeation rate can be explained by the increase in the degree of swelling and a dense skin layer structure with increasing the Al ion in membranes. The constant permeation rates



**Figure 7** Effect of the degree of substitution on glassy transition temperature ( $T_g$ ) of Al substituted polysulfone membrane. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



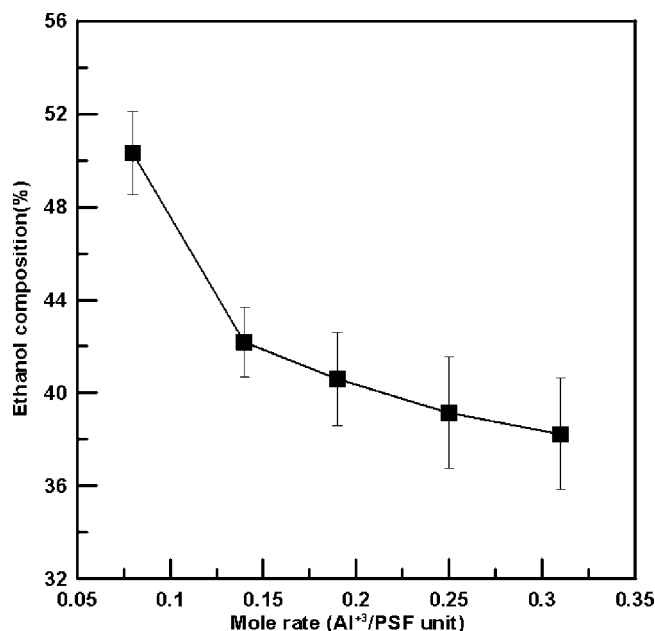
**Figure 8** Pervaporation performance of Al substituted membranes for the feed of 90-wt % ethanol solution.

of modified membrane usually show a less influence on its separation factor. But the Al substituted membranes showed the inverse results of permselectivity. Thus, it is necessary to further understand the possible transport mechanism of water and ethanol in asymmetric ion exchange membranes. To further distinguish the dominant factor of water and ethanol transport through membranes, the sorption property of Al substituted membranes were measured.

#### Sorption properties of aluminum substituted polysulfone membranes

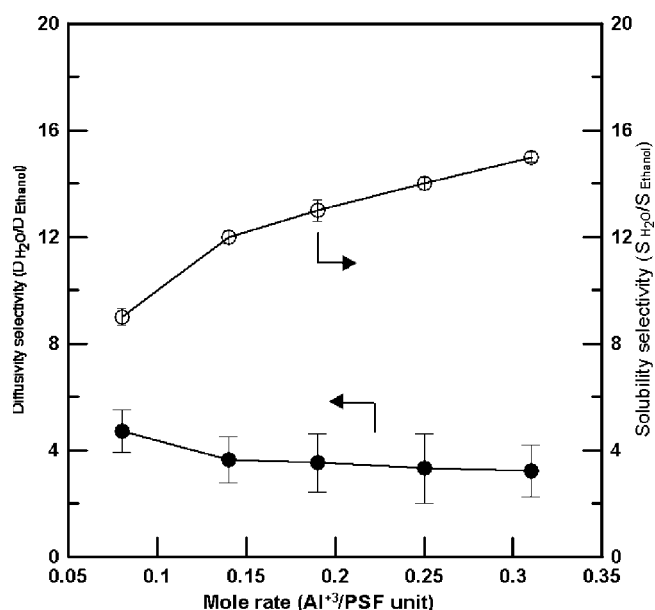
Figure 9 shows the relationship between the degree of substitution and the weight fraction of alcohol content in the membrane with 90 wt % ethanol solution at 25°C. It can be seen that the weight fraction of alcohol content in the membrane decreased as the degree of substitution increased. The sorption selectivity of water to ethanol was calculated by dividing the amount of water content by the amount of ethanol content in Aluminum substituted membranes. On the basis of the solution-diffusion mechanism, the diffusion selectivity ( $\alpha^d$ ) can be defined as the ratio of permeation selectivity ( $\alpha^p$ ) and sorption selectivity ( $\alpha^s$ )<sup>20</sup>:  $\alpha^p = \alpha^d \alpha^s$ .

Figure 10 shows the effect of degree of ion substitution on solubility selectivity and diffusion selectivity of water to ethanol. It can be seen that the sorption selectivity increased and the diffusion selectivity slightly decreased upon increasing the ion substitution in membranes. It is also implied that the ion substitution in membranes increased the sorption selectivity and decreased the diffusion selectivity of asymmetric ion exchange membranes. Moreover,

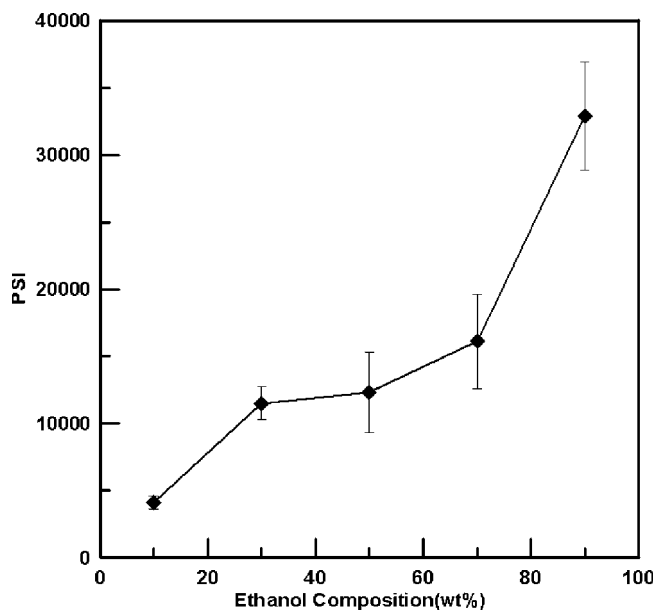


**Figure 9** Effect of degree of substitution on the weight fraction of alcohol content in the membrane with 90 wt % ethanol solution at 25°C.

Figure 8 shows the constant permeation rate and an increase in the separation factors with increasing the Al ion substitution in membranes. Therefore, it is proposed that the constant permeation rate may be required to restrain the degree of swelling and polymer packing density of skin layer. On the other hand, the increase in separation factors may be due to the increase in sorption selectivity, which was



**Figure 10** Effect of degree of substitution on solubility selectivity and diffusion selectivity of water to ethanol Al substituted membranes.



**Figure 11** Effect of ethanol composition in feed on PSI value of ion exchange membranes with degree substitution of 0.31.

caused by the ion hydration in pervaporation. The increase in water permeation rate is due to the enhancement in the hydrophilicity of ion substituted membrane by inducing hydrophilic groups (ion) on the PSf matrix. On the other hand, the swelling properties did not show any significantly decrease in permselectivity of asymmetric ion exchange membranes. Therefore, the hydration of ion substitution in polysulfone membrane enhanced the degree of swelling and sorption selectivity of water to ethanol. Thus the diffusion selectivity slightly decreased with increasing the degree of swelling. It can be concluded that the increase in separation factor was due to the increase in sorption selectivity, but the relatively less decrease in the diffusion selectivity of membrane was caused by the swelling effect in polymer matrix and hydration of ion in pervaporation.

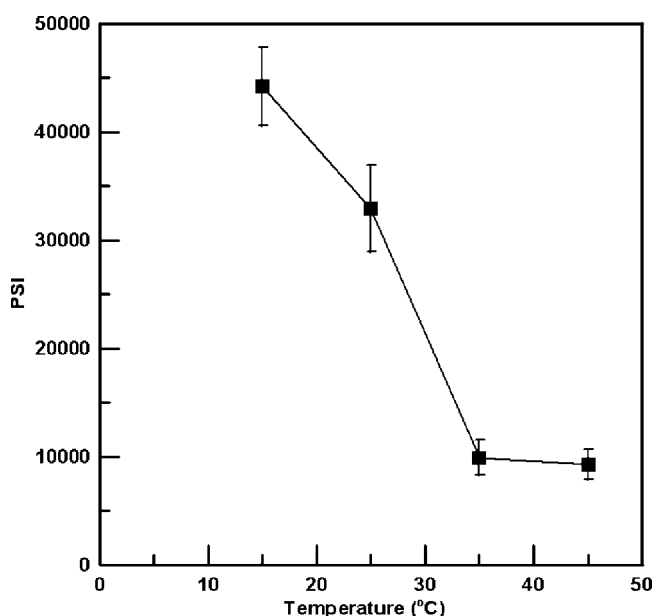
#### Effect of ethanol concentration on the PSI value of asymmetric ion exchange membrane

It has been reported that the value of separation factor tended to increase and the permeation flux tended to decrease upon increasing the concentration of ethanol in the feed solution if the ionic hydration affects the ionic membranes (Nafion membrane). For the purpose of exploring the dependence of feed concentration on the hydration of ion in asymmetric ion exchange membranes, the effect of composition in feed solution on the PSI (pervaporation separation index) value were made. The effect of ethanol composition in feed on PSI value of asymmetric ion exchange membranes with the degree of ion substi-

tution of 0.31 is shown in Figure 11. It can be seen that the PSI value is increased as the ethanol concentration in the feed is increased. Because of the less change in permeation rate, the increase in PSI value mainly contributed by the enhancement on sorption selectivity of asymmetric ion exchange membranes, which was contributed by the ion hydration in the membrane. It was indicated that the degree of swelling increased with increasing ethanol concentration in the feed. This result implied that the permselectivity of asymmetric ion exchange membranes were strongly affected by the ethanol concentration in the feed. Therefore, the permselectivity of permeates in asymmetric ion exchange membrane should be considered during the pervaporation process.

#### Effect of operation temperature

Figure 12 shows the effect of the feed temperature on the PSI value of Al substituted membrane with 90% ethanol in the feed solution. The PSI value showed a rapid decrease with increasing the operating temperature. It has been shown that the decrease in PSI value may be due to lost membrane structure upon increasing the operating temperature. The loosen structure resulted that the increment of ethanol flux was higher than the water flux at high temperature operation in pervaporation process. On the other hand, it is worth noting that a higher separation performance is obtained at low temperature than at high temperature.



**Figure 12** Effect of operating temperature on PSI value of asymmetric ion exchange membranes with degree substitution of 0.31.



## CONCLUSION

The asymmetric ion exchange polysulfone membranes were prepared for dehydration of ethanol-water mixture by pervaporation process. It was found that the hydration of Al ion not only enhanced the solubility ratio of water to ethanol but also enriched the degree of swelling of asymmetric ion exchange membranes. Both of them induced an increase in separation pervaporation performance of Al ion exchange membranes. The operating temperature and feed composition showed a significant influence on the hydration and separation performance of asymmetric ion exchange membranes.

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