Pervaporation Separation of Water/Ethanol Mixture by Poly(phenylene oxide) and Sulfonated Poly(phenylene oxide) Membranes

Chi-Yu Shih,[1] Shih-Hsiung Chen,[2] Ray-May Liou,[2] Juin-Yih Lai,[3] Jang-Song Chang[4]

[1]Department of Chemical Engineering, Cheng Shiu University, Kaohsiung 83305, Taiwan, Republic of China
[2]Department of Environmental Resource and Management, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan, Republic of China
[3]Department of Chemical Engineering, Research and Development Center for Membrane Technology Chung Yuan University, Chung-Li 32034, Taiwan, Republic of China
[4]Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan, Republic of China

ABSTRACT: Sulfonated poly(phenylene oxide) (SPPO) membranes were prepared for dehydrating water/ethanol mixtures. The effects of hydration of sulfonated membranes on pervaporation (PV) performance were discussed by comparing the characteristics of pure PPO and SPPO membranes. The differences in microstructural and hydrophilic properties of membranes were characterized by means of atomic force microscopy and swelling test. The degree of sulfonation of PPO dominates the hydrophilicity of sulfonated membranes and it plays an important role to determine the dehydration performance of PV membranes. The sulfonated membranes present excellent water permeation rate of about 300 g m^{-2} h^{-1} with good selectivity up to 700. The experimental results also show that SPPO membranes exhibit better PV performance than pure PPO membranes due to the improvement in hydrophilicity of modified membranes with sulfonation method. The hydrophilic sulfonated membranes enhance the permeate hydration process in membrane matrix and increase the separation performance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1566–1574, 2007

Key words: poly(phenylene oxide); membrane; pervaporation; sulfonation; hydroplilic; water/ethanol mixture

INTRODUCTION

Separation by pervaporation includes dehydration of water from water/organic mixture and organic–organic separation. The dehydration membrane attracted much more attentions for their industrial applications. Mostly, water-permselective pervaporation membranes focus on separation based on solubility selectivity rather than mobility selectivity. Generally, high water-permselective membranes[1–5] can be achieved by increasing either the sorption ratio of water to ethanol or the diffusion ratio of water to ethanol. Introduction of hydrophilic moiety into the polymer chain to enhance the water selectivity is one of the effective methods to achieve high water-permselective membranes. However, more hydrophilic moiety in membrane is usually accompanied with excessive swelling and loss of its selectivity.[6,7]

Several membrane modification technologies can be used to improve the hydrophilicity of membrane, such as surface modification, blending, copolymerization, and grafting a selective species onto an inert film.[8–11] However, only a few hydrophilic polymers can be prepared and they own a high separation performance in pervaporation process. Direct sulfonation was a powerful method, which can be used to simultaneously render these polymers proton-conductive as well as hydrophilic in nature. Sulfonation reaction was a popular modification technique for improving the hydrophilicity of polymer.[12–15] Commercial polymers with aryl backbones such as polystyrene, polycarbonate, polysulfone, and poly(phenylene oxide) (PPO) were sulfonated in fuel cells application by Smitha et al.[11] On the other hand, the synthesis of sulfonated poly(phenylene oxide) (SPPO) was investigated for the enhancement in hydrophilic properties of PPO.[16,17] However, few literatures investigated the influence of sulfonation of PPO membranes on the separation performance of sulfonated membranes for dehydration from ethanol solution.

For the purpose of improving separation performance of PPO membrane, this study prepared SPPO membranes for dehydration of water/ethanol mixture. The sulfonic groups were induced onto PPO backbone

by using direct sulfonation method,[18] improving the hydrophilic properties of polymer. Those hydrophilic SPPOs were prepared to form dense membranes and applied to separate water from a water/ethanol mixture. The relationship between the degree of sulfonation and hydrophilic properties of sulfonated membrane were discussed by measuring the permeation and swelling properties. For the purpose of evidencing the improvement in dehydration properties, the swelling properties and contact angle of sulfonated membrane were measured. The analyses of sorption components in sulfonated membranes were also made to calculate the selective permeate during pervaporation process.

EXPERIMENTAL

Materials

Poly(phenylene oxide) (PPO) was obtained from Sigma Chemical. Merck Chemical supplied chlorosulfonic acid, chloroform, and ethanol.

Membrane preparation

The sulfonated PPO (SPPO) was prepared from direct sulfonation method by adding chlorosulfonic acid[18] into the polymer solution. The SPPO membrane was prepared from a casting solution in chloroform. The casting solution was casted onto a glass plate to a predetermined thickness of 400 μm, using a Gardner Knife. The PPO and SPPO membranes were dried at 60°C for 30 min, then peeled off and immersed in distilled water for 24 h, and finally put into vacuum oven for 24 h before sorption and pervaporation measurements.

Pervaporation experiment

A traditional pervaporation process was used.[19] In pervaporation, the feed solution of 90 wt % ethanol solution was in direct contact with the membrane and was kept at 25°C. The effective membrane area was 10.2 cm^2. The down stream pressure was maintained at about 5–8 Torr. The permeation rate was determined by measuring the weights of permeate. The concentration of the feed solution permeate and solution adsorbed in the membranes was measured by gas chromatography (GC, 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).

Sorption measurements

The membranes were immersed in the ethanol–water mixture for 24 h at 25°C. They were subsequently blotted between tissue paper to remove the excess solvent and were then placed in the left half of a twin tube set-up. The system was evacuated while the tube was heated with hot water for 30 min and the right tube was cooled in liquid nitrogen. The concentration of the condensed liquid in the right tube was determined by GC. The separation factor of sorption was calculated by

$$\alpha_{sorp} = (Y_w/Y_e)/(X_w/X_e)$$

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

Swelling measurement

The degree of swelling of sulfonated membranes were determined in distilled water and in aqueous ethanol solution at 25°C. The weight of dry membrane (W_{dry}) was determined first. After equilibrium with water or ethanol solution, the fully swollen membrane was wiped with tissue paper and weighed. 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_{wet}) of the membrane. The degree of swelling was calculated by following equation:

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

Contact angle measurements

The contact angle of water was measured with a FACE contact angle meter CA-D type (Kyowa interface Science).

Atomic force microscope

The membrane structures were examined by an atomic force microscope (AFM; Digital Instrument, DI 5000) in the tapping mode. The root mean square of Z values (Rms), mean roughness (R_a), and maximum roughness (R_{max}) were used to express differences in the membrane surface morphology. The mean roughness is the mean value of the surface relative to the center plane, the plane for which the volumes enclosed by the images above and below this plane are equal. The roughness parameters depend on the treatment of the captured surface data.

RESULTS AND DISCUSSION

Pervaporation properties and characteristics of poly(phenyl oxide) membranes

The separation performances of aqueous ethanol solution through poly(phenyl oxide) (PPO) membranes were measured by various feed ethanol concentrations at 25°C, as shown in Figure 1. It can be seen that a good separation factor but low permeation rate of pure PPO membranes were observed in those measurements. Because of the hydrophobic structure of PPO molecules, a low interaction force between hydrophobic polymers and polar permeates was expected. It is expected that the PPO membranes have low degree of swelling in ethanol/water solution. Therefore, the less free volume can be form due to low degree of swelling and then lead to a low permeation rate of membranes. The low degree of swelling of PPO membranes could be measured by the amount of permeate uptake after the equilibrium in water/ethanol solution. Figure 2 shows the effect of ethanol concentrations in feed solution on the degree of swelling of PPO membranes at 25°C. The degrees of swelling of membranes were low in all concentrations range. As can be seen, the degree of swelling increased with increasing feed ethanol concentration. The low degree of swelling evidenced that the hydrophobic structure of PPO leads to a lower interaction between permeate and polymers. As expected, the low degree of swelling contributed a decrease in permeation rate and an increase in separation factor. Therefore, it was found that the lower permeation rate of PPO membrane was obtained in low ethanol concentration but the separation factor of PPO membrane increased slightly with increasing ethanol concentration in feed.
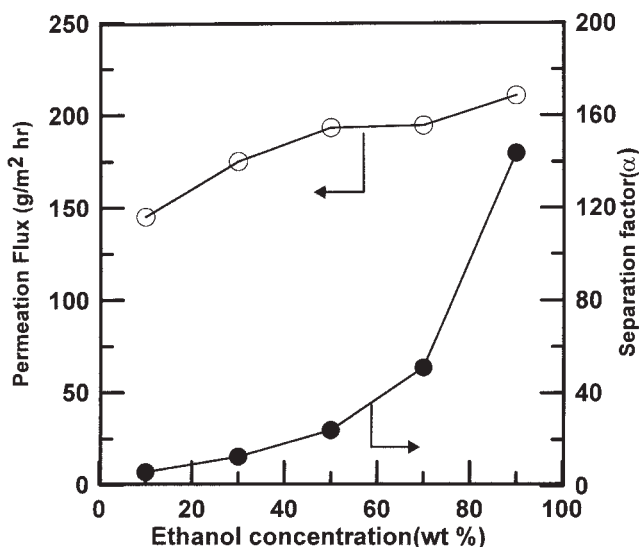

Figure 1 Effect of water content in feed on the permeation flux and separation factor of pure PPO membrane in pervaporation of water/ethanol mixture at 25°C.
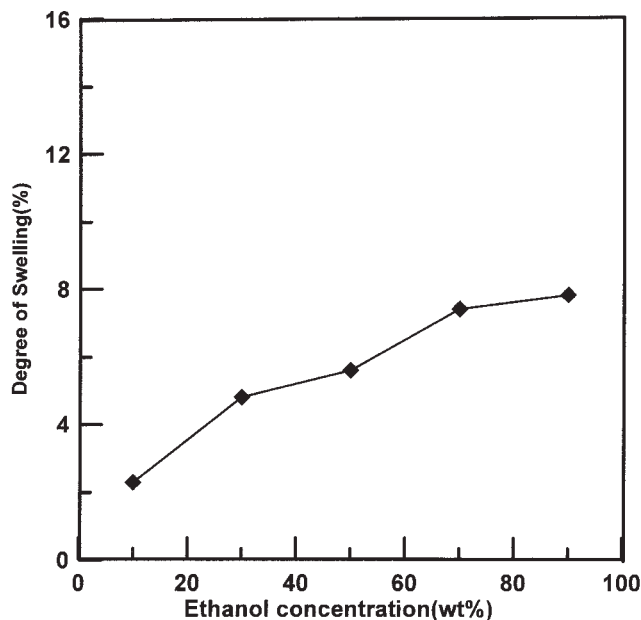
Figure 2 Effect of feed concentration in water/ethanol mixture on the degree of swelling of PPO membranes at 25°C.

Generally, a higher degree of swelling of membranes implies a free volume for permeate transport through the membrane. Based on the result of swelling measurements, it was found that the degree of swelling of PPO membranes increased with increasing feed ethanol concentration, indicating that the PPO polymer chains were swelled in higher concentration ethanol solution and offered an excess pathway for permeates to transport through the membrane. It was possible to induce a decrease in separation factor during pervaporation. As shown in Figure 1, the negative result indicated that the separation factor increased with increasing ethanol concentration in feed. It is interesting to clarify that the higher swelling properties of PPO membranes did not deteriorate the separation factor of PPO membranes. For further distinguishing the increase in the separation factor with increasing feed ethanol concentration, the permeate analyses were made. The amount of permeates were analyzed and shown in Figure 3. As can be seen, both water and ethanol permeation flux increased slightly in the concentration range tested. The increase in permeation rate was consistent with the increase in swelling properties of PPO membrane with increasing feed ethanol concentration. This result indicated that the swelling properties of PPO membrane significantly dominated both water and ethanol molecules to transport through the PPO membranes.

According to the solution-diffusion mechanism, the diffusion selectivity (α^d) can be defined as the ratio of permeation selectivity (α^p) and sorption selectivity (α^s)[20,21] : $\alpha^p = \alpha^d \alpha^s$. The sorption and diffusion selectivity of PPO membranes were calculated to clarify the real dominant factor of permeate transport through
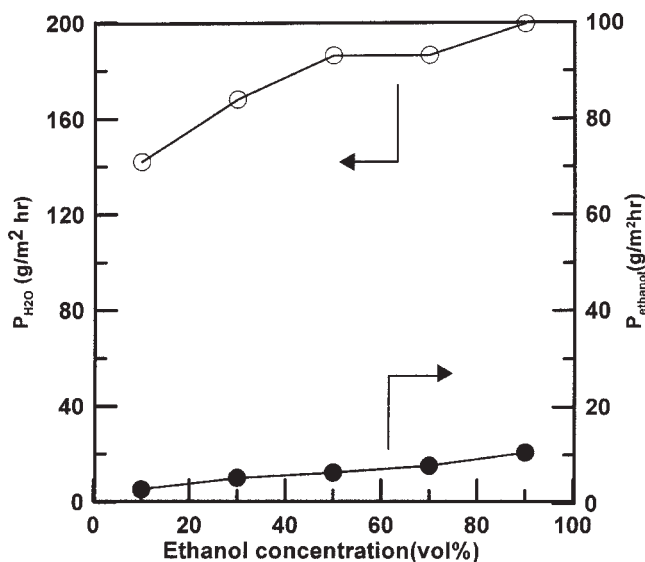
Figure 3 Effect of feed ethanol concentration on the amount of permeation fluxes of PPO membranes at 25°C.

the PPO membranes. Figure 4 shows the effect of feed ethanol concentration on the permeate content in PPO membranes. As can be seen, the ethanol content increased with increasing ethanol concentration in feed solution but the water content only showed a slight increase in membrane content. The permeate content analyses showed that the interaction of polymer–ethanol were stronger than the interaction of polymer–water in all concentration range in the PPO membrane. It was also evidenced that the hydrophobic polymer preferred ethanol molecules than water in water/ethanol mixture.

For clarifying the dominant factor on permeate transport through membrane, the sorption and diffusion selectivities of water to ethanol were calculated.
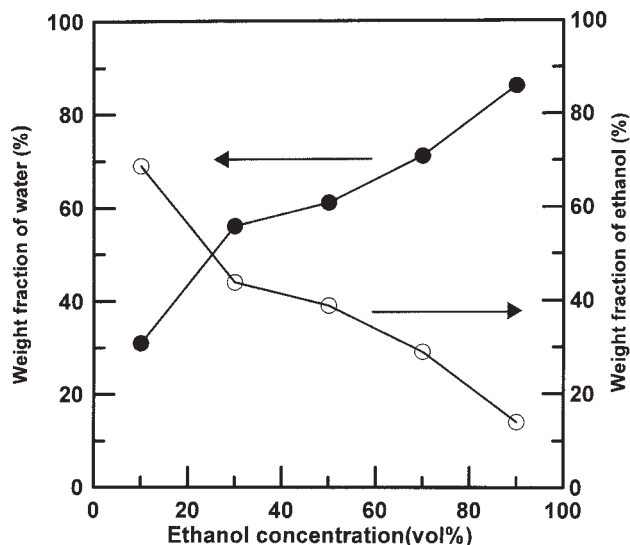

Figure 4 Effect of feed concentration on the water and ethanol content in PPO membranes at 25°C.

The sorption and diffusion selectivities of water to ethanol in PPO membranes were shown in Figure 5. As can be seen that the sorption selectivity was only slightly increased with increasing the feed ethanol concentration but the diffusion selectivity increased rapidly with increasing feed ethanol concentration. Therefore, it can be noted that the high selectivity of PPO membranes for dehydration of ethanol mixture was contributed by the diffusion rate difference of permeate molecules during pervaporation.

Characteristics of sulfonated PPO membranes

According to the pervaporation measurements, the poor permeation rate of PPO membranes was the disadvantage for dehydration of water from water/ethanol mixture. To improve the permeation flux, the PPO membranes were sulfonated to enhance the hydrophilic and permeation properties during pervaporation. Sulfonated PPO (SPPO) was prepared by direction chlorination method.[18] The degree of substitution (DS) of PPO was determined by elementary analyses. In direct chlorination method, the degree of substitution of sulfonic group on aromatic ring depends on the chlorosulfonic acid concentration in sulfonation. The effect of chlorosulfonic acid concentration in sulfonation on the degree of substitution is shown in Figure 6. As seen, the increase in concentration of chlorosulfonic acid increased the degree of substitution of PPO up to 0.10. Despite a higher degree of substitution obtained degradation of PPO after sulfonation. A higher degree of substitution caused the poor membrane formation. To evidence the sulfonation
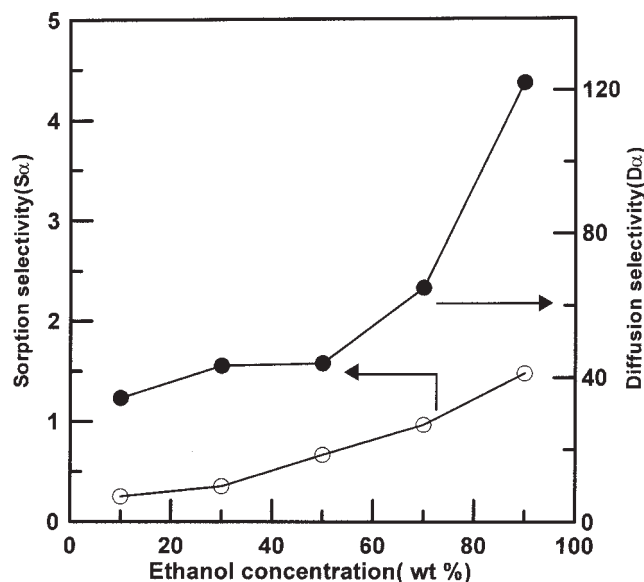

Figure 5 Effect of feed concentration on the sorption selectivity (S_α) and diffusion selectivity (D_α) of water to ethanol in PPO membrane at 25°C.
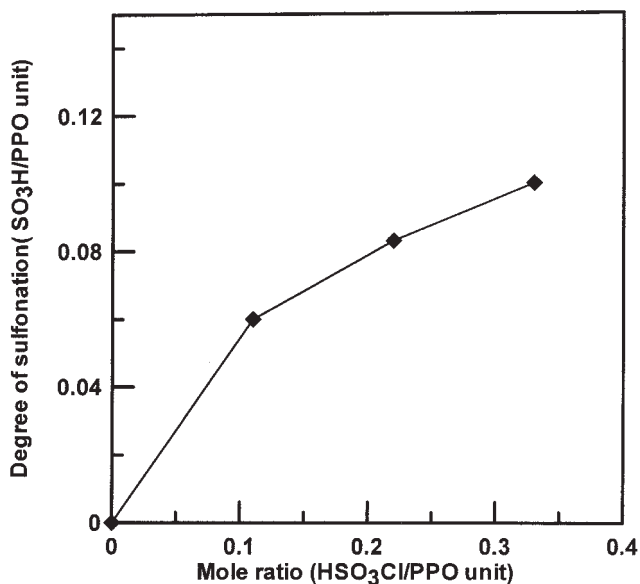
Figure 6 The effect of chlorosulfonic acid/PPO unit ratio in sulfonation on the degree of substitution of PPO membranes.

on PPO polymer backbone, FTIR spectra were also measured. According to previous reports on the IR spectral analysis of sulfonation of PPO, the peak at 635 cm^{-1} was assigned as the C—S bond[22] due to the substitution of sulfonic group on aromatic ring. However, the peak at 635 cm^{-1} was not observed in the IR spectra of SPPO membrane (FTIR did not show). It may be due to a lower absorbance of the C—S bond in the spectra of SPPO membranes.

Usually, a hydrophilic membrane has a superior separation performance than hydrophobic membranes in pervaporation for dehydrating water from ethanol/
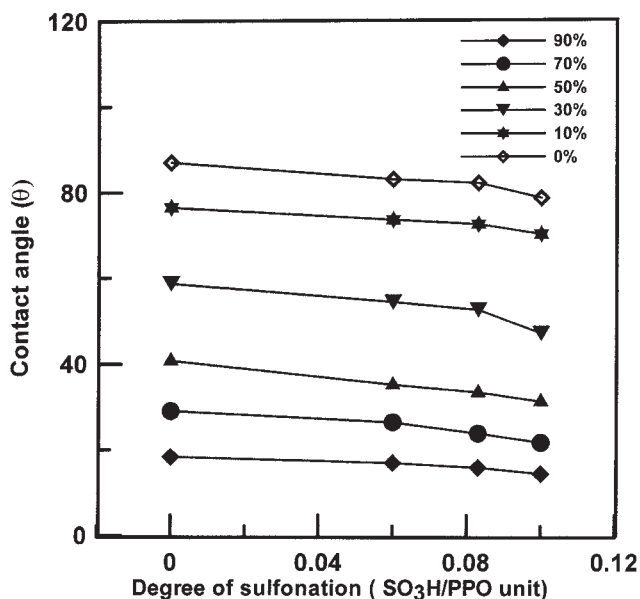

Figure 7 Effect of ethanol concentration in solution on the contact angle of sulfonated PPO membranes at 25°C.

water mixture. The hydrophilicity of membrane was indicated by measuring the water contact angle on membrane surface. A low contact angle of water on sulfonated membrane implied that the membrane has a higher hydrophilicity than pure PPO membrane. Therefore, the contact angle of water on membrane surface was measured to verify the improvement in hydrophilicity of SPPO. Figure 7 shows the contact angle of sulfonated membranes with various ethanol concentrations. It can be seen that the lower contact angle evidenced the increase in hydrophilicity of sulfonated membranes. Atomic force microscopy (AFM) was used to measure the surface structure and roughness of sulfonated membranes. We used AFM to examine the surface structure of the PPO and SPPO membranes. The values of surface roughness and the AFM photographs are shown in Table I and Figure 8, respectively. It could be seen that the surface structure of PPO is significantly different from that of SPPO membranes, with the PPO surface roughness 70 times higher than that of the SPPO membranes. In other words, the SPPO membranes showed a smoother surface structure than the pure PPO membranes.

Pervaporation properties of sulfonated membranes

The separation performance of SPPO membranes, for the feed of 90 wt % ethanol solution, is shown in Figure 9 as a function of degree of substitution. It can be seen that both the permeation flux and separation increased as the degree of substitution increased. However, the hydrophilicity of SPPO membrane increased with increasing degree of sulfonation. It is well known that the increase in membrane uptake swelled the polymer chains and led to an increase in the free volume of membranes. An excess swelling of membrane leads to an increase in permeation rate and a decrease in separation factor in dehydration membranes. However, a different result was observed in the sulfonated membranes. Thus, the possible reasons should be distinguished, which induced the increase in both permeation rate and separation of sulfonated membranes. Considering solution-diffusion mechanism, the dominant factors were discussed by considering the permeate transport mechanism through sulfonated membranes. The measurements of the sorption and swelling property of sulfonated membranes

TABLE I
Effect of Different Substitution of Sulfonic Groups in PPO Membranes on the Surface Roughness

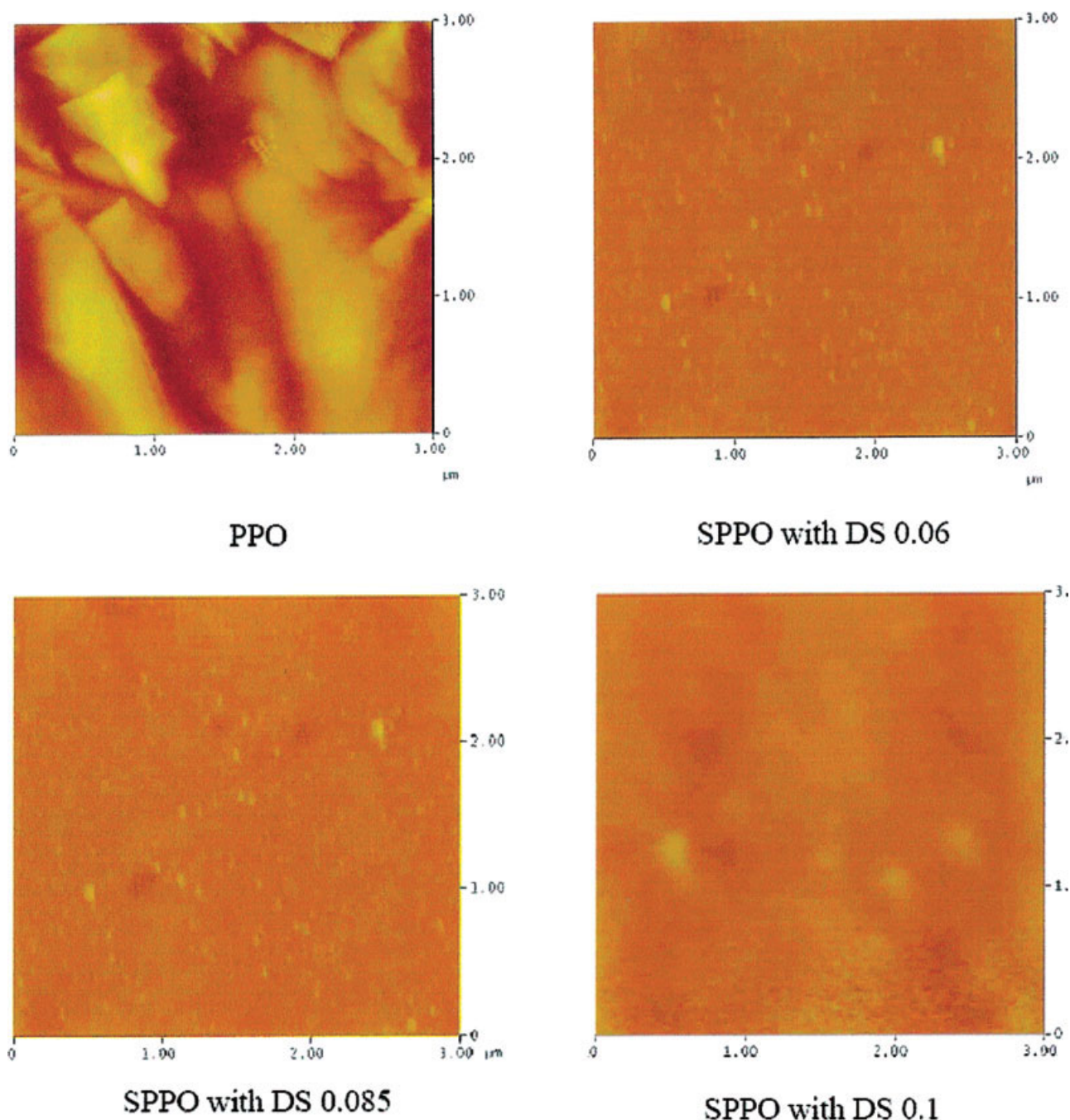| Degree of substitution (SO$_3$H/PPO unit)	Rms (R_a) (nm)	R_a (nm)	R_{max} (nm)
0	82.40	65.65	544.7
0.05	0.89	0.63	16.4
0.08	1.23	0.96	16.2
0.10	0.86	0.60	15.3

Figure 8 AFM images of the PPO and SPPO membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were made to evaluate the hydration effect of sulfonated membranes on pervaporation performance.

The swelling properties were measured with 90% ethanol content in testing solution, as shown in Figure 10. As seen in Figure 10, the increase in degree of swelling is proportional to the increase in the degree of sulfonation of PPO membranes. It was indicated that permeate free volume and permeate content in membranes increased with increasing the sulfonic group substitution in aromatic range. It can be expected that an increase in permeation rate and decline of separation factor can be found during permeation measurements. The increase in permeation rate may be due to the enhancement of hydrophilicity of sulfonated membrane with the introduction of more sulfonyl groups on the PPO backbone and loosened membrane structure due to the incorporated sulfonic group. Those permeation and swelling measurements evidenced the effect of introduction of sulfonic groups on the hydrophilicity of SPPO membrane.

Generally, the increase in swelling usually reduced the diffusion selectivity of permeates and decreased
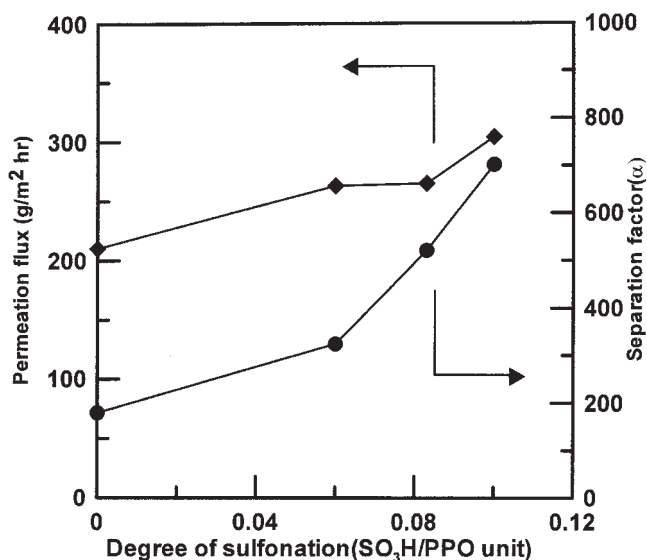
Figure 9 Effect of degree of substitution on the permeation flux and separation factor of sulfonated PPO membrane in pervaporation of water/ethanol mixture at 25°C.

the separation factor. However, as shown in Figure 9, the sulfonation of PPO membrane also enhanced the separation of membranes. The possible reasons for this phenomenon is that the introduction of sulfonic groups into matrix enhanced diffusion selectivity more than the selectivity loss in solubility, or both diffusion and solubility selectivity were increased due to enhancement of the hydrophilicity of membranes. Generally, hydrophilic sulfonic groups on SPPO enhanced polar channel for the selective transport of water molecules. Therefore, the sorption mea-
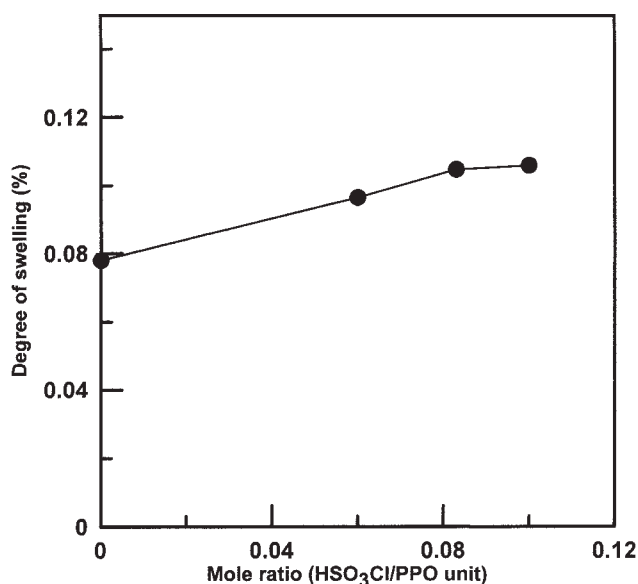
surement of SPPO membranes helps clarify the possible factor influencing separation performance.

Figure 11 shows the relationship between the degree of substitution and the weight fraction of water and alcohol content in the membrane in 90 wt % ethanol solution at 25°C. It can be seen that the weight fraction of water content in the membrane with 90% ethanol solution in feed slightly increased with increase in the degree of substitution. Thus, the increase in water content of SPPO membranes illuminated the enhancement on polymer–water interaction due to the hydration of PPO membranes. It was also implied that the hydrophilicity of membrane increased with the increase in degree of substitution. The sorption selectivity of water to ethanol was calculated by dividing the amount of water content by the amount of ethanol content in sulfonated membranes. The permselectivity behavior can be described as diffusion and sorption selectivity of permeates. Figure 12 shows the effect of degree of substitution on sorption selectivity and diffusion selectivity of water to ethanol. It can be seen that the sorption selectivity increased only slightly but the diffusion selectivity increased significantly with increasing degree of substitution. These results evidenced that the polar sulfonic group of SPPO enhanced the water content in membrane but the hydrophilic group only induced a slight increase in sorption selectivity. Both the increase in swelling properties and diffusion selectivity indicate that the hydration effect may be formed in sulfonated membranes and this effect induced a higher diffusion rate of water molecules than ethanol molecules in sulfonated membrane.
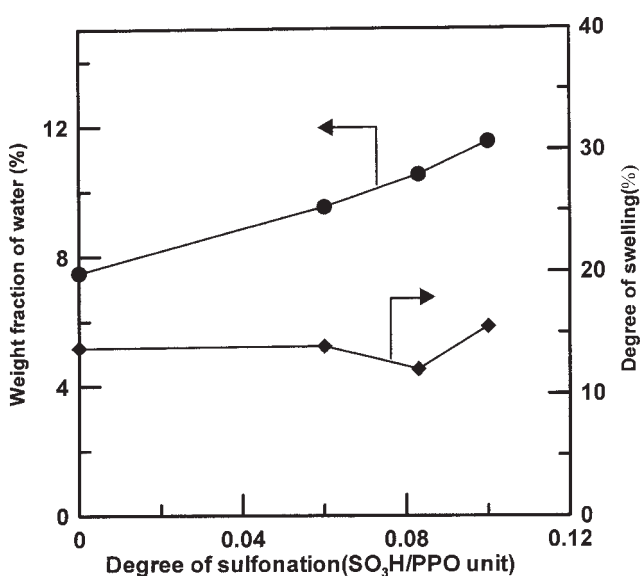

Figure 10 Effect of degree of substitution on the swelling properties of sulfonated PPO membranes with 90% ethanol in testing solution.

Figure 11 The relationship between the degree of substitution and the weight fraction of water and alcohol content in the membrane with 90 wt % ethanol in feed at 25°C.
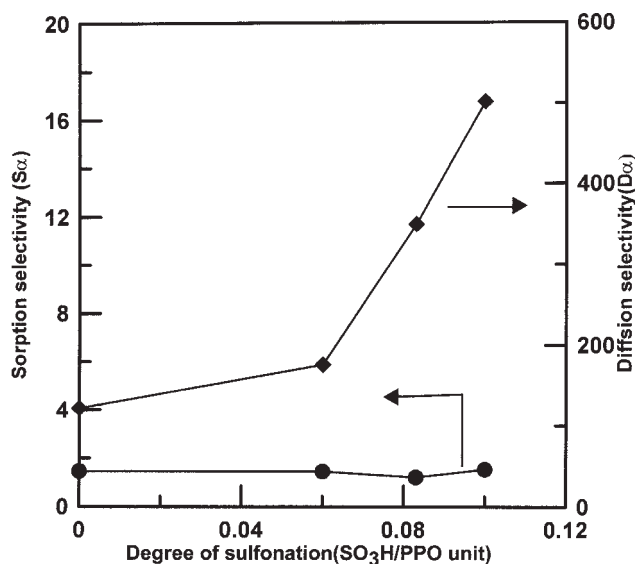
Figure 12 Effect of degree of substitution of sulfonated PPO membranes on sorption selectivity and diffusion selectivity of water to ethanol at 25°C.

The polar group on polymer backbone significantly affects permeate sorption in membranes. It was reported[23] that the polar sulfonic groups as water sorption sites enhanced the swelling properties. The addition of water molecules in membrane also increased the diffusion pathways and enlarged the diffusion rate of water molecule.[24,25] As can be seen in Figure 12, the diffusion selectivity increased with increasing amount of sulfonic groups on the PPO membrane. It is also concluded that the increase in separation factor was mainly contributed by the increase in hydration effect of water molecule. This result induced a significant increase in diffusion selectivity of sulfonated membranes.
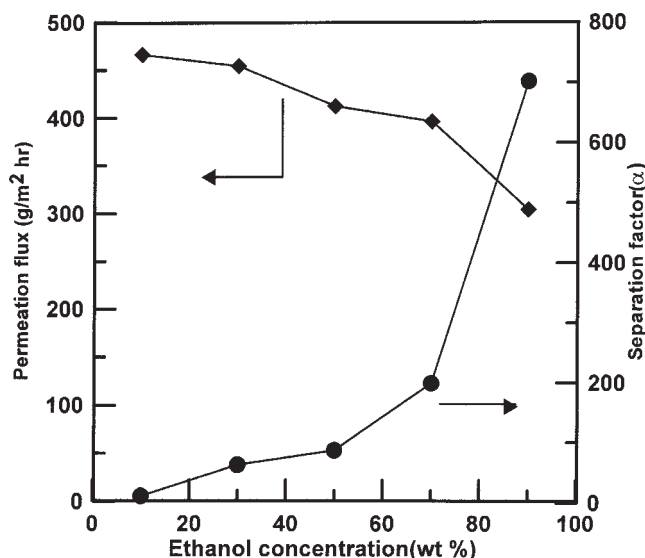
Effect of feed concentration on pervaporation properties

The polar properties of SPPO membranes tend to increase the separation factor and permeation flux. The effect of ethanol concentration in feed on permeation flux and separation of sulfonated membranes with degree substitution of 0.1 is shown in Figure 13. It can be seen that the permeation flux decreased and the selectivity increased as the ethanol concentration in feed increased. If the permeation flux depends on the water concentration in the feed, it would be a strong support for the hydration effect on sulfonated membranes. As shown in Figure 13, both the total permeation and water flux were strongly dependent on the water concentration in the feed. Figure 14 shows the effect of water concentration in feed on sorption and diffusion selectivity of sulfonated membrane. It can be seen that the degree of sorption selectivity increased slightly as ethanol concentration in the feed increased. This indicates that the sulfonated membrane did not significantly enhance the sorption selectivity of SPPO membrane with increasing ethanol concentration in the feed. However, the diffusion selectivity increased with increase in the ethanol concentration in feed. It reveals superior separation performance of SPPO membranes at high ethanol concentration. It may be due to the controlled diffusion of water molecules in membrane dominating the separation, contributing to the diffusion selectivity during pervaporation.

CONCLUSIONS

Introduction of a sulfonic group in the PPO unit increased the hydrophilicity and separation perform-

Figure 13 Effect of ethanol concentration in feed on permeation flux and separation factor of sulfonated membranes with degree of substitution 0.1 in PPO membrane.
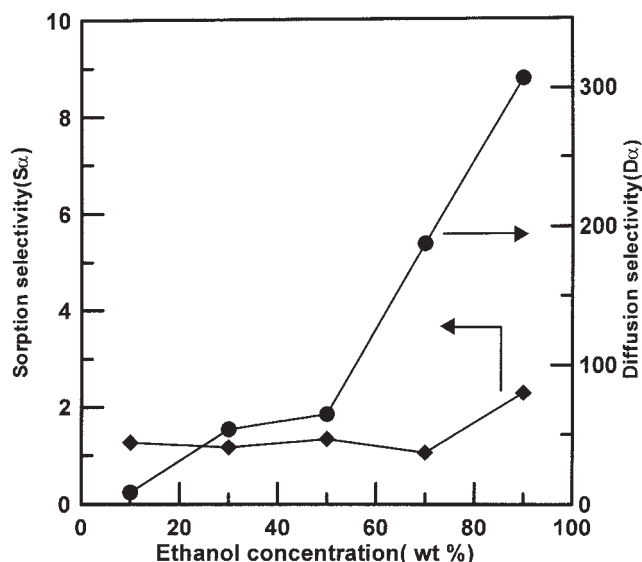

Figure 14 The effect of water concentration in feed on sorption and diffusion selectivity of sulfonated membrane with degree of substitution 0.1 in PPO membrane.

ance of PPO membranes. The increase in hydrophilicity of sulfonated membranes was evidenced by the degree of swelling and the contact angle measurements. This investigation also evidenced that the polar sulfonic group of SPPO enhanced the hydration effect in membranes. However, the enhancement in hydrophilic properties of membranes induced only a slight increase in sorption selectivity but a significant improvement in diffusion selectivity of permeates. The hydration effect of sulfonated membrane plays an important role on the enhancement of pervaporation separation. The increase in separation was mainly contributed by the increase in diffusion selectivity. The superior separation performance of SPPO membrane was found at high ethanol concentration. The experiment indicated that the hydration effect of water and permeate diffusion rate difference in membranes dominated the separation factor, mainly contributed by the diffusion selectivity in pervaporation.

References

 1. Kujawski, W.; Waczynski, M.; Lasota, M. Sep Sci Technol 1996, 31, 953.
 2. Freger, V.; Korin, E.; Wisniak, J.; Korngold, E. J Membr Sci 1997, 133, 255.
 3. Freger, V.; Korin, E.; Wisniak, J.; Korngold, E. J Membr Sci 1997, 128, 151.
 4. Qariouh, H.; Schue, R.; Schue, F.; Bailly, C. Polym Int 1999, 48, 171.
 5. Cao, S.; Shi, Y.; Chen, G. J Membr Sci 2000, 165, 89.
 6. Yeom, C. K.; Lee, K. H. J Appl Polym Sci 1998, 67, 949.
 7. Sang, Y. N.; Young, M. L. J Membr Sci 1997, 135, 161.
 8. Yamaguchi, T.; Yamahara, S.; Nakao, S.; Kimura, S. J Membr Sci 1994, 95, 39.
 9. Lee, Y. M. Desalination 1993, 90, 277.
10. Lee, Y. M.; Nam, S. Y.; Kim, J. H. Polym Bull 1992, 29, 423.
11. Smitha, B.; Sridhar, S.; Kham, A. A. J Membr Sci 2003, 225, 63.
12. Byun, I. S.; Kim, I. C.; Seo, J. W. J Appl Polym Sci 2000, 76, 787.
13. Carreta, N.; Tricoli, V.; Picchioni, F. J Membr Sci 2000, 166, 189.
14. Fu, H.; Jia, L.; Xu, J. J Appl Polym Sci 1994, 51, 1405.
15. Wycisk, R.; Pintauro, P. N. J Membr Sci 1996, 119, 155.
16. Acosta, J. L.; Firro, J. L.; Linares, A.; Casannva, M. J. Polym Int 2000, 49, 1534.
17. Hamad, F.; Chowdhury, G.; Matsuura, T. Desalination 2002, 145, 365.
18. Zschocke, P.; Quellmalz, D. J Membr Sci 1985, 22, 332.
19. Lee, K. R.; Lai, J. Y. J Polym Res 1994, 1, 247.
20. Yoshikawa, M.; Yukoshi, T.; Sanvi, K.; Ugata, N. J Polym Sci Polym Lett Ed 1984, 22, 475.
21. Chen, S.-H.; Yu, K.-C.; Lin, S.-S.; Chang, D.-J.; Liou, R. M. J Membr Sci 2001, 183, 29.
22. Kruczek, B.; Matsuura, T. J Membr Sci 1998, 146, 263.
23. Kirsh, Y. E.; Fedotov, Y. A.; Semenova, S. I.; Vdovin, P. A.; Valuev, V. V.; Zemlianova, O. Y. J Membr Sci 1995, 103, 95.
24. Lu, J.; Nguyen, Q.; Zhou, L.; Xu, B.; Ping, Z. J Membr Sci 2003, 226, 135.
25. Ito, A.; Feng, Y.; Sasaki, H. J Membr Sci 1997, 133, 95.