Pervaporation Separation of a Water/Ethanol Mixture by a Sodium Sulfonate Polysulfone Membrane

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ABSTRACT: A sodium sulfonate polysulfone membrane was prepared for the dehydration of a water/ethanol mixture by pervaporation. The separation performances of water and ethanol were examined by the testing of the ethanol/water mixture under operating conditions. The permselectivity of the sodium sulfonate polysulfone membrane was found to strongly depend on the sodium content in the membrane. The sodium sulfonate ratio showed a significant influence on the hydrophilicity and diffusion behavior of the polysulfone membrane. Moreover, the difference in the diffusion of the permeates played an important role in the sulfonate polysulfone membrane. It was found that a high-performance pervaporation membrane could be achieved with a sodium sulfonate polysulfone membrane. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3374–3383, 2003

Key words: polysulfone; membrane; pervaporation

INTRODUCTION

The balance between hydrophilic and hydrophobic moieties in membrane materials is an important factor in achieving high-performance pervaporation membranes.[1] Some previous studies applied hydrophilic polymers such as poly(acrylic acid) (PAA), poly(vinyl acetate) (PVA), and chitosan to the preparation of pervaporation membranes. However, a high content of hydrophilic moieties in the membranes induced excessive swelling during the pervaporation process. Therefore, membranes prepared from those hydrophilic polymers were developed with another modified method to avoid excessive swelling during the pervaporation process. Polymer crosslinking and blending were usually applied to modify the hydrophilic materials.[2,3] However, those modified technologies not only reduced the excessive swelling of hydrophilic membranes but also reduced the water permeation rate because of the decrease in the free volume of the membranes. Thus, other methods must be considered to resolve these disadvantages.

Many previous investigations have focused on the preparation of an ionic charge membrane to enhance the dehydration performance of an organic solution by a pervaporation process.[4,8] The well-known cation-exchange membrane Nafion showed a strong interaction between water and the ionic groups of the membrane, and it presented good mechanical properties. However, the selectivity of water to alcohol and the water permeation rate were still too low for pervaporation applications.[4,9] To improve the separation performance of the Nafion membrane, researchers proposed some modifications, such as chemical modification[4] and a bilayer composite method.[10] The permselectivity was improved with these methods, but the water permeation rate usually decreased with an increasing degree of modification. The other potential polymers for the preparation of high-performance pervaporation membranes are polyelectrolyte and alginate materials. Krasemann et al.[11] reported that composite membranes with ultrathin polyelectrolyte separation layers showed good separation performance. It was also indicated that the separation performance of polyelectrolyte membranes was strongly dependent on the charge density in the membranes. Alginate is a possible material for the preparation of membranes with high separation performance. Alginate composite membranes presented an outstanding performance for the dehydration of organic solutions.[12,13] An alginate membrane was crosslinked ionically with various divalent and trivalent metal ions to improve the separation performance. Alginate membranes crosslinked with Ca^{2+} showed the highest pervaporation performance in terms of the permeation flux and separation factor for the dehydration of ethanol/water and isopropanol/water mixtures.[14] An alginate compos-

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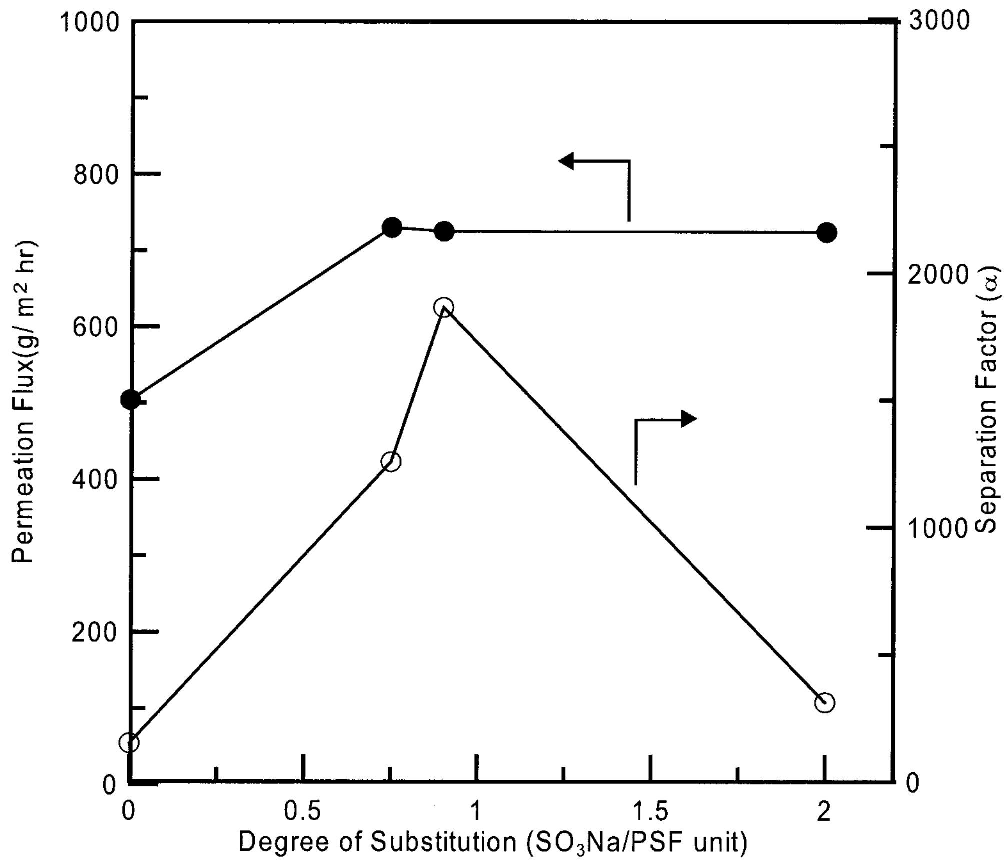

Figure 1 Effect of the substitution molar ratio of sodium sulfonate to the polysulfone unit on the pervaporation performance of sodium sulfonate membranes for 90 wt % ethanol solutions in the feed at 25°C.

ite membrane[15,16] was also prepared for the dehydration of aqueous ethanol. The formation conditions and materials of the alginate membrane strongly influenced the pervaporation performance and mechanical properties. The dominant factors of alginate membranes, including the polymer type in contact with the feed stream, the NaOH treatment, and the type of crosslinking agent, play important roles in performance. Although alginate membranes have presented good pervaporation performance with a certain modified method, the weak mechanical properties and stability of alginate membranes are still a challenge.

In this study, a sodium sulfonate membrane was prepared by the sulfonation of polysulfone. The pervaporation characteristics and the temperature dependence of the sulfonate membrane were examined with respect to the dehydration of an ethanol/water mixture. The permeation rate and degree of swelling were measured independently. The relationship between the microstructural changes of the sulfonated membrane and the pervaporation properties was also examined in this study. The effects of the feed composition and operating conditions were studied through the measurement of the pervaporation properties.

EXPERIMENTAL

Materials

Udel Polysulfone P-3500 was obtained from Amoco Performance Products, and Merck Chemical Co. supplied chlorosulfonic acid and ethanol.

Membrane preparation

The sulfonated polysulfone was prepared by the direct sulfonation method by the addition of chlorosulfonic acid.[17,18] The sulfonation of polysulfone was achieved with chlorosulfonic acid, and then it was cast at room temperature. The polymer solution was cast onto a glass plate to a predetermined thickness of 350 μm with a Gardner knife (Braive Instruments, B-4000, Switzerland). The membrane was dried at room temperature for 30 min, peeled off, and immersed in distilled water for 12 h. The sodium sulfonate polysulfone (Na-PSF) membrane was prepared by the immersion of the sulfonated membrane into a 0.1*N* NaOH solution for 12 h and then was dried in a vacuum oven for 24 h before the sorption and pervaporation measurements.

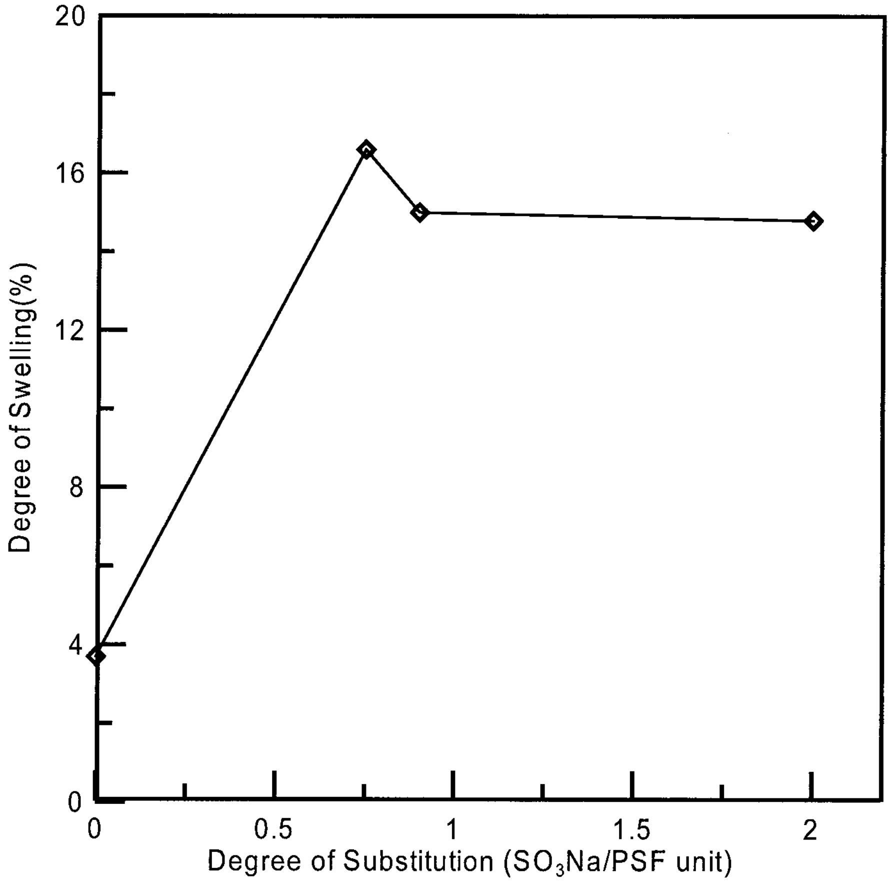

Figure 2 Effect of the substitution molar ratio of sodium sulfonate to the polysulfone unit on the degree of swelling of sodium sulfonate membranes for 90 wt % ethanol solutions in the feed at 25°C.

Pervaporation experimentation

A traditional pervaporation process was used.[19] In pervaporation, a feed solution of 90 wt % ethanol was in direct contact with the membrane and was kept at 25°C. The effective membrane area was 10.2 cm^2. The effect of the operating temperature on the pervaporation performance was measured at constant temperatures of 25, 35, 45, and 55°C. The downstream pressure was kept at about 5–8 Torr. The permeation rate was determined from the weights of the permeates. The compositions of the feed solution permeate and the solution adsorbed in the membrane were measured by gas chromatography (China Chromatography, Taiwan). The separation factor ($\alpha_{A/B}$) was calculated as follows:

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

where X_A and X_B and Y_A and 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 membrane was immersed in an ethanol/water mixture for 24 h at 25°C. It was subsequently blotted between tissue papers for the removal of the excess solvent and placed in the left half of a twin-tube setup. 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 composition of the condensed liquid with the right tube was determined by gas chromatography. The separation factor of sorption (α_{sorp}) was calculated as follows:

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

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

RESULTS AND DISCUSSION

Degree of substitution and physical properties of the sodium sulfonate membrane

The Na-PSF membrane was prepared by the ion-exchange method with a sulfonated polysulfone membrane. Elementary analysis and an atomic adsorption spectrum identified the degree of substitution. Figure 1 shows the relationship between the molar ratio of the sodium sulfonate groups to the polysulfone units

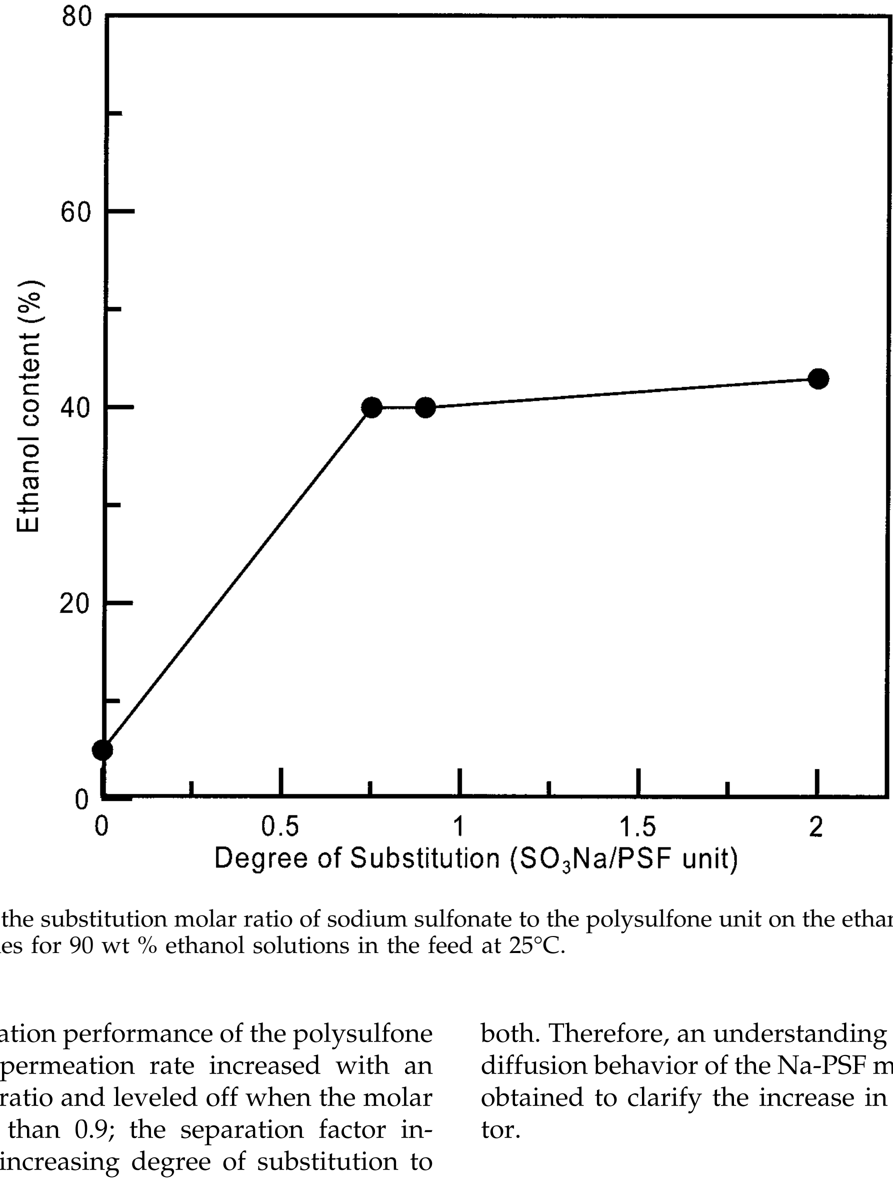

Figure 3 Effect of the substitution molar ratio of sodium sulfonate to the polysulfone unit on the ethanol content in sodium sulfonate membranes for 90 wt % ethanol solutions in the feed at 25°C.

and the pervaporation performance of the polysulfone membrane. The permeation rate increased with an increasing molar ratio and leveled off when the molar ratio was larger than 0.9; the separation factor increased with an increasing degree of substitution to 0.9 and then decreased. An increase in the permeation rate of a dehydrated membrane usually reduces its separation factor because of the high permeation rate due to the high degree of swelling in the dehydrated membrane. However, the sodium sulfonate membrane behaved differently than those dehydrated membranes.[20–22] Based on the solution–diffusion mechanism, an evaluation of the diffusion and sorption behavior of the sodium sulfonate membrane in a feed solution could further clarify the permeation properties. According to the solution–diffusion mechanism, an understanding of permeate diffusion and interaction behavior in membranes could be helpful in clarifying the transport mechanism of the sodium sulfonate membrane. In Figure 1, it can be seen that the fraction of the permeate content in the membrane indicated the favorable permeate in the membrane in a 90 wt % ethanol solution at 25°C. The increase in the separation factor should be due to increases in the sorption selectivity (α^s), diffusion selectivity (α^d), or both. Therefore, an understanding of the sorption and diffusion behavior of the Na-PSF membrane should be obtained to clarify the increase in the separation factor.

Effect of sodium substitution on the swelling properties and sorption properties

Figure 2 shows the effect of the degree of substitution on the swelling properties for 90 wt % ethanol solutions in the feed. The degree of swelling increased as the degree of substitution increased, and it was almost constant, whereas the substitution ratio was higher than 0.5. The increase in the degree of swelling showed that the flexibility of the polymer chain in the sodium sulfonate membrane increased with an increasing degree of substitution. On the basis of the swelling measurement results, it can be implied that the decrease in α^d should be observed with an increase in substitution. However, it was found that the separation factor increased when the degree of substitution was increased up to 0.9 and then slightly decreased with the degree of substitution further increasing. Moreover, it was indicated that the degree of sodium substitution enhanced the degree of swelling of the

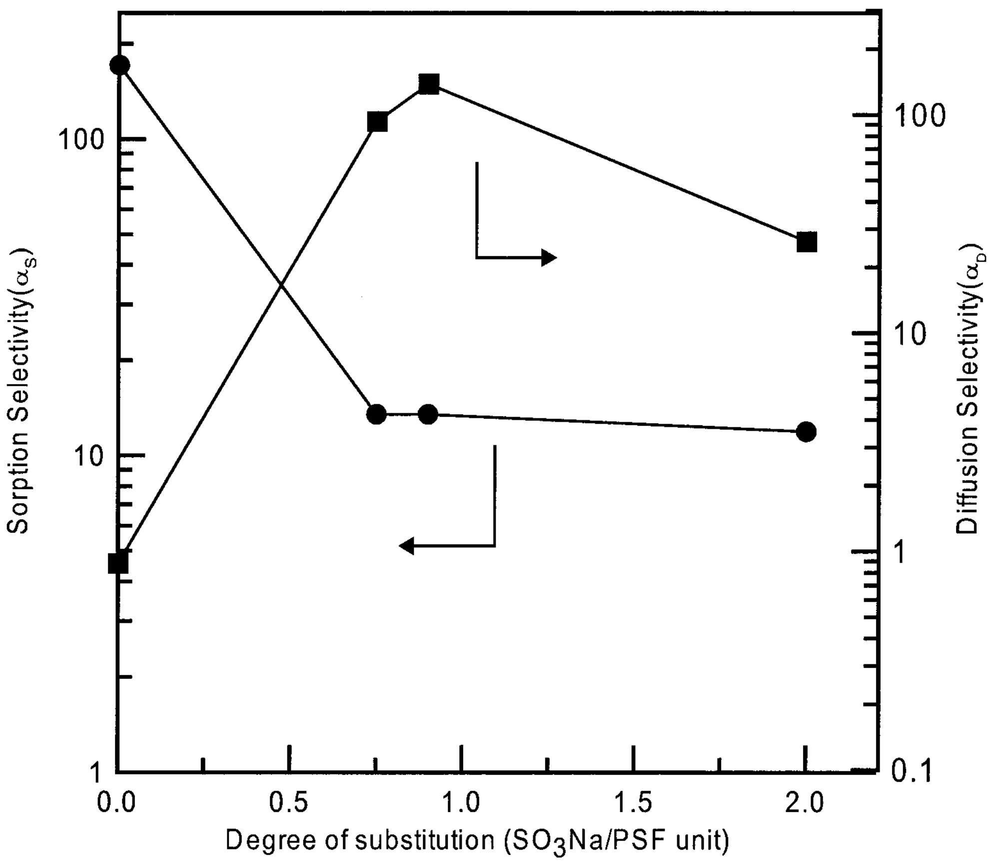

Figure 4 Effect of the substitution molar ratio of sodium sulfonate to the polysulfone unit on α^s and α^d of sodium sulfonate membranes for 90 wt % ethanol solutions in the feed at 25°C.

Na-PSF membrane in a 90% ethanol solution, and this increase did not reduce the separation factor at a degree of substitution of 0.9. The results of permeation and swelling measurements indicated that the permeate transport behavior was dominated not only by the diffusion behavior of the permeate but also by the sorption behavior in the membrane.

On the basis of the sorption–diffusion mechanism, α^d can be defined as the ratio of the permeation selectivity (α^P) and α^s:[23] $\alpha^P = \alpha^d\alpha^s$. To demonstrate the diffusion behavior through a pervaporation membrane, Figure 3 shows the relationship between the degree of substitution and the weight fraction of alcohol in the membrane in a 90 wt % ethanol solution at 25°C. The weight fraction of alcohol in the membrane increased with an increasing degree of substitution. α^s of water with respect to ethanol was calculated by the division of the amount of water by the amount of ethanol in the sulfonated membrane. α^d and α^s were calculated with the previous equation. Figure 4 shows the effect of the degree of substitution on the solubility selectivity and α^d of water with respect to ethanol in Na-PSF membranes. α^s decreased and α^d increased as the degree of substitution increased. As mentioned previously, the separation factor (α^P) and α^s showed different trends with increasing contents of sodium sulfonate groups in the polysulfone membranes. The different trends of the permeation and sorption behavior may be attributed to the interaction force between the permeate and membrane. Therefore, the increase in the permeation rate may be due to the high degree of swelling of the sulfonate polysulfone membrane, which was caused by the hydration effect of sodium ions with water and ethanol. The high degree of swelling induced an increase in the permeation flux. Then, the water molecules had a higher diffusion rate than ethanol because of the size of the molecules. Therefore, the higher degree of swelling and high permeation flux were obtained by the introduction of a sodium sulfonate group into the polysulfone membrane. The decrease in the separation factor may be due to the defect in the membrane with a high sodium sulfonate content when the degree of substitution was up to 0.9. However, the increase in the degree of swelling was due to the effect of permeate (water or ethanol) plasticization by the sodium sulfonate group in the membrane. Huang et al.[14] reported that the same behavior was found in an alginate/chitosan membrane. They proposed that the nature of the membrane and the interaction between the feed compound and mem-

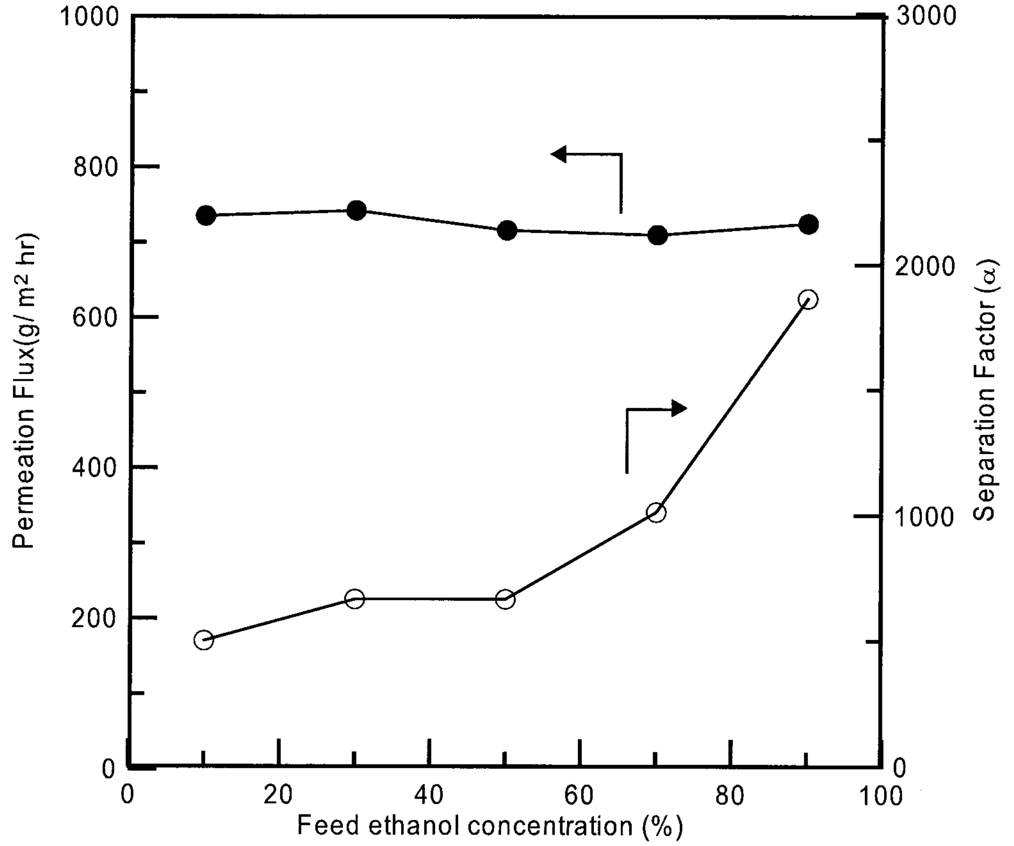

Figure 5 Effect of the feed ethanol composition on the pervaporation performance of sodium sulfonate membranes with a degree of substitution of 0.9 at 25°C.

brane dominated the degree of swelling. Therefore, the permeation behavior may be attributed to the diffusion behavior, which was due to the solubility difference in the sulfonate membrane. The higher degree of permeate plasticization of the Na-PSF membrane increased the free volume of the membrane and resulted in the decreases in α^d and the separation factor.

Effect of the feed concentration on the pervaporation properties

The effect of the ethanol composition in the feed on the permeation flux and separation factor of sodium sulfonate membranes with a degree substitution of 0.9 is shown in Figure 5. The permeation flux was almost constant, and the separation factor increased with an increasing ethanol concentration in the feed. Generally, a change in the permeate flux would lead to a change in the permselectivity of the pervaporation membrane. As shown in Figure 5, the sodium-substituted membrane presented a constant permeation rate and an increase in the separation factor over the entire feed concentration range. The behavior of the sodium sulfonate membrane was quite different from that of hydrophilic pervaporation membranes. Thus, it was proposed that the permeate transport behavior may have been influenced by the hydration effect of the sodium ion with water when the permeate passed through the membrane. Figure 6 shows the effect of the water concentration in the feed on the degree of swelling of sodium sulfonate membranes. The degree of swelling was almost independent of the water concentration over the entire concentration range. Moreover, the degree of swelling was about 20% for all test range. According to the results of the swelling tests, the interaction force between the permeates and Na-PSF membrane did not significantly change with the feed concentration. In other words, the sodium hydration effect did not influence the degree of swelling or the sorption amount of the feed solution. However, the separation factor of the sodium sulfonate membrane increased with an increasing ethanol concentration in the feed. The increase in the separation factor may have been due to an increase in the water permeation rate with an increasing feed ethanol concentration. This result was further clarified by an analysis of the permeate. As shown in Figure 5, the water permeation flux increased with an increasing feed ethanol concentration over the entire concentration range of the feed solutions. The

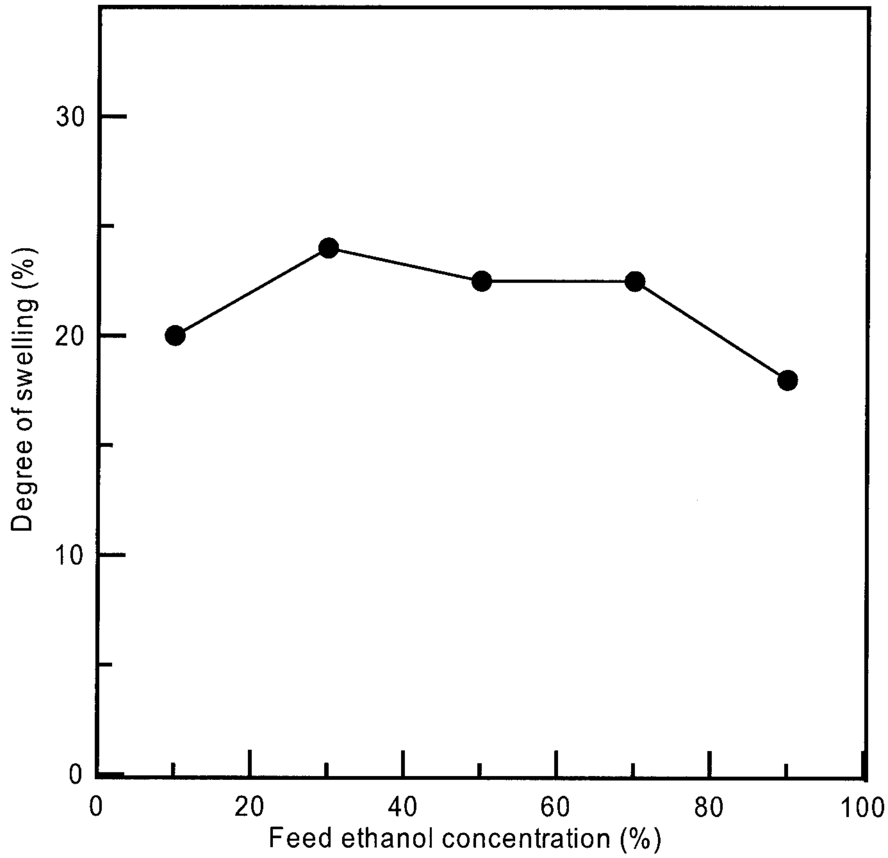

Figure 6 Effect of the feed ethanol composition on the degree of swelling of sodium sulfonate membranes with a degree of substitution of 0.9 at 25°C.

permeation behavior was almost dominated by the diffusion behavior of the permeate in the pervaporation membrane for the separation of the ethanol/water mixture. Therefore, an understanding of the diffusion behavior of the permeates in the sodium-substituted membrane over the entire concentration range would be helpful for further clarifying the real transport behavior in the membrane. The effect of the feed concentration on the sorption composition in the sodium sulfonate membrane is shown in Figure 7. The sodium membrane preferred water to ethanol at all concentrations, and the sodium membrane preferred water to ethanol at 90% in the feed solution much more. α^s and α^d were calculated by the previous equation, $\alpha^P = \alpha^d \alpha^s$. Figure 8 shows the effect of the feed concentration on α^s and α^d of the Na-PSF membrane. α^s increased and α^d remained almost constant for all feed concentration ranges. As shown in Figure 6, the degree of swelling of the sulfonated membrane was nearly constant with an increasing ethanol concentration in the feed solution. This result indicated that the sorption amount of the permeate in the sodium sulfonate membrane was not affected by the change in the ethanol concentration in the feed solution. This result implied that the hydration effect of water decreased with an increasing ethanol concentration and that the sorption amount of water molecules also decreased with an increasing ethanol concentration. According to the constant degree of swelling of the Na-PSF membrane, the sorption amount of ethanol increased with an increasing feed ethanol concentration. However, the separation factor of the Na-PSF membrane increased with an increasing feed concentration. Therefore, it can be concluded that the increase in the separation factor was due to the water molecules being smaller than the ethanol molecules. This size difference induced the difference in the diffusion rates between water and ethanol. The ethanol content in the membrane increased with an increasing ethanol concentration in the feed solution. However, the diffusion rate of water was faster than that of ethanol in the membrane because of the molecular size difference between water and ethanol. Therefore, the influence of the polar interaction of the permeate between the permeate and the membrane resulted in a constant permeation rate, and the influence of their size difference resulted in an increase in the separation factor at higher ethanol concentrations in the feed.

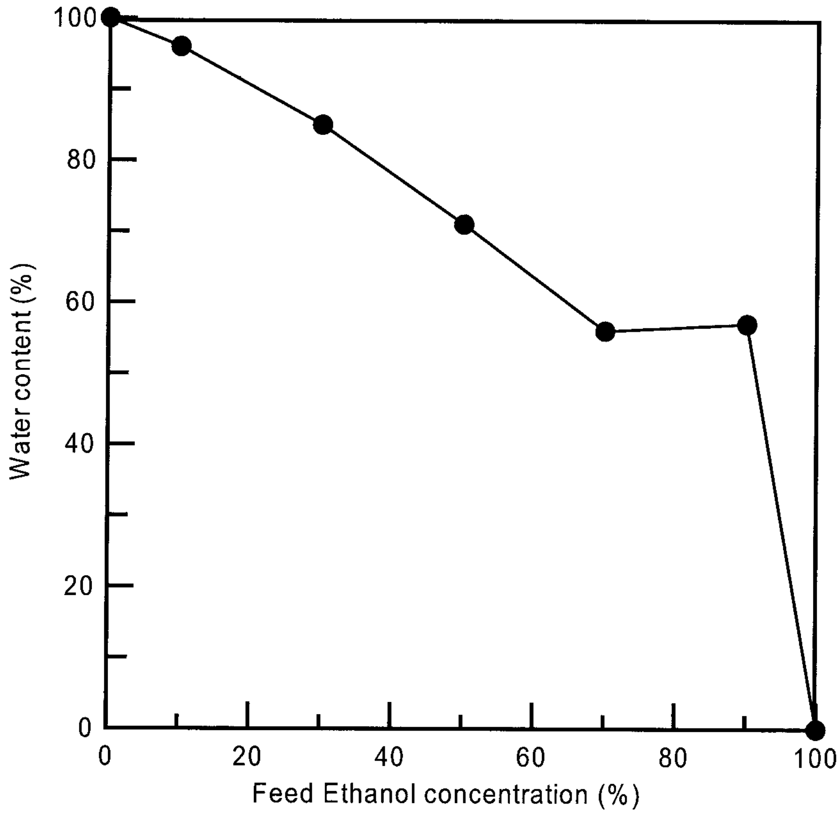

Figure 7 Effect of the feed ethanol composition on the water content in sodium sulfonate membranes with a degree of substitution of 0.9 at 25°C.

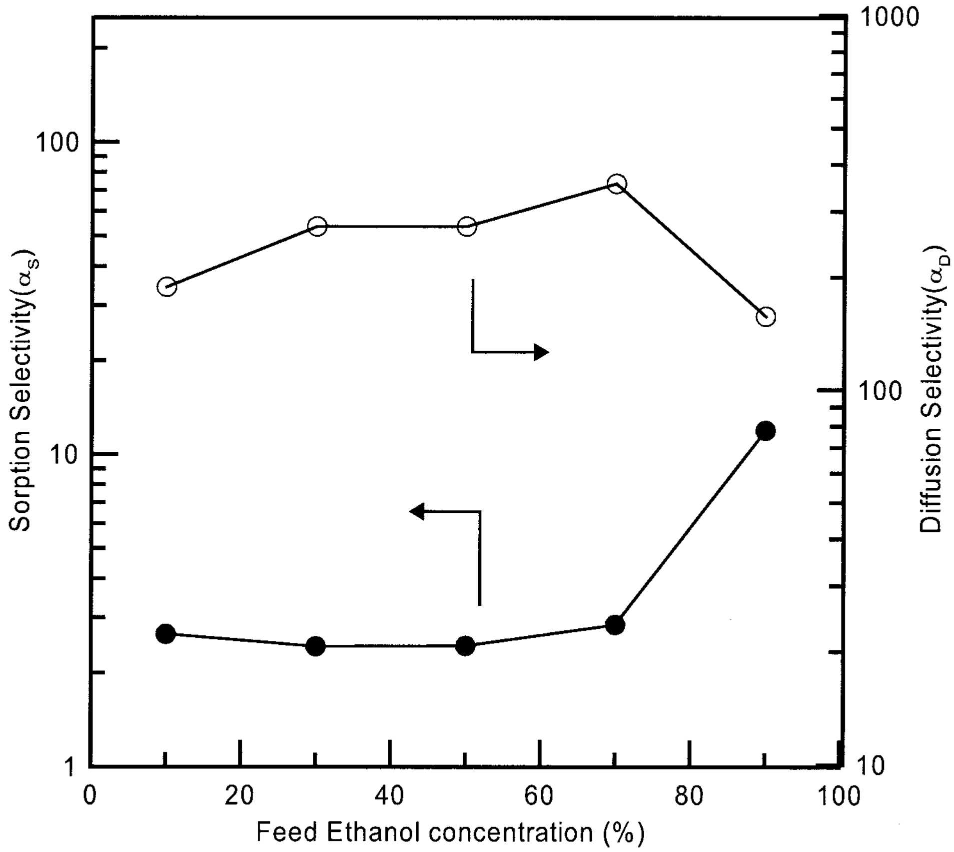

Figure 8 Effect of the feed ethanol composition on α^s and α^d of sodium sulfonate membranes with a degree of substitution of 0.9 at 25°C.

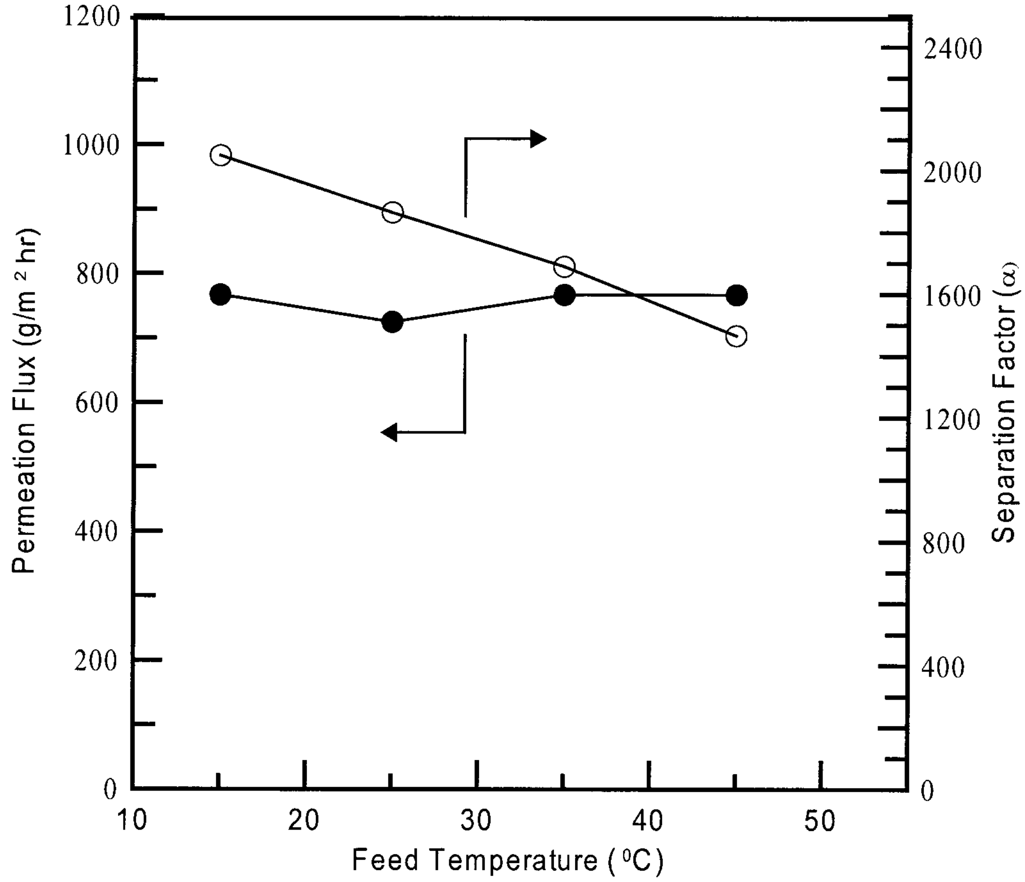

Figure 9 Effect of the operating temperature on the pervaporation performance of sodium sulfonate membranes with a degree of substitution of 0.9 for 90 wt % ethanol solutions in the feed.

Effect of the operating temperature on the pervaporation properties

Figure 9 shows the effect of the feed temperature on the permeation flux and separation factor of the sulfonated membrane with 90% ethanol in the feed solution. The permeation flux was almost constant for all temperature ranges. Generally, the temperature influenced both the permeate transport behavior and the membrane structure. The mass-transfer coefficients of both water and ethanol increased with an increasing feed temperature. In addition, the polymer chain of the membrane became more flexible with an increasing feed temperature, and this resulted in a freer space for permeate diffusion through the membrane. Therefore, higher permeation flux and lower separation would be expected in the pervaporation system at a higher operating temperature. As shown in Figure 9, the permeation flux was almost constant for all temperature ranges, but the separation factor declined with an increasing feed temperature. The decrease in the separation factor was due to a loosened membrane structure with an increasing operating temperature. The loosened membrane structure should have increased the permeation flux, but a different behavior is shown in Figure 9. The constant permeation flux may be attributed to both a thermodynamic influence on the polymer chain mobility and hydrogen bonding between the permeates and the modified membrane. The degree of swelling was enhanced by the thermodynamic factor. However, the increase in the feed temperature reduced the interaction force between the permeate and the membrane. Therefore, the degree of swelling was almost constant for all temperature ranges, whereas the equilibrium of the thermodynamic influence and polar interaction was reached under feed conditions. The decrease in the separation factor with increasing temperature was due to the coupling effect of the permeate. Because of the high degree of swelling of the sodium sulfonate membrane at high temperatures, more water and ethanol were sorbed into the membrane, and the coupling effect of the permeate resulted in more ethanol transport through the membrane. These factors were essentially responsible for the loss in the separation factor at high temperatures.

CONCLUSIONS

Sodium substitution successfully improved the pervaporation performance of a polysulfone membrane. The introduction of a sodium group into the polymer unit increased the hydrophilicity of the polysulfone membrane. The high separation performance of the Na-PSF membrane was attributed to the ion hydration effect and the difference in the diffusion rates of water and ethanol molecules in the membrane. It was also shown that the sodium sulfonate membrane was strongly affected by the ethanol concentration in the feed. The transport mechanism of the sodium sulfonate membrane was dominated by α^{d} of water with respect to ethanol. Because of a high degree of swelling, the permeation flux showed minor changes with the operating temperature, although the separation factor decreased with an increasing operating temperature. The influence of the polar interaction of the permeate between the permeate and the membrane resulted in a constant permeation rate, and the influence of their size difference resulted in an increase in the separation factor at higher ethanol concentrations in the feed. Because of the high degree of swelling of the Na-PSF membranes at high temperatures, more water and ethanol were sorbed into the membrane, and the coupling effect of the permeate resulted in more ethanol transport through the membrane. These phenomena induced the loss in the separation factor at higher temperatures.

References

1. Huang, R. Y. M. Pervaporation Separation Process; Elsevier: Amsterdam, 1991.
2. Yoshikawa, M.; Yukoshi, T.; Sanui, K.; Ogata, N. J Appl Polym Sci 1987, 33, 2369.
3. Lee, Y. M.; Oh, B. K. J Membr Sci 1993, 85, 13.
4. Kusumocahyo, S. P.; Sudoh, M. J Membr Sci 1999, 161, 77.
5. Cabasso, I.; Liu, Z. Z.; Makenzie, T. J Membr Sci 1986, 28, 109.
6. Wenzlaff, A.; Boddeker, K. W.; Hattenbach, K. J Membr Sci 1985, 22, 333.
7. Yeom, G. Y.; Pal, R.; Huang, R. Y. M. J Membr Sci 1999, 156, 207.
8. Jegal, J. G.; Lee, K. H. J Appl Polym Sci 1996, 60, 1177.
9. Ray, S. K.; Sawant, S. B.; Joshi, J. B. J Membr Sci 1998, 138, 1.
10. Sportsman, K. S.; Way, J. D.; Chen, W.-J.; Pez, G. P.; Laciak, D. V. J Membr Sci 2002, 203, 155.
11. Krasemann, L.; Toutianoush, A.; Tieke, B. J Membr Sci 2001, 181, 221.
12. Shi, Y. Q.; Wang, X. W.; Chen, G. W. J Appl Polym Sci 1996, 61, 1387.
13. Mochizuki, A.; Amiya, S.; Sato, Y.; Ogawara, H.; Yamashita, S. J Appl Polym Sci 1990, 40, 385.
14. Huang, R. Y. M.; Pal, R.; Moon, G. Y. J Membr Sci 1999, 160, 101.
15. Huang, R. Y. M.; Pal, R.; Moon, G. Y. J Membr Sci 2000, 167, 275.
16. Moon, G. Y.; Pal, R.; Huang, R. Y. M. J Membr Sci 1999, 156, 17.
17. Zschocke, P.; Quellmalz, D. J Membr Sci 1985, 22, 325.
18. Chen, S.-H.; Yu, K.-C.; Lin, S.-S.; Chang, D.-J.; Liou, R. M. J Membr Sci 2001, 183, 29.
19. Lee, K. R.; Lai, J. Y. J Polym Res 1994, 1, 247
20. Luo, G. S.; Niang, M.; Schaetzel, P. J Appl Polym Sci 1997, 66, 1631.
21. Chen, S.-H.; Liou, R. M.; Hsu, C.-S.; Yu, K.-C. J Membr Sci 2001, 93, 59.
22. Freger, V.; Korin, E.; Wisniak, J.; Korngold, E. J Membr Sci 1997, 133, 255.
23. Shieh, J. J.; Huang, R. Y. M. J Membr Sci 1997, 127, 185.