Separation of Liquid Mixtures by Using Polymer Membranes. I. Water–Alcohol Separation by Pervaporation through PVA-g-MMA/MA Membrane

WEN-YEN CHIANG* and CHUN-MIN HU

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd. Sec., Taipei 10451, Taiwan, Republic of China

SYNOPSIS

A membrane was designed for the separation of a water–alcohol mixture by pervaporation on the basis of the difference in hydrogen-bonding interaction between two components of the membrane. Two kinds of poly(vinyl alcohol)-g-maleic anhydride/methyl methacrylate membrane were prepared by different methods: (1) A homogeneous membrane was formed by casting from dimethyl sulfoxide solution after purification. (2) A porous membrane was obtained directly by casting from the reaction solution, and then was purified. It is found that water was permeated through a homogeneous membrane preferentially in all ranges of feed compositions. Moreover, the flux was found to decrease with increasing PVA content in the membrane. The porous membrane after heat treatment has selective permeability for methanol. Pervaporation of water was investigated with respect to the feed concentration and also to the operating conditions. The effect of the molecular size of the permeating species on both permeation and separation is also discussed.

INTRODUCTION

Separation carried out by membranes is considered to be one of the most promising processes in energy-saving separation technology. The pervaporation technique is potentially useful in fields where distillation techniques are difficult, such as fractionation of close-boiling components, azeotropic mixtures, or isomeric mixtures.[1-19] In the pervaporation process (liquid–vapor transport), the membrane is brought in contact with the liquid mixture at atmospheric pressure and the liquids permeate into the membrane to vaporize downstream at a reduced pressure. This technique was first developed in the mid-1950s.[20,21]

Specific and selective separation of substances by membranes may be realized by incorporating a group into membranes that may cause a strong interaction such as a hydrogen-bonding interaction. Differences in strength of the hydrogen-bonding interaction may lead to a selective separation by membranes.[22-26] It is expected that the hydroxy group might have a strong interaction with water through hydrogen bonding and a membrane-containing hydroxy group might permeate water with high selectivity.

Poly (vinyl alcohol) (PVA) contains many hydroxy groups and is a very "tight" membrane that is caused by high degree of inter- and intramolecular hydrogen bonding. When PVA membrane was used for separation of alcohol and water, it was found that although the flux was very low the membrane possessed a high degree of selectivity toward water.[27-32] A useful procedure to improve the permeability characteristics of PVA membrane and yet maintain the selectivity lies in graft copolymerization of hydrophobic monomers onto the backbone.[33]

From this point of view, water-insoluble but more hydrophilic PVA graft terpolymers were synthesized in our previous papers.[34-37] In this study, PVA-g-maleic anhydride (MA)/methyl methacrylate (MMA) graft terpolymer obtained by the coupling condensation of PVA with MMA-co-MA[36] was used as a permselective membrane. Moreover, the major purpose of this study is to develop new membranes

that have high selectivity and acceptable flux rates for separating the alcohol–water system by pervaporation and also to investigate the dependence of permeation behavior on the membrane structure and composition as well as operating conditions.

EXPERIMENTAL

Sample Preparation

The materials and grafting procedure were previously described in detail.[36]

Membrane Preparation

Membranes were prepared by two different methods as follows:

Homogeneous PVA-g-MMA/MA Membrane

First, the product mixture was extracted by water and acetone to remove the unreacted PVA and MMA-co-MA, and then PVA-g-MMA/MA membrane was obtained by casting from dimethyl sulfoxide (DMSO) solution. The solution was poured into glass plates, and the solvent was allowed to evaporate at 60°C in a vacuum. This procedure provided a nonporous and homogeneous membrane. The thickness of the membrane is 100–120 μm.

Porous PVA-g-MMA/MA Membrane

The membrane was formed directly by casting from the reaction solution and then was purified. This procedure provided a porous membrane.

Heat Treatment of the Membrane

As described in the previous paper,[36] PVA-g-MMA/MA is a highly water-swellable graft terpolymer. However, too much hydrophilicity often leads to weak mechanical properties of the membrane. To avoid such defects, all the membranes were treated in an oven at temperature 100°C for 20 min. Moreover, to study the effect of cross-linking density on the permeation behavior, some membranes were treated at 100°C for a longer time.

Pervaporation Experiment

The apparatus and procedure for pervaporation was essentially the same as described in the literature.[11] Its upper compartment with a capacity of 250 cm^3, containing the liquid mixture, was equipped with a stirrer, a thermometer, and a heating spiral con-

nected to a circulating thermostatted bath. The membrane used was 5 cm in diameter and placed in a stainless steel pressure holder. A constant downstream pressure was maintained by a vacuum pump. The pervaporate was condensed in either of the two traps cooled with liquid nitrogen. The pervaporation experiments were usually carried out at 30°C and were also done in the temperature range of 10–50°C to observe the temperature dependence.

To keep the feed composition constant, the mass of pervaporate collected during a run was kept small compared with the mass of the feed. The separation analysis was carried out on a Hitachi gas chromatography equipped with a 2 m-long column packed with Porapak Q.

Two factors were used to evaluate the performance of a pervaporation run:

1. The permeation flux, expressed in kg/hm^2.
2. The selectivity factor α, defined as

$$\alpha = \frac{y_{water}/y_{alcohol}}{x_{water}/x_{alcohol}}$$

where x and y denote the weight fraction of water and alcohol in the feed solution and in the pervaporate, respectively.

Swelling Ratio

A piece of membrane was immersed in a water-alcohol mixture solvent at 30°C temperature. After reaching equilibrium, the membrane was rapidly removed from the mixture solvent, wiped with tissue paper to remove adherent solvent, and weighed. The swelling ratio S is defined as

$$S = \frac{W_s - W_d}{W_d}$$

where W_d and W_s denote the weight of dry and solvent-swollen membranes, respectively.

Solvent Composition in the Membrane

Several pieces of solvent-swollen membrane with the same composition were removed from the mixture solvent, and the surface solvent was blotted. The solvent in the membrane was allowed to evaporate under reduced pressure and collected in a cold trap. The composition of the solvent was determined by gas chromatography and used to calculate the separation factor defined as

Table I   Synthesis of PVA-*g*-MMA/MA Graft Copolymer

Membrane No.	PVA Feed[a] (wt %)	Mol Fraction of MA in MMA-*co*-MA	Wt % of PVA in PVA-*g*-MMA/MA	Yield (%)	Intrinsic Viscosity[b] $[\eta]$ (dL/g)
1	66.7	0.53	68.3	87.1	4.47
2	50.0	0.53	53.8	80.0	3.89
3	33.3	0.53	39.2	76.4	3.42
4	50.0	0.24	51.1	68.2	2.48
5	50.0	0.72	56.2	87.2	5.65
6[c]	33.3	0.24	50.3	70.2	2.51

[a] Reaction temperature = 100°C.
[b] Solvent: DMSO, T = 30°C.
[c] Membrane no. 6 is a porous membrane.
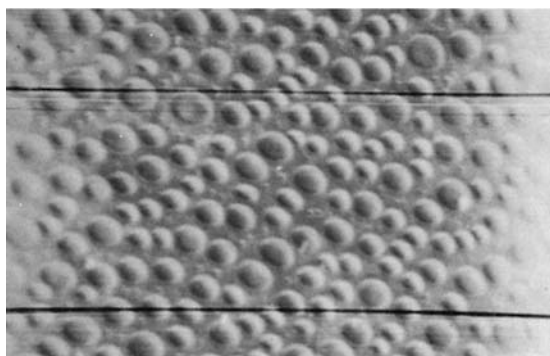
$$\alpha_s = \frac{S_{water}/S_{alcohol}}{X_{water}/X_{alcohol}}$$

where $S_{water}/S_{alcohol}$ and $X_{water}/X_{alcohol}$ denote the weight ratio of the solvent in the membrane and feed solution, respectively.

RESULTS AND DISCUSSION

Homogeneous Membrane

Results of the coupling–condensation reaction of PVA and MMA-*co*-MA are shown in Table I. The composition and structure of the graft terpolymer were determined previously.[36] Figure 1 shows the scanning electron micrograph of the nonporous membrane no. 2.

Figure 2 shows the relation between the swelling ratio in water–alcohol mixtures at 30°C and the composition of graft terpolymer membranes. The water causes swelling of the membranes to a far greater degree than does alcohol. Moreover, the swelling ratio increases monotonically with an increasing level of PVA in the membrane because of the increase of hydrophilicity. As the water concentration is increased, the swelling ratio is increased. It should be noted that the membranes in the water–ethanol system have a larger swelling ratio than in the water–methanol system. It is well known that the degree of swelling of the polymer membrane by water–alcohol mixtures increases as the number of carbon atoms in the alcohol mixtures increases.[38]
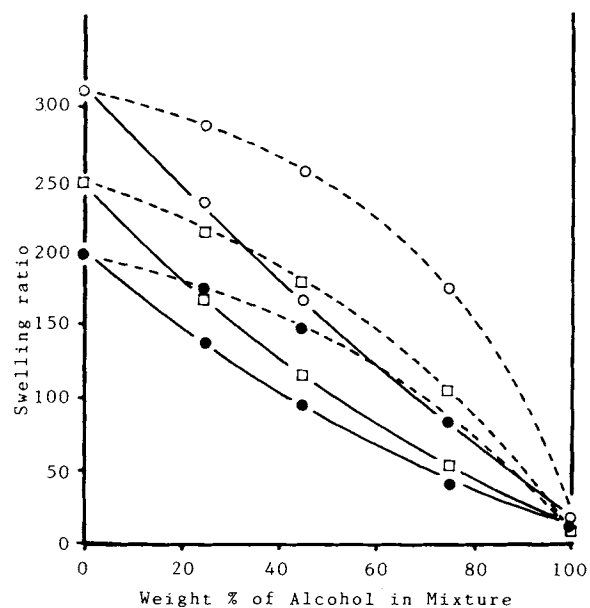
Figure 1   Scanning electron micrograph of membrane no. 2.

10 μm

Figure 2   Dependence of swelling degree on the PVA feed wt % in water–alcohol mixtures at 30°C. (○) Membrane no. 1; (□) no. 2; (●) no. 3. (——) Water–methanol system; (----) water–ethanol system.

Figure 3 shows the composition of the solvents sorbed into the membranes. Water is found to be preferentially sorbed into the membrane. A good separation is expected in the systems of water–alcohol mixtures by pervaporation. Membrane of higher hydroxy content shows a higher selectivity to water. Therefore, the separation factor increases with an increasing PVA content in the membrane. From this result, it could be also seen that this membrane has a stronger affinity to methanol than to ethanol. On the other hand, methanol is more easily sorbed into the membrane than is ethanol. In this case, the separation characteristics of the membrane for a water–methanol mixture are worse than for a water–ethanol mixture (Fig. 4).

It has been postulated by several workers[5,39] that if the interaction between water and the polar group of the polymer membrane is too strong water clusters are formed which suppress the permeation. Therefore, when the number of hydrophilic groups (hydroxy groups) increases, the permeation flux decreases, but the selectivity increases (Figs. 4 and 5). Some studies[9,11,40] have shown that the permeation rate increases with an increasing swelling ratio, due to the enhancement of the mobility of polymer chains in membrane. In our experimental results, however, membranes with higher PVA content have a higher swelling ratio (Fig. 2) but a lower permeation flux (Fig. 3). This means that there is no certain relationship between the swelling ratio and permeation flux when the membrane has different
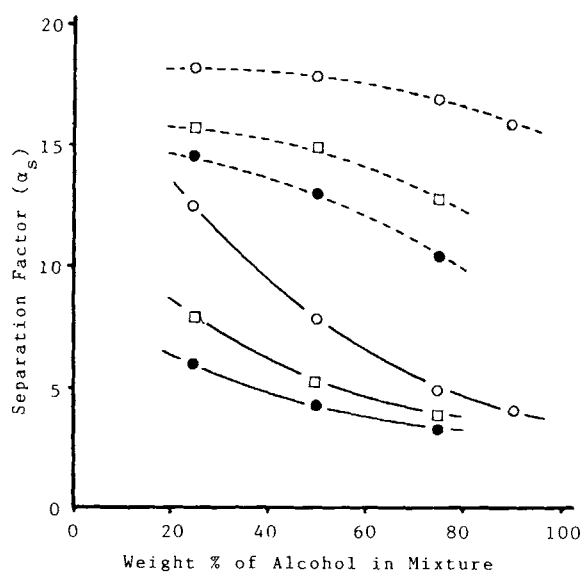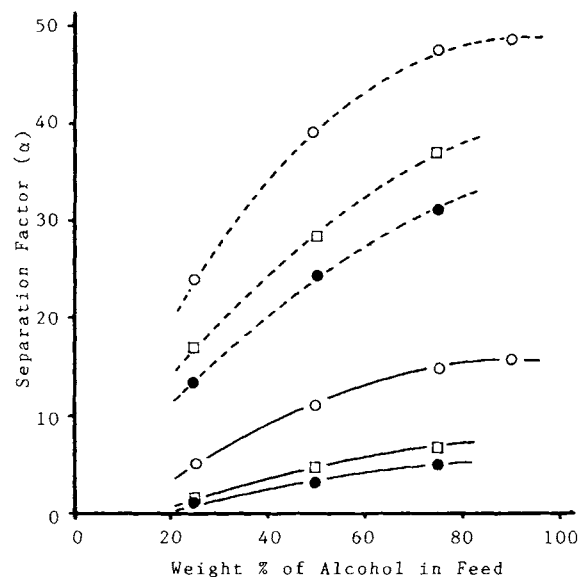

Figure 4   Dependence of separation factor of water on the PVA feed wt % and composition of feed mixtures at 30°C. Symbols the same as in Figure 2.

degrees of hydrophilicity. However, a high swelling degree always results in a high permeation rate of the membrane with the same composition. The separation factor increases gradually with increasing alcohol concentration in the feed. This can be easily seen in Figure 3: The PVA-g-MMA/MA membrane still possesses a very high selectivity for water even in high alcohol concentration.

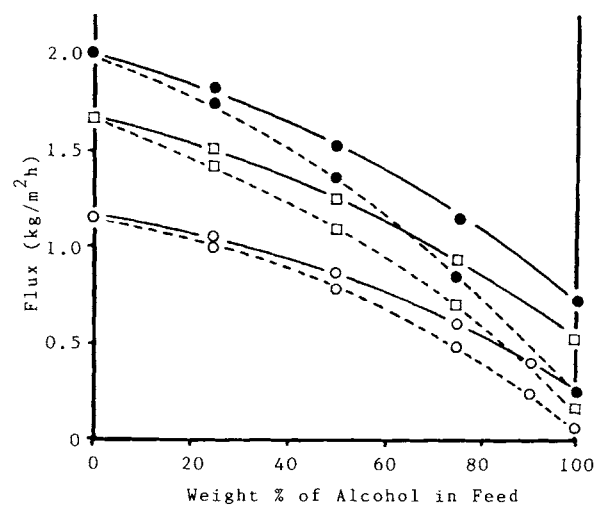As can be seen in Figure 6, the permeation flux increases whereas the separation factor decreases

Figure 3   Dependence of separation factor on the PVA feed wt % in water–alcohol mixtures at 30°C. Symbols the same as in Figure 2.

Figure 5   Dependence of permeation flux on the PVA feed wt % and composition of feed mixtures at 30°C. Symbols the same as in Figure 2.
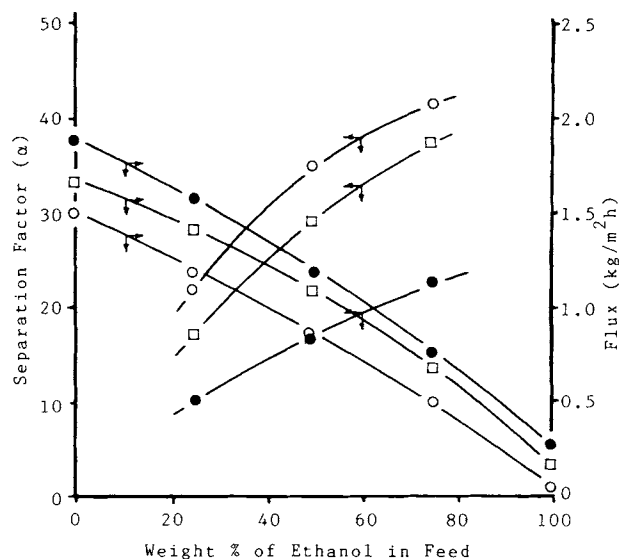
Figure 6 Dependence of separation factor and permeation flux on the mol fraction of MA in MMA-*co*-MA and composition of feed mixtures at 30°C. (□) Membrane no. 2; (○) no. 4; (●) no. 5.
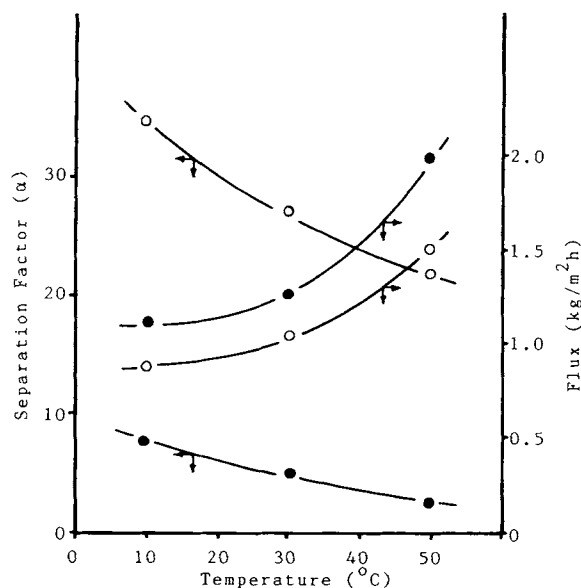

Figure 7 Dependence of separation factor and permeation flux on operating temperature through membrane no. 2: (●) methanol; (○) ethanol. (Weight fraction of alcohol in feed is 0.5.)

when the MMA-*co*-MA with higher MA content is used. As mentioned previously,[36] the higher MA content in MMA-*co*-MA provides higher reactivity with PVA since it contains more anhydride groups. This results in an increase of the number of side chains in PVA. The increase of the level of grafting loosens up the membrane structure and decreases the crystalline content in the membrane.

Many researchers reported the dependence of pervaporation results on the operating temperature.[41-43] Accordingly, changing the operating temperature is one of the plausible ways to improve membrane performance. On the basis of this idea, the effect of operating temperature on the permeation through present membranes is investigated (Fig. 7). By lowering the operating temperature from 50 to 10°C, the hydrogen-bonding interaction between water and hydroxy groups becomes strong. As a result, the selectivity toward water increases, while the flux decreases. This decrease of flux is attributed to the decrease of diffusivity of water through the membrane.

PVA-*g*-MMA/MA forms a cross-linked network as a result of the interchain ester linkage between hydroxy and anhydride groups during the heat treatment. Figures 8 and 9 show the influence of heating time (cross-linking time) on separation factor, α; the swelling ratio, αs; and the permeation flux. The maximum separation factor is reached in 3 h and there is no further increase with longer

heating time. The cross-linking degree increases with the cross-linking time. As a result, the hydrophilic properties of the membrane are reduced while the membrane becomes more dense. Thus, as can be seen from these figures, the swelling degree and the permeation flux decrease with heating time.
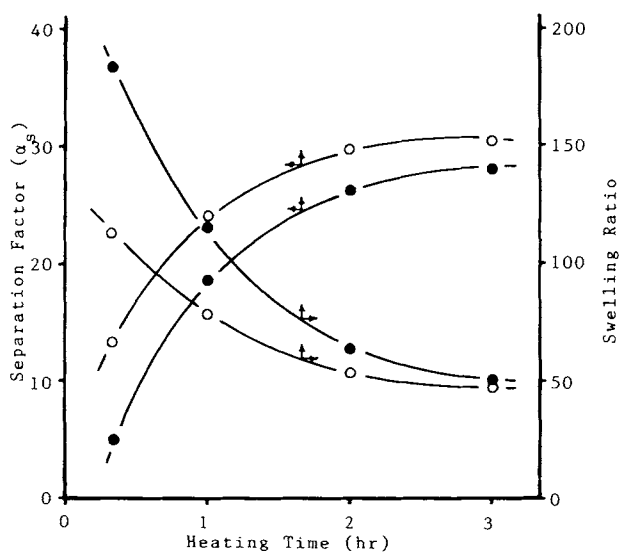

Figure 8 Dependence of separation factor and swelling ratio on the heating time of membrane no. 2 at 100°C: (●) methanol; (○) ethanol. (Weight fraction of ethanol in feed is 0.5.)
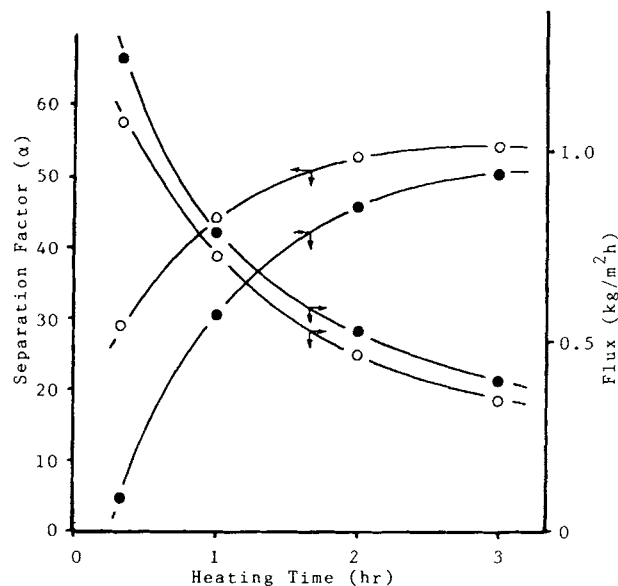
Figure 9   Dependence of separation factor and permeation flux on the heating time of membrane no. 2 at 100°C: methanol (●); ethanol (○). (Weight fraction of ethanol in feed is 0.5.)

Huang et al.[3,31] have shown that as the molecular weight of compounds in a given homologous series increases the permeation flux decreases and the separation increases. The present study shows that the same relationships hold for the homologous series of methanol, ethanol, n-propanol, and n-butanol for the PVA-g-MMA/MA membrane. Table II shows that the permeation flux increases as the molecular length decreases. Membrane selectivity is also found to depend on the molecular length for this series of linear alcohols. Separation of water–alcohol solutions at given water content increases as the molecular length of the alcohols increases. Isopropanol, with the larger cross section, is sepa-

Table II   Effect of Size and Shape of Permeating Species on the Flux and Separation Factor through Membrane No. 2 at 30°C

Mixture	Flux[a] (kg/m² h)	Separation Factor
Water–methanol	1.25	5
Water–ethanol	1.03	28
Water–n-propanol	0.91	36
Water–i-propanol	0.87	38
Water–butanol	0.70	43

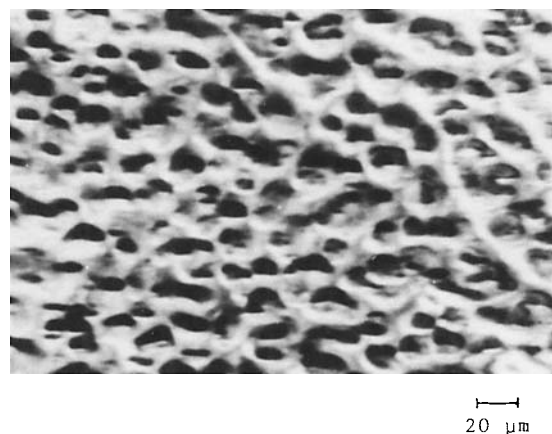[a] Wt % of alcohol in feed is 50%.

Figure 10   Scanning electron micrograph of membrane no. 6.

rated from water–alcohol mixtures better than is n-propanol.

Porous Membranes

Figure 10 shows a typical scanning electron micograph of the surface of porous membrane no. 6. Figure 11 shows the swelling ratio and separation factor of membrane no. 6 at 30°C in an water–ethanol mixture. By comparing Figure 10 with Figures 1 and 2, these curves show a similar trend such that the porous membrane should be expected to have a high selectivity of water in water–alcohol mixtures.

Table III shows the permeation flux of pure solvents through membrane no. 6 at 30°C. It can be seen that water and high molecular weight alcohols
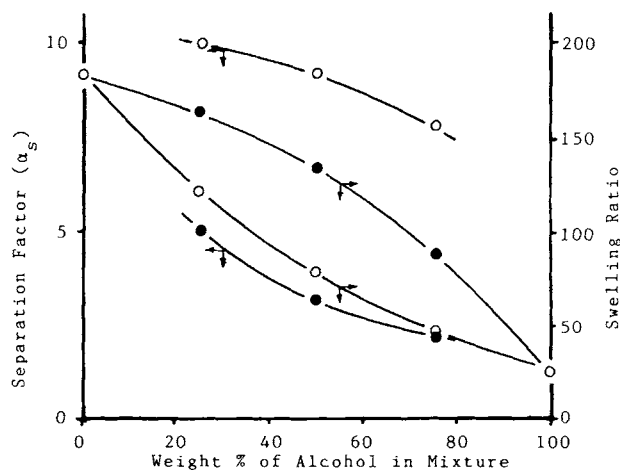

Figure 11   Dependence of separation factor and swelling degree on the weight fraction of alcohol in the mixture of a porous membrane no. 6: (●) methanol; (○) ethanol.

Table III   Effect of Size and Shape of Permeating Species on Flux through Porous Membrane No. 6 at 30°C

Solvent	Water	Methanol	Ethanol	n-Propanol	i-Propanol	n-Butanol
Flux (kg/m² h)	1.03	2.68	1.36	0.47	0.39	0.15

(ethanol and propanol) are more difficult to diffuse through the pores than is methanol. The former could be due to the strong hydrogen bonding between water and hydroxy groups within pores, and the latter could be attributed to the larger molecular size. From the above results, it is suggested that such porous membranes should exhibit a higher selectivity of methanol than of water. But Table IV, shows, on the contrary, that membrane no. 6 is still a water-permselective membrane. This could be explained by the fact that a more hydrophilic membrane is surrounded by water molecules and that methanol cannot easily pass through the pores.

A methanol-permselective membrane is obtained by decreasing the hydrophilicity of membrane through slight cross-linking (Table IV). However, longer heating times result in a high degree of cross-linking and not only decreases the hydrophilicity but also decreases the pore size, and the membrane becomes water-permselective once more. Therefore, control of the pore size and the hydrophilicity of PVA-g-MMA/MA porous membranes is important to obtain a alcohol-permselective membrane in water–alcohol mixtures. This will be reported in detail in our next paper.

Table IV   Effect of Heating Time of Membrane at 100°C on Flux and Separation Factor through Porous Membrane No. 6

Mixture	Heating Time (h)	Flux[a] (kg/m² h)	Separation Factor
Water–methanol	0	1.34	4.26
	1	1.15	0.27
	3	0.87	12.3
Water–ethanol	0	1.02	11.5
	1	0.88	6.4
	3	0.62	29.6
Water–n-propanol	0	0.72	14.7
	1	0.55	27.6
Water–i-propanol	0	0.58	19.2
	1	0.41	40.2

[a] Operating temperature = 30°C; wt % of alcohol in feed is 50%.

CONCLUSIONS

Homogeneous and porous PVA-g-MMA/MA membranes are obtained by different experimental procedures. Both of them show higher selectivity of water in water–alcohol mixtures. Increase of PVA content in the membrane causes the selectivity to increase. When alcohol concentration in the feed increases, the permeation flux decreases, but the separation factor increases. Both preheat treatment of the membrane and increases of the operating temperature result in an increase of selectivity for water. Porous membranes after heat treatment at 100°C for 1 h become methanol-permselective membranes.

REFERENCES

1. A. S. Michaels, R. F. Baddour, H. J. Bixter, and C. Y. Choo, *Ind. Eng. Chem. Proc. Design Dev.*, **1**, 14 (1962).
2. R. F. Baddour, A. S. Michaels, H. J. Bixter, and J. A. Barrie, *J. Appl. Polym. Sci.*, **8**, 897 (1964).
3. R. Y. M. Huang and V. J. C. Lin, *J. Appl. Polym. Sci.*, **12**, 2615 (1968).
4. I. Cabasso, J. J. Grudzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, **18**, 2117 (1974).
5. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Membr. Sci.*, **1**, 271 (1976).
6. S. Yoshimasu, H. Nomura, K. Kamyi, T. Okano, and I. Shinohara, *Nippon Kagaku Kaishi*, 785 (1980).
7. S. Yoshimasu, H. Nomura, K. Kamyi, T. Okano, and I. Shinohara, *Nippon Kagaku Kaishi*, 276 (1981).
8. E. Nagy, O. Borlai, and A. Ujhidy, *J. Membr. Sci.*, **7**, 109 (1980).
9. T. Terada, T. Hohjoh, S. Yoshimasu, and M. Ikemi, *Polym. J.*, **14**, 347 (1982).
10. G. F. Tusel and H. H. Bruschke, *Desalination*, **53**, 327 (1985).
11. T. Itoh, H. Toya, K. Ishihara, and I. Shinohara, *J. Appl. Polym. Sci.*, **30**, 179 (1985).

12. F. Suzuki, H. Kimua, K. Onozato, and S. Kuroda, *J. Appl. Polym. Sci.,* **32,** 4573 (1986).

13. T. Masuda, B. Z. Tang, and T. Higashimura, *Polym. J.,* **18,** 565 (1986).

14. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.,* **33,** 2369 (1987).

15. T. Hirotsu, *J. Appl. Polym. Sci.,* **34,** 1159 (1987).

16. C. H. Hsiue and Y. S. Yang, *J. Appl. Polym. Sci.,* **34,** 2187 (1987).

17. T. Q. Nguyen, A. Essamri, R. Clement, and J. Neel, *Makromol. Chem.,* **188,** 1973 (1987).

18. J. Nieuwenhuis and Y. Y. Tan, *Die Angew. Makromol. Chem.,* **147,** 83 (1987).

19. R. Y. M. Huang, A. Moreiva, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.,* **35,** 191 (1988).

20. R. C. Binning and J. L. Robert, U. S. Pat. 2,953,502 (1955).

21. R. C. Binning and F. E. James, *Petrol. Refin.,* **37,** 214 (1958).

22. R. F. Sweeny and A. Rose, *Ind. Eng. Chem. Prod. Res. Dev.,* **4,** 248 (1965).

23. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Chem. Ed.,* **22,** 2159 (1984).

24. M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, and T. Shimidzu, *Polym. J.,* **17,** 653 (1986).

25. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *Polym. J.,* **17,** 363 (1985).

26. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *Macromolecules,* **19,** 47 (1986).

27. V. N. Schodt, R. F. Sweeny, and A. Rose, *Am. Chem. Soc. Div. Petrol. Chem. Symp.,* **6**(A), 29 (1961).

28. R. C. Binning, J. F. Jennings, and E. C. Martin, U. S. Pat. 3,035,060 (1962).

29. R. A. Markle, R. D. Falb, and R. I. Leninger, *Trans. Am. Soc. Artif. Int. Organs.,* **10,** 22 (1964).

30. M. Odian and E. F. Leonard, *Trans. Am. Soc. Artif. Int. Organs.,* **14,** 19 (1968).

31. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.,* **14,** 2341 (1970).

32. J. C. Bray and E. W. Merrill, *J. Appl. Polym. Sci.,* **17,** 3779 (1973).

33. V. Shantora and R. Y. M. Huang, *J. Appl. Polym. Sci.,* **26,** 3223 (1981).

34. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.,* **30,** 3895 (1985).

35. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.,* **30,** 4045 (1985).

36. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.,* **36,** 1479 (1988).

37. W. Y. Chiang and C. M. Hu, *Angew. Makromol. Chem.,* **165,** 133 (1989).

38. A. G. Mitchell and W. E. K. Wynne-Jones, *Trans. Faraday Soc.,* **49,** 161 (1953).

39. H. Yasuda and V. Stannett, *J. Polym. Sci.,* **57,** 906 (1962).

40. T. Itoh, Y. Ohkawa, K. Ishihara, and I. Shinohara, *Polym. J.,* **15,** 827 (1983).

41. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.,* **53,** 45 (1961).

42. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.,* **18,** 351 (1974).

43. S. Yomada and T. Hamaya, *Kobunshi Ronbunshu,* **33,** 217 (1976).