Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Permselective Properties for Aqueous Ethanol Solutions through Copolymer Membranes from Benzyl Methacrylate and Polyethylene Glycol Dimethacrylate

Hiroshi Okuno[a]; Takashi Okado[a]; Akira Matsumoto[a]; Masayoshi Oiwa[a]; Tadashi Uragami[a]
[a] FACULTY OF ENGINEERING, KANSAI UNIVERSITY, SUITA, OSAKA, JAPAN

To cite this Article Okuno, Hiroshi , Okado, Takashi , Matsumoto, Akira , Oiwa, Masayoshi and Uragami, Tadashi(1992) 'Permselective Properties for Aqueous Ethanol Solutions through Copolymer Membranes from Benzyl Methacrylate and Polyethylene Glycol Dimethacrylate', Separation Science and Technology, 27: 12, 1599 — 1617

To link to this Article: DOI: 10.1080/01496399208029226

URL: http://dx.doi.org/10.1080/01496399208029226

SEPARATION SCIENCE AND TECHNOLOGY, **27**(12), pp. 1599–1617, 1992

Permselective Properties for Aqueous Ethanol Solutions through Copolymer Membranes from Benzyl Methacrylate and Polyethylene Glycol Dimethacrylate

---

HIROSHI OKUNO, TAKASHI OKADO, AKIRA MATSUMOTO, MASAYOSHI OIWA, and TADASHI URAGAMI
FACULTY OF ENGINEERING
KANSAI UNIVERSITY
SUITA OSAKA 564, JAPAN

Abstract

Copolymer membranes prepared by bulk copolymerization of polyethylene glycol dimethacrylates of three different degrees of polymerization as macromonomer and benzyl methacrylate as comonomer were used for the separation of aqueous ethanol solutions in both pervaporation and evapomeation. The copolymer membranes preferentially permeated water from an aqueous ethanol solution in evapomeation. In pervaporation, ethanol was predominantly permeated from an aqueous ethanol solution through the copolymer membranes containing a long polyethylene glycol (PEG) chain above about 20 wt% PEG content in a copolymer. This result was attributed to a remarkable swelling of the copolymer membrane containing a long PEG chain by the aqueous ethanol solution in pervaporation. In evapomeation, both the separation factors and the permeation rates through these membranes are not much affected by the ethanol concentration in the feed vapor. In pervaporation, they were significantly dependent on the ethanol concentration in the feed solution. The above results are discussed from the viewpoint of the physical structure of the membrane in evapomeation and pervaporation.

INTRODUCTION

Pervaporation is a useful technique for the separation of azeotropic mixtures, close-boiling mixtures, and mixtures of heat-sensitive compounds (*1*). In pervaporation, polymer membranes are often swollen by a feed solution because the membranes are in direct contact with a feed solution; consequently their selectivities are significantly decreased. We presented a new membrane separation technique "evapomeation" (*2*), and we have reported the permeation and separation characteristics of aqueous alcohol solutions through various polymer membranes in evapomeation (*2–8*). In evapomeation, a polymer membrane is not swollen much by a feed solution because the membrane is not in contact with the feed solution; that is, a feed vapor is supplied to the membrane. It has been found that the behavior of permeation and separation in evapomeation differs from that in pervaporation owing to the difference in the physical structure of the membrane. In general, permeation rates in evapomeation are lower than those in pervaporation, and selectivities in the former are higher than those in the latter. Hydrophilic polymer membranes such as alginic acid (*2*), crosslinked chitosan (*3*), and crosslinked pullulan (*7*) showed very high permselectivity for water from aqueous ethanol solutions but low permeability in evapomeation. On the other hand, hydrophobic polymer membranes such as polystyrene (*4*), poly(vinyl chloride) (*5*), and poly(vinyl *p-tert*-butyl benzoate) (*6*) showed higher selectivity for water and had the same permeation rate as in pervaporation.

It is unfortunate if the polymer membrane for the separation of liquid mixtures is greatly swollen by the feed solution because selectivity through the membrane is thereby lowered. To prevent swelling of the membrane, various techniques have been tried. Crosslinking is available for preventing the swelling or dissolution of polymer membranes by a feed solution under permeation conditions. Furthermore, this leads to a high selectivity for water from an aqueous alcohol solution because the resulting membrane becomes a dense and stable structure (*3*, *7*).

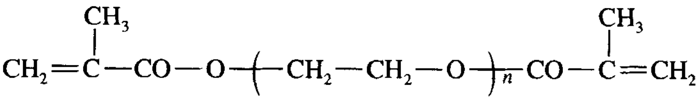
Many studies on the preparation and application of macromonomers as membranes have been reported recently (*9–13*). The preparation of copolymers from a macromonomer and a small monomer is better for the exact design of a membrane material than is the use of copolymers resulting from the usual graft polymerization because the length of a macromonomer as a grafted chain is determined in advance. Copolymer membranes prepared from macromonomers and comonomers were used for the separation of aqueous organic solutions, and their advantages have been discussed (*12*, *13*). However, there are no reports of detailed investigations of separation membranes using bifunctional macromonomers which can form a crosslinked structure. It is very interesting that the characteristics of crosslinking and the copolymerization of a macromonomer are reflected in the structural design of the membrane material. When a reactive bifunctional macromonomer is employed as one of the membrane materials, the above characteristics may be satisfied.

For this paper, polyethylene glycol dimethacrylate as the hydrophilic crosslinker macromonomer and benzyl methacrylate as the hydrophobic comonomer were selected as the membrane materials. The copolymer membranes were prepared from these monomers by bulk polymerization. The effects of the hydrophilicity–hydrophobicity balance and of the fine structure of the copolymer membrane on the permselectivity of aqueous alcohol solutions in both pervaporation and evapomeation are discussed.

EXPERIMENTAL

Materials and Preparation of Membrane

Polyethylene glycol dimethacrylates (PEGDMA) as hydrophilic macromonomers were used with three different degrees of polymerization as follows:



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-CO-O\left(CH_2-CH_2-O\right)_n CO-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

PEGDMA, $n = 4, 23, 136$

PEGDMAs having 4 and 23 ethylene glycol units were produced by Shin-Nakamura Chemical Co., Ltd., and a PEGDMA containing 136 ethylene glycol units was produced by Kyoeisha Chemical Co., Ltd. Benzyl methacrylate (BzMA) was the hydrophobic monomer, and benzoyl peroxide (BPO) was the initiator. They and the other solvents and reagents were of pure commercial grade.

A mixture of BzMA and PEGDMA containing 1 wt% BPO was placed between two glass plates having a thin rim and copolymerized in bulk at 80°C for 6 h in an oven. The copolymer membrane was immersed in benzene at 25°C for 24 h in order to extract the homopolymer and unreacted monomer, and then treated with methanol. This membrane was dried in a desiccator under reduced pressure for a few days. It was difficult to extract the homopolymer of PEGDMA because of the insoluble crosslinked structure of the PEGDMA homopolymer. Therefore, the reactivity ratios of PEGDMA and BzMA could not be calculated. The PEG content in the copolymer was determined by elemental analysis. The membrane was homogeneous and transparent. The thickness of the membrane was approximately 25 μm. In this study the copolymer membranes prepared from PEGDMA with degrees of polymerization of PEG of 4, 23, and 136 and BzMA are abbreviated as CM-4, CM-23, and CM-136, respectively.

Pervaporation and Evapomeation Measurements

The pervaporation and evapomeation techniques used in this study have been published elsewhere (*6*). The measurements of both pervaporation and evapomeation were carried out under the following conditions: 40°C permeation temperature and 0.01 torr reduced pressure. The effective membrane area was 13.8 cm^2. The concentrations of aqueous ethanol solution in the feed and permeate were determined by gas chromatography (Shimadzu GC-9A).

The separation factors ($\alpha_{B/A}$) in pervaporation and evapomeation were calculated by

$$\alpha_{B/A} = (P_B/P_A)/(F_B/F_A) \tag{1}$$

where F_A and P_A are the compositions of Component A in the feed and permeate, respectively. F_B and P_B are the compositions of Component B. B is a preferentially permeating component. In evapomeation, the separation factor was calculated by using the vapor compositions of A and B vaporized from the feed solutions instead of the liquid compositions because the membrane was in contact with the feed vapor on the feed side of the membrane.

The permeation rates for both pervaporation and evapomeation were determined by the weight of permeant collected in a cold trap, the permeation time, and the effective membrane area.

Degree of Swelling of Membrane

The membrane was dried completely under reduced pressure at room temperature and was then weighed. The dry membrane was immersed in an aqueous ethanol solution in a sealed vessel at 40°C for 24 h. Then the membrane was taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (DS) of the membrane was calculated from

$$DS = W_S/W_D \tag{2}$$

where W_S is the weight of the membrane swollen by an aqueous ethanol solution and W_D is the weight of the dry membrane.

Composition of Solution in Membrane

The dry membrane was immersed in an aqueous ethanol solution in a sealed vessel at 40°C for 24 h. Then the membrane was removed from the vessel and wiped quickly with filter paper. The membranes swollen in the feed solution were placed under the reduced pressure system (*5*), and the aqueous ethanol solution adsorbed in the membrane was completely vaporized by heating and trapped by liquid nitrogen. The composition was determined by gas chromatography.

Observation with Scanning Electron Microscopy

The surface of the membranes was observed with a scanning electron microscope (SEM) (JEOL, JSM-6100). Specimens were completely dried *in vacuo* and coated with Au.

RESULTS AND DISCUSSION

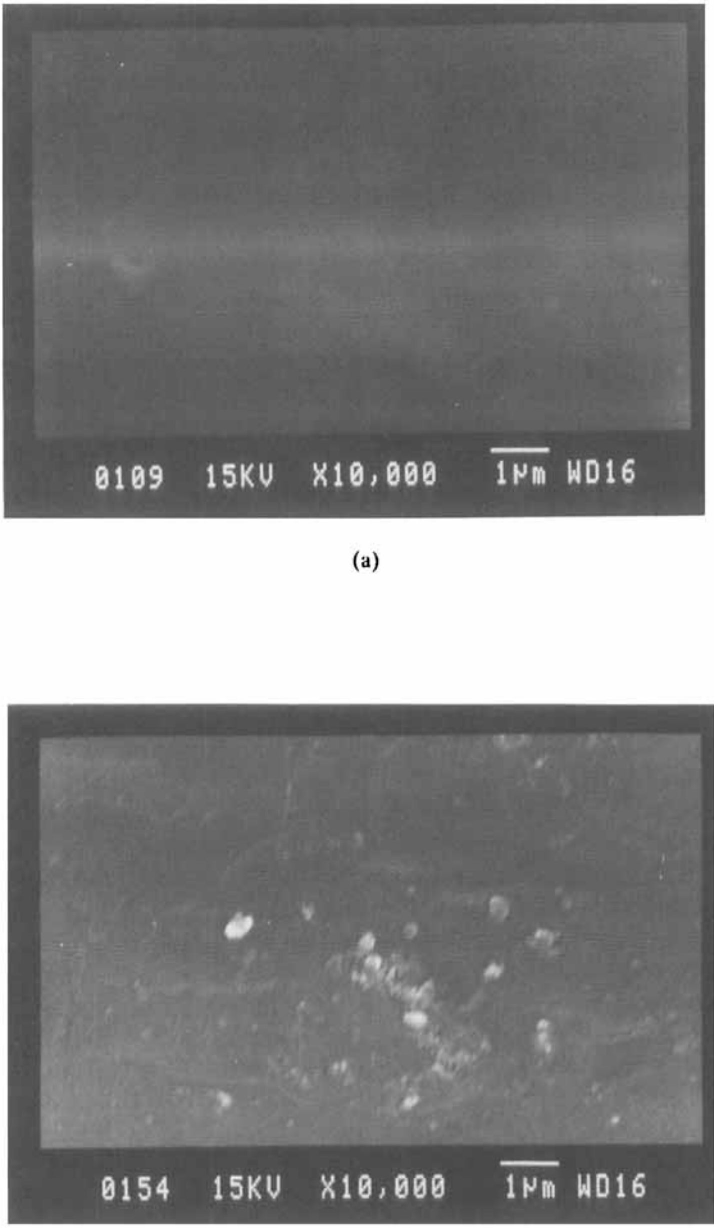
Morphology of Membrane

Figure 1 shows SEM photographs of the surface of the polyBzMA and CM-136 membranes. The surface of the polyBzMA membrane is homogeneous, as shown in Fig. 1(a). In the CM-136 membrane, the PEG microphases are observed. Their sizes grow with increasing PEG content in the copolymer, and they are dispersed uniformly in the continuous phase, as shown in Fig. 1(b)–(d).

Figure 2 shows SEM photographs of the surfaces of the CM-4 and CM-23 membranes. The PEG contents of these membranes are approximately 50 wt%. As shown in Fig. 2(a), 2(b) and Fig. 1(c), the size of the PEG microphases changes in the order CM-4 < CM-23 < CM-136. This result implies that the miscibility of BzMA and PEGDMA is high and in the order CM-4 > CM-23 > CM-136. It is expected that the size of the PEG microphases will affect the permselectivity of an aqueous ethanol solution.

Effect of PEG Content of Permselectivity of Aqueous Ethanol Solution

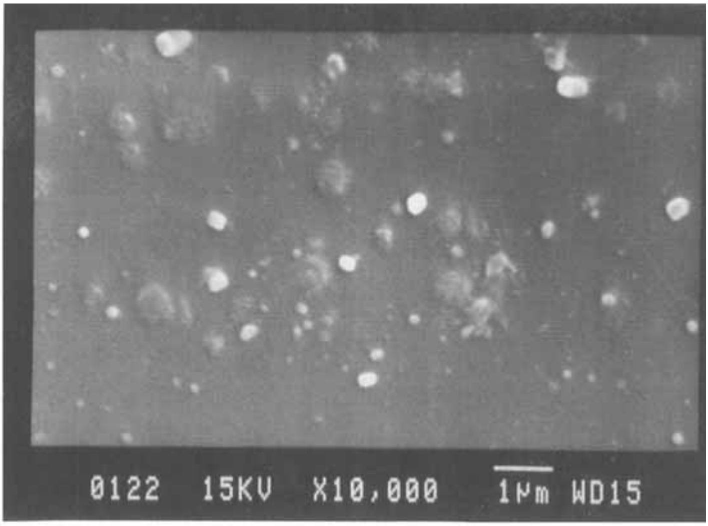
The effect of the PEG content in copolymer membranes on the ethanol concentration in the permeate for aqueous solutions of 10 wt% ethanol through these membranes in evapomeation (a) and pervaporation (b), and on the degree of swelling of these membranes (c) by an aqueous solution of 10 wt% ethanol under the pervaporation conditions are shown in Fig. 3. In evapomeation, all plots in Fig. 3(a) stay below the feed vapor composition for an aqueous solution of 10 wt% ethanol. This shows that these copolymer membranes preferentially permeated water from an aqueous ethanol solution. The ethanol concentration in the permeate increased with increasing PEG content in each copolymer membrane. This is due to the fact that the copolymer membranes are easily swollen by the feed vapor with an increase of the hydrophilic PEG content in these membranes, as shown in Fig. 3(c). In Fig. 3(a) it is clear that the permselectivity for water through the copolymer membrane containing shorter PEG chain is higher. This result is attributed to the fact that these copolymer membranes have different fine structures, as shown in Fig. 1(c) and Fig. 2. The copolymer containing a longer PEG chain has larger PEG microphases in the copol-



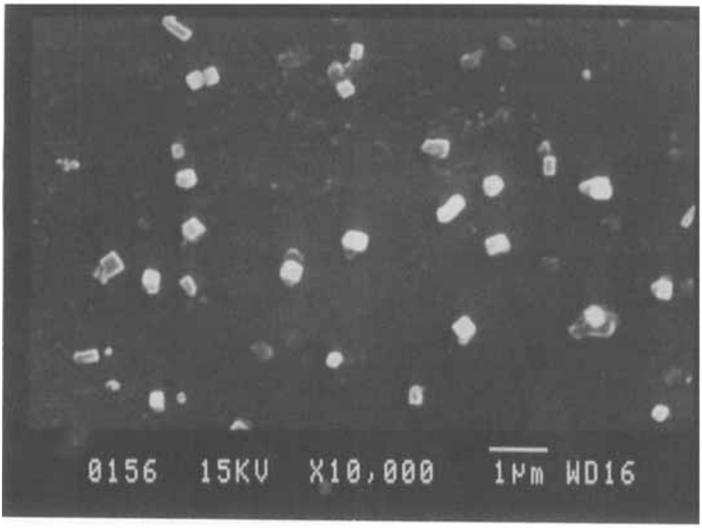
(a)

(b)

FIG. 1. SEM photographs of the surface of the polyBzMA (a) and CM-136 [PEG content: 19.8 wt% (b), 50.9 wt% (c), and 60.5 wt% (d)] membranes.



(c)



(d)

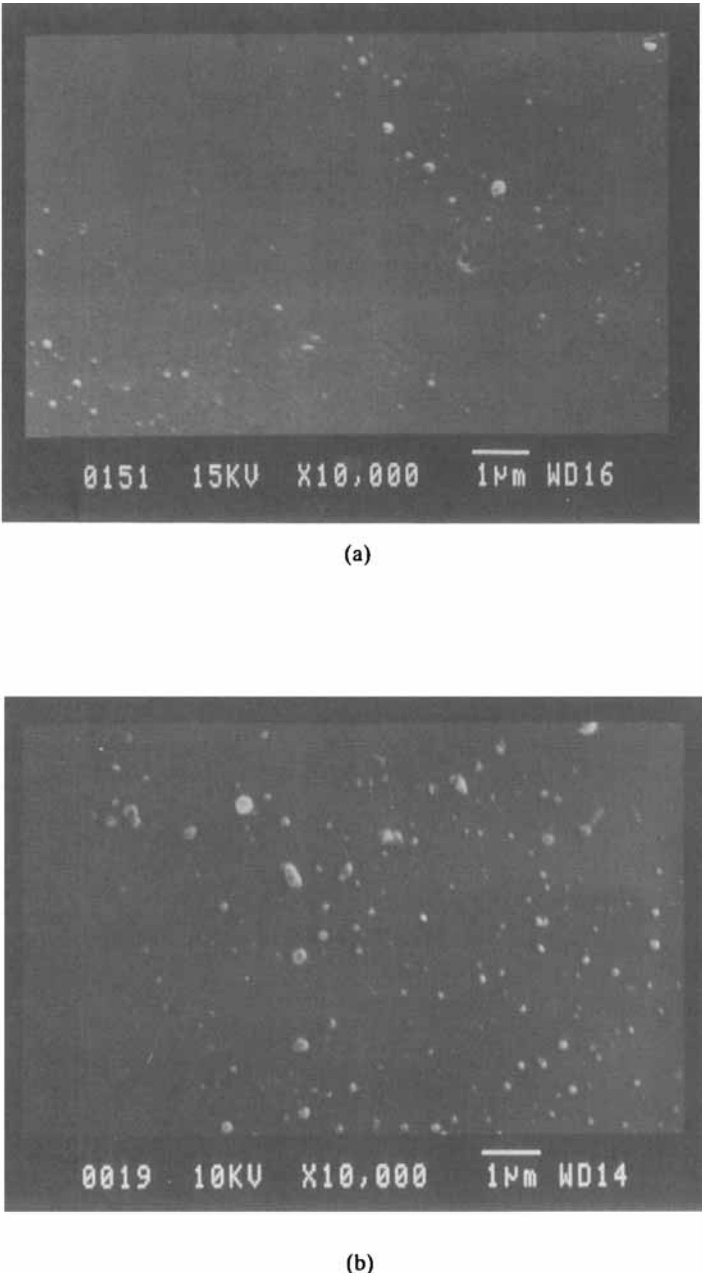


FIG. 2. SEM photographs of the surfaces of the CM-4 (PEG content: 53.3 wt%) (a) and CM-23 (PEG content: 43.8 wt%) (b) membranes.

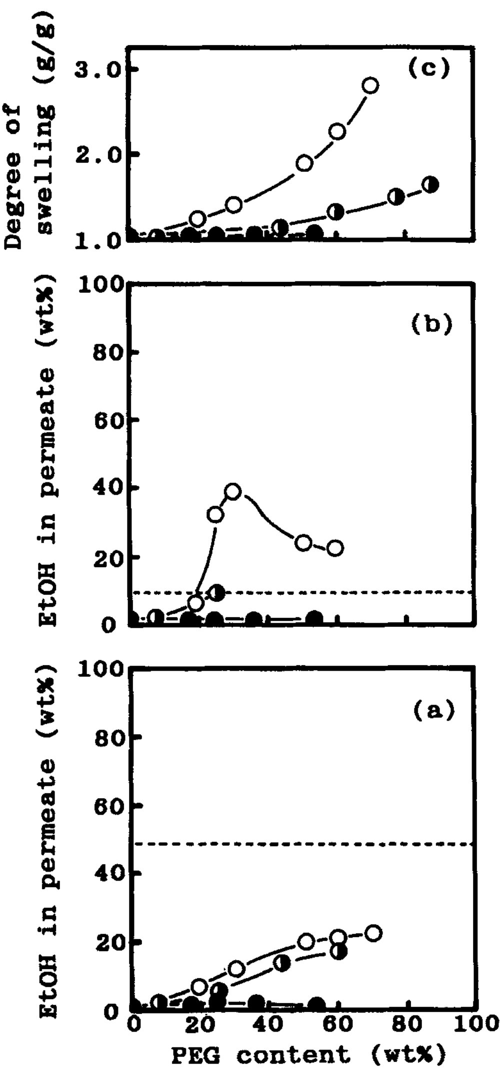


FIG. 3. Ethanol concentrations in the permeate through the copolymer membranes in evapomeation (a) and pervaporation (b), and the degree of swelling of the copolymer membranes (c) as a function of the PEG content in the copolymer membrane. Feed solution: aqueous ethanol solution of 10 wt% ethanol. Membrane: (●) CM-4, (◑) CM-23 and (○) CM-136. [Dashed lines are the compositions of the feed vapor in evapomeation (a) and feed solution in pervaporation (b).]

ymer membrane. The PEG microphases in the copolymer membrane affect the permeation and separation characteristics because such permeants as water and ethanol are more easily permeated through the soft region of hydrophilic PEG.

In pervaporation (Fig. 3b), the CM-136 membranes above 20 wt% of the PEG content in the copolymer membrane permeated ethanol from an aqueous solution of 10 wt% ethanol. The CM-4 and CM-23 membranes permeated water from an aqueous solution of 10 wt% ethanol. In general, the permeant having a smaller molecular size diffuses more easily than that having a larger molecular size. Consequently, most of the polymer membranes predominantly permeate water from an aqueous ethanol solution, although a few membranes, such as silicone rubber (*14*) and poly[1-(trimethylsilyl)-1-propyne] (*15*), do not do so in pervaporation. The permeation behavior of the CM-136 membrane in pervaporation is due to the fact that the CM-136 membrane is swollen so much by the feed solution, as shown in Fig. 3(c). The CM-136 membrane has large PEG microphases which easily make the membrane swell because of their high hydrophilicity. As the membrane is swollen by an aqueous ethanol solution, the selectivity of the membrane becomes lower. The reason is that the skin layer (active layer) (*16*) of the membrane, in which diffusive separation mainly occurs, is destroyed by an aqueous ethanol solution. Consequently, the thickness of the swollen layer is increased, as illustrated in Fig. 4. The relatively high volatility of the ethanol molecule on the surface of the permeation side of the membrane leads to ethanol being selectively permeated through the CM-136 membrane in pervaporation. Such a preferential permeation of

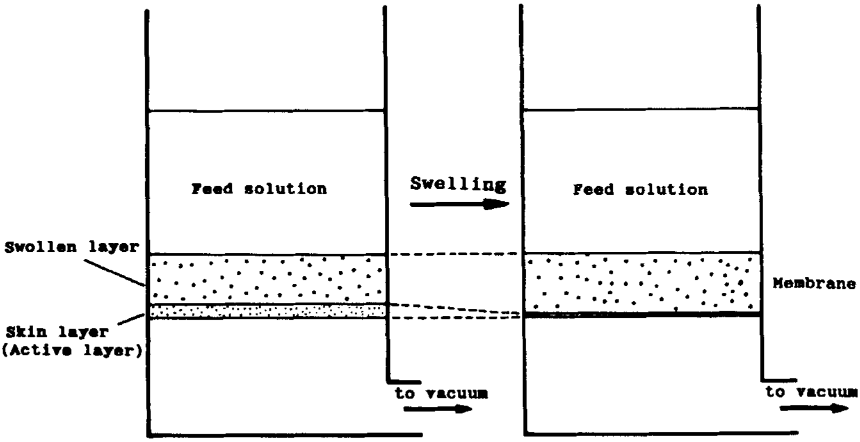


FIG. 4. Model of the structure of swollen membrane under the pervaporation condition.

ethanol through the swollen membrane has also been observed in crosslinked pullulan (*7*) and chitosan (*8*) membranes. The ethanol concentration in the permeate through the CM-136 membrane decreases with increasing PEG content above about 30 wt% PEG content in the copolymer membrane. This is attributed to the fact that the ethanol concentration in the CM-136 membrane is very low in the range of high PEG content in the copolymer membrane, as shown in Fig. 5.

The relationships between the ethanol concentration in the copolymer membranes for an aqueous solution of 10 wt% ethanol under pervaporation conditions and the PEG content in the membranes are shown in Fig. 5. The ethanol concentration in the polyBzMA membrane, without PEG, was 35.5 wt%. Ethanol was predominantly incorporated from an aqueous solution of 10 wt% ethanol into the polyBzMA membrane because the polyBzMA was hydrophobic. The ethanol concentrations in the CM-23 and CM-136 membranes decreased with increasing PEG content in the copolymer membrane. This is due to the high hydrophilicity of the PEG. The ethanol concentration in the CM-4 membrane was not as greatly affected by the PEG content in the copolymer membrane. This implies that the short PEG chain does not play a hydrophilic role. On the other hand, the ethanol concentration in CM-136 was significantly dependent on the PEG content in the copolymer. Water was preferentially incorporated from an aqueous solution of 10 wt% ethanol above about 20 wt% of the PEG content into the CM-136 membrane. The difference in the ethanol concentration in the membrane between the CM-4 and CM-136 membranes

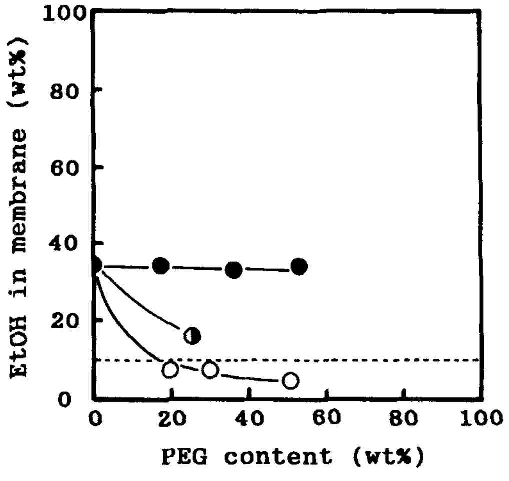


FIG. 5. Relationships between the ethanol concentration and the PEG content in the copolymer membranes. Feed solution and membranes are the same as in Fig. 3.

is due to differences in the fine structures of the two copolymers as described above. The CM-136 membrane has larger PEG microphases, and the CM-4 membrane has a structure in which the PEG is homogeneously dispersed. Water is predominantly sorbed in the PEG region. These results show that the copolymer membrane containing shorter PEG chains has a more homogeneous membrane structure in spite of the fact that the PEG content in each copolymer is the same.

Comparison of Fig. 3(b) and Fig. 5 suggests that the CM-4 membrane predominantly incorporates ethanol and permeates water from an aqueous solution of 10 wt% ethanol. This is due to the fact that ethanol has a stronger interaction with the CM-4 membrane than does water. Ethanol molecules are easily incorporated into the CM-4 membrane, but they don't diffuse much through the CM-4 membrane because of the strong interactions between the ethanol molecule and the CM-4 membrane. On the other hand, water molecules are not incorporated much in the CM-4 membrane but quickly diffuse through it because of their weak interaction with the membrane and their small molecular size. This behavior was also observed in such hydrophobic homogeneous polymer membranes as polystyrene (*4*), poly(vinyl chloride) (*5*), and poly(vinyl *p*-*tert*-butyl benzoate) (*6*). It may be a characteristic phenomenon for the hydrophobic polymer membrane that alcohol is predominantly incorporated into the membrane and water is preferentially permeated through the membrane. The CM-136 membrane preferentially incorporated water and predominantly permeated ethanol from an aqueous solution of 10 wt% ethanol above about 20 wt% of the PEG content. The reason for this result was described above.

The effect of the PEG content on the permeation rates for an aqueous solution of 10 wt% ethanol through the copolymer membranes by evapomeation and pervaporation is shown in Fig. 6. The permeation rates in evapomeation (Fig. 6a) increase with an increase of the PEG content in the copolymer membrane. This is due to the fact that the quantity of soft PEG increases with the introduction of PEG into the copolymer. The permeants are more easily permeated through the soft region than through the hard region of the membrane. The permeation rate for the copolymer membrane containing longer PEG chains was higher than that for the copolymer membrane containing shorter PEG chain. The former membrane had large PEG microphases which could easily transport the permeants.

The permeation rates for the CM-23 and CM-136 membranes in pervaporation (Fig. 6b) were higher than those in evapomeation. This is explained from the result in Fig. 3(c). The physical structures of these membranes in evapomeation are different from those in pervaporation. That is, these copolymer membranes are remarkably swollen by the feed solution

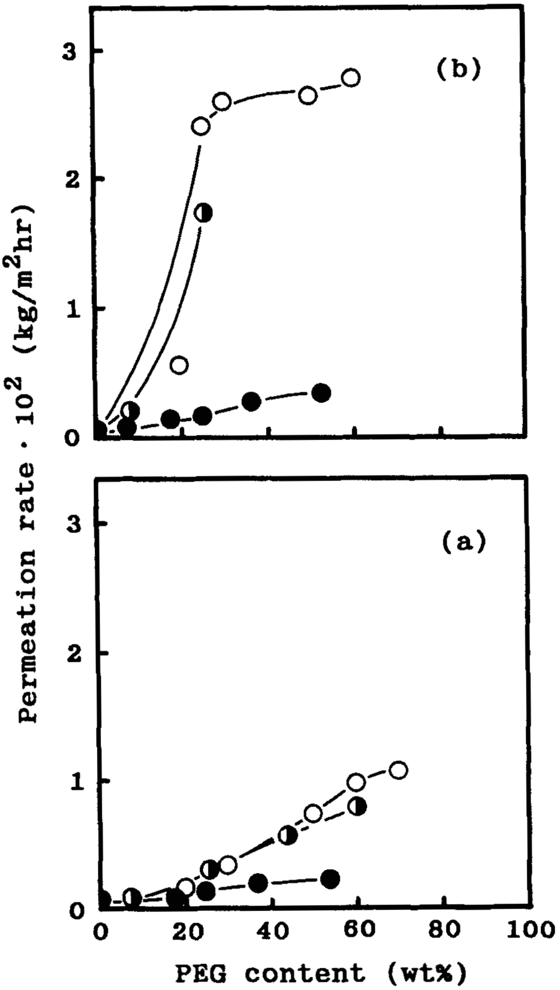


FIG. 6. Effect of PEG content in the copolymers on the permeation rates through the copolymer membranes in evapomeation (a) and pervaporation (b). Feed solution and membranes are the same as in Fig. 3.

under the pervaporation conditions because the membranes are in direct contact with the feed solution. In general, the permeation rate for a swollen membrane is high, but the CM-4 membrane was not swollen much, as shown in Fig. 3(c). Therefore, the differences between the permeation rates in evapomeation and pervaporation were very small, as shown in Figs. 6(a) and 6(b).

Effect of Feed Composition on Permselectivity of Aqueous Ethanol Solution

Figure 7 shows the relationships between the ethanol concentrations in the feed vapor and in the permeate through three different membranes (polyBzMA, CM-23, and CM-136) in evapomeation. The PEG contents in the CM-23 and CM-136 membranes were 43.8 and 50.9 wt%, respectively. These membranes preferentially permeated water from an aqueous ethanol solution. The ethanol concentration in the permeate through the polyBzMA membrane was the lowest of these three membranes. This result implies that the polyBzMA membrane has the highest selectivity for water. In other words, the selectivity for water through the copolymer membrane containing a longer PEG chain is lower. The CM-136 membrane has the largest PEG microphases; it may be easily swollen, and consequently the selectivity for water is lowered. On the other hand, since the polyBzMA membrane without PEG is dense, the selectivity is higher than that of other membranes.

The effect of ethanol concentration in the feed vapor on the separation factors of two kinds of copolymer membranes and the polyBzMA membrane in evapomeation is shown in Fig. 8(a). The separation factor through

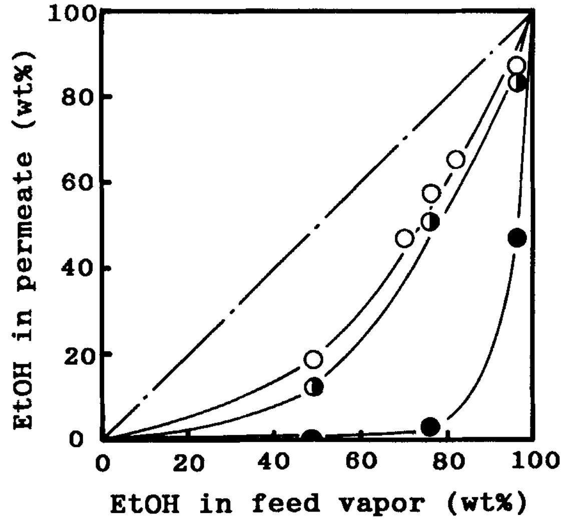


FIG. 7. Relationships between the ethanol concentration in the permeate and in the feed vapor through three different membranes in evapomeation. Feed solution: aqueous ethanol solutions (40°C), Membrane: (●) polyBzMA, (◑) CM-23 (43.8 wt% of PEG content), (○) CM-136 (50.9 wt% of PEG content).

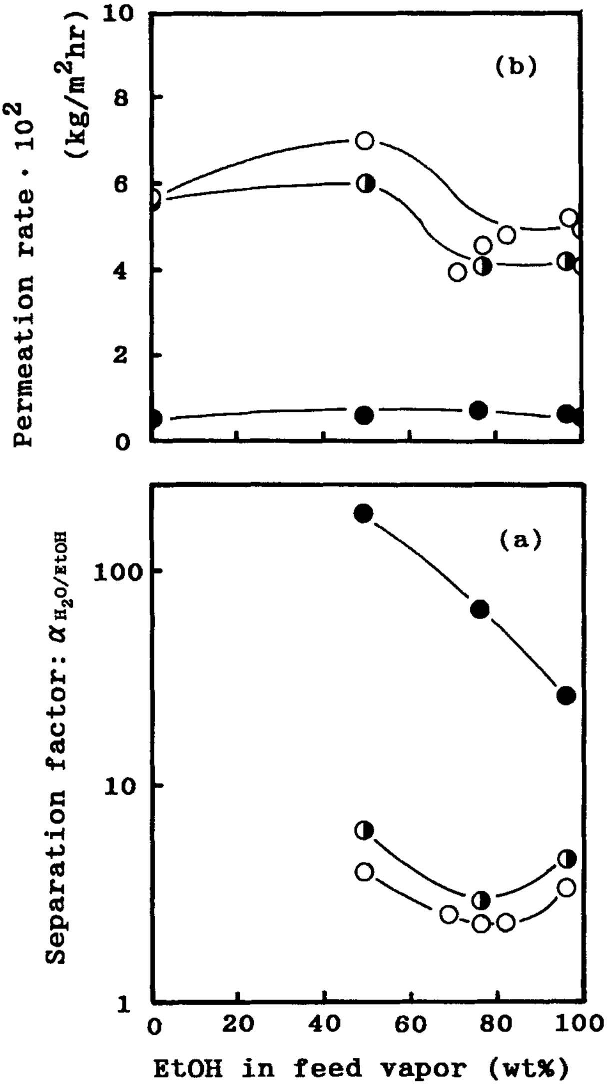


FIG. 8. Effect of the ethanol concentration in the feed vapor on the separation factor (a) and the permeation rate (b) through three different copolymer membranes in evapomeation. Membrane: Same as in Fig. 7.

the polyBzMA membrane is higher than those through the copolymer membranes. This is due to the dense structure of the polyBzMA membrane. However, the separation factor for this membrane decreased with an increase of the ethanol concentration in the feed vapor. This result is due to the fact that the polyBzMA membrane may be swollen by the ethanol vapor in the feed vapor because the polyBzMA membrane is hydrophobic.

The separation factors for the copolymer membranes had minimum values at about 70 wt% of ethanol concentration in the feed vapor. As predicted from the results in Fig. 10(c), this is attributed to the fact that the copolymer membranes are easily swollen at this feed vapor composition.

The relationships between the ethanol concentration in the feed vapor and the permeation rates through two kinds of copolymer membranes and the polyBzMA membrane in evapomeation are shown in Fig. 8(b). The permeation rate of the polyBzMA membrane was much lower than those of the copolymer membranes. The permeation rate of the CM-136 membrane was somewhat larger than that of the CM-23 membrane. The permeation rate of the polyBzMA membrane was apparently not much affected by the ethanol concentration in the feed vapor. In general, the permeation rate through a water-selective membrane (e.g., hydrophilic polymer membrane) decreases with an increase in the ethanol concentration in the feed solution. This is mainly due to decreasing swelling of the membrane and to a decrease in the number of water molecules incorporated into the membrane with an increase of the ethanol concentration in the feed solution. In the case of the polyBzMA membrane, the swelling of the membrane increases and the number of water molecules incorporated into the membrane decreases with the ethanol concentration in the feed solution. That is, the positive and negative factors for the permeation rate compensate each other. Consequently, the permeation rate of the polyBzMA membrane is not significantly influenced by the ethanol vapor concentration.

The permeation rates for the CM-23 and CM-136 membranes had maximum values at about 50 wt% of ethanol concentration in the feed vapor. The general behavior is that the permeation rate varies inversely with the separation factor. In this case, however, the ethanol concentration at the maximum value of the permeation rate did not agree with that at the minimum value of the separation factor in Fig. 8(a). Although the fact that both the permeation rate and separation factor are higher at about 50 wt% of ethanol concentration in the feed vapor is very good for the membrane performance of the separation process, the reason for this result is not clear at present.

Figure 9 shows the relationship between ethanol concentrations in the feed and in the permeate through the CM-136 membrane whose PEG content is 50.9 wt% in pervaporation. Ethanol was preferentially per-

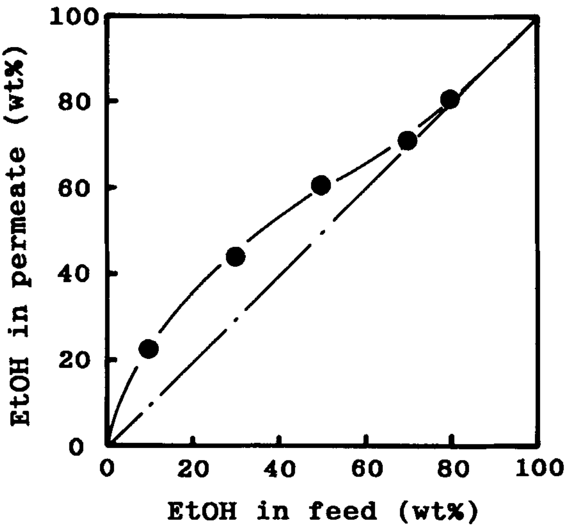


FIG. 9. Relationship between the ethanol concentration in the permeate and in the feed solution through the CM-136 membrane (50.9 wt% of PEG content) in pervaporation.

meated from aqueous ethanol solutions through the CM-136 membrane in pervaporation. It is clear that selectivity through the CM-136 membrane in pervaporation is different from that in evapomeation (Fig. 7). The CM-136 membrane, which has long PEG chains, was significantly swollen by the feed solution in pervaporation. Therefore, the skin layer of the membrane, as illustrated in Fig. 4, was destroyed by the feed solution. As a result of the destruction of the skin layer, the CM-136 membrane predominantly permeated ethanol from aqueous ethanol solutions because the relative volatility of the ethanol molecule on the surface of the permeation side of the membrane was higher than that of the water molecules.

Figure 10(a) shows the effect of the ethanol concentration in the feed on the separation factor for ethanol through the CM-136 membrane in pervaporation. The separation factor had a minimum value at about 70 wt% of ethanol concentration in the feed solution. In other words, at this feed solution composition, the preferential permeability for water is the highest in all ethanol concentration ranges of the feed solution. Figure 10(b) shows the permeation rate under this condition. The permeation rate for the CM-136 membrane had a maximum value at about 70 wt% of ethanol concentration in the feed solution. It was found that the ethanol concentration at the minimum value of the separation factor agrees with that at the maximum value of the permeation rate in pervaporation. The

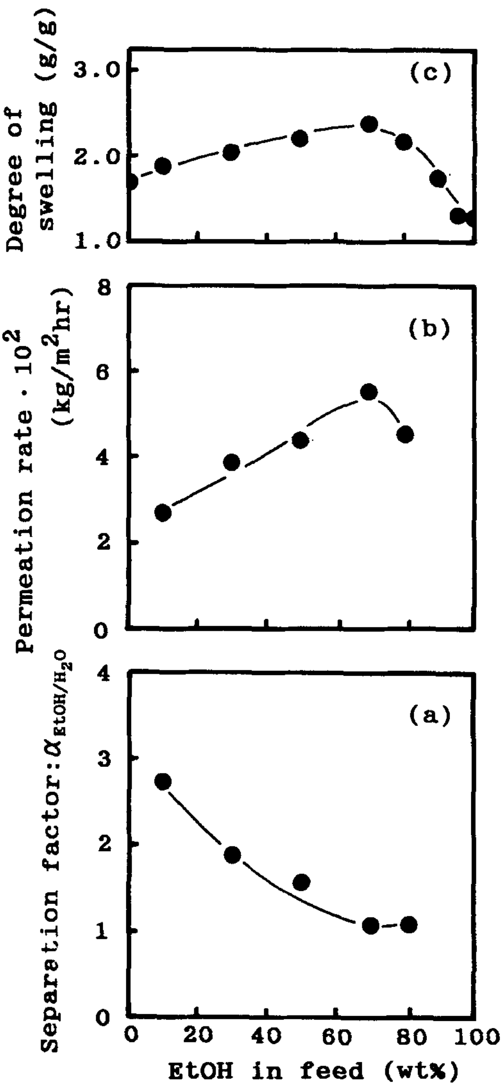


FIG. 10. Effect of ethanol concentration in the feed solution on the separation factor (a), the permeation rate (b) through the CM-136 membrane (50.9 wt% of PEG content) in pervaporation, and the degree of swelling of the CM-136 membrane (c).

result that the separation factor shows a minimum and the permeation rate a maximum is attributable to the fact that the CM-136 membrane is remarkably swollen by an aqueous solution of 70 wt% ethanol, as shown in Fig. 10(c). It is clear that the separation factor and the permeation rate for the CM-136 membrane in pervaporation are significantly dependent on the degree of swelling of the membrane by the feed solution.

Acknowledgment

This work was supported by The Science Research Promotion Fund of the Japan Private School Promotion Foundation.

REFERENCES

1. J. Neel, P. Aptel, and R. Clement, *Desalination, 53,* 297 (1985).
2. T. Uragami and M. Saito, *Sep. Sci. Technol., 24,* 541 (1989).
3. T. Uragami, M. Saito, and K. Takigawa, *Makromol. Chem., Rapid Commun., 9,* 361 (1988).
4. T. Uragami and T. Morikawa, *Makromol. Chem., 190,* 399 (1989).
5. T. Uragami, T. Morikawa, and H. Okuno, *Polymer, 30,* 1117 (1989).
6. H. Okuno, M. Tsuchioka, and T. Uragami, *Sen-i Gakkaishi, 46,* 367 (1990).
7. H. Okuno and T. Uragami, *Polymer,* To Be Published.
8. T. Uragami and K. Takigawa, *Ibid., 31,* 668 (1990).
9. J. P. Kennedy and C. Y. Lo, *Polym. Bull., 13,* 343 (1985).
10. Y. Kawakami, K. Inagaki, Y. Yamashita, and L. J. Mathias, *J. Polym. Sci., Part B, 19,* 629 (1981).
11. G. G. Cameron and M. S. Chisholm, *Polymer, 26,* 437 (1985).
12. Y. Nagase, J. Ochiai, K. Matsui, and M. Uchikura, *Polym. Commun., 29,* 10 (1988).
13. Y. Nagase, A. Naruse, and K. Matsui, *Polymer, 30,* 1931 (1989).
14. S. Kimura and T. Nomura, *Membrane, 8,* 177 (1983).
15. T. Masuda, B.-Z. Tang, and T. Higashimura, *Polym. J., 18,* 565 (1986).
16. S. Yamada, *Membrane, 6,* 168 (1981).

Received by editor October 21, 1991