Characteristics of permeation and separation of aqueous alcohol solutions through crosslinked pullulan membranes

Hiroshi Okuno
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

and Tadashi Uragami*
Chemical Branch, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

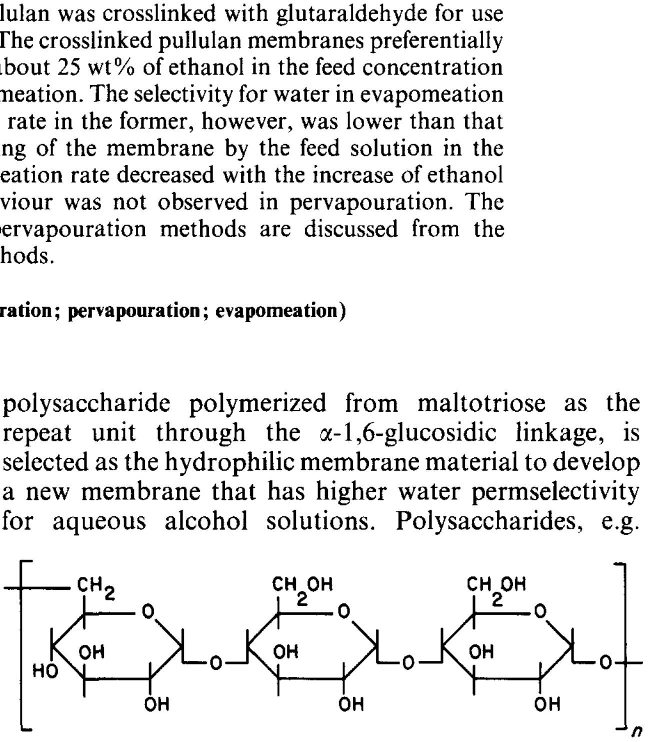
(Received 28 August 1990; revised 18 February 1991; accepted 20 March 1991)

The permeation and separation characteristics of aqueous alcohol solutions through crosslinked pullulan membranes were investigated in pervapouration and evapomeation. Pullulan is a highly hydrophilic polysaccharide that is easily soluble in water, so that pullulan was crosslinked with glutaraldehyde for use as a separation membrane for aqueous alcohol solutions. The crosslinked pullulan membranes preferentially permeated water from aqueous ethanol solutions above about 25 wt% of ethanol in the feed concentration in pervapouration and below 90 wt% of ethanol in evapomeation. The selectivity for water in evapomeation was higher than that in pervapouration. The permeation rate in the former, however, was lower than that in the latter. These results were attributed to the swelling of the membrane by the feed solution in the latter method. In evapomeation, the selectivity and permeation rate decreased with the increase of ethanol concentration in the feed vapour. However, such behaviour was not observed in pervapouration. The different results between the evapomeation and the pervapouration methods are discussed from the viewpoint of the structure of the membrane in both methods.

(Keywords: pullulan; membrane; aqueous alcohol solution; separation; pervapouration; evapomeation)

INTRODUCTION

Pervapouration is a membrane separation technique that is useful in separating organic liquid mixtures, such as azeotropic mixtures, close-boiling-point mixtures and so on[1]. In pervapouration, the membrane is often swollen by the feed solution because the polymer membrane directly contacts with the feed solution, and consequently the selectivity decreases remarkably. In attempts to solve this problem, many studies have been carried out, and we devised an 'evapomeation' method[2], which is a new membrane separation technique. In evapomeation, the membrane is some distance from the feed solution; that is, the vapour from the feed solution is supplied to the membrane, so that it is not swollen so much by the feed mixture. We have studied the permeation and separation characteristics for aqueous alcohol solutions through various polymer membranes by evapomeation[2–7]. The selectivities for aqueous alcohol solutions in evapomeation were generally higher than those in pervapouration. Especially, in hydrophilic polymer membranes such as alginic acid[2], chitosan[3] and crosslinked chitosan[7], a great difference was found in selectivity between pervapouration and evapomeation[2,3,7]. A hydrophilic polymer is a good material for a water-selective membrane unless the membrane is swollen remarkably by the feed solution. Recently, many polymer membranes have been prepared in order to extract water efficiently from aqueous alcohol solutions[8–12]. In this paper, pullulan (**1**), which is a polysaccharide polymerized from maltotriose as the repeat unit through the α-1,6-glucosidic linkage, is selected as the hydrophilic membrane material to develop a new membrane that has higher water permselectivity for aqueous alcohol solutions. Polysaccharides, e.g. cellulose acetate, alginic acid, chitosan and so on, have previously been used for membrane materials. The characterization and application[13,14] of pullulan have been studied by many workers. But pullulan has not been used as a membrane for the separation of organic liquid mixtures. This paper deals with the permeation and separation characteristics of aqueous alcohol solutions through the hydrophilic crosslinked pullulan membrane in the pervapouration and evapomeation methods.



1

EXPERIMENTAL

Membrane

Pullulan powder (PF-20) was a commercial product from Hayashibara Biochemical Laboratories Inc. and had a molecular weight of about 2 × 10^5. A solution of

---

* To whom correspondence should be addressed

0032-3861/92/071459–05

pullulan powder (1.0 g) in water (99 ml) was stirred for about 5 h. An aqueous solution of 25% glutaraldehyde (1.0 ml) and a trace of magnesium chloride were added to this solution. Crosslinked pullulan (CPL) membranes were prepared by casting this mixed solution on a rimmed glass plate at 25°C for 4 days to evaporate water completely, and furthermore annealing at 120°C for 4 h in an oven in order to make them insoluble in water. The thickness of these membranes was about 15 μm.

The reagents used in this study were of commercial grade.

Permeation measurements

The pervapouration and evapomeation measurements were carried out under the following conditions: permeation temperature 40°C, pressure of permeation side 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. The pervapouration and evapomeation apparatuses used in this study were reported in an earlier paper[6]. The compositions of the feed mixture and permeate were determined by gas chromatography (Shimadzu GC-9A).

The separation factor ($\alpha_{B/A}$) of the pervapouration and evapomeation was computed by the equation:

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

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

The permeation rates in both pervapouration and evapomeation were determined in terms of 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 then weighed. The dry membrane was immersed into an aqueous alcohol 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 of the membrane (DS) was calculated from the equation:

$$DS = W_S/W_D \qquad (2)$$

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

Composition of solution in membrane

The dry membrane was immersed into an aqueous alcohol solution or was exposed to its vapour in a sealed vessel at 40°C for 24 h. Then the membrane was taken out of the vessel, and wiped quickly with filter paper. The aqueous alcohol solution adsorbed in the membrane was completely vaporized under reduced pressure and was collected in a cold trap[5]. The composition adsorbed in the membrane was determined by gas chromatography.

RESULTS AND DISCUSSION

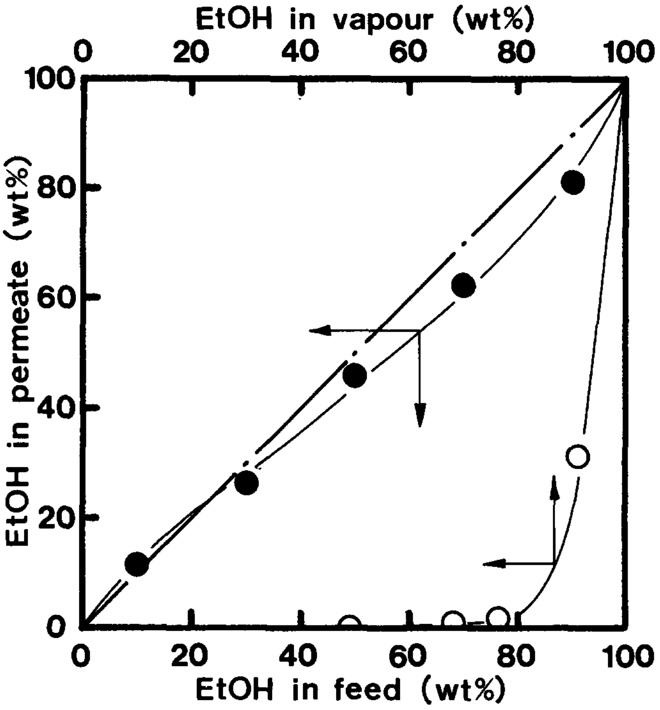


Figure 1 Relationships between the compositions of aqueous ethanol solution in the feed solution or feed vapour and in the permeate through the CPL membrane in pervapouration (●) and evapomeation (○)

The relationships between the composition of aqueous ethanol solution in the permeate through the CPL membrane in pervapouration and evapomeation and the feed composition or feed vapour composition are shown in *Figure 1*. In pervapouration, an equisorptive composition, at which separation cannot be observed, appeared at about 25 wt% of ethanol concentration in the feed solution. Below this point, the ethanol concentration in the permeate was somewhat higher than that in the feed solution. This result was unexpected because hydrophilic polymer membranes, in general, predominantly permeate water from an aqueous solution. It is dependent on too high hydrophilicity of the CPL membrane. Namely, the CPL membrane was swollen remarkably by water because the membrane directly contacted with the feed solution in pervapouration. This swelling of the membrane introduced a reduction of the separation capability, which is contrary to the purpose in this study. At a high concentration of water in the feed solution (below 25 wt% of ethanol concentration), the higher relative volatility of ethanol molecules on the permeation side of the interface of the CPL membrane mainly affects the permselectivity in pervapouration because of the significant swelling of the membrane. On the other hand, at a low concentration of water, the selectivity for water appeared because the membrane was not swollen so much.

In evapomeation, water was preferentially permeated through the CPL membrane below 90 wt% of ethanol in the feed concentration and the concentration of ethanol in the permeate was lower than that in pervapouration. The equisorptive composition disappeared. These results are attributed to the fact that the CPL membrane was not swollen so much by an aqueous ethanol solution in evapomeation because the membrane did not contact with the feed solution and was exposed to the feed vapour. Therefore, there is a difference between the physical structure of the membrane in both pervapouration and evapomeation in spite of the fact that the chemical

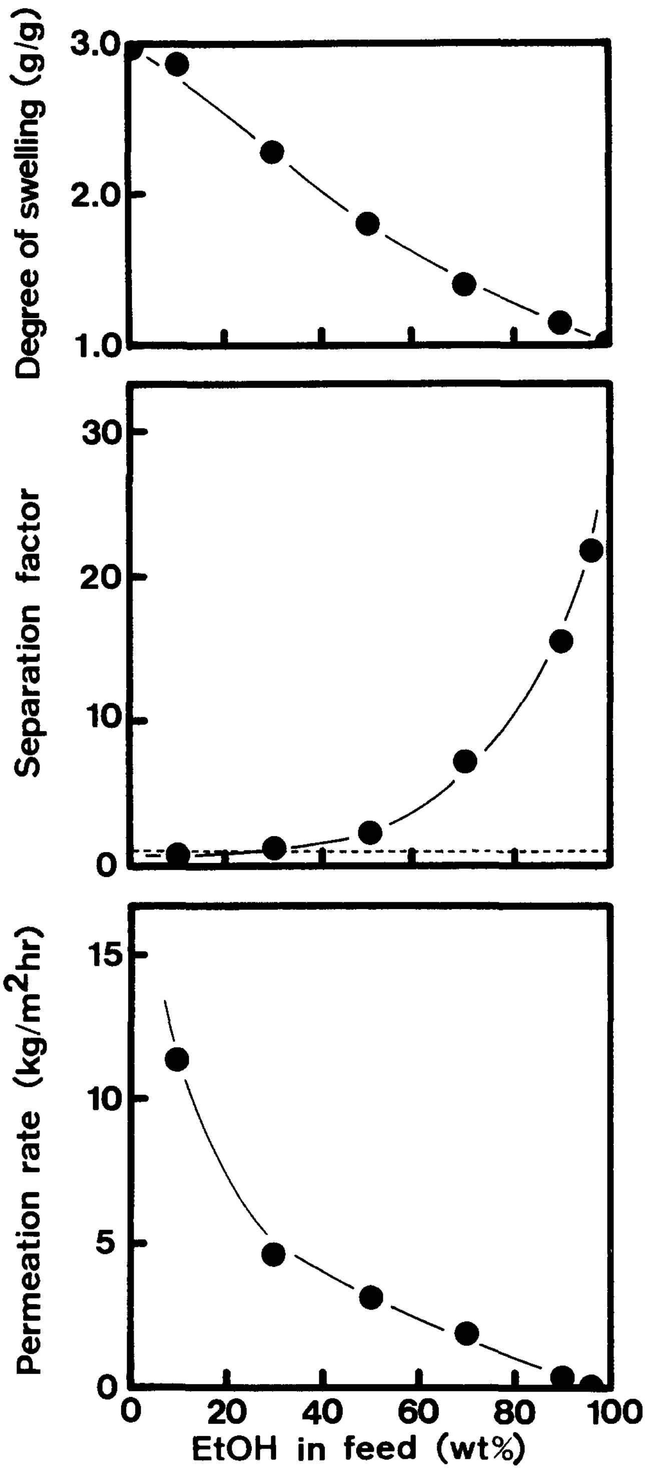


Figure 2 Effect of ethanol concentration in the feed solution on the permeation rate and separation factor through the CPL membrane, and the degree of swelling of the CPL membrane by aqueous ethanol solution in pervapouration

structure of the membrane in pervapouration is the same as that in evapomeation. Consequently, the CPL membrane in pervapouration was swollen by the feed solution, but in evapomeation was not swollen so much by the feed vapour. It is understood that the CPL membrane has a high water selectivity from an aqueous ethanol solution when the membrane was not swollen by water in the feed solution in evapomeation.

Figure 2 shows the effect of the ethanol concentration in the feed solution on the permeation rate, separation factor and degree of swelling of the CPL membrane in pervapouration. The dotted line, on which the feed mixture is not separated at all, shows a separation factor of unity. The separation factor at 10 wt% of ethanol in the feed solution is less than unity. This implies that ethanol was predominantly permeated from an aqueous ethanol solution of 10 wt% of ethanol through the CPL membrane as described above. The permeation rate decreased and the separation factor increased with the increase in the ethanol concentration in the feed solution. These results are mainly caused by the decrease in the swelling of the CPL membrane by an aqueous ethanol solution with increase of the ethanol content in the feed solution as shown at the top of *Figure 2*. These phenomena are general in a binary liquid system in pervapouration. The decrease of the separation capability and the increase of the permeability are due to plasticization of the membrane by the adsorption of permeants. From the above discussion, it is found that a highly hydrophilic polymer membrane does not necessarily show high selectivity for water from an aqueous liquid mixture.

Figure 3 shows the effect of the ethanol concentration in the feed vapour on the permeation rate and separation

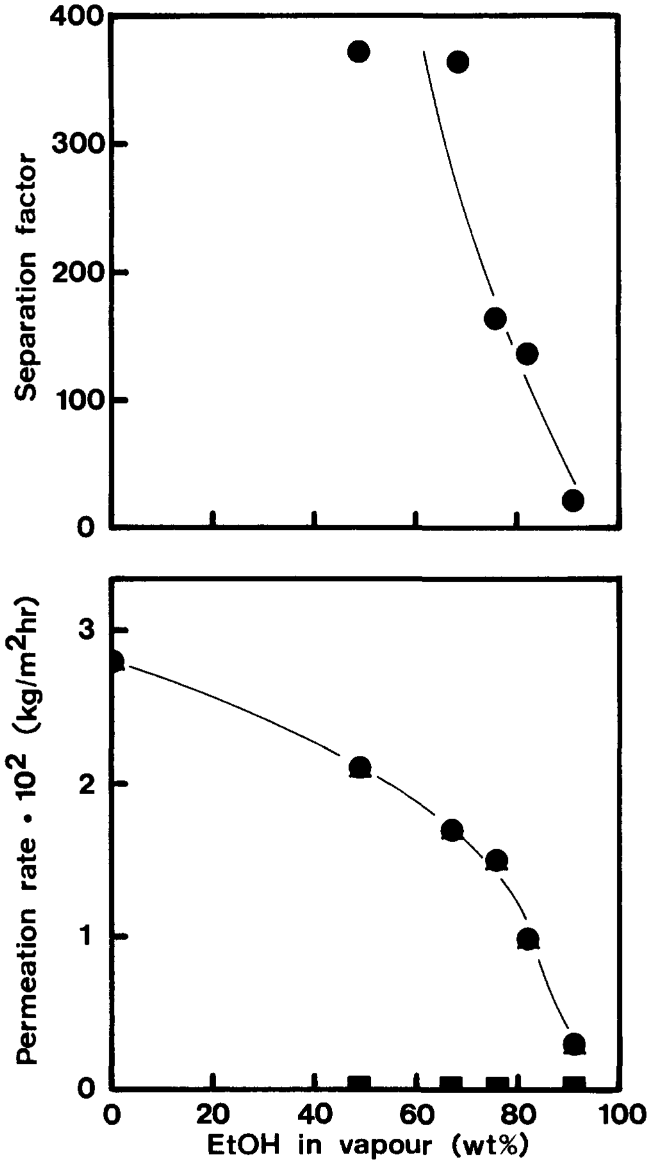


Figure 3 Effect of ethanol concentration in the feed vapour on the permeation rate (total (●), water (▲) and ethanol (■)) and separation factor through the CPL membrane in evapomeation

Table 1 The permeation rates (Q) and separation factors (α) for various aqueous alcohol solutions through the CPL membrane in evapomeation

Alcohol concentration in feed (wt%)	Methanol		Ethanol		1-Propanol		2-Propanol	
	$Q \times 10^2$ (kg m^{-2} h^{-1})	α	$Q \times 10^2$ (kg m^{-2} h^{-1})	α	$Q \times 10^2$ (kg m^{-2} h^{-1})	α	$Q \times 10^2$ (kg m^{-2} h^{-1})	α
0	2.80	–	2.80	–	2.80	–	2.80	–
10	1.97	152	2.12	372	2.31	1074	2.01	5710
30	2.23	136	1.69	368	0.86	3012	1.05	3795
50	1.72	50	1.47	163	1.13	1267	0.97	5280
70	membrane breakage		0.98	136	0.97	1074	1.22	930
90	membrane breakage		0.30	22	0.36	138	0.44	281
100	membrane breakage		membrane breakage		0.18	–	0.12	–

factor in evapomeation. The total permeation rate decreased with increasing ethanol content in the feed vapour. The permeation rate for water had almost the same value as the total permeation rate. The fact that the total permeation rate in evapomeation decreases also was found in pervapouration in *Figure 2*. It seems that the decrease of the total permeation rate with the ethanol concentration in evapomeation is not due to the same reason as that in pervapouration, because the CPL membrane is not swollen so much by the feed vapour in evapomeation. The result in evapomeation is due to the fact that the amount of water molecules adsorbed into the CPL membrane, which selectively permeates water molecules, decreases as the ethanol concentration in the feed vapour is increased. The permeation rate in evapomeation was remarkably small in comparison with that in pervapouration. This is attributed to significantly small swelling of the CPL membrane by water in evapomeation. The separation factor in evapomeation was much larger than that in pervapouration. Higher values of the separation factors in evapomeation resulted from retaining the dense structure of the CPL membrane in evapomeation as described above. In evapomeation, it was observed that separation factors decrease with the increase of ethanol concentration in the feed vapour. This tendency differs greatly from that in pervapouration. Above 96 wt% of ethanol concentration in the feed vapour, the CPL membrane broke after the steady state of permeation was reached. To find the reason for this, experiments were carried out using various aqueous alcohol solutions, such as methanol, 1-propanol and 2-propanol, in evapomeation.

Table 1 lists the permeation rates and separation factors for aqueous alcohol solutions, such as methanol, ethanol, 1-propanol and 2-propanol, through the CPL membrane in evapomeation. In all aqueous alcohol solutions, water was preferentially permeated through the CPL membrane in evapomeation. In the methanol/water mixture, the CPL membrane was broken above 70 wt% of methanol in the feed vapour during the steady state of permeation. In the 1-propanol/water and 2-propanol/water mixtures, however, the durability of the CPL membrane was satisfactory for all the feed vapour compositions in the mixtures. From the results in *Table 1*, it was found that the CPL membrane was broken by lower alcohol solutions (methanol and ethanol) at high concentration in the feed vapour. The reason for these results is not understood at the present time, but it seems phenomenally that the CPL membrane was remarkably shrunk by methanol or ethanol vapour in evapomeation. It may be attributed to a strong dehydration ability of methanol and ethanol for the CPL membrane.

The separation factor decreased with increase of alcohol concentration in the feed vapour as listed in *Table 1*. A lowering of the separation factor $\alpha_{B/A}$ is phenomenally due to the following three causes: (1) the permeation rate for component B is constant and that for component A increases; (2) the permeation rate for component B decreases and that for component A is constant; or (3) the permeation rate for component B decreases and that for component A increases. The permeation rates for water and ethanol through the CPL membrane in evapomeation are shown at the bottom of *Figure 3*. As can be seen from *Figure 3*, the permeation rates for water decrease remarkably with increase of the ethanol content in the feed vapour, but those for ethanol are almost zero regardless of the feed vapour composition. Therefore, the results in evapomeation in this study correspond to case (2) above. The permeation rate for ethanol, in general, increases as the ethanol concentration in the feed vapour increases. It is presumed that the permeation rate for ethanol in evapomeation is apparently constant on account of the shrinkage of the CPL membrane with increasing ethanol concentration in the feed vapour. The permeation of the ethanol molecule is more significantly affected by membrane shrinkage than that of the water molecule because of the larger molecular size of ethanol.

Table 2 summarizes the concentrations of ethanol sorbed into the CPL membrane and the ethanol concentrations in permeate in pervapouration and evapomeation. It is clear that the ethanol concentration in the CPL membrane in evapomeation was lower than that in pervapouration. This result indicates that the solubility selectivity for water on the feed side of the interface of the CPL membrane in evapomeation is higher than that in pervapouration. In evapomeation, the CPL membrane is not swollen so much by the feed vapour, so that it is difficult for an ethanol molecule, having a larger molecular size, to be incorporated into the CPL membrane. On the other hand, in pervapouration the CPL membrane is remarkably swollen by the feed solution, and ethanol molecules, which have a weaker affinity for the CPL membrane than water molecules, can be more easily absorbed with water molecules into the CPL membrane. Consequently, it is also considered that preferential adsorption of water in evapomeation greatly affects the high selectivity for aqueous ethanol solutions.

In *Table 2*, it is found that the separation mechanism

Table 2 The ethanol concentration in the CPL membrane and in the permeate as a function of the ethanol concentration in the feed in pervapouration and evapomeation

Ethanol in feed (in vapour)	Pervapouration		Evapomeation	
(wt%)	Ethanol in membrane (wt%)	Ethanol in permeate (wt%)	Ethanol in membrane (wt%)	Ethanol in permeate (wt%)
0	0	0	0	0
10 (49.2)	5.8	12	1.7	0.3
30 (68.6)	8.6	27	1.8	0.6
50 (75.9)	18	46	2.2	1.9
70 (81.7)	17	63		3.2
90 (91.2)	1.4	82	0.9	32
100	100	100	100	100

of an aqueous ethanol solution through the CPL membrane in evapomeation is different from that in pervapouration. In general, water has a higher diffusivity through a polymer membrane than ethanol in a binary mixture of ethanol/water because of the smaller size of water molecules. So the ethanol concentration in the permeate will be lower than that in the CPL membrane. The evapomeation result in *Table 2* shows the lower ethanol concentration in the permeate than that in the CPL membrane. Namely, high selectivity for water in evapomeation results from the predominant solubility of water into the CPL membrane and preferential diffusivity of water through the CPL membrane. On the other hand, in pervapouration the ethanol concentration in the CPL membrane was lower than that in the feed solution. This suggests that water was preferentially incorporated into the CPL membrane. The ethanol concentration in the permeate was higher than that in the CPL membrane. The result in pervapouration differs from that in evapomeation. In pervapouration, in spite of the fact that the diffusivity of ethanol through the CPL membrane is lower than that of water, the high ethanol concentration in the permeate is mainly caused by the desorption of ethanol molecules, which is governed by the interaction with the membrane and the relative volatility. The CPL membrane thus has a different mechanism of permselectivity for aqueous ethanol solution between pervapouration and evapomeation. This is due to the fact that the physical structure of the CPL membrane in the above two permeation methods is different.

CONCLUSIONS

The following results were obtained by studying the permselective characteristics for aqueous alcohol solutions through the crosslinked pullulan membrane by pervapouration and evapomeation.

(1) The crosslinked pullulan membrane preferentially permeated water from aqueous alcohol solutions in evapomeation. In pervapouration, ethanol was predominantly permeated from aqueous ethanol solution below about 25 wt% of ethanol in the feed solution. The difference of selectivity in pervapouration and in evapomeation was mainly due to the difference in physical structure with the swelling of the CPL membrane.

(2) The permeation rates through the crosslinked pullulan membrane in pervapouration were much larger than those in evapomeation. The separation factors in the former were lower than those in the latter. These results were explained in terms of the swelling of the CPL membrane.

(3) Water was preferentially incorporated into the crosslinked pullulan membrane in both pervapouration and evapomeation. Especially, in pervapouration the concentration of water adsorbed in the crosslinked pullulan membrane was higher than that in the permeate.

(4) The selectivity for water from aqueous alcohol solutions through the crosslinked pullulan membrane in evapomeation was governed by preferential dissolution of water molecules into the membrane and diffusion of water through the membrane. In pervapouration, it was significantly influenced by the desorption of ethanol molecules on the permeation side of the interface of the membrane.

REFERENCES

1 Neel, J., Aptel, P. and Clement, R. *Desalination* 1985, **53**, 297
2 Uragami, T. and Saito, M. *Sep. Sci. Technol.* 1989, **24**, 541
3 Uragami, T., Saito, M. and Takigawa, K. *Makromol. Chem., Rapid Commun.* 1988, **9**, 361
4 Uragami, T. and Morikawa, T. *Makromol. Chem.* 1989, **190**, 399
5 Uragami, T., Morikawa, T. and Okuno, H. *Polymer* 1989, **30**, 1117
6 Okuno, H., Tsuchioka, M. and Uragami, T. *Sen-i Gakkaishi* 1990, **46**, 367
7 Uragami, T. and Takigawa, K. *Polymer* 1990, **31**, 668
8 Reineke, C. E., Jagodzinski, J. A. and Denslow, K. R. *J. Membr. Sci.* 1987, **32**, 207
9 Xu, Y. F. and Huang, R. Y. M. *J. Appl. Polym. Sci.* 1988, **36**, 1121
10 Hirotsu, T., Ichimura, K., Mizoguchi, K. and Nakamura, E. *J. Appl. Polym. Sci.* 1988, **36**, 1717
11 Mochizuki, A., Amiya, S., Sato, Y., Ogawara, H. and Yamashita, S. *J. Appl. Polym. Sci.* 1990, **40**, 633
12 Mochizuki, A., Amiya, S., Sato, Y., Ogawara, H. and Yamashita, S. *J. Appl. Polym. Sci.* 1990, **40**, 385
13 Kato, T., Okamoto, T., Tokuya, T. and Takahashi, A. *Biopolymers* 1982, **21**, 1623
14 Kamiya, S., Onishi, Y. and Yamauchi, A. *J. Japan. Contact Lens Soc.* 1985, **27**, 242