

# Modified polysulphone membranes: 1. Pervaporation of water/alcohol mixtures through modified polysulphone membranes having methyl ester moiety\*

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Membranes were prepared from modified Udel P-3500 polysulphone having methyl carboxylate groups, of which the degree of substitution ranged from 0.05 to 1.90 ester groups per repeat unit. The membranes showed permselectivity towards water in the pervaporation of aqueous alcohol solutions.

(Keywords: pervaporation; membranes; permselectivity; functionalized polysulphones; chemical modification)

## INTRODUCTION

Polysulphone is widely used for synthetic polymeric membranes, particularly in ultrafiltration processes and as porous backing supports for thin-film composite reverse osmosis membranes. It is a high-performance thermoplastic with excellent mechanical strength and film-forming quality. However, its relatively hydrophobic nature limits its utility as a material for water-permeable pervaporation membranes. The introduction of polar functional moieties onto the polymer chain increases the hydrophilicity, allowing greater water permeability.

Polysulphone has been modified in a number of ways with the aim of obtaining membrane materials having higher performance<sup>1-17</sup>. We know, however, of only a few examples of modification of polysulphone as membrane materials for pervaporation<sup>10,12</sup>. We have been investigating novel membrane materials for water-permeable pervaporation by using hydrogen-bonding interaction<sup>18,19</sup> or ion-dipole interaction<sup>20,21</sup> as a specific interaction to recognize the water molecule with high selectivity.

In continuation of these studies, we report the pervaporation of various water/alcohol mixtures, especially water/ethanol solutions, through modified polysulphone membranes having methyl ester moiety as a hydrophilic site.

## EXPERIMENTAL

### Materials

Udel P-3500 was obtained from Amoco Performance Products.

Modification of polysulphone Udel P-3500 to introduce methyl ester moieties onto the polymer consists of three steps shown in *Scheme 1*, as reported previously<sup>11</sup>: (1) lithiation with *n*-butyllithium; (2) carboxylation with carbon dioxide; (3) esterification with iodomethane. Five polymers containing 0.05, 0.29, 1.05, 1.43 and 1.90 methyl carboxylate groups per repeat unit (designated ME005, ME029, ME105, ME143 and ME190) were prepared.

Various alcohols were purified in the usual manner<sup>22</sup>. Deionized water was used.

### Preparation of membranes

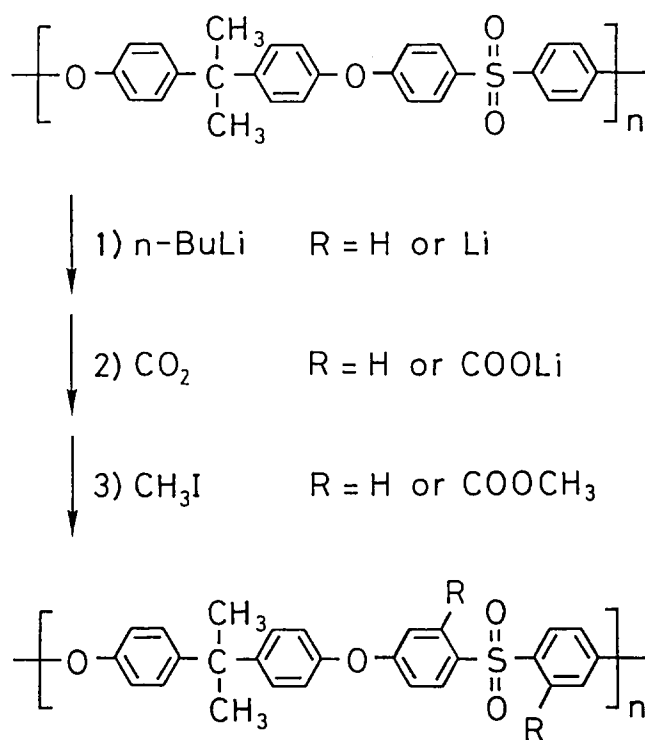
All membranes were prepared by casting from chloroform solution (50 g dm<sup>-3</sup>). The solutions were cast onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at ambient temperature overnight. The resulting membranes were dried at 45°C for 8 h and ranged in thickness from 7 to 12 μm.

### Determination of membrane polarity

Membrane polarity in terms of Dimroth's solvent polarity value  $E_T(25^\circ\text{C})$  was measured according to the method described previously, using 1-octadecyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2*H*-benzopyran) as the indicator<sup>23</sup>. A 500 W xenon lamp was used as the

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Scheme 1

light source. The membrane was illuminated with u.v. light using Corning colour filter no. 7-54. Absorption spectra were measured with a Spectro Multichannel Photo Detector MCPD-110A (Photal).

#### Pervaporation

Permeation of water/alcohol mixture through the membrane was carried out as described previously<sup>24</sup>. The membrane area in contact with liquid was 10.5 cm<sup>2</sup>. The downstream pressure was maintained at 400 Pa (3.0 mmHg).

The flux was determined by weighing the permeate sample collected in a cold trap. The separation factor  $\alpha$  was calculated by determining the composition of the feed liquid mixtures and the permeates. The composition analysis was carried out on a Shimadzu GC-8A gas chromatograph equipped with a 3.1 m column packed with poly(ethylene glycol) PEG 6000 on Shimalite TPA. The separation factor is defined by:

$$\alpha = (Y_{\text{water}}/Y_{\text{alcohol}})/(X_{\text{water}}/X_{\text{alcohol}}) \quad (1)$$

where  $Y_i$  is the weight fraction of the component  $i$  in the permeate and  $X_i$  that in the feed.

#### Spectroscopic measurement

I.r. spectra of Udel P-3500 and ME190 in chloroform and in chloroform containing either water or ethanol were measured at ca. 27°C using a Nicolet 20 DXB FTi.r. spectrometer. The polymer concentrations were 1.75 g dm<sup>-3</sup> for Udel P-3500 solution and 2.18 g dm<sup>-3</sup> for ME190 solution. Concentrations of water and ethanol were adjusted to be 4.24 × 10<sup>-2</sup> mol dm<sup>-3</sup> for Udel P-3500/chloroform solution and 4.14 × 10<sup>-2</sup> mol dm<sup>-3</sup> for ME190/chloroform solution, respectively. The molar ratio of water or ethanol to that of Udel P-3500 in the solution was 10.7 and that of ME190 system was 10.5.

#### Measurement of degree of swelling

A sample of membrane that had been dried to constant weight ( $W_d$ ) was immersed in water or ethanol at 25°C. When the sorption equilibrium was reached, the sample was weighed rapidly after blotting free surface liquid. The degree of swelling of membranes was defined by:

$$\text{Degree of swelling} = 100 \times (W_s - W_d)/W_d \quad (2)$$

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

## RESULTS AND DISCUSSION

#### Characterization of membranes

Membrane polarity  $E_T(25^\circ\text{C})$ , together with the wavelength of the absorption maximum of the indicator, and the degree of swelling for water and ethanol, are summarized in Table 1.

Membrane polarity increased with an increase in the methyl ester content in the polymer.

From the data on the degree of swelling, these membranes showed a tendency to swell in both ethanol and water. This suggests that pervaporation phenomena in the present study were highly dependent on the internal concentration both of water and of ethanol. This speculation is tested in the section 'Permeation mechanism of water/ethanol mixture'.

#### Pervaporation of water/ethanol mixture

Figure 1 shows results of the pervaporation experiments, where the weight fraction of water in the permeate is plotted as a function of water fraction in the feed. Figure 2 shows the separation factor ( $\alpha$ ) and the total flux values plotted versus the weight fraction of water in the feed. All six membranes, both parent polysulphone membrane and modified polysulphone membranes having methyl ester group, are preferentially permeable to water. The full curves in Figures 1 and 2 are calculated according to equations (8), (13) and (15), and associated pervaporation parameters summarized in Table 2. The method of calculation is described in detail in the next section.

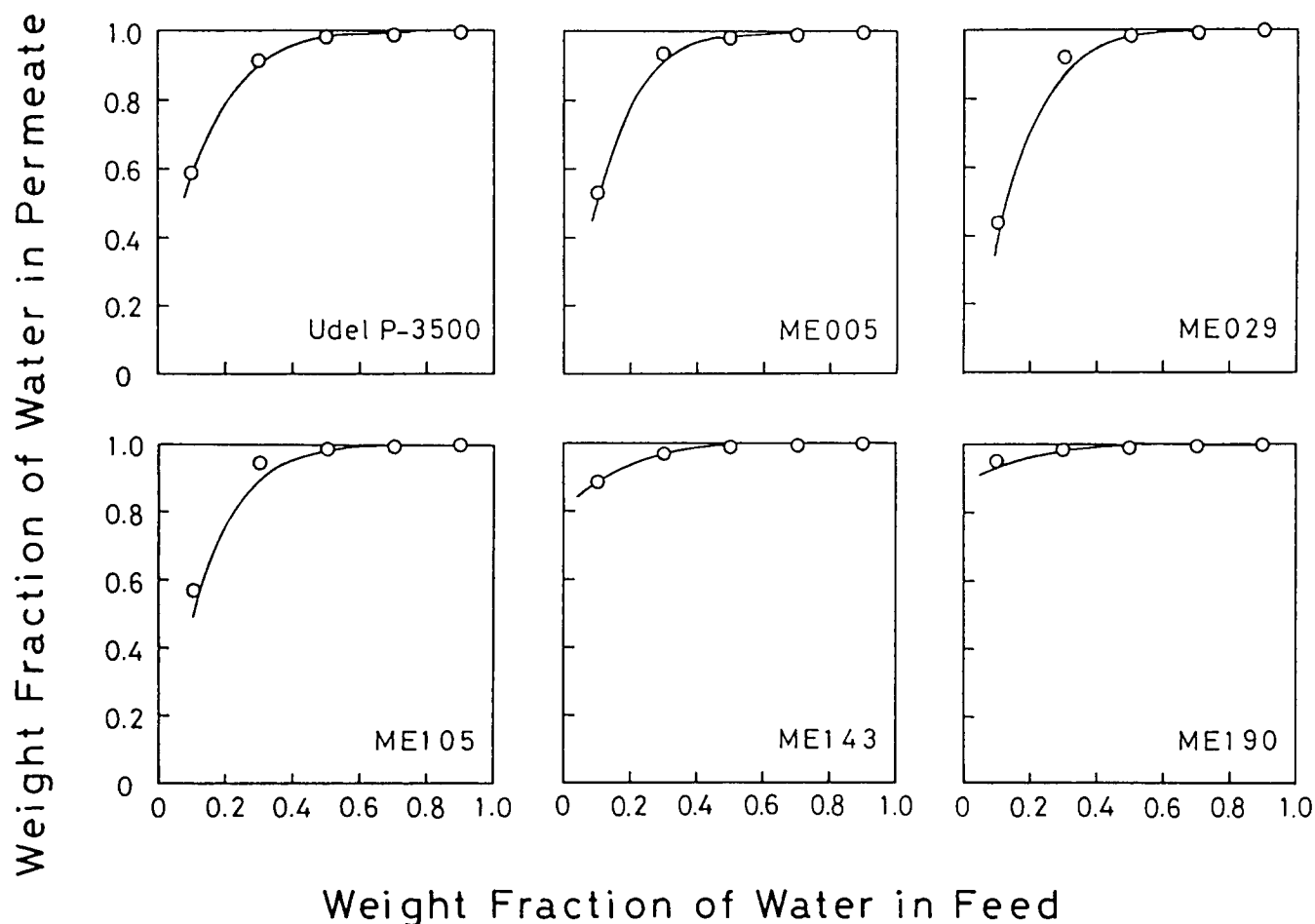
In Figure 3, the separation factor and the total flux are plotted versus the degree of substitution of methyl ester, for the feed water mole fraction of 0.50. The selectivity towards water tended to increase with the increase in degree of substitution, while the flux showed a tendency to decrease. Thus, the introduction of the methyl ester moiety onto the polymer improved the dehydration capacity of the membrane by raising its permselectivity towards water.

Table 1 Characterization of membranes

Polymer membrane	$\lambda$ (nm)	$E_T(25^\circ\text{C})^a$ (kcal mol <sup>-1</sup> )	Degree of swelling <sup>b</sup>	
			In water	In ethanol
Udel P-3500	599	33.2	3.4	10.1
ME005	598	33.6	3.0	10.1
ME029	598	33.6	3.8	13.4
ME105	596	34.3	1.6	9.2
ME143	594	35.1	1.3	8.6
ME190	594	35.1	0.8	8.2

<sup>a</sup>  $E_T(25^\circ\text{C}) = (688.3 - \lambda_{\text{max}}^{\text{vis}})/2.69$

<sup>b</sup> Degree of swelling = 100 × ( $W_s - W_d$ )/ $W_d$ , where  $W_d$  = weight of dry membrane and  $W_s$  = weight of solvent-swollen membrane



**Figure 1** Effect of feed composition on the separation of aqueous ethanol solution: downstream pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C; (—) calculated, according to equations (8) and (13), and using the coefficient numerical values summarized in Table 2

**Table 2** Transport parameters applicable for the system water/ethanol mixture and polysulphone and methyl ester polysulphone membranes<sup>a</sup>

Polymer membrane	$10^6 l$ (m)	$10^{13} P_{0,E}$ ( $m^2 h^{-1}$ )	$10^{13} P_{0,W}$ ( $m^2 h^{-1}$ )	$10^4 B_{EE}$ ( $m^3 mol^{-1}$ )	$10^4 B_{WE}$ ( $m^3 mol^{-1}$ )	$10^4 B_{WW}$ ( $m^3 mol^{-1}$ )
Udel P-3500	12	3.8	22	5.0	5.5	1.2
ME005	8	0.27	13	6.6	4.6	1.1
ME029	9	0.60	2.3	6.4	5.6	1.5
ME105	9	0.70	23	6.0	4.3	1.0
ME143	10	2.6	120	3.0	3.2	0.31
ME190	7	4.3	220	2.0	2.7	0.28

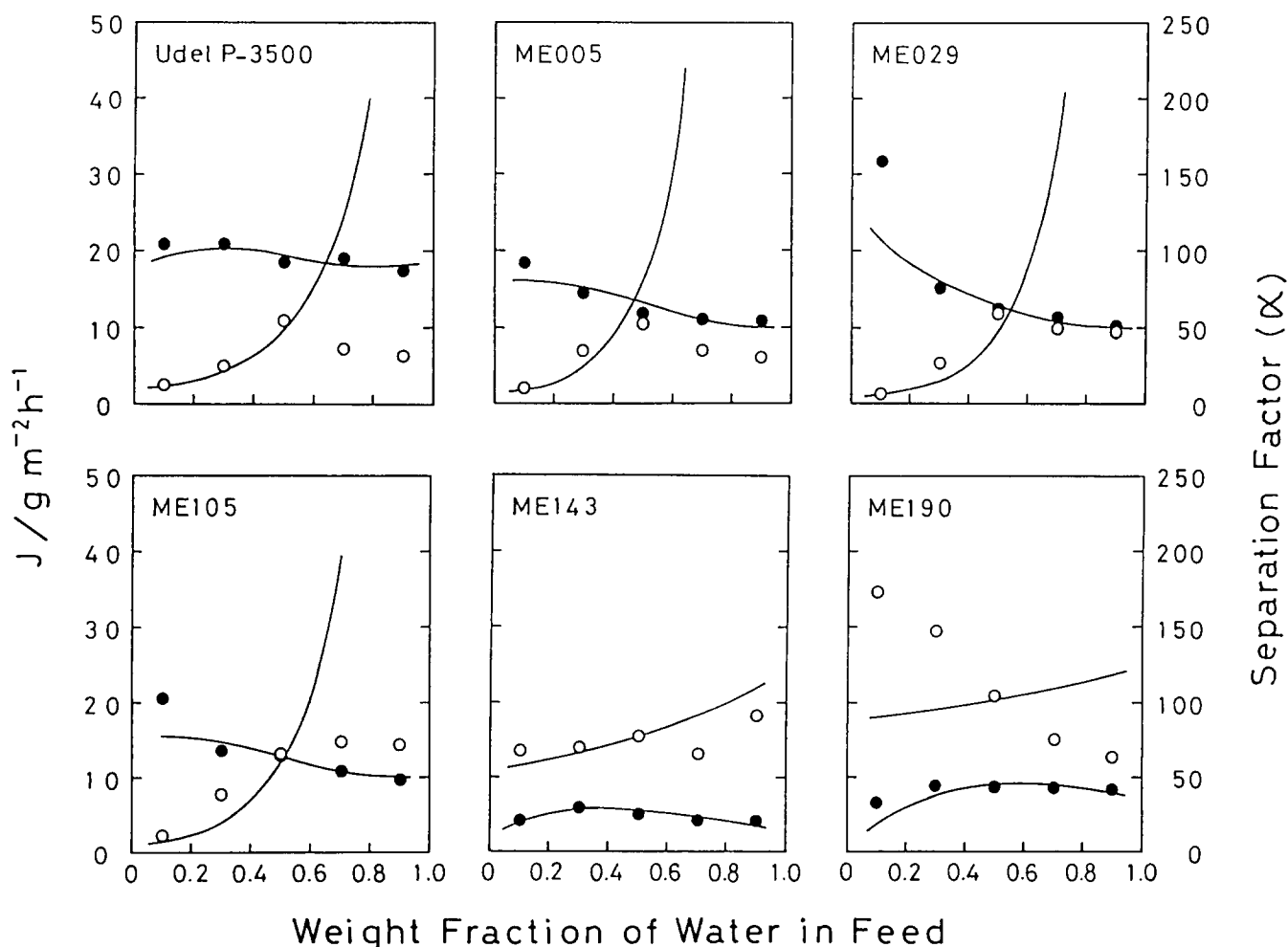
<sup>a</sup>Operating pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C

The interaction between the introduced ester moiety and the permeants, water and ethanol, were investigated by i.r. The ester group carbonyl ( $>C=O$ ) stretching band was  $1738\text{ cm}^{-1}$  when the polymer was dissolved in chloroform. A small but measurable band shift to  $1737\text{ cm}^{-1}$  was observed when water or ethanol were present. These results suggest that the hydrogen-bonding ability of the ester group both with water and with ethanol is nearly equal. Both water and ethanol may therefore interact with the ester group equally, as previously observed in the pervaporation of water/ethanol mixture through poly(methyl methacrylate-co-styrene) membranes<sup>25</sup>. This indiscriminate hydrogen-bonding interaction hinders a greater improvement of permselectivity towards water in the presence of the

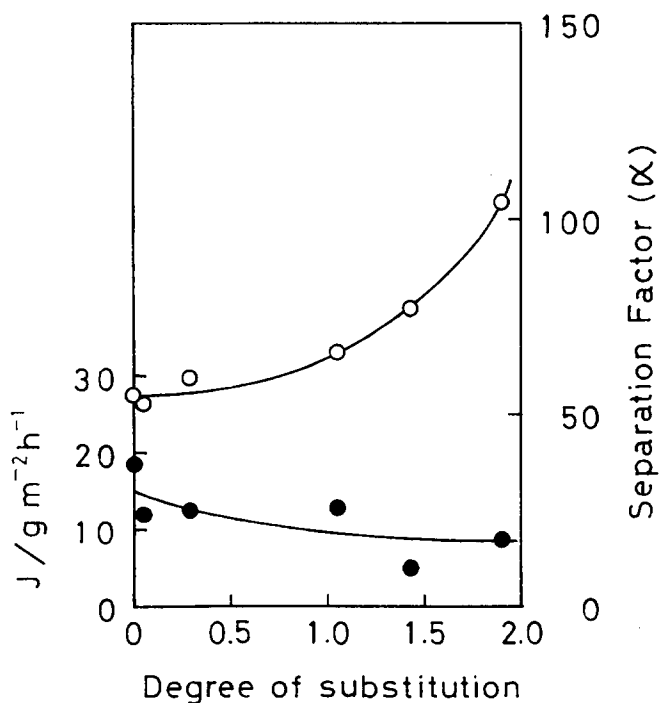
methyl ester moiety. On the other hand, an interaction between sulphone moieties in both parent and modified polymers and permeants was scarcely observed.

#### Permeation mechanism of water/ethanol mixture

In order to study the permeation mechanism of water and ethanol through the membrane, the observed total fluxes were separated into their respective water and ethanol fluxes, so that they could be plotted against their feed concentration. The same method was reported previously<sup>18-20,24</sup>. The relationship between each component flux and feed concentration is shown in Figure 4, for membrane ME143 as an example. The ethanol curve (on the right) shows an exponential profile. On the other hand, water flux dependence (on the left) on



**Figure 2** Effect of feed composition on total flux and separation factor ( $\alpha$ ) in water/ethanol pervaporation: downstream pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C; (●) flux; (○) separation factor,  $\alpha$ ; (—) calculated, according to equations (8), (13) and (15), and using the coefficient numerical values summarized in Table 2



**Figure 3** Effect of degree of substitution on flux and separation factor ( $\alpha$ ) in water/ethanol pervaporation: (●) flux; (○) separation factor,  $\alpha$ ; downstream pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C; weight fraction of water in feed, ca. 0.5

its feed concentration appears more complicated. Similar relationships to Figure 4 were obtained for other membranes. The relationships in Figure 4 show the dependence of water flux on the water concentration in the feed and the relationship between ethanol flux and the ethanol concentration in the feed.

For permeation of ethanol, the diffusion coefficient  $D$  usually depends on the local concentration of ethanol<sup>26-33</sup>. In some cases the concentration dependence of the diffusion coefficient has been reported to be linear<sup>30</sup>:

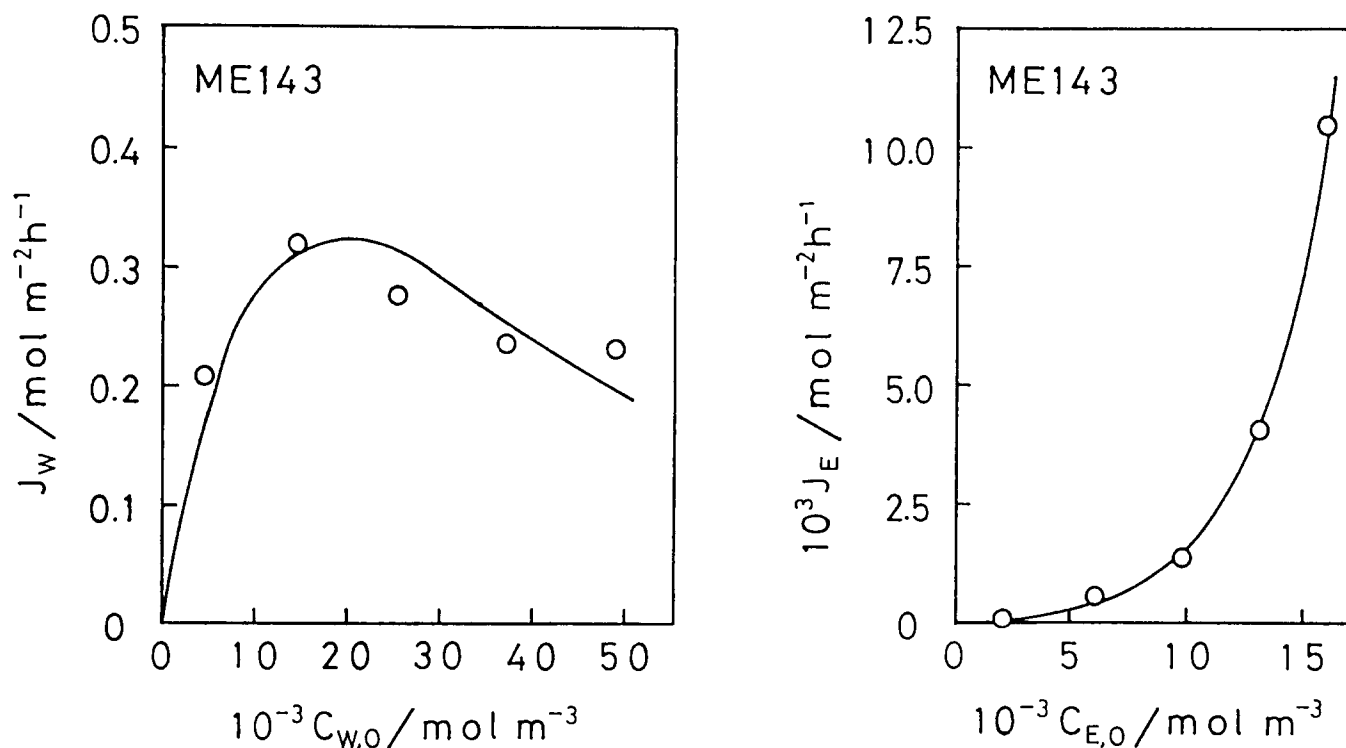
$$D = D_0(1 + a\bar{C}) \quad (3)$$

and in the other cases, an exponential form was observed<sup>30</sup>:

$$D = D_0 \exp(b\bar{C}) \quad (4)$$

In these two equations,  $D_0$  is the  $D$  value as the permeant concentration approaches zero;  $a$  and  $b$  are coefficients characteristic of the membrane/permeant interaction;  $\bar{C}$  denotes the permeant concentration in the membrane. Equation (4) will be used hereafter, since it is more suitable in cases where the diffusion coefficient is more dependent on concentration. For ethanol permeation through these membranes, equation (4) becomes:

$$D_E = D_{0,E} \exp(b_{EE}\bar{C}_E) \quad (5)$$



**Figure 4** Effect of feed composition on the separation of aqueous ethanol solution for membrane ME143: downstream pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C; (—) calculated, according to equations (8) and (13), and using the coefficient numerical values summarized in Table 2

From equation (5) and Fick's first law of diffusion, ethanol flux through the membrane is given by:

$$J_E = -D_{0,E} \exp(b_{EE} \bar{C}_E) d\bar{C}_E/dx \quad (6)$$

In the steady state, equation (6) can be solved in terms of:

$$\bar{C}_E = \bar{C}_{E,x} \quad \text{at } x = x$$

with boundary condition:

$$\bar{C}_E = \bar{C}_{E,0} (= K_E C_{E,0}) \quad \text{at } x = 0$$

where  $K_E$  is the solubility coefficient of ethanol. The result is

$$\frac{\bar{C}_{E,x}}{\bar{C}_{E,0}} = \frac{1}{B_{EE} C_{E,0}} \ln \left( \exp(B_{EE} C_{E,0}) - \frac{B_{EE} J_E}{P_{0,E}} x \right) \quad (7)$$

By making use of equation (7), we are able to obtain the concentration profile in the steady state across the membrane as shown in Figure 5. With an assumption of ethanol concentration ( $\bar{C}_E$ ) at the downstream side of the membrane ( $x = l$ ) being zero, which is generally regarded as being acceptable, equation (8) is derived from equation (7):

$$J_E = (P_{0,E}/B_{EE}l) [\exp(B_{EE} C_{E,0}) - 1] \quad (8)$$

where  $P_{0,E} (= D_{E,0} K_E)$  is the permeability coefficient at zero concentration of ethanol.

Next, we describe the water permeation through the membranes. As shown in Figure 4, a complicated profile for water flux dependence was obtained. From the fact that these membranes were swollen by both water and ethanol, and the relationship between separated water flux and water concentration shown in Figure 4, the diffusion coefficient for water was considered to

depend on the local concentration of both water and ethanol. The general expression may be given in equation (9), in which the exponential depends separately on the local concentrations of ethanol and water:

$$D_W = D_{0,W} \exp(b_{WW} \bar{C}_W + b_{WE} \bar{C}_E) \quad (9)$$

Combination of equation (9) and Fick's first law of diffusion gives the water flux through the membrane:

$$J_W = -D_{0,W} \exp(b_{WW} \bar{C}_W + b_{WE} \bar{C}_E) d\bar{C}_W/dx \quad (10)$$

In the steady state, integration of equation (10) when the boundary conditions are

$$\begin{aligned} \bar{C}_E &= \bar{C}_{E,0} (= K_E C_{E,0}) \\ \bar{C}_W &= \bar{C}_{W,0} (= K_W C_{W,0}) \end{aligned} \quad \text{at } x = 0$$

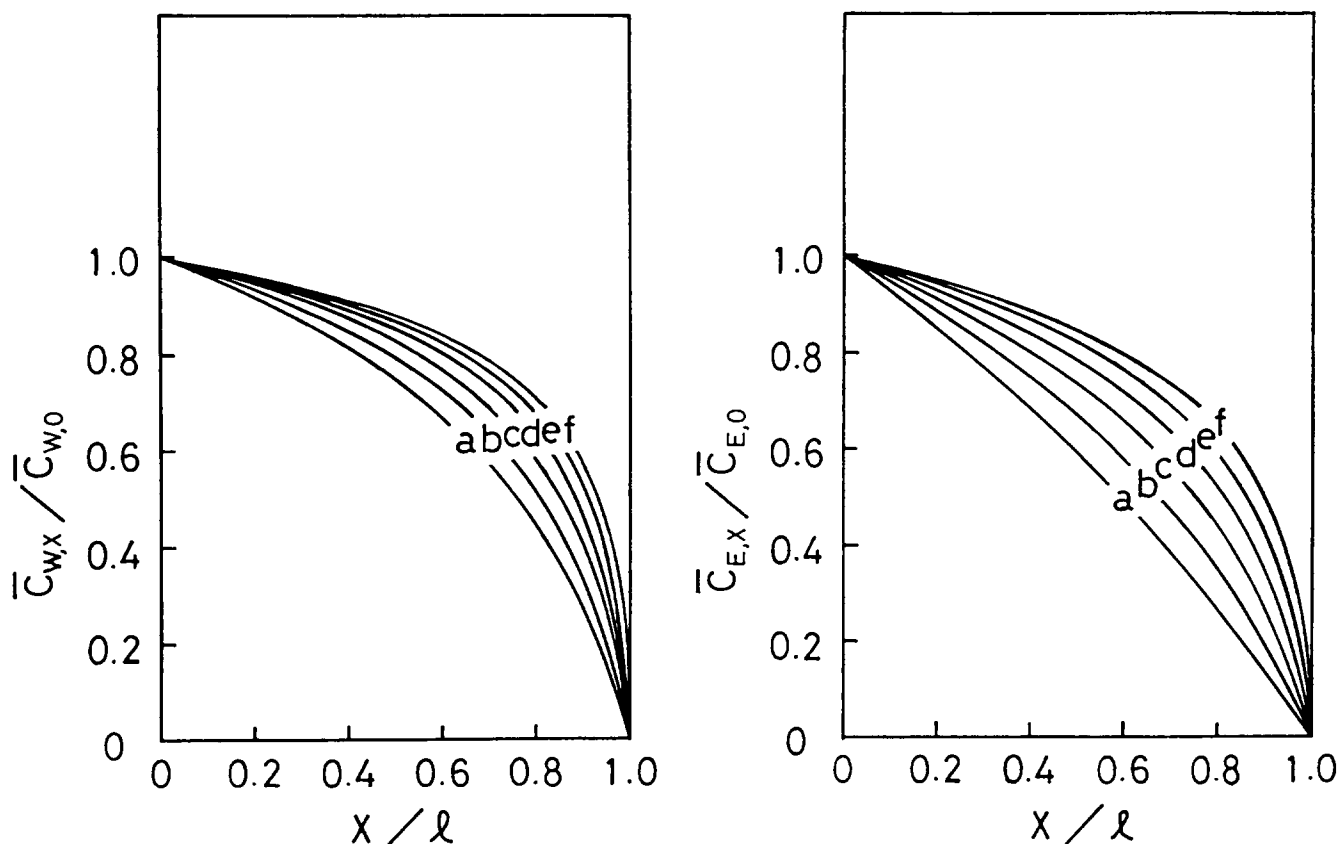
and

$$\bar{C}_E = \bar{C}_{E,x} \quad \bar{C}_W = \bar{C}_{W,x} \quad \text{at } x = x$$

is given by:

(i) In the case  $B_{EE} \neq B_{WE}$ ,

$$\begin{aligned} \frac{\bar{C}_{W,x}}{\bar{C}_{W,0}} &= \frac{1}{B_{WW} C_{W,0}} \ln \left\{ \exp(B_{WW} C_{W,0}) \right. \\ &\quad - \frac{J_W P_{0,E}}{J_E P_{0,W} B_{EE} - B_{WE}} \\ &\quad \times \left[ \exp(B_{EE} C_{E,0}) \right]^{1 - B_{WE}/B_{EE}} \\ &\quad \left. - \left( \exp(B_{EE} C_{E,0}) - \frac{B_{EE} J_E}{P_{0,E}} x \right)^{1 - B_{WE}/B_{EE}} \right\} \end{aligned} \quad (11)$$



**Figure 5** Calculated concentration profiles for membrane ME143 under the operating pressure of 400 Pa (3.0 mmHg): (—) calculated, according to equations (7) and (11), and using the coefficient numerical values summarized in Table 2. The curves as follows:

Conc. (mol m <sup>-3</sup> )	a	b	c	d	e	f
10 <sup>-3</sup> C <sub>w,0</sub>	47.74	40.51	32.78	24.68	16.47	7.846
10 <sup>-3</sup> C <sub>e,0</sub>	2.546	5.003	7.528	10.05	12.50	14.98

(ii) In the case  $B_{EE} = B_{WE} = B_E$ ,

$$\frac{\bar{C}_{w,x}}{\bar{C}_{w,0}} = \frac{1}{B_{WW}C_{w,0}} \ln \left\{ \exp(B_{WW}C_{w,0}) - \frac{P_{0,E} J_W B_{WW}}{P_{0,W} J_E B_E} \right. \\ \left. \times \left[ B_E C_{E,0} - \ln \left( \exp(B_E C_{E,0}) - \frac{B_E J_E}{P_{0,E}} x \right) \right] \right\} \quad (12)$$

Concentration profiles of water in the membrane can be given by either equation (11) or (12). Some results are shown in Figure 5. Furthermore, the assumption of both water and ethanol concentration ( $\bar{C}_w$  and  $\bar{C}_e$ ) at the downstream side of the membrane ( $x = l$ ) being zero results in equations (13) and (14), respectively, from equations (11) and (12):

(i) In the case  $B_{EE} \neq B_{WE}$ ,

$$J_W = \frac{P_{0,W} B_{EE} - B_{WE}}{l B_{WW} B_{EE}} \\ \times \frac{[\exp(B_{EE} C_{E,0}) - 1][\exp(B_{WW} C_{w,0}) - 1]}{\exp[(B_{EE} - B_{WE}) C_{E,0}] - 1} \quad (13)$$

(ii) In the case  $B_{EE} = B_{WE} = B_E$ ,

$$J_W = \frac{P_{0,W}}{B_{WW} l B_E C_{E,0}} [\exp(B_{WW} C_{w,0}) - 1] \\ \times [\exp(B_E C_{E,0}) - 1] \quad (14)$$

Equations for the separation factor may be obtained from equations (8), (13) and (14):

(i) In the case  $B_{EE} \neq B_{WE}$ ,

$$\alpha = \frac{J_W / J_E}{C_{w,0} / C_{e,0}} \\ = \frac{P_{0,W} B_{EE} - B_{WE}}{P_{0,E} B_{WW}} \frac{[\exp(B_{WW} C_{w,0}) - 1] C_{E,0}}{\{\exp[(B_{EE} - B_{WE}) C_{E,0}] - 1\} C_{w,0}} \quad (15)$$

(ii) In the case  $B_{EE} = B_{WE} = B_E$ ,

$$\alpha = \frac{P_{0,W} \exp(B_{WW} C_{w,0}) - 1}{P_{0,E} B_{WW} C_{w,0}} \quad (16)$$

In the present paper, equations (13) and (15) were considered valid.  $B_{EE}$  and  $P_{0,E}$  were determined first by using the ethanol flux–ethanol feed concentration relation and then  $P_{0,W}$ ,  $B_{WE}$  and  $B_{WW}$  were determined to fit the observed data. The five parameters in the flux equations, determined to fit Figure 4 best, are summarized in Table 2. It is difficult to correlate intrinsic permeability coefficients  $P_0$  of both water and ethanol with some characteristic properties of polymers.  $P_{0,W}$  and  $P_{0,E}$ , however, tend to increase with an increase in methyl ester content in the membrane. The coefficients of the exponential model,  $B_{EE}$ ,  $B_{WE}$  and  $B_{WW}$ , showed

tendencies to decrease with increase in methyl ester content in the membrane. This suggests that the introduction of methyl ester onto the polymer leads to the suppression of the swelling effect of water and ethanol on polymeric membranes.

The curves for weight fractions of water in permeate in *Figure 1*, fluxes in *Figures 2* and *4*, and separation factors in *Figure 2* are the ones calculated according to equations (8), (13) and (15) and using numerical coefficient values summarized in *Table 2*. Theoretical curves except those for separation factor agreed well with the observed value. It was concluded, therefore, that the pervaporation flux observed experimentally under the downstream pressure of 400 Pa (3.0 mmHg) could be obtained by calculation using equations (8), (13) and (15), and zero downstream pressure. On the other hand, theoretical curves for separation factor in *Figure 2*, which is thought to be very sensitive to small variations in calculated flux values, could not simulate the observed results well.

As mentioned above, we can obtain the concentration distribution at steady state in the membrane according to equations (7) and (11), and taking the obtained coefficient values in these two equations. As an example, water and ethanol distributions in membrane ME143 is shown in *Figure 5*.

#### Relationship between membrane polarity and membrane performance

It is important to correlate membrane performance to some parameters characteristic to the polymer material, since it may lead to the effective molecular design of novel membrane materials. Based on this idea, one of the authors proposed in earlier work that membrane polarity is one of the most promising parameters in the development of membrane materials for pervaporation<sup>34,35</sup>.

*Figure 6* shows the relationship between separation factor and polarity of the membrane under study. The correlation coefficient for the present relationship was determined to be 0.866. As previously reported<sup>34,35</sup>, the separation factor tends to increase as the membrane polarity comes closer to that of water, 63.1 kcal mol<sup>-1</sup> (ref. 36). It is considered that a membrane having membrane polarity close to that of water can incorporate water more easily into the membrane, causing an increase in the permselectivity towards water.

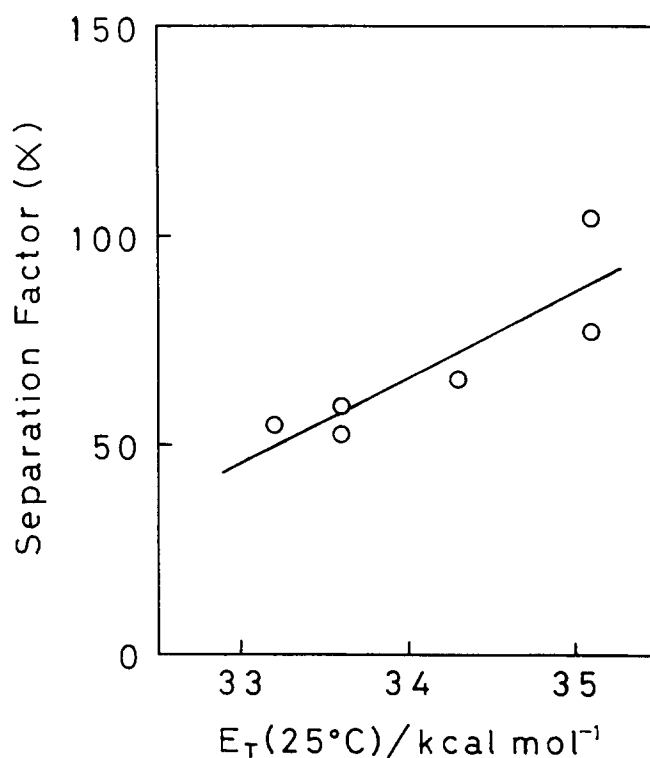
#### Pervaporation of various water/alcohol mixtures

*Table 3* shows the separation factor and the total flux

of the membrane prepared from ME190 and the membrane prepared from Udel P-3500 towards aqueous solutions of various alcohols containing 0.90 weight fraction of water. In these pervaporation systems, water permeated preferentially through both membranes. Furthermore, the modified polysulphone membranes gave higher selectivity towards water than the parent polysulphone membrane. These results suggest that the present membranes are potentially applicable for dewatering aqueous organic solutions. It is, however, necessary to give higher flux values with the present membranes so that they can be applicable to such a purpose. An improvement in membrane performance might be accomplished by the formation of composite membranes.

#### CONCLUSIONS

Modified Udel P-3500 membranes having methyl carboxylate groups showed selective permeation of water



**Figure 6** Relationship between separation factor ( $\alpha$ ) and membrane polarity for polysulphone and modified polysulphone with various degrees of substitution: downstream pressure, 400 Pa (3.0 mmHg); operating temperature, 25°C; weight fraction of water in feed, ca. 0.5

**Table 3** Results of pervaporation of water/alcohol binary mixture<sup>a</sup>

Alcohol	ME190		Udel P-3500	
	Separation factor, $\alpha$	Flux (g m <sup>-2</sup> h <sup>-1</sup> )	Separation factor, $\alpha$	Flux (g m <sup>-2</sup> h <sup>-1</sup> )
Methanol	4.32	8.09	3.03	12.1
Ethanol	63.8	8.37	32.2	17.5
1-Propanol	$\infty$	10.1	153	18.0
2-Propanol	1290	7.74	1060	9.32
2-Butanol	408	7.13	322	14.2
3-Methyl-2-propanol	$\infty$	11.8	573	10.5

<sup>a</sup>Operating temperature 25°C; downstream pressure, 400 Pa (3.0 mmHg); weight fraction of water in feed, ca. 0.90

from various aqueous alcohol solutions. The presence of methyl carboxylate groups was effective in improving the membrane performance. According to the analysis of the permeation data by the solution-diffusion model, the diffusion coefficient for water was an exponential function of both water and ethanol concentrations, while that for ethanol was an exponential function of ethanol concentration alone.

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#### APPENDIX: NOMENCLATURE

- |                 |   |
|-----------------|---|
| $b_{EE}$        | coefficient of the exponential model for ethanol diffusion, which depends on the ethanol concentration ( $\text{mol}^{-1} \text{m}^3$ ) |
| $b_{WE}$        | coefficient of the exponential model for water diffusion, which depends on the ethanol concentration ( $\text{mol}^{-1} \text{m}^3$ )   |
| $b_{WW}$        | coefficient of the exponential model for water diffusion, which depends on the water concentration ( $\text{mol}^{-1} \text{m}^3$ )     |
| $B_E$           | coefficient of the exponential model for both water and ethanol ( $= B_{EE} = B_{WE}$ ) ( $\text{mol}^{-1} \text{m}^3$ )                |
| $B_{EE}$        | coefficient of the exponential model for ethanol ( $= K_E b_{EE}$ ) ( $\text{mol}^{-1} \text{m}^3$ )                                    |
| $B_{WE}$        | coefficient of the exponential model for water ( $= K_E b_{WE}$ ) ( $\text{mol}^{-1} \text{m}^3$ )                                      |
| $B_{WW}$        | coefficient of the exponential model for water ( $= K_W b_{WW}$ ) ( $\text{mol}^{-1} \text{m}^3$ )                                      |
| $\bar{C}_E$     | concentration of ethanol in the membrane ( $\text{mol m}^{-3}$ )  |
| $\bar{C}_W$     | concentration of water in the membrane ( $\text{mol m}^{-3}$ )  |
| $\bar{C}_{E,0}$ | concentration of ethanol in the membrane at the upstream face of the membrane ( $\text{mol m}^{-3}$ )                                   |
| $\bar{C}_{W,0}$ | concentration of water in the membrane at the upstream face of the membrane ( $\text{mol m}^{-3}$ )                                     |
| $\bar{C}_{E,x}$ | concentration of ethanol in the membrane at distance $x$ ( $\text{mol m}^{-3}$ )  |
| $\bar{C}_{W,x}$ | concentration of water in the membrane at distance $x$ ( $\text{mol m}^{-3}$ )  |
| $\bar{C}_{E,l}$ | concentration of ethanol in the membrane at the downstream face of the membrane ( $\text{mol m}^{-3}$ )                                 |
| $\bar{C}_{W,l}$ | concentration of water in the membrane at the downstream face of the membrane ( $\text{mol m}^{-3}$ )                                   |
| $C_{E,0}$       | concentration of ethanol in the feed solution ( $\text{mol m}^{-3}$ )   |
| $C_{W,0}$       | concentration of water in the feed solution ( $\text{mol m}^{-3}$ )   |
| $D_E$           | diffusion coefficient of ethanol ( $\text{m}^2 \text{h}^{-1}$ )   |
| $D_W$           | diffusion coefficient of water ( $\text{m}^2 \text{h}^{-1}$ )   |
| $D_{0,E}$       | diffusion coefficient of ethanol in the membrane ( $\text{m}^2 \text{h}^{-1}$ )   |
| $D_{0,W}$       | diffusion coefficient of water in the membrane ( $\text{m}^2 \text{h}^{-1}$ )   |
| $J$             | total permeant flux ( $\text{g m}^{-2} \text{h}^{-1}$ )   |
| $J_E$           | flux of ethanol ( $\text{mol m}^{-2} \text{h}^{-1}$ )   |
| $J_W$           | flux of water ( $\text{mol m}^{-2} \text{h}^{-1}$ )   |
| $K_E$           | solubility coefficient of ethanol ( $\text{mol m}^{-3}$ -membrane polymer/ $\text{mol m}^{-3}$ )  |



$K_w$	solubility coefficient of water (mol m <sup>-3</sup> -membrane polymer/mol m <sup>-3</sup> )	$P_{0,w}$	permeability coefficient of water in the membrane (= $D_{0,w}K_w$ ) (m <sup>2</sup> h <sup>-1</sup> )
$l$	thickness of the membrane (m)	$x$	distance from the upstream face of the membrane along the flow of the permeant (m)
$P_{0,E}$	permeability coefficient of ethanol in the membrane (= $D_{0,E}K_E$ ) (m <sup>2</sup> h <sup>-1</sup> )	$\alpha$	separation factor