

# Permeation and Separation Characteristics of Alcohol–Water Mixtures through Poly(dimethyl Siloxane) Membrane by Pervaporation and Evapomeation

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## SYNOPSIS

Permeation and separation characteristics for aqueous alcoholic solutions such as methanol/water, ethanol/water and 1-propanol/water were studied using a poly(dimethyl siloxane) membrane by pervaporation and evapomeation. Poly(dimethyl siloxane) membrane preferentially permeated alcohol from aqueous alcoholic solutions in both methods. The concentration of alcohol in the permeate by evapomeation was higher than that by pervaporation. However, the permeation rate for the former method was smaller than that for the latter method. In evapomeation with a temperature difference between the feed solution and the membrane surroundings, when the temperature of the membrane surroundings was kept constant and the temperature of the feed solution was raised, both the permeation rate and the permselectivity for ethanol increased with increasing temperature of the feed solution. On the other hand, as the temperature of the feed solution was kept constant and the temperature of the membrane surroundings was changed, the permeation rate decreased, but the permselectivity for ethanol increased remarkably with dropping temperature in the membrane surroundings. Under permeation conditions of a feed solution of 40°C and a membrane surrounding temperature of –30°C in evapomeation, an aqueous solution of 10 wt % ethanol in the feed was concentrated to about 90 wt % in the permeate. The permselectivity for alcohol was in the order of methanol < ethanol < 1-propanol. The above permeation and separation characteristics are discussed from the viewpoint of the physicochemical properties of the poly(dimethyl siloxane) membrane and the permeating molecules.

## INTRODUCTION

Aqueous ethanol solutions are known to have an azeotropic composition which prevents their separation by distillation. Although azeotropic mixtures are separable by some methods, in recent years a membrane separation technique such as pervaporation is applied to separate the azeotropic mixtures. For such azeotropic mixtures, preferential permeation of water through the membrane is advantageous because the amount of water in this azeotropic mixture is small. Such permselective membranes for water have been prepared from hydrophilic polymers

such as cellulose acetate,<sup>1</sup> poly(vinyl alcohol),<sup>2,3</sup> sulfonated polyethylene,<sup>4</sup> Nafion,<sup>5</sup> alginic acid,<sup>6,7</sup> chitosan,<sup>8–12</sup> quaternized poly(vinyl pyridine),<sup>13</sup> and so on. When an aqueous solution of low ethanol concentration is distilled, high heat energy is required. Permselective membranes for ethanol should be developed in order to solve this problem. Some permselective membranes for ethanol in pervaporation have been developed by some workers,<sup>14–23,25</sup> but the membrane performance was insufficient; namely, high selectivity and high permeation rate do not coincide.

In this study, polymer membranes with high permeability and high selectivity for alcohol in aqueous solutions of low alcohol content were sought. The permeation and separation characteristics for aqueous alcoholic solutions were investigated using

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a poly(dimethyl siloxane) membrane by pervaporation and evapomeation,<sup>6,8</sup> which was proposed as a new membrane separation technique for separation of organic liquid mixtures. Also evapomeation having a temperature difference between the feed solution and the membrane surroundings<sup>24</sup> was applied. The mechanism for the permeation and separation of aqueous alcoholic solutions is discussed.

## EXPERIMENTAL

### Materials

Oligo(dimethyl siloxane) KE-10 and catalyst RA, produced by Shin-etsu Chemical Co. Ltd., were employed as the material for membrane preparation. All reagents used were of the best grade from commercial sources.

### Preparation of Membrane

Casting solutions were prepared from oligo(dimethyl siloxane) KE-10 (7.0 g) and catalyst RA (0.25 g) in benzene (49 g) at 25°C. Poly(dimethyl siloxane) (PDMS) membranes were prepared by pouring a desired amount of the casting solution onto a flat dish of stainless steel and allowing the solvent to evaporate completely at 25°C. The thickness used in this work was 120  $\mu\text{m}$ .

### Apparatus and Measurements

The principle schemes for pervaporation (PV) and evapomeation (EV) are shown in Figure 1(a) and (b), respectively. In PV the feed solution and in EV only vapor are in direct contact with the membrane.<sup>6,8</sup> The experiments on PV and EV were carried out at a desired temperature under a desired reduced pressure using a conventional apparatus. The principle scheme for the temperature difference controlling EV (TDEV) method<sup>24</sup> is shown in Figure 2, in which the temperature of the feed solution (A) and the membrane surroundings (B) are controlled.

Compositions of the feed mixture and permeate were measured by means of gas chromatography (Shimadzu GC-9A). The degree of swelling of the membrane (DS) was calculated as follows:

$$DS = W_S/W_D \quad (1)$$

where  $W_S$  is the weight of the swollen membrane in the feed solution or feed vapor and  $W_D$  is the weight of the dried membrane.

The separation factor,  $(\alpha_{\text{alcohol}/\text{H}_2\text{O}})_F$ , based on the compositions of feed solution and permeate, was calculated as follows:

$$(\alpha_{\text{alcohol}/\text{H}_2\text{O}})_F = (Y_{\text{alcohol}}/Y_{\text{H}_2\text{O}})/(X_{\text{alcohol}}/X_{\text{H}_2\text{O}}) \quad (2)$$

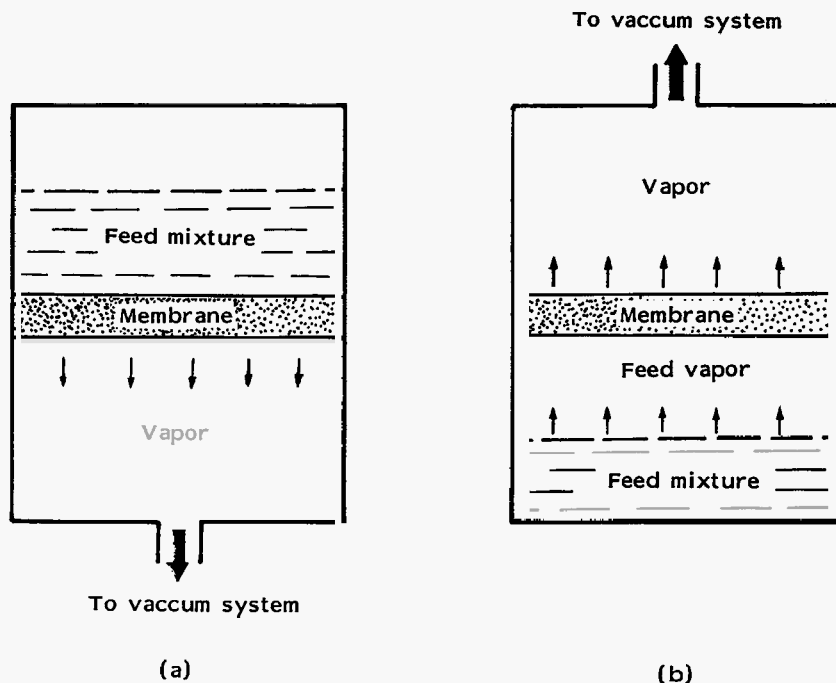
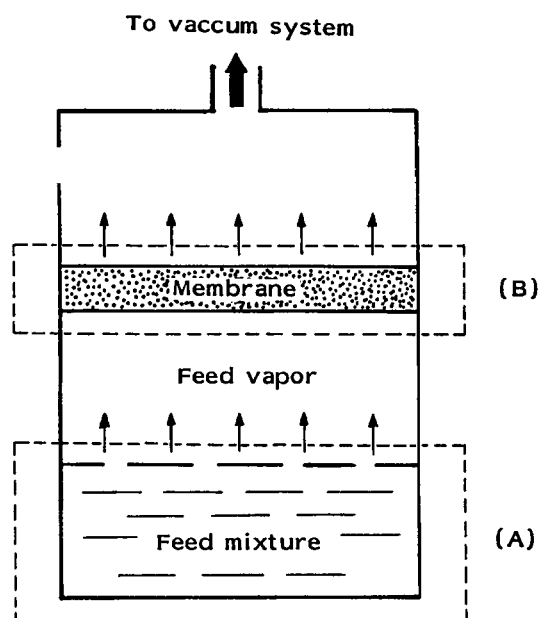


Figure 1 Principles of pervaporation (PV) (a) and evapomeation (EV) (b).



where  $X_{\text{H}_2\text{O}}$ ,  $X_{\text{alcohol}}$  and  $Y_{\text{H}_2\text{O}}$ ,  $Y_{\text{alcohol}}$  are the weight fractions of water and alcohol in the feed and permeate, respectively.

The separation factor,  $(\alpha_{\text{alcohol}/\text{H}_2\text{O}})_v$ , based on the compositions of feed vapor and permeate, was calculated as follows:

$$(\alpha_{\text{alcohol}/\text{H}_2\text{O}})_v = (Y_{\text{alcohol}}/Y_{\text{H}_2\text{O}})/(V_{\text{alcohol}}/V_{\text{H}_2\text{O}}) \quad (3)$$

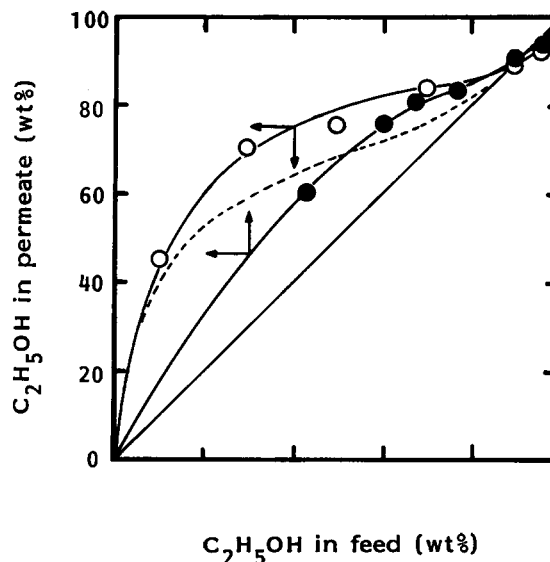
where  $V_{\text{alcohol}}$  and  $V_{\text{H}_2\text{O}}$  are the weight fractions of alcohol and water vapor from the feed solution.

### Permeation and Separation Characteristics

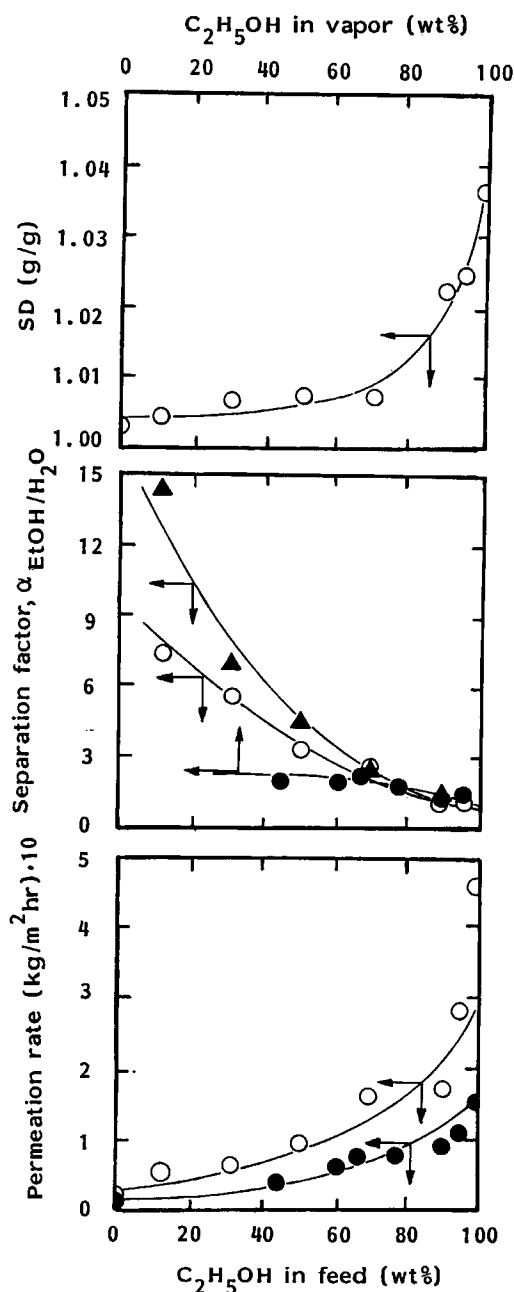
Relationships between the compositions of the mixtures of ethanol/water in the feed solution or feed vapor and in the permeate through the PDMS membrane by PV and EV are shown in Figure 3. The open circle plots are for the PV experiment which was carried out at 40°C and a pressure of  $1.5 \times 10^{-2}$  Torr (=1.995 Pa). The dashed line is a vapor-liquid equilibrium curve for the mixtures of ethanol/water. The plots for the ethanol concentration in the permeate in PV are on the upper side of the dashed line. These results support the assumption that ethanol predominantly permeates in

PV. Similar results have been reported by some workers.<sup>2,11,14,19</sup> The permselectivity for ethanol in the mixtures of ethanol/water through the PDMS membrane is attributed to the fact that ethanol has a higher affinity for the PDMS membrane than water and easily diffuses through the PDMS membrane which is hydrophobic and rubbery. The solid circle plots are the results for the EV experiment which was carried out at a feed solution temperature of 40°C, a membrane surroundings temperature of 25°C, and a pressure of  $1.5 \times 10^{-2}$  Torr (=1.995 Pa). In this EV method since vapor molecules, vaporized from the feed solution, are in direct contact with the PDMS membrane, the composition in the permeate is shown for the feed vapor composition. In this case also, ethanol predominantly permeated from aqueous ethanol solutions through the PDMS membrane.

Figure 4 shows the permeation rate, separation factor, and degree of swelling of the PDMS membrane as a function of the feed composition of aqueous ethanol solution or the feed vapor composition. The permeation rates increased with increasing ethanol concentration in the feed solution or feed vapor in both PV and EV. This is due to the fact that the PDMS membrane predominantly per-



**Figure 3** Effect of feed solution or feed vapor composition on the ethanol concentration in the permeate through the PDMS membrane by PV at 40°C (O), EV at feed solution of 40°C and membrane neighborhood of 25°C (●). Reduced pressure:  $1.5 \times 10^{-2}$  Torr (=1.995 Pa).



**Figure 4** Permeation rate, separation factor, and degree of swelling of the PDMS membrane as a function of the composition of feed solution or feed vapor. Permeation conditions: same as in Figure 3.

meates ethanol, the ethanol amount which is in contact with the membrane increases, and the degree of swelling of the PDMS membrane increases with increasing ethanol concentration in the feed.

The separation factors based on the feed vapor composition in EV were relatively smaller than those based on the feed solution concentration in PV. The

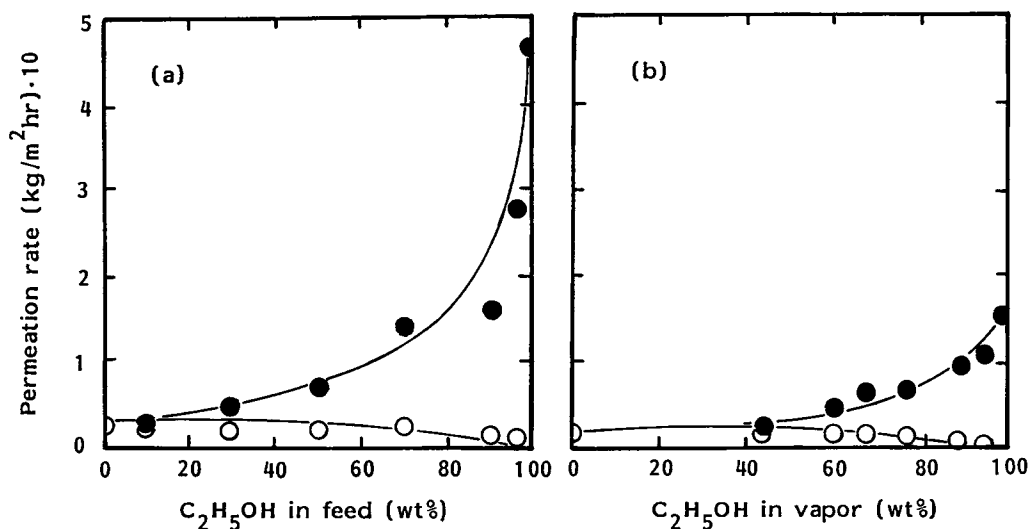
separation factors, calculated from the compositions of feed solution and permeate, were higher than those in PV. This is due to the fact that in EV the vapor with higher ethanol concentration than that in the feed solution is in contact with the membrane and the vapor is concentrated through the membrane.

The separation factors in both PV and EV decreased with increasing ethanol concentration in the feed. In order to clarify these results, the permeation rates for water and ethanol in both PV and EV were plotted against the ethanol concentration in the feed solution or feed vapor in Figure 5. The permeation rates for ethanol in both methods increased with an increase in ethanol concentration in the feed. The increase of the permeation rate for ethanol is apparently related to an increase in the separation factor with an increase of ethanol concentration in the feed. As seen in Figure 5, however, the permeation rates for water in both methods were approximately constant regardless of the feed composition. These results imply that almost the same amount of water is permeated through the PDMS membrane in all feed compositions. Namely, in the feed with a high ethanol concentration a relatively large amount of water is permeated. Consequently, the separation factors that are expressed as permselectivity for ethanol in both methods are decreased with increasing ethanol concentration in the feed.

### Effect of Alcohol

The permeation rates and separation factors for various alcoholic solutions through the PDMS membrane by PV and EV are summarized in Table I, in which the permeation conditions in PV and EV are same as those in Figure 4, and the values in parentheses are for the feed vapor in EV.

In both PV and EV, the permeation rate for all aqueous alcoholic solutions increased and the separation factors decreased as the alcohol concentration in the feed was increased. The results obtained for aqueous methanol and 1-propanol solutions were similar to those for an aqueous ethanol solution. Namely, alcohol predominantly permeated from aqueous alcoholic solutions. In spite of that, the molecular size increases in order of methanol < ethanol < 1-propanol. The permeation rates and separation factors for aqueous alcoholic solutions through the PDMS membrane in both PV and EV increased with the molecular size. These permeation and separation characteristics suggest that both the solubility of the permeating molecule in the membrane and the diffusivity of the permeating molecule through the



**Figure 5** Permeation rates for water (O) and ethanol (●) through the PDMS membrane by PV (a) and EV (b) as a function of the composition of feed solution and feed vapor, respectively.

membrane are very significant. Table II lists the solubility parameter ( $\delta$ ) of the permeating molecule,<sup>26</sup> and the difference between the  $\delta$  values of the PDMS and permeating molecules. The difference in the  $\delta$  value between the PDMS and alcohol is in order of  $(\delta_{\text{PDMS}} - \delta_{\text{MeOH}}) > (\delta_{\text{PDMS}} - \delta_{\text{EtOH}}) > (\delta_{\text{PDMS}} - \delta_{1\text{-PrOH}})$ . This implies that the PDMS membrane has the strongest affinity for 1-propanol among the above alcohols. Namely, 1-propanol is the easiest to dissolve in the PDMS membrane. On the other hand, since the PDMS membrane is rubbery, the PDMS chain is very flexible. Therefore,

the permeating molecule can easily diffuse through the PDMS membrane. Consequently, 1-propanol that has a high solubility can be easily permeated through the PDMS membrane, and a high permselectivity for 1-propanol is shown.

#### Effect of Permeation Temperature

The effect of permeation temperature on the permeation rates and separation factors for aqueous ethanol solutions through the PDMS membrane in PV is shown in Figure 6. The permeation rates in-

**Table I** Effect of Feed Composition of Aqueous Alcoholic Solutions on the Permeation and Separation Characteristics through the PDMS Membrane by Pervaporation and Evaporation

Feed		Aqueous Solution of 10 wt% Alcohol		Aqueous Solution of 30 wt % Alcohol	
		Permeation Rate $\times 10^2$ (kg/m <sup>2</sup> h)	Separation Factor ( $\alpha_{\text{alcohol}/\text{H}_2\text{O}}$ )	Permeation Rate $\times 10^2$ (kg/m <sup>2</sup> h)	Separation Factor ( $\alpha_{\text{alcohol}/\text{H}_2\text{O}}$ )
Method	Alcohol				
Pervaporation <sup>a</sup>	MeOH	4.03	6.03	6.85	4.72
	EtOH	5.33	7.44	6.90	5.79
	1-PrOH	8.04	16.24	18.10	9.06
Evaporation <sup>b</sup>	MeOH	2.29	9.96 (1.32)	5.84	10.16 (1.37)
	EtOH	4.01	14.36 (2.04)	6.24	7.20 (2.02)
	1-PrOH	6.73	30.70 (6.59)	10.43	9.63 (6.54)

<sup>a</sup> Permeation temperature: 40°C.

<sup>b</sup> Temperature of feed solutions. 40°C; temperature of membrane surroundings 25°C.

**Table II** Difference between the Solubility Parameters of Permeating Molecules and PDMS<sup>a</sup>

Permeating Molecule	$\delta_p^b$	$(\delta_p - \delta_{PDMS})^b$
Water	47.9	45.5
Methanol	29.7	27.3
Ethanol	26.0	23.6
1-Propanol	25.8	23.4

<sup>a</sup> Solubility parameter of PDMS ( $\delta_{PDMS}$ ) was  $2.4 \text{ (J m}^{-3}\text{)}^{1/2} \times 10^{-3}$ .

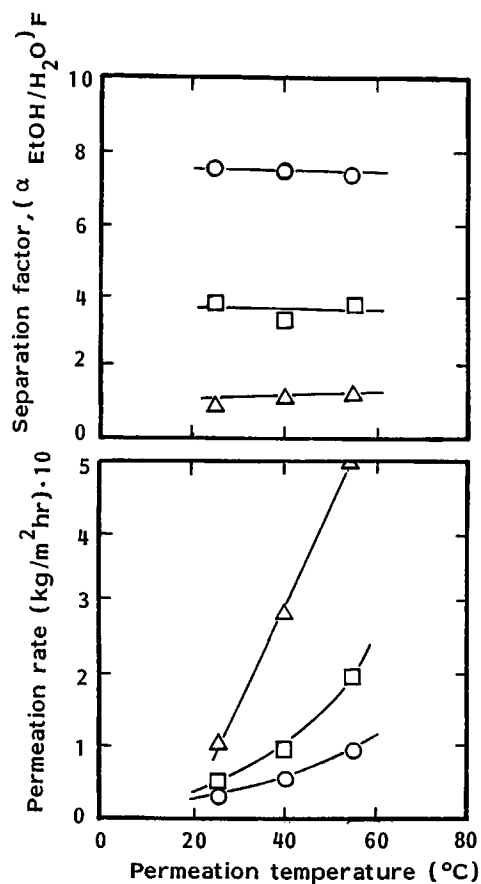
<sup>b</sup>  $(\text{J m}^{-3})^{1/2} \times 10^{-3}$ .

creased with increasing permeation temperature. This is attributed to an increase in motion of the PDMS chain and of the permeating molecule. On the other hand, the separation factors were kept constant regardless of the permeation temperature. In Figure 7(a), the permeation rates for ethanol and water are shown plotted against the permeation temperature. The ratios of the permeation rate for water to that for ethanol at each permeation temperature are constant. In order to easily understand them, the relationship between these permeation rates and the permeation temperature for an aqueous solution of 50 wt % ethanol in PV is illustrated by magnifying in Figure 7(b) as an example. In this figure, the ratios of the permeation rate for water to that for ethanol at 25, 40, and 55°C are 1/4, 2/8, and 4/16, respectively. Consequently, the separation factor is constant regardless of the permeation temperature in PV.

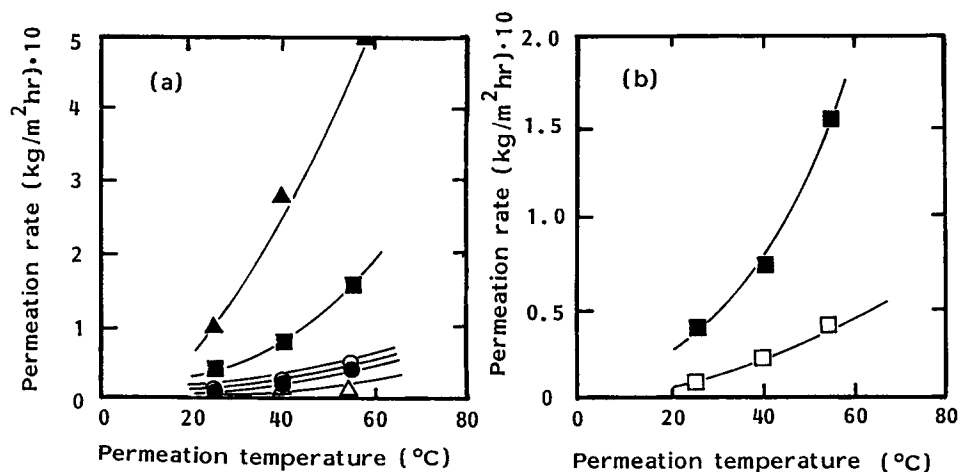
In Figure 8, the permeation rates and separation factors for aqueous ethanol solutions through the PDMS membrane in the TDEV method, in which the temperature of membrane surroundings was kept constant at 25°C and the temperature of the feed solution was changed, are shown. Both the permeation rate and separation factor for each aqueous ethanol solution increased with increasing feed solution temperature. The increase in permeation rate is due to increased motility of the permeating molecules. The increase in the separation factor can be understood from Figure 9, which shows the permeation rates for ethanol and water with increasing temperature of the feed solution. As seen from Figure 9, the permeation rates for water in aqueous ethanol solutions were approximately constant regardless of the feed solution temperature, but those for ethanol increased remarkably with increasing temperature of the feed solution. Therefore, the separation factor increases also.

The permeation and separation characteristics for an aqueous solution of 10 wt % ethanol through the

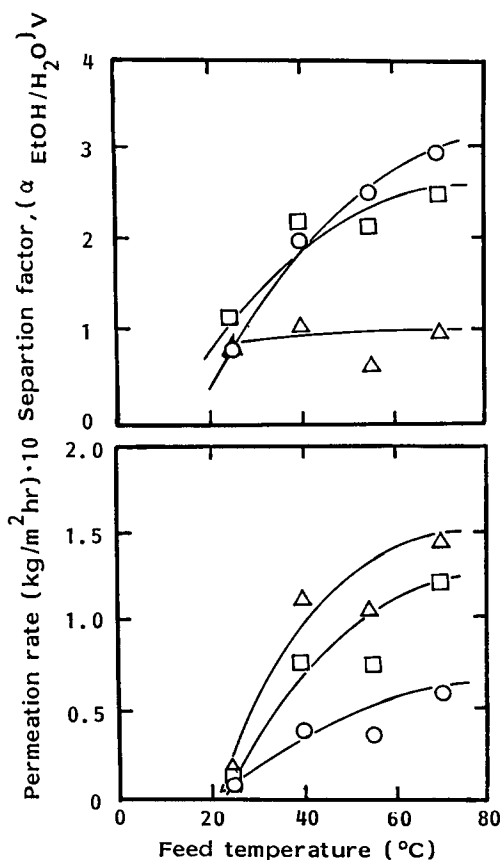
PDMS membrane in TDEV, in which the temperature of the feed solution was kept constant at 40°C and the temperature of the membrane surroundings was changed, are shown in Figure 10. The permeation rate decreased but the ethanol concentration in the permeate increased with lowering of the temperature in the membrane surroundings. The decrease in the permeation rate is attributed to the lowering of the motion of both the permeating molecules and polymer chains constituting the PDMS membrane. On the other hand, the increase in separation factor is explained by the illustration shown in Figure 11. At first, ethanol and water molecules are vaporized from the feed mixture at higher temperature. When these vaporized molecules come close to the membrane surroundings kept at a lower temperature, the water molecules are liable to be aggregated more than the ethanol molecules. It is very difficult for these aggregated water molecules to be incorporated into the PDMS membrane and



**Figure 6** Effect of permeation temperature on the permeation rates and separation factors for 10 wt % (O), 50 wt % (□), and 96 wt % (Δ) of an aqueous ethanol solution through the PDMS membrane by PV.



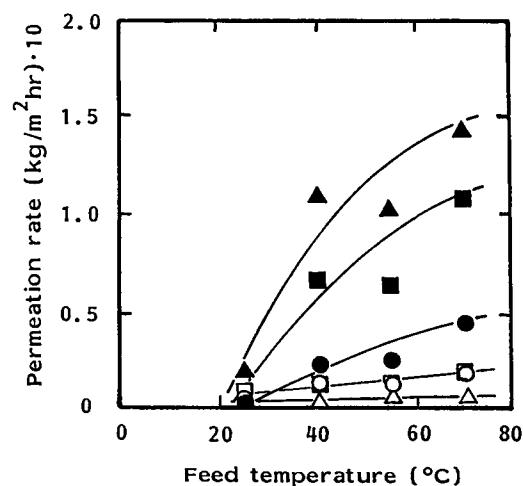
**Figure 7** Effect of permeation temperature on the permeation rates for water and ethanol: (a) for aqueous solutions of 10 wt % (○, ●), 50 wt % (□, ■), and 96 wt % (△, ▲) ethanol, ○, □, and △ for water, ●, ■, and ▲ for ethanol; (b) for an aqueous solution of 50 wt % ethanol, □ for water, ■ for ethanol.



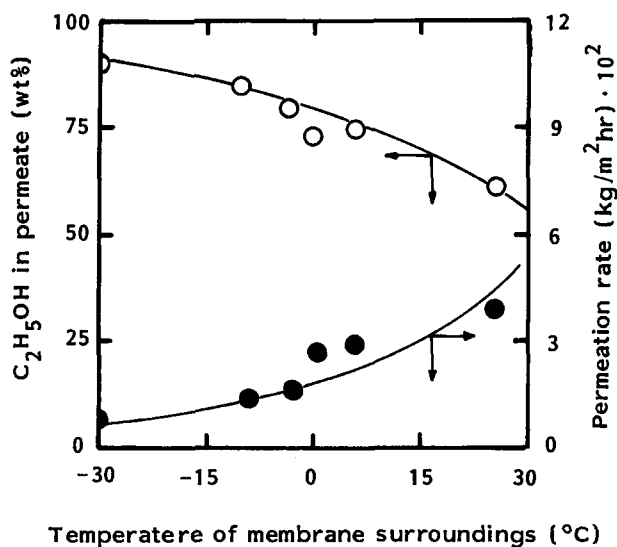
**Figure 8** Effect of temperature of feed solution on the permeation rates and separation factors for aqueous solutions of 10 wt % (○), 50 wt % (□), and 96 wt % (△) ethanol through the PDMS membrane by TDEV. Temperature of membrane surroundings: 25°C.

be diffused through the PDMS membrane. However, the ethanol molecules are not aggregated in the range of the temperature in the membrane surroundings in this study. The degree of aggregation of the water molecules depends on the temperature in the membrane surroundings. The increase in the separation factor is due to the aggregation of water molecules and is significantly governed by the degree of aggregation of the water molecules.

Table III summarizes the permeation and separation characteristics for an aqueous solution of 10



**Figure 9** Effect of temperature of feed solution on the permeation rates for water (open plots) and ethanol (solid plots) of aqueous solutions of 10 wt % (○, ●), 50 wt % (□, ■), and 96 wt % (△, ▲).



**Figure 10** Effect of temperature of membrane surroundings on the permeation and separation factors for an aqueous solution of 10 wt % ethanol through the PDMS membrane. Temperature of feed solution: 40°C.

wt % ethanol through the PDMS membrane in EV, in which the temperatures of the feed and membrane surroundings are controlled. When the temperature in the membrane surroundings was kept constant and the temperature of the feed solution was raised (nos. 1–5 in Table III), both the permeation rate and separation factor increased. As the temperature of the feed solution was kept constant and the temperature in the membrane surroundings was changed (nos. 2, 6–10), the permeation rate decreased and the separation factor remarkably increased with lowering of the temperature in the membrane surroundings. However, when the temperature of the feed was kept constant and the temperature in the membrane surroundings was set higher than the temperature of the feed solution (nos. 11–13), the selectivity for ethanol was very low.

Table III also includes the permeation and separation characteristics for an aqueous solution of 10 wt % ethanol through the PDMS in PV at 40°C (no. 15). The separation factors,  $(\alpha_{\text{EtOH}/\text{H}_2\text{O}})_F$ , for TDEV in nos. 2–5 and 6–11 are greater than these for PV in no. 15. In particular, when the temperature of the feed solution was 40°C and the temperature in the membrane surroundings was –30°C (no. 6),  $(\alpha_{\text{EtOH}/\text{H}_2\text{O}})_F$  was 85.7 and the ethanol concentration in the permeate was 90.5 wt %.

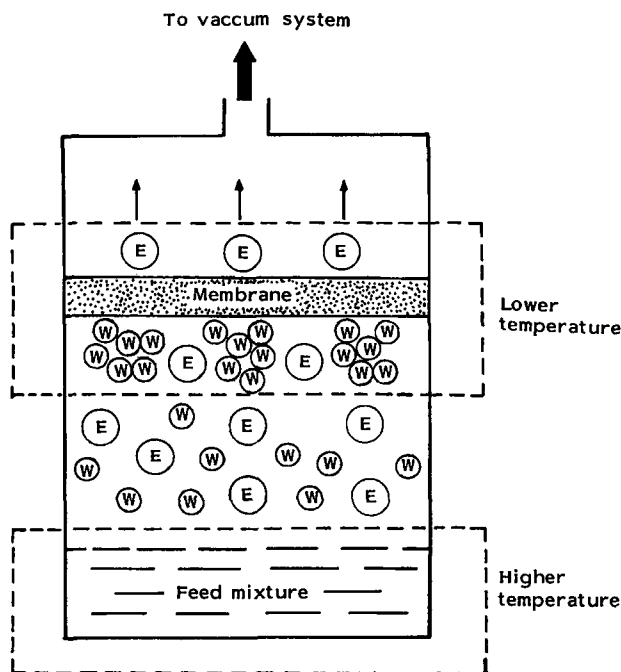
From the above results in TDEV, it was found that the selectivity for ethanol in aqueous ethanol solutions through the PDMS membrane is improved as the temperature of the feed solution is raised, the

temperature in the membrane surroundings is dropped, and also a larger difference between these temperatures is created. In order to provide a larger temperature difference, the temperatures of the feed solution and the membrane surroundings were set at 70 and –30°C, respectively. The result obtained is shown in Table III, no. 14. However, contrary to our expectations, a high selectivity cannot be obtained. This result may be due to the fact that the temperature in the membrane surroundings could not be kept at –30°C because the temperature of the feed solution was too high.

In Table IV, the performances for ethanol permselective membranes with aqueous ethanol solutions are summarized. As can be seen in this table, the selectivity for ethanol through the PDMS membrane in TDEV is very high compared with those for other membranes in PV but its permeation rate is small.

## CONCLUSIONS

In order to obtain a high permeation rate and high permselectivity for alcohol in aqueous alcohol solutions of low alcohol content, a poly(dimethyl siloxane) membrane, which had permselectivity for



**Figure 11** Tentative separation mechanism for ethanol/water mixture through the PDMS membrane by the TDEV method, in which the temperature of the membrane surroundings is lower than that of the feed solution.



**Table III Effect of Temperature of the Feed and Membrane Surroundings on the Permeation and Separation Characteristics for an Aqueous Solution of 10 wt % Ethanol through the PDMS Membrane by the TDEV Method**

Run No.	1	2	3	4	5	15
Feed temperature (°C)	25	40	55	70	85	PV
Membrane surroundings temperature (°C)	25	25	25	25	25	40
Ethanol concentration in permeate (wt %)	38.2	61.5	68.5	71.8	70.6	45.3
Separation factor $(\alpha_{EtOH/H_2O})_V$	0.8	2.0	2.8	3.3	3.1	
$(\alpha_{EtOH/H_2O})_F$	5.6	14.4	19.6	22.9	21.6	7.4
Permeation rate for total (kg/m <sup>2</sup> hr) × 10 <sup>2</sup>	0.85	4.01	8.12	11.50	9.57	5.33
Permeation rate for ethanol (kg/m <sup>2</sup> h) × 10 <sup>2</sup>	0.33	2.47	5.56	8.25	6.75	2.92
Permeation rate for water (kg/m <sup>2</sup> h) × 10 <sup>2</sup>	0.52	1.54	2.56	3.24	2.81	2.41

6	7	8	9	10	11	12	13	14
40	40	40	40	40	40	40	40	70
-30	-10	-3	0	5	40	55	70	-30
90.5	85.4	80.1	73.2	75.7	38.5	38.6	31.1	77.3
12.2	7.4	5.2	3.5	4.0	0.8	0.8	0.7	4.3
85.7	52.4	36.3	24.5	28.1	5.6	5.6	4.1	30.6
0.74	1.41	1.71	2.74	3.03	1.63	1.58	1.37	1.78
0.67	1.21	1.37	2.00	2.30	0.63	0.61	0.49	1.38
0.07	0.20	0.34	0.74	0.73	1.00	0.97	0.88	0.40

**Table IV Performance of Permselective Membranes for Ethanol**

Membrane	Feed (wt %)	Applied Temperature (°C)	Permeate (wt %)	$\alpha_{EtOH/H_2O}$	Permeation Rate × 10 <sup>4</sup> (g/m <sup>2</sup> h)	References
St-DMA graft copolymers (87.5/5.0/7.5)	7	25	65.7	25.4	2.70	20
PDMS	7	25	47.0	11.8	20.5	2
PTMSP	7	25	47.6	11.2	11.2	6
PTMSP	10	30	57.1	12.0	45.0	16
PPP/PDMS graft copolymer	7.28	30	63.85	22.5	5.53	22
PDMS containing zeolite (60%)	5-5.5	22.5	48.6	16.5	4.49 × 10 <sup>-2</sup> (g/m <sup>2</sup> h)	19
St-HdFDA graft copolymer (87.6/12.4)	8	30	80.0	45.9	6.00	18
Plasma-polymerized perfluoropropane	4.8		26.9	7.31	7.53 (kg/m <sup>2</sup> h)	7
TFE/ <i>i</i> -OcVE/C <sub>18</sub> VE terpolymer(50/25/25)	15	50	55.6	7.13	50.0	20
Plasma-polymerized hexamethyltrisiloxane	4	25	42.9	18.0	1.51 × 10 <sup>-2</sup> (kg/m <sup>2</sup> h)	21
Modified silicone (PV), 80 μm	10	40	28.8	3.65	110	23
Modified silicone (EV), 80 μm	10	-30/70	68.2	19.3	166	23
PDMS (PV) 120 μm	10	40	45.3	7.44	63.9	This work
PDMS (EV) 120 μm	10	-30/40	90.5	85.7	8.93	This work

alcohols in pervaporation, was selected, and the permeation and separation characteristics for aqueous alcohol solutions through this membrane were investigated in detail by evapomeation with a temperature difference. When both the temperatures of the feed solution and the membrane surroundings were reasonably set up, high permeability and high selectivity for ethanol were observed. In particular, when the temperature of feed solution was kept constant and the temperature of the membrane surroundings was lowered, the permselectivity for ethanol remarkably increased. This high selectivity for ethanol was attributed to a difference in the aggregation in the membrane surroundings at a lower temperature of water and ethanol molecules vaporized from the feed solution.

It was found that evapomeation with a temperature difference was effective for the separation of aqueous alcohols. This membrane separation technique may be advantageous for separation in combinations with other membranes and other organic liquid mixtures.

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