Characteristics of permeation and separation of aqueous alcohol solutions through hydrophobic polymer membranes

Tadashi Uragami, Takeshi Morikawa and Hiroshi Okuno
Chemical Branch, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan
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Characteristics of the permeation and separation of aqueous alcohol solutions through hydrophobic polymer membranes, such as polystyrene and poly(vinyl chloride), were studied under various conditions by pervaporation and 'evapomeation' techniques. These hydrophobic membranes predominantly permeated water molecules from aqueous alcohol solutions in both pervaporation and evapomeation methods. Permeation rates in evapomeation were approximately equal to those in pervaporation, but the separation factors in the former were greater than those in the latter method. The permeation rate decreased and the separation factor increased as the alcohol molecule in aqueous solution increased in size. When the temperature of the feed vapour in evapomeation was raised, both permeation rate and separation factor were increased. Mechanisms for permeation and separation of aqueous alcohol solutions through hydrophobic polymer membranes by pervaporation and evapomeation techniques are discussed from physicochemical viewpoints.

(Keywords: hydrophobic polymer membrane; aqueous alcohol solution; permeation; separation; pervaporation; evapomeation)

INTRODUCTION

Polymer membranes for materials separation have been considered in various fields. The separation and concentration of organic liquid mixtures are very important in the chemical industry, for example. It is well known that pervaporation in membrane separation techniques is an advantage in the separation and concentration of organic liquid mixtures. We also proposed[1,2] a new membrane separation technique, named 'evapomeation', as a membrane separation technique that has the several advantages of pervaporation and also improves on it.

In earlier papers, permeation and separation characteristics for aqueous alcohol solutions through hydrophilic polymer membranes such as alginic acid[1], chitosan[2] and crosslinked chitosan[3] via the pervaporation and evapomeation methods were reported. The permeation and separation characteristics of these membranes in pervaporation were significantly different from those in evapomeation. For example, the selectivity for aqueous ethanol solution through the alginic acid membrane by pervaporation depended on the composition of the feed solution, but the selectivity in the case of evapomeation did not change over all the feed compositions. These phenomena were closely related to the swelling of the membrane due to the feed solution. In this paper, poly(vinyl chloride) (PVC) and polystyrene (PSt) membranes are selected as hydrophobic polymer membranes in order to reveal more about the relation between the permeation and separation characteristics and membrane structure in pervaporation and evapomeation methods. Mechanisms for the permeation and separation of aqueous alcohol solutions through these membranes by both methods are discussed.

EXPERIMENTAL

Materials

The three kinds of poly(vinyl chloride) (produced by Kanegafuchi Chemical Industry Co. Ltd) used as membrane material were PVC 400, PVC 1008 and PVC 3000, whose average degrees of polymerization were 440, 773 and 3340, respectively. Polystyrene (produced by Shinnitetsu Chemical Industry Co. Ltd), having an average degree of polymerization of 730, was also employed as a membrane material. The tetrahydrofuran and benzene used as casting solvents and the alcohols used as feed solutions for the permeation were supplied as pure commercial sources.

Preparation of membranes

The casting solutions of PVC and PSt consisted of 10 wt% of PVC in tetrahydrofuran and 3.5 wt% of PSt in benzene, respectively. The PVC and PSt membranes were made by pouring the casting solutions onto a rimmed glass plate and allowing the solvent to evaporate completely at 25°C. The thickness of the PVC and PSt membranes was 15 and 25 μm, respectively.

Apparatus and measurements

The apparatus for the pervaporation and evapomeation experiment has been reported in earlier papers[1,2]. In pervaporation, the feed solution is in direct contact with the membrane; whereas, in evapomeation, the feed mixture is not in contact with the membrane and only vapour in equilibrium with the liquid mixture is supplied to the membrane. The pervaporation and evapomeation experiments were carried out at the desired temperature,

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and the pressure maintained at the downstream face of the membrane in both methods was 5×10^{-3} Torr. Permeation rates were determined by weighing the permeate. The compositions of the feed solutions, permeates and solutions adsorbed in the membrane were measured by means of gas chromatography (Shimadzu GC-4CPTF).

The degree of swelling of the membrane was defined by the following equation:

$$\text{Degree of swelling} = \frac{\text{Weight of swollen membrane}}{\text{Weight of dry membrane}}$$

The composition of solution adsorbed in the membrane was measured using the system shown in *Figure 1*. The membrane was completely swollen with the feed solution and the solution on the surface of the swollen membrane quickly wiped off with a filter paper. Then the desired amount of the swollen membrane was placed in a container. This container was connected to the system as shown in *Figure 1*, the system was evacuated and the container with the swollen membrane heated to evaporate completely the liquid adsorbed in the membrane. The evaporated vapour was trapped in the U-tube by cooling with liquid nitrogen, and the collected liquid was analysed by gas chromatography.

The separation factor, $\alpha_{H_2O/alcohol}$, was computed from the following equation:

$$\alpha_{H_2O/alcohol} = (Y_{H_2O}/Y_{alcohol})/(X_{H_2O}/X_{alcohol})$$

In pervaporation, X_{H_2O}, $X_{alcohol}$, Y_{H_2O} and $Y_{alcohol}$ are weight fractions of water and alcohol in the feed and permeate, respectively. In evapomeation, X_{H_2O} and $X_{alcohol}$ are weight fractions of water and alcohol vapours in the feed solution, and Y_{H_2O} and $Y_{alcohol}$ are weight fractions of water and alcohol in the permeate.

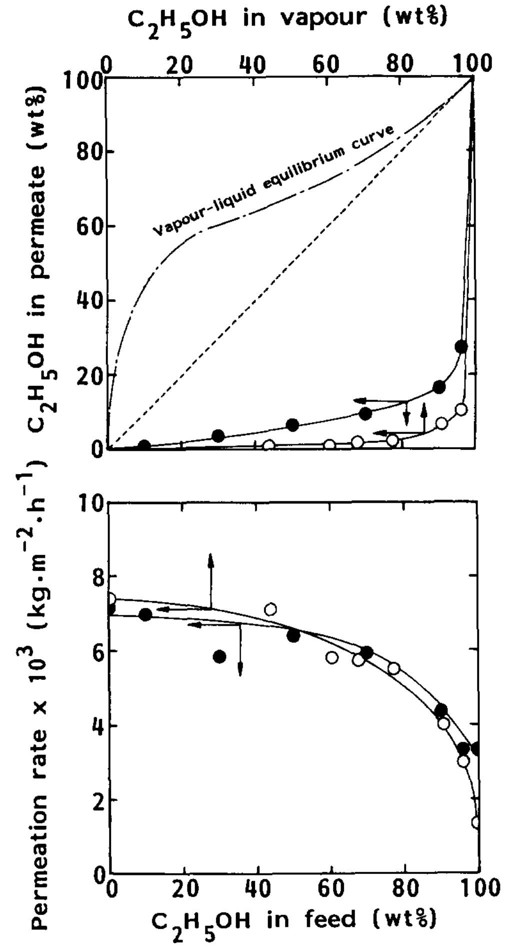

Figure 2 Effect of composition of both the feed solution and the feed vapour on the permeation rate and ethanol concentration in the permeate through the PVC 400 membrane by (●) pervaporation and (○) evapomeation. Permeation conditions: 40°C, 5×10^{-3} Torr

RESULTS AND DISCUSSION

Permeation and separation characteristics

The characteristics of permeation and separation of aqueous ethanol solutions through the PVC 400 membrane via pervaporation and evapomeation are shown in *Figure 2*. Since the vaporized molecules are in contact with the membrane in the case of evapomeation, the abscissa in this case is represented by vapour composition. The chain curve in *Figure 2* is a vapour–liquid equilibrium curve for aqueous ethanol solution. The plots for the concentration of ethanol in the permeate through the PVC 400 membrane in both pervaporation and evapomeation are below the chain curve. These results support the assumption that water molecules predominantly permeate through the hydrophobic PVC membrane in both methods. Similar results were obtained in the hydrophobic PSt membranes[4]. In order to reveal that the PVC membrane predominantly permeated water from aqueous ethanol solution in spite of the fact that the PVC membrane was hydrophobic, the composition of the solution adsorbed in the PVC membrane was measured. The results are shown in *Figure 3*. As can be seen, ethanol is preferentially incorporated into the PVC membrane in all feed solutions. This result is attributed to the fact that the difference in solubility parameter[5] between the PVC membrane ($\delta_{PVC}=19.3$) and ethanol ($\delta_{EtOH}=26.9$) is smaller than that between the PVC membrane ($\delta_{PVC}=19.3$) and water ($\delta_{H_2O}=47.9$). In spite of the ethanol molecules in the feed solution being preferentially sorbed by the PVC membrane, the fact that the water was preferentially predominantly permeated through the PVC membrane from aqueous ethanol

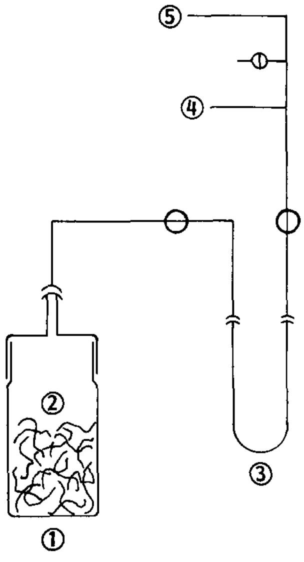

Figure 1 Diagram of the apparatus used to determine the composition of solution adsorbed inside the membrane: 1, container; 2, membrane; 3, U-tube trap; 4, Pirani gauge; 5, to vacuum system

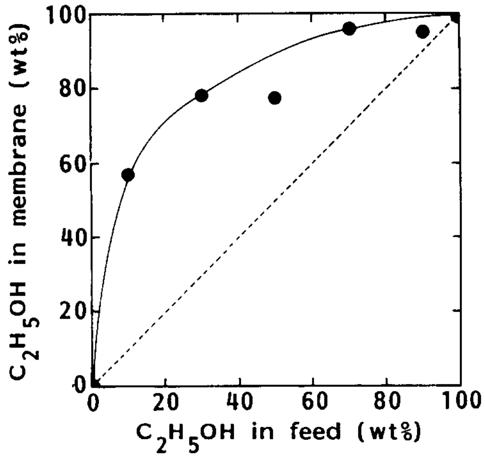

Figure 3 Relationship between the ethanol concentrations in the feed solution and in the PVC 400 membrane. Experimental conditions: 40°C, 1 atm

solution is interpreted as follows. The ethanol molecules are preferentially incorporated into the PVC membrane but it is very difficult for the ethanol molecules to diffuse through the PVC membrane, because the affinity between the ethanol molecules and the PVC membrane is very strong and also the molecular size of ethanol is rather large. On the other hand, it is very difficult for the water molecules to dissolve into the PVC membrane. However, once the water molecules are incorporated into the membrane, they can easily diffuse through the PVC membrane because the interaction between the water molecule and the PVC membrane is very weak and also the molecular size of the water is smaller than that of ethanol. Consequently, the water molecules are predominantly permeated through the hydrophobic PVC membrane.

In *Figure 2*, the permeation rates through the PVC membrane obtained for pervaporation and evapomeation were found to decrease with increase in the ethanol concentration in the feed solution. This decrease in the permeation rate is attributed to the fact that the amount of water molecules incorporated into the PVC membrane, which selectively permeates water molecules, decreases as the ethanol content in the feed solution or feed vapour is decreased. Because the polymer membranes used in pervaporation are directly in contact with the feed solutions, the membranes are often swollen due to the feed mixtures. On the other hand, in evapomeation, since the feed solution is not in contact with the membrane and only vapour is supplied to the membrane, the swelling of membrane is remarkably prevented compared with that in pervaporation. Consequently, the permeation rates for pervaporation were greater than those for evapomeation[1,2,4]. These phenomena may be attributed to the difference in interfacial tension between the permeating species and the membrane. However, the difference between the permeation rates from aqueous ethanol solutions through the PVC membrane by pervaporation and evapomeation is very small, as shown in *Figure 2*. In *Figure 4* the relationship between the ethanol concentration in the feed solution and the degree of swelling of the PVC 400 membrane in the case of pervaporation is shown. As can be seen, the swelling of the PVC membrane with aqueous ethanol solutions is very small. Therefore, no difference between the permeation rates in the pervaporation and evapomeation methods was found.

Separation factor

The effect of feed concentrations on the separation factors through the PVC 400 membrane via pervaporation and evapomeation is shown in *Figure 5*. The separation factors in both methods increase as the ethanol concentration in the feed is increased. This increase in separation factor is due to the fact that water can be predominantly permeated from the feed solution with a higher ethanol content. In *Figure 5*, the separation factors in evapomeation are about 10 times higher than those in pervaporation. In pervaporation, there exist interactions between water molecules, between water and ethanol molecules, and between ethanol molecules in the feed solutions. On the other hand, in evapomeation, the feed solution is vaporized and the water and ethanol molecules can behave as a monomolecule. When the permeation of species through the membrane is due to the solution–diffusion mechanism, the size of the permeating species is very important in the solution or diffusion processes. Therefore, these molecules in evapomeation can be selectively incorporated into the membrane or predomi-

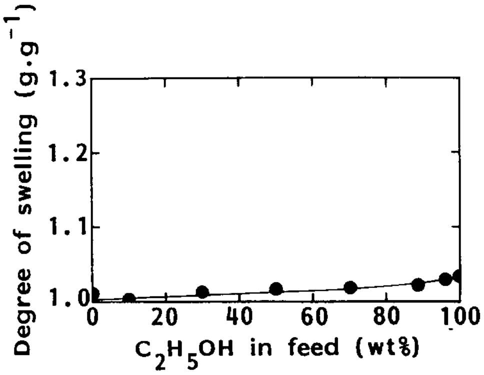

Figure 4 Effect of ethanol concentration in the feed solution on the degree of swelling of the PVC 400 membrane. Experimental conditions: 40°C, 1 atm

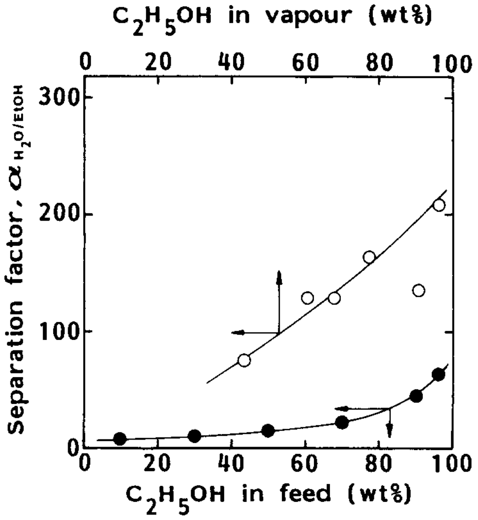

Figure 5 Relationship between the ethanol concentration in the feed and the separation factor through the PVC 400 membrane by (●) pervaporation and (○) evapomeation. Permeation conditions: 40°C, 5×10^{-3} Torr

nantly diffused through the membrane, and consequently the selectivity for the feed mixture is increased.

Figures 6 and *7* show the permeation rates and separation factors for aqueous methanol, ethanol and 2-propanol solutions through the PVC 400 membrane and for aqueous methanol and ethanol solutions through the PSt membrane by evapomeation. The permeation rates for aqueous alcohol solutions in both PVC and PSt membranes increase with increase in alcohol concentration in the feed mixtures. Also the permeation rates for an aqueous solution of higher alcohol are smaller than those for lower alcohol in both membranes. The separation factors for all aqueous alcohol solutions through both membranes decrease with increasing alcohol concentration in the feed and become larger for an aqueous solution of higher alcohol.

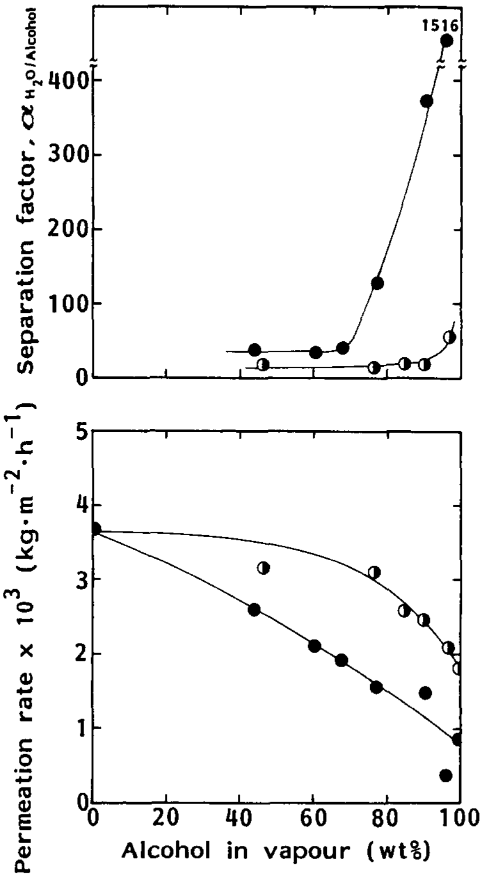

Figure 7 Effect of alcohol concentration in the feed vapour on the permeation rate and separation factor through the PSt membrane by evapomeation. Aqueous solutions: (◑) methanol; (●) ethanol. Permeation conditions: 40°C, 5×10^{-3} Torr

Table 1 Molecular size and solubility parameter of the permeating molecule

Permeating molecule	$V_s \times 10^3$ (l mol^{-1})	$R_s \times 10^{10}$ (m)	$P_s \times 10^{28}$ (m^2)	$\delta \times 10^{-3}$ (J m^{-3})$^{1/2}$
Water	–	–	–	47.9
Methanol	40.7	1.44	17.8	29.7
Ethanol	58.5	1.94	18.1	26.0
2-Propanol	76.8	2.28	28.0	23.5

Table 2 Difference between the solubility parameters of polymer and alcohol

Permeating molecule	$\delta_{PVC} - \delta_{alcohol}$	$\delta_{PSt} - \delta_{alcohol}$
Methanol	10.4	10.2
Ethanol	6.7	6.5
2-Propanol	4.2	4.0

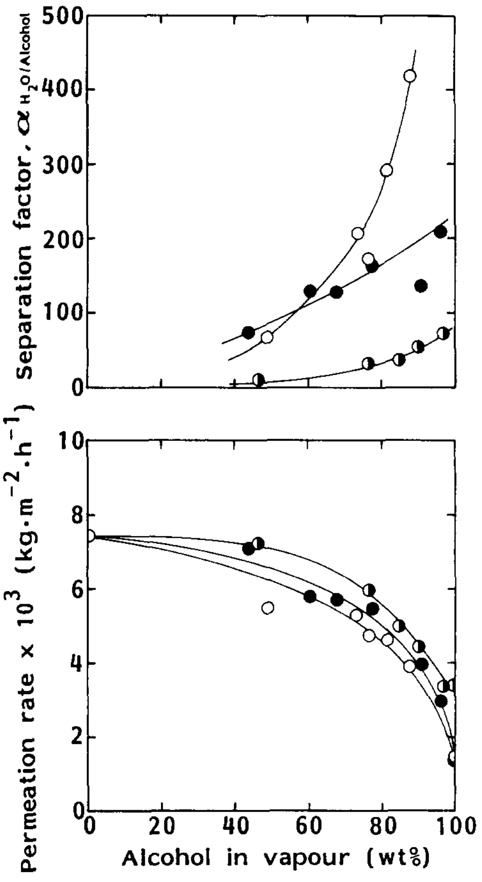

Figure 6 Effect of alcohol concentration in the feed vapour on the permeation rate and separation factor through the PVC 400 membrane by evapomeation. Aqueous solutions: (◑) methanol; (●) ethanol; (○) 2-propanol. Permeation conditions: 40°C, 5×10^{-3} Torr

The molecular size[6] and solubility parameter[5] of the permeating molecule are summarized in *Table 1*, where V_s is the molar volume, R_s is the Stokes radius, P_s is the cross-sectional area of permeating molecule, perpendicular to the larger axis of the molecule, and δ is the solubility parameter. The values of V_s, R_s and P_s for the higher alcohol are larger. The diffusivity of alcohol molecules through the PVC and PSt membranes decreases as the molecular size increases. Therefore, the permeation rate for an aqueous solution of a higher alcohol is smaller. On the other hand, the solubility parameters[5] for PVC and PSt are 19.3 and 19.5, respectively. The difference between the solubility parameters of polymer and alcohol molecules is summarized in *Table 2*. When this difference between the solubility parameters is small, the interaction between the polymer membrane and the permeating molecule becomes large. Consequently, the larger separation factor for the higher alcohols can be explained from the viewpoints of molecular size and the affinity between polymer membrane and permeating species.

Effect of permeation temperature

The effect of temperature of the feed solution on the permeation and separation characteristics for an aqueous

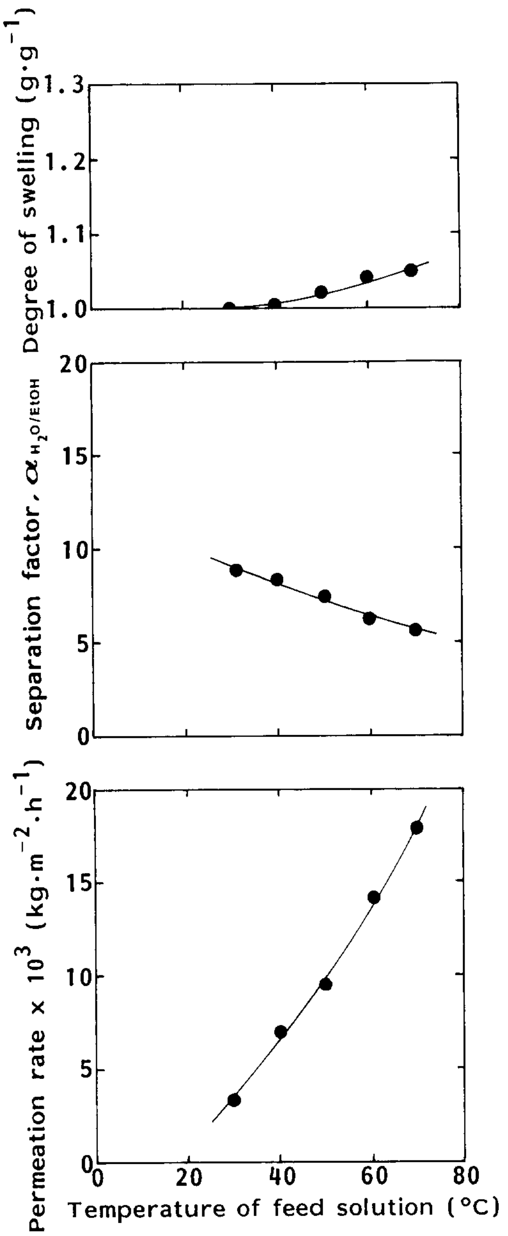

Figure 8 Permeation rate and separation factor through the PVC 400 membrane by evapomeation and degree of swelling of the PVC 400 membrane as a function of temperature of the feed solution. Ethanol concentration in the feed solution is 10 wt%. Reduced pressure: 5×10^{-3} Torr

solution of 10 wt% ethanol through the PVC 400 membrane in pervaporation is shown in *Figure 8*. The permeation rate is increased and the separation factor is decreased on raising the temperature of the feed solution. The increase in permeation rate is attributable to the increase in activity of permeating molecules and molecular motion of the polymer chain of the PVC membrane. *Figure 8* also includes the degree of swelling of the PVC 400 membrane with change in the temperature of the feed solution. The decrease in separation factor is dependent on the increase in degree of swelling of the membrane, which facilitates the permeation rates of both water and ethanol through the membrane.

The effect of temperature of the feed vapour on the permeation rate and separation factor for aqueous solutions of 10 wt% and 95.6 wt% ethanol (viz. an azeotropic composition) through the PVC membrane in evapomeation is shown in *Figure 9*. Both permeation rate and separation factor increase as the temperature of the feed vapour is raised. In *Table 3*, the total permeation rate, the permeation rates for water and ethanol, and the separation factor for various temperatures of feed vapour from aqueous solution of 10 wt% ethanol are summarized. As can be seen, the permeation rates for ethanol are almost constant regardless of the temperature of the feed vapour but those for water increase with increasing temperature. For the former result, although there is no evidence, it is presumed that the temperature dependence of the diffusion coefficient of the ethanol molecule through the PVC membrane may be very small because the interaction between the ethanol molecule and the PVC membrane is very strong. On the other hand, the diffusion coefficient of water molecules through the

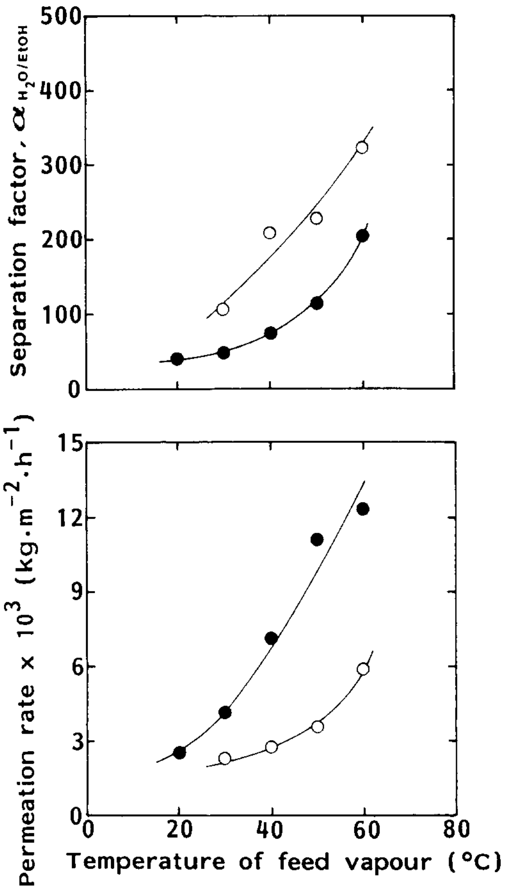

Figure 9 Effect of temperature of the feed vapour on the permeation rate and separation factor through the PVC 400 membrane by evapomeation. Ethanol concentration in the feed solution: (●) 10 wt%; (○) 95.6 wt%. Reduced pressure: 5×10^{-3} Torr

Table 3 Effect of temperature of the feed vapour on the permeation rate and separation factor by evapomeation[a]

Temperature of feed vapour (°C)	Separation factor	Permeation rate × 10^{-3} (kg m^{-2} h^{-1})		
		Total	H_2O	C_2H_5OH
20	41.3	2.55	2.50	0.05
30	48.9	4.20	4.13	0.07
40	74.7	7.22	7.15	0.07
50	114	11.18	11.1	0.08
60	206	12.35	12.3	0.05

[a] Feed solution is aqueous solution of 10 wt% ethanol, viz. 43.9 wt% ethanol in feed vapour

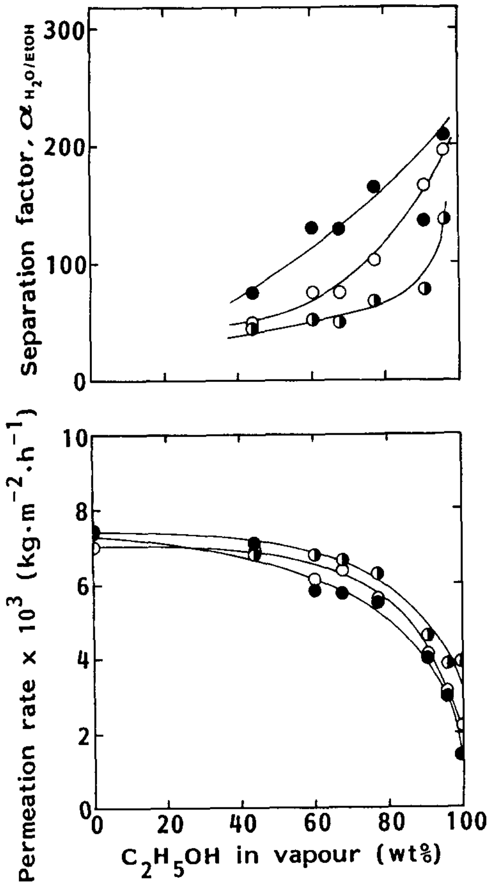

Figure 10 Effect of ethanol concentration in the feed vapour on the permeation rate and separation factor through various PVC membranes by evapomeation: (●) PVC 400 membranes; (○) PVC 1008 membrane; (◑) PVC 3000 membrane. Permeation conditions: 40°C, 5×10^{-3} Torr

membrane is increased because the activity of water molecules increases remarkably with an increase in temperature. Consequently, the total permeation rate and the separation factor are significantly governed by those of water.

In *Figure 9*, the increase in both permeation rate and separation factor with increase in temperature of the feed vapour in evapomeation is of much interest for membrane performance.

Effect of degree of polymerization of PVC membrane

The effect of ethanol concentration in the feed vapour on the permeation and separation characteristics by evapomeation through some PVC membranes, which were prepared from PVC having different degrees of polymerization, is shown in *Figure 10*. The permeation rates are increased but the separation factors are decreased for the PVC membrane with the higher degree of polymerization. These PVC membranes were prepared under the same conditions. Therefore, polymer chains of PVC molecules with the higher degree of polymerization are not satisfactorily extended in the casting solution compared with those of PVC molecules with a lower degree of polymerization. Consequently, the PVC with the higher degree of polymerization does not form a dense membrane. It is also that the permeation and separation characteristics in *Figure 10* depend on the packing density of the resulting PVC membrane.

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