AWARD ACCOUNTS
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Structural Design of Polymer Membranes for Concentration of Bio-ethanol

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This review paper introduces the preparation of porous PDMS membranes and the development of a new membrane separation technique for the concentration of bio-ethanol. Porous PDMS membranes were prepared by freeze-drying aqueous emulsions of organopolysiloxane, and were applied to a temperature-difference controlled evapomeation (TDEV) method developed as a new membrane separation technique. When the temperature of membrane surroundings was lowered, while keeping the temperature of the feed solution constant. The permeation rate of porous membrane in TDEV was higher by three orders of magnitude than that of dense membrane, although the ethanol/water selectivity was almost the same to each other. The relationship between the permeation and separation characteristics of porous PDMS membrane was discussed.
KEY WORDS: Poly(dimethylsiloxane) / Porous Membrane / Freeze Dry / Temperature-Difference Controlled Evapomeation / Bio-ethanol / Ethanol Permselectivity /

Bio-ethanol is a clean energy source that can be made by fermentation of biomass and has been noticed as one of the most important energy sources in the future. Aqueous dilute solutions made by this method contain only about 10 wt % ethanol which must be concentrated before industrial use. In general, an aqueous solution of dilute ethanol can be concentrated to an azeotrope (96.5 wt % ethanol) that cannot be separated furthermore by distillation. An entrainer such as benzene is then added to the azeotrope of ethanol and water, and this mixture is distilled to produce absolute ethanol.

Recently, membrane separation techniques have attracted considerable industrial attention in a wide variety of medical, food, energy, and environmental applications. Pervaporation is very useful for the separation of azeotropic mixtues[1,2] and close-boiling-point chemicals[3,4] and, in addition, can also offer advantages in energy savings. The chemical and physical properties of polymer membranes for pervaporation to remove water from an azeotrope of ethanol/water can be tailored by several methods to improve their performance.

Cross-linked poly (vinyl alcohol) composite membranes have been used in commercial pervaporation plants for dehydration of ethanol beyond the azeotrope. However aqueous ethanol solutions that can be produced by bio-fermentation are dilute (about 10 wt %). Therefore, if ethanol/water selective membranes with high efficiency can be prepared, the distillation process in the first stage to obtain an azeotrope can be replaced which is very advantageous for reduction of energy cost. There are fewer reports on ethanol/water selective membranes compared with those of water/ethanol selective membranes. One reason why the development of efficient high-performance ethanol/water selective membranes is difficult can be attributed to the fact that ethanol has a larger molecular size than water and must be preferentially permeated through the membrane. In fact, permeation and separation in a pervaporation process through dense membranes is based on the solution-diffusion mechanism.[5,6] Therefore, when it is required that ethanol molecules with larger molecular size preferentially permeate from an aqueous ethanol solution, it cannot be expected to be separated by the diffusion process. Consequently, only a difference of sorption selectivity in the solution process in which both ethanol and water components are dissolved can contribute to the separation. However, if the affinity of ethanol for polymer membranes is very high, the polymer membrane is extremely swollen when exposed to the liquid feed during pervaporation. Consequently, the permeation rate increases but the ethanol/water selectivity decreases remarkably because water molecules can be easily incorporated into the polymer membrane. In order to solve this problem, polymer membranes were modified by copolymerization, graft-, block-copolymerization, blending and cross-linking. In these approaches, the affinity and the hydrophobic balance of polymer membranes were investigated. However, the development of these methods showed a limit in improvement of the pervaporation properties of polymer membranes.

In order to develop practical ethanol/water selective polymer membranes, new membrane separation techniques instead of pervaporation must be developed. In this paper, the structural design of ethanol/water selective polymer membranes and the improvement of membrane separation techniques were investigated. In addition, a developmental study for the practicality of concentrating of bio-ethanol by membrane separation is reviewed.

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MEMBRANE SEPARATION TECHNIQUES

There are two methods for the concentration of an aqueous bio-ethanol solution that is produced by bio-fermentation. One uses both a hybrid process that combines distillation and membrane separation. In this case, an aqueous bio-ethanol solution is distillated first, and then an azeotrope is dehydrated by a water/ethanol selective membrane. The second method applies only a membrane separation technique, that is, an aqueous bio-ethanol solution is concentrated by an ethanol/ water selective membrane for bio-ethanol production. Presently, pervaporation is applied as the chosen membrane separation technique in both methods. However, it seems that conventional pervaporation is not the most efficient membrane separation process for bio-ethanol treatment as follows. Because the polymer membranes used in pervaporation are directly in contact with the liquid feed solutions, however, specifically designed chemical and physical membrane properties are often impaired by swelling or shrinking of the membrane due to sorption of the feed components. Swelling or shrinking of the polymer membranes is disadvantageous for the membrane performance with respect to the separation of mixtures. A novel membrane separation technique known as "evapomeation"[5–14] makes use of the advantages of pervaporation, but reduces the negative effects of swelling on membrane performance. In this technique, the feed solution is fed to the membrane without directly contacting the polymer membrane. This is accomplished by vaporizing the liquid feed so that only vapor is supplied to the polymer membrane. Therefore, swelling or shrinking of the polymer membranes due to contact with the feed solutions is minimized.

As mentioned above, a new evapomeation method for membrane separation that improves the shortcomings of pervaporation while keeping the advantages of this technique was developed.[5–14] In evapomeation, the temperatures of the feed solution (A) and the membrane surroundings (B) are controlled, and consequently a differential between these temperatur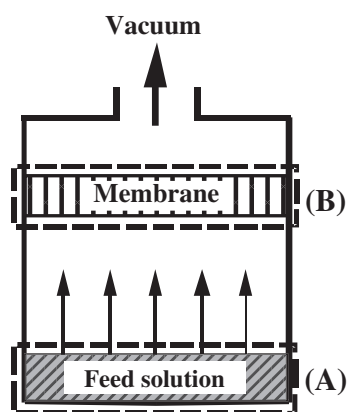es can be established, as shown in Figure 1. Such an evapomeation method, in which this temperature difference is controlled, is called "temperature-difference controlled evapermeation" (TDEV).[5,6,13–21] In TDEV, the most permeable solute has a lower freezing point in a binary liquid mixture and is selectively permeated, as shown in Table II. In addition, when the membrane has a stronger affinity to the preferentially permeating mixture component, an increase in selectivity can result.

COMPARISON OF PERFORMANCE OF DENSE PDMS MEMBRANES DURING PERVAPORATION AND EVAPOMEATION

Figure 2 shows the effect of the ethanol concentration in the feed solution on the permeation rate and the separation factor through a dense PDMS membrane during pervaporation and evapomeation.[19] The permeation rate in pervaporation was higher than that in evapomeation, but the separation factor for ethanol/water in the former was lower than that in the latter. With increasing the ethanol concentration in the feed solution the permeation rate increased but the separation factor decreased in both processes. These results can be attributed to the fact that the degree of swelling of the membrane in
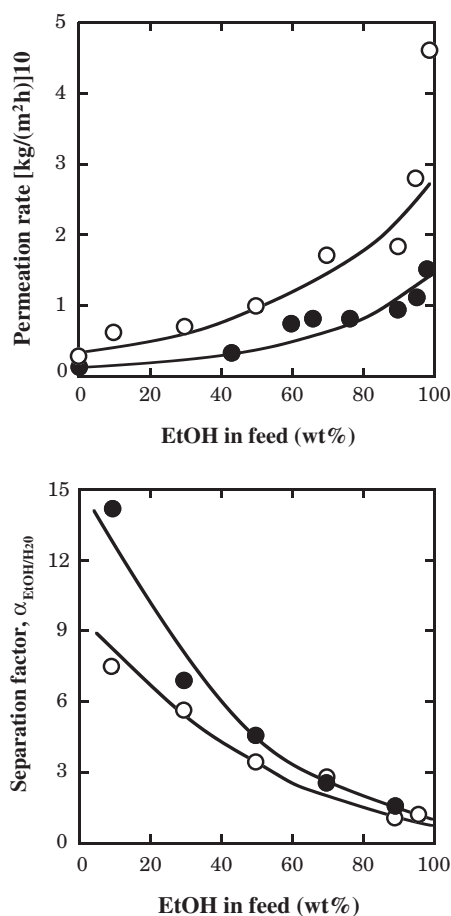
Figure 1. Principle of temperature difference-controlled evapomeation (TDEV).

Figure 2. Permeation rate and the separation factor through a dense PDMS membrane by pervaporation (○) and evapomeation (●) as a function of the ethanol concentration in the feed solution.
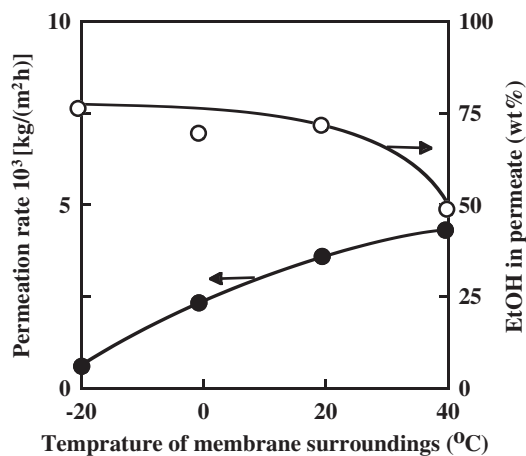
Figure 3. Permeation rate (●) and the ethanol concentration in the permeate (○) for an aqueous solution of 10 wt % ethanol through a dense PDMS membrane during TDEV, in which the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed.

Figure 4. Tentative mechanism of the separation for an aqueous ethanol solution through a dense PDMS membrane in TDEV.

Table I. Effect of the freezing point on the selectivity of the permeant in the organic liquid mixtures through polymer membranes in TDEV

Membrane	Chitosan	PVC	PDMS
Freezing point of permeant	$(CH_3)_2SO/H_2O$ $18.5\,°C > 0\,°C$	CH_3COOH/H_2O $16.7\,°C > 0\,°C$	C_2H_5OH/H_2O $-114.4\,°C < 0\,°C$
Selectivity	H_2O	H_2O	C_2H_5OH

pervaporation was higher than that in evapomeation. Based on above results, the higher ethanol/water selectivity of a dense PDMS membrane in evapomeation is very interesting. Hence, a dense PDMS membrane can be applied to TDEV for the concentration of aqueous ethanol solutions.

PERMEATION AND SEPARATION CHARACTERISTICS OF DENSE PDMS MEMBRANES IN TDEV

The permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt % ethanol through the dense PDMS membrane during TDEV is shown in Figure 3. The temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed as shown in Figure 3. 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 can be attributed to lowering the motion of both the permeating molecules and polymer chains consisting the PDMS membrane. On the other hand, the increase in the ethanol/water selectivity is explained by the illustration shown in Figure 4. 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 more aggregated than the ethanol molecules (because the freezing points of water and ethanol are 0 and $-114.4\,°C$, respectively) It is very difficult for these aggregated water molecules to be incorporated into the dense PDMS membrane and diffuse through the dense PDMS membrane. However, the ethanol molecules are not aggregated in the range of the temperature in the membrane surroundings under these permeation conditions. The increase in the ethanol/water selectivity is due to the aggregation of water molecules and is significantly governed by the degree of aggregation of the water molecules.
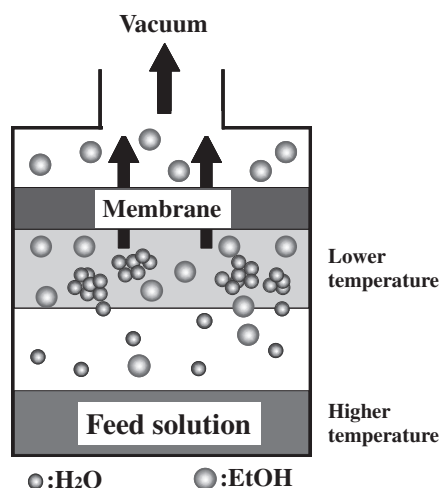
In order to confirm the generality of the mechanism for the ethanol/water selectivity shown in Figure 4, some other case were also studied. In Table I, the effect of the freezing point of the permeant in aqueous organic liquid mixtures on the selectivity through some polymer membranes in TDEV in which the feed solution was kept constant and the temperature of membrane surroundings was changed to a temperature less than the temperature of the feed solution is summarized. As can be seen from Table I, the permeant having a lower freezing point in the feed mixture is selectively permeated. In addition, the membrane has stronger affinity to the permeant which is selectively permeated. Therefore, a much higher selectivity can be achieved in TDEV.[22] In Figure 5, a chitosan membrane which is water selective was applied to the separation of aqueous dimethyl sulfoxide solutions (DMSO) in TDEV.[20] As can be seen from this figure, when the feed solution was kept constant at 40 °C and the temperature of membrane surroundings was changed to a temperature less than the temperature of the feed solution, with decreasing temperature of the membrane surroundings both the permeation rate and the water/DMSO selectivity increased. The increase in the permeation rate may be due to an increase of the vapor solubility in the chitosan membrane with a drop of the temperature of the membrane surroundings according to Henry's law. The increase in the water/DMSO selectivity is explained as follows. When the DMSO and water molecules which had vaporized from the feed solution come close to the membrane surroundings, the DMSO vapor aggregates much easier than of the water vapor because the freezing points of DMSO and
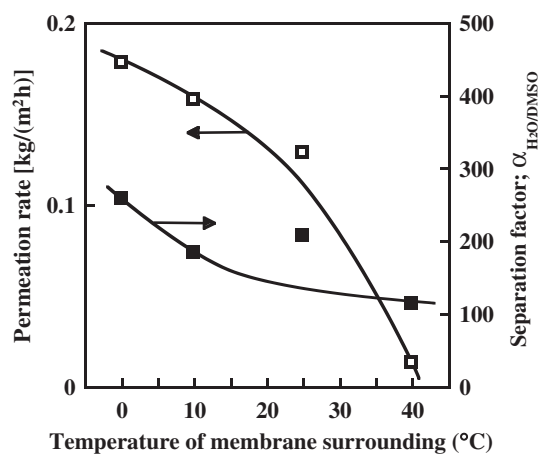
Figure 5. Effects of the temperature of the membrane surroundings in TDEV in which the temperature of the feed solution is kept constant at 40 °C on the permeation rate (■) and the separation factor (□) for the water/DMSO selectivity for an aqueous solution of 50 wt % DMSO through a chitosan membrane.

Table II. Permeation and separation characteristics for an aqueous solution of 10 wt % ethanol through a PTMSP membrane in TDEV

	TDEV					PV[a]
Temperature of membrane surroundings (°C)	0	10	20	30	40	40
EtOH in permeate (wt %)	89.6	87.1	85.3	76.8	62.4	58.8
Separation factor (α_{EtOH/H_2O})	77.5	60.7	52.2	29.7	14.9	12.8
Permeation rate [kg/(m²h)]	0.38	0.51	0.76	0.67	0.53	0.59

[a]Pervaporation.

$\alpha_{EtOH/H2O} = \{Y_{EtOH}/(1-Y_{EtOH})/X_{EtOH}/(1-X_{EtOH})\}$

X_{EtOH}: weight fraction of ethanol in the feed. Y_{EtOH}: weight fraction of ethanol in the permeate. Feed temperature: 40 °C.

water are 18.4 and 0 °C, respectively and tends to liquefy as the temperature of the membrane surroundings becomes lower. This aggregation of the DMSO molecules is responsible for the increase of the water/DMSO selectivity through the chitosan membrane. The results in the separation for aqueous DMSO solutions through a water selective chitosan membrane in TDEV could support the mechanism in the concentration of ethanol for aqueous ethanol solutions through an ethanol selective PDMS membrane in TDEV.

In Table II, the characteristics of permeation and separation for an aqueous solution of 10 wt % ethanol through the glassy poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane, which is organic solvent selective, is shown operated in TDEV and pervaporation mode. For comparison, the properties of PDMS membrane are also listed. The permeation and separation characteristics in TDEV and pevaporation at 40 °C are very similar. However, in TDEV with decreasing temperature of the membrane surroundings the ethanol/water selectivity increased remarkably. The permeation rate and the ethanol/water selectivity of the PTMSP membrane in TDEV are considerably higher than those of the PDMS membrane in TDEV in

Table III. Performance of commercial porous polymer membranes for an aqueous solution of 10 wt % ethanol in TDEV[a]

Membrane	Average pore size[b] (μm)	EtOH in permeate (wt %)	Permeation rate [kg/(m²h)]
PTFE[c]	0.45	39.7	36.59
	0.30	43.6	29.73
	0.22	44.6	31.21
	0.10	51.3	20.17
	0.05	54.3	13.80
PP[d]	0.125 x 0.05	55.9	8.27
	0.07 x 0.03	57.1	8.31
CN[e]	0.01	51.2	28.24
PC[f]	0.015	59.6	0.27
PP[g]	0.125 x 0.05	20.0	1.02
PDMS[h]		86.0	0.023

[a]Temperatures of the feed solution and the membrane surroundings are 40 and −20 °C, respectively. [b]Value in catalogue. [c]Poly(tetrafluoro ethylene). [d]Polypropyrene. [e]Cellulose nitrate. [f]Polycarbonate. [g]In pervaporation (40 °C). [h]Dense membrane.

Figure 3. It is well-known that the glassy, nanoporous PTMSP membranes has lower density, and, hence, higher free volume than other polymer membranes.[23] These results suggest that if a porous polymer membrane is applied to TDEV for the concentration of aqueous ethanol solutions, high permeation and separation characteristics can be obtained. Thus, we tried to apply various commercial porous membranes to the concentration of aqueous ethanol solutions in TDEV.

PERFORMANCE OF COMMERCIAL POROUS POLYMER MEMBRANES IN TDEV

Table III lists the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt % ethanol through various commercial porous polymer membranes in TDEV. In this Table, the properties of the dense PDMS in TDEV are also included. From the results in Table III, it is found that an aqueous solution of 10 wt % ethanol could be concentrated to about 40–60 wt % by applying porous polymer membranes using TDEV and the permeation rates were about 10–1,000 times than those of a PDMS membrane.

Figure 6 shows the effect of the average pore size of porous PTFE membranes on the ethanol concentration in the permeate for an aqueous solution of 10 wt % in TDEV. It can be presumed that there is any correlation between the pore size and the ethanol/water selectivity, because a porous PTFE membrane with smaller pore size had higher ethanol/water selectivity.

The contact angle for water on the surface of the porous polymer membranes and the ratio of adhesion work of porous polymer membranes are listed in Table IV. A membrane which is highly water repellent but has affinity for ethanol can give high ethanol/water selectivity. On the basis of these aforementioned results, it was found that the ethanol/water selectivity of porous polymer membranes was significantly influenced by both the pore size and the character of the pore wall. Specifically, a microporous polymer membrane which has the smallest possible critical surface tension relative to the
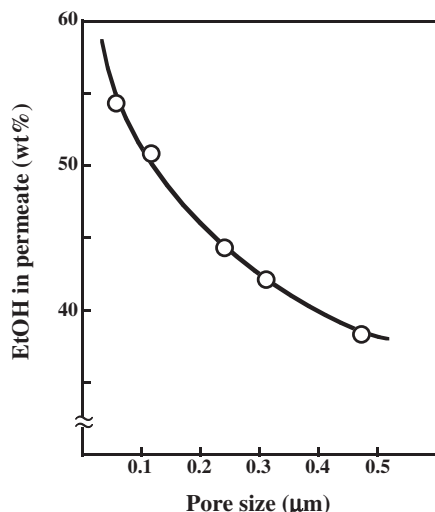
Figure 6. Effect of the pore size of porous PTFE membrane on the ethanol/water selectivity for an aqueous solution of 10 wt% ethanol in TDEV.

Table IV. Contact angle for water of porous polymer membranes

Membrane	Contact angle for water	Ration of adhesion work[a]
PTFE	112–116	0.92–0.97
PP	98–105	0.77–0.83
PC	80	0.70

[a]Contact angle for 10 wt% EtOH/contact angle for water.

surface tension of water (δ_{H2O}: 72.8 dyne/cm) and is a little larger than that of ethanol (δ_{EtOH}: 22.6 dyne/cm), is optimum. Thus, we investigated to prepare porous PDMS membranes.

PREPARATION OF POROUS PDMS MEMBRANES[24–26]

When an aqueous emulsion of organopolysiloxane, that can be cured by removing water at room temperature or by heating to form a water repellent elastomer, was frozen, a half-cured elastomer could be formed. Because this frozen elastomer was dried by a conventional method, an elastomer-like sponge with a dense skin layer was produced. However, when the water in the frozen elastomer was removed without the freeze-drying method, porous materials having a continuous pore structure were obtained as shown in Figure 7. Porous PDMS membranes were prepared by using this technique. In this membrane preparation method, the pore size and porosity can be controlled by changing the freeze conditions of aqueous emulsions of organopolysiloxane.

PERMEATION AND SEPARATION CHARACTERISTICS OF POROUS PDMS MEMBRANE IN TDEV

Figure 8 shows the effect of the temperature of the membrane surroundings on the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol through a dense PDMS membrane (a) and
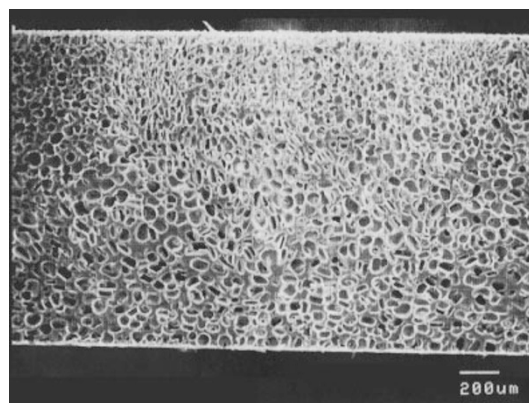

Figure 7. Scanning electron micrograph image of the cross-section of a porous PDMS membrane.
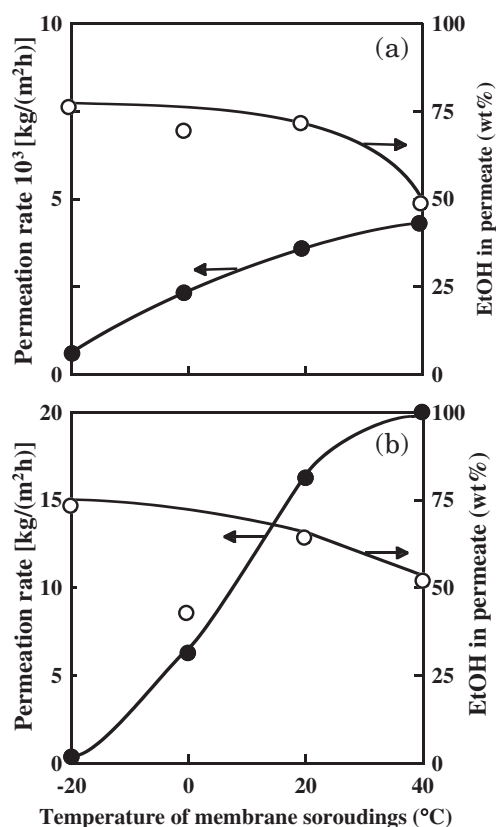

Figure 8. Comparison of the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol of a dense PDMS membrane (a) and a porous PDMS membrane (b) in TDEV, in which the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed.

a porous PDMS membrane (b) in TDEV. In Figure 8, the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed; the pressure on the downstream side was kept at 665 Pa. In Figure 8(b), with decreasing temperature of the membrane surroundings, the permeation rate decreased and the ethanol concentration in the permeate increased. This decrease in the

Table V. Permeation and separation characteristic for an aqueous solution of 10 wt% ethanol through a porous PDMS membrane during TDEV and the permeation conditions in TDEV with changing the temperature of the membrane surroundings as the temperature of the feed solution was kept constant

	Temperature of membrane surroundings (°C)			
	−20	0	20	40
EtOH in permeate (wt%)	71.8	71.1	62.1	49.8
Permeation rate ([kg/(m²h)])	0.14	7.8	16.1	20.1
T_L	33.0	33.8	35.2	40.0
T_V	17.2	22.0	30.2	38.0
ΔT	15.8	11.8	5.0	2.0
ΔP	4934	5692	6357	6903
P_F	5599	6357	7022	7568

T_L, temperature of the feed solution. T_V, temperature of the feed vapor. P_p, pressure on the downstream side. P_f, pressure on the feed side. $\Delta T = T_L - Y_V$, $\Delta P = P_F - P_p$.

permeation rate can be explained by the permeation conditions in Table V, where ΔT is the temperature difference between the temperature of the feed solution, T_L, and that of the feed vapor, T_V, and ΔP is the pressure difference between the pressure on the feed side, P_f, and that on the permeate side, P_p. In Figure 9(a), 9(b), and 9(c), the relationships between ΔT and ΔP, and between ΔP and ΔT and the characteristics of permeation and separation are shown, respectively. It is suggested that an increase in ΔT results in a decrease in ΔP and a decrease in the permeation rate. Consequently, the decrease in the permeation rate with decreasing temperature of the membrane surroundings in Figure 8(b) significantly depend upon a decrease in ΔP.

On the other hand, the increase in the ethanol concentration in the permeate shown in Figure 8(b), *i.e.*, the increase in the ethanol/water selectivity through a porous PDMS membrane with decreasing temperature of the membrane surroundings, can be attributed to a tentative mechanism shown in Figure 10.

When water and ethanol molecules, vaporized from the feed solution, come close to the membrane surroundings kept at lower temperature in TDEV, the water vapor aggregates much easier than the ethanol vapor, because the freezing point of water molecules (0 °C) is much higher than that of ethanol molecules (−114.4 °C), and the aggregated water molecules tend to be liquefied as the temperature of the membrane surroundings becomes lower. On the other hand, because the PDMS membrane has a relatively high affinity to the ethanol molecules, they are sorbed inside the pores in a porous PDMS membrane and this sorbed layer of the ethanol molecules is formed in an initial stage of the permeation. The vaporized ethanol molecule may be able to permeate across the membrane by surface diffusion on the sorbed layer of the ethanol molecules inside the pores.

Both the aggregation of the water molecules and the surface diffusion of the ethanol molecules in the pores are responsible for the increase in the ethanol/water selectivity through a porous PDMS membrane in TDEV. The increase of the ethanol/water selectivity in TDEV can be attributed to both the degree of aggregation of the water molecules on the membrane surroundings and the thickness of the sorbed layer of the
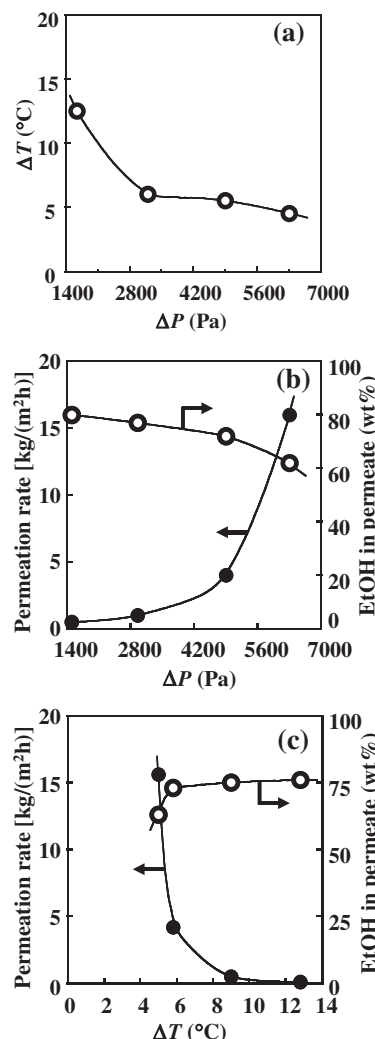

Figure 9. Relationships between the temperature difference, ΔT, and the pressure difference, ΔP (a), between ΔP and the permeation and separation characteristic (b), and between ΔT and the permeation and separation characteristics (c) in TDEV.
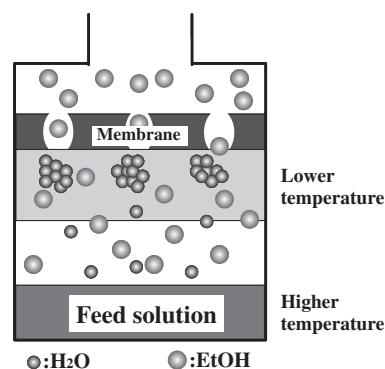

Figure 10. Tentative mechanism of the separation for aqueous ethanol solutions through porous PDMS membrane in TDEV.

ethanol molecules inside the pores, which are significantly governed by the temperature of the membrane surroundings. When the temperature of the membrane surroundings becomes

lower, the degree of aggregation of the water molecules and the thickness of the sorbed layer of the ethanol molecules are increased. Therefore, an increase in the ethanol/water selectivity for aqueous ethanol solutions was observed with decreasing temperature of the membrane surroundings.

As shown in Figure 8(a) and 8(b), the tendency of the decrease in the permeation rate and increase in the ethanol/water selectivity with lowering temperature of the membrane surroundings through these two PDMS membranes was very similar. In spite of the fact that the ethanol/water selectivity in these PDMS membranes was almost equal, however, the permeation rates through these PDMS membranes was remarkably different, *i.e.*, the permeation rates in a porous PDMS membrane were higher by three orders of magnitude than those of a dense PDMS membrane.

A remarkable difference in the permeation rate between dense and porous PDMS membranes can be attributed to the fact that the permeation through a dense PDMS membrane is due to the solution-diffusion model and that through a porous PDMS membrane is based on pore flow, as shown in Figure 10.

On the basis of the above results, it is suggested that an application of porous hydrophobic polymer membranes to TDEV for the concentration of aqueous ethanol solutions is very advantageous.

IMPROVEMENT OF PERFORMANCE OF POROUS PDMS MEMBRANE IN TDEV BY CHANGE OF CONDITIONDS IN PERMEATION AND MEMBRANE PREPARATION

Figure 11 shows the effects of the reduced pressure on the downstream side on the permeation rate and the ethanol concentration in the permeate for an aqueous solution of
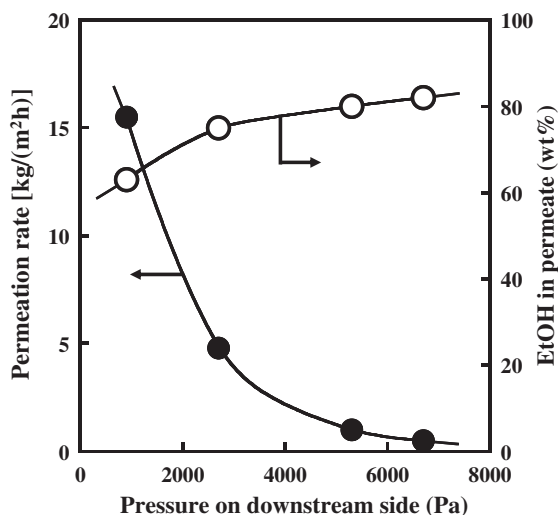
10 wt % ethanol through a porous PDMS membrane without additive during TDEV. The temperatures of the feed solution and the membrane surroundings were kept at 40 and 20 °C, respectively, and the pressure on the downstream side was changed. As can be seen in Figure 11, by increasing pressure on the downstream side, the permeation rate decreased but the ethanol concentration in the permeate increased. This decrease in the permeation rate can be understood by the permeation conditions in Table VI. It is suggested that an increase in ΔP results in a decrease in ΔT and an increase in the permeation rate. Consequently, the decrease in the permeation rate with increasing pressure of the downstream side in Figure 12 is dependent on a decrease in ΔP.

In a previous section, we explained the ethanol/water selectivity for aqueous ethanol solutions through porous PDMS membranes in TDED using a tentative mechanism shown in Figure 10. The increase in the ethanol concentration in the permeate shown in Figure 11, *i.e.*, the increase in the ethanol/water selectivity through a porous PDMS membrane without additive with increasing pressure on the downstream side, may be governed by the following factor. As can be seen in

Table VI. Permeation and separation characteristics for an aqueous solution of 10 wt % ethanol through a porous PDMS membrane during TDEV and the permeation conditions in TDEV with changing the pressure on the downstream side as the temperature the feed solution and the membrane surroundings were 40 and 20 °C, respectively

	Pressure on downstream (Pa)			
	665	266	5320	6650
EtOH in permeate (wt %)	62.1	72.4	79.7	80.3
Permeation rate ([kg/(m²h)])	16.1	4.2	0.11	0.03
T_L	35.2	35.2	37.5	37.2
T_V	30.2	29.5	28.5	24.5
ΔT	5.0	5.7	9.0	12.7
ΔP	6257	5080	2766	1609
P_F	7022	7740	8086	8259

Figure 11. Effects of the reduced pressure on the downstream side on the permeation rate (●) and the ethanol concentration in the permeate (○) through a porous PDMS membrane without additive during TDEV. Feed solution was an aqueous solution of 10 wt % ethanol. Temperatures of the feed solution and the membrane surroundings were 40 and 20 °C, respectively.
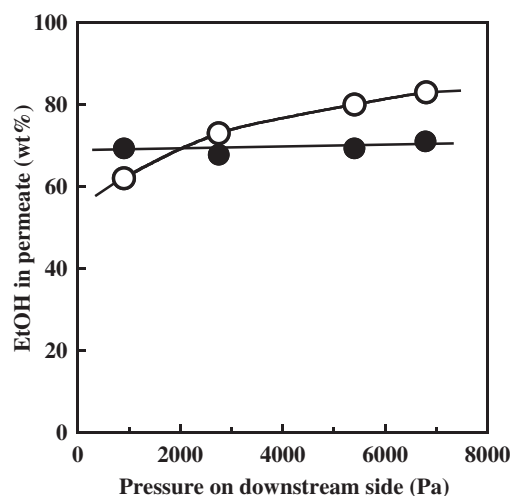

Figure 12. Effect of the reduced pressure on the ethanol concentration in the permeate for an aqueous solution of 10 wt % ethanol through a porous (○) and dense (●) PDMS membrane during TDEV. Temperatures of the feed solution and the membrane surroundings were 40 and 20 °C, respectively.

Table VI, the temperature of feed vapor, T_v decreased with an increase of the pressure on the downstream side. Lower temperature of feed vapor can accelerate the aggregation of the water molecules on the membrane surroundings. Consequently, as the pressure in the downstream side becomes higher, the degree of aggregation of the water molecules is increased. Therefore, an increase in the ethanol/water selectivity for aqueous ethanol solutions was observed with increasing pressure on the downstream side.

To make the mechanism of permeation and separation for aqueous ethanol solutions through porous PDMS membranes more clear, the separation characteristics for an aqueous solution of 10 wt % ethanol through porous and dense PDMS membranes during TDEV as a function of the pressure on the downstream side are compared in Figure 12. As can be seen in this figure, with increasing pressure on the downstream side the ethanol concentration in the permeate through a porous PDMS membrane increased but that through a dense PDMS membrane did not change. This result suggests that there is a difference between the mechanisms of permeation and separation through porous and dense PDMS membranes. The mechanism of permeation and separation for aqueous solutions through a dense PDMS membrane in TDEV is due to the solution-diffusion model. Namely, the water vapors are aggregated on the membrane surroundings kept at lower temperature, and it is very difficult that the aggregated water molecules dissolve into the dense PDMS membrane. On the other hand, the ethanol vapors are easily dissolved into the dense PDMS membrane. Therefore, the ethanol molecules can be preferentially permeated through the dense PDMS membrane. The fact that the ethanol/water selectivity did not change with an increase of the pressure on the downstream side can be attributed to the fact that the temperature and pressure of feed vapor in TDEV using the dense PDMS membrane were not changed by the pressure on the downstream side.

On the other hand, the mechanism of permeation and separation for aqueous ethanol solution through porous PDMS membranes in TDEV is due to the pore flow model shown in Figure 10. Namely, the ethanol/water selectivity through porous PDMS membranes is attributed to both the aggregation of the water molecules on the membrane surroundings and surface diffusion of the ethanol molecules on the sorbed layer of the ethanol molecules inside the pores. This discussion can be supported by the results in Table VI. In porous PDMS membranes, when the pressure on the downstream is increased, the pressure on the feed vapor side, P_f increased and the temperature on the feed vapor side, T_v decreased, and the degree of aggregation of the water molecules and of the thickness of the sorbed layer of the ethanol molecules inside pore are increased. Consequently, the ethanol/water selectivity is increased with increasing pressure on the downstream side.

From the above results, if the pore size of porous PDMS membranes can be controlled, it can be expected to get better membrane performance for the concentration of aqueous ethanol solutions. Hence, the effect of additives in aqueous organo polysiloxane emulsions was investigated.
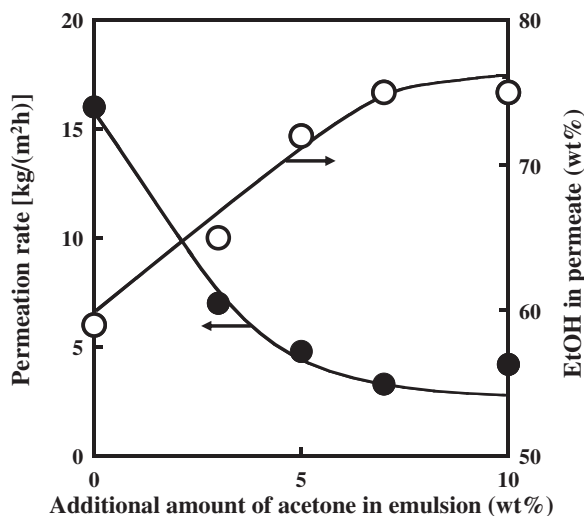
Figure 13. Effects of the additional amount of acetone in the casting emulsion on the permeation rate (●) and the ethanol concentration in the permeate (○) for an aqueous solution of 10 wt % ethanol through porous PDMS membranes in TDEV, in which the temperatures of the feed solution and the membrane surroundings were 40 and 20 °C, respectively.

Figure 13 shows the effect of adding acetone to the casting emulsion on the permeation rate and the ethanol concentration in the permeate through porous PDMS membranes during TDEV. The feed solution was an aqueous solution of 10 wt % ethanol, the feed temperature was 40 °C, the temperature of the membrane surroundings was 20 °C, and the pressure on the downstream side was 655 Pa. As can be seen in Figure 13, with increasing amount of acetone in the casting emulsion the ethanol/water selectivity increased remarkably but the permeation rate decreased. This result suggests that the addition and amount of acetone in the casting emulsion significantly affects the physical structure of the resulting porous PDMS membranes.

In Figure 14, scanning electron microscope pictures of porous PDMS membranes without and with acetone are shown. A porous PDMS membrane prepared from a casting emulsion with the addition of acetone has smaller pores than that without acetone. These observations of pore structure suggest mechanisms for the permeation and separation for aqueous ethanol
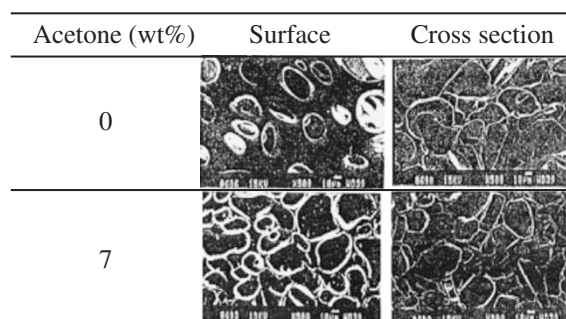
Acetone (wt%)	Surface	Cross section
0		
7		

Figure 14. Scanning electron micrograph images of porous PDMS membranes with and without acetone as an additive.
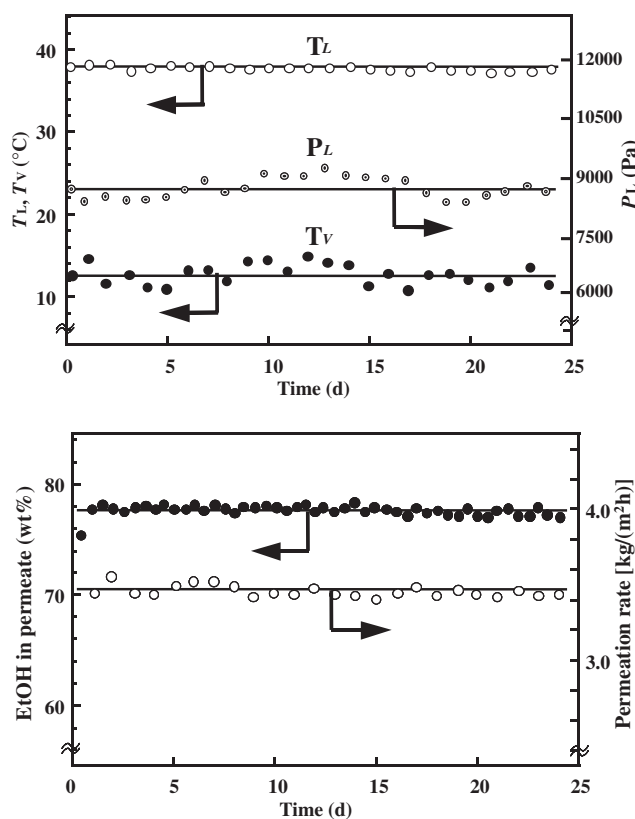
Figure 15. Membrane performance and experimental conditions for an aqueous solution of 10 w % ethanol through a porous PDMS membrane during TDEV in continuous long-term experiments.

solutions through porous PDMS membranes with different pore sizes in TDEV. A porous PDMS membrane with smaller pore size can disturb the permeation of the aggregated water molecules much more compared to a porous PDMS membrane with larger pore size.

MEMBRANE PERFORMANCE IN CONTINUOUS PERMEATION EXPERIMENT

The membrane performance and the experimental conditions for an aqueous solution of 10 wt % ethanol through a porous PDMS membrane during TDEV in continuous long-term experiments are shown in Figure 15 The temperatures of the feed solution and membrane surroundings were 40 and 20 °C, respectively. As can be seen in Figure 15, T_L, T_V and P_L did not change with time and a stable operation was observed. This result is advantageous for a long-term continuous operation. More importantly, both the permeation rate and the ethanol/water selectivity also were very stable.

CONCLUSION

In this review, a new membrane separation technique and novel membrane preparation methods for the concentration of bio-ethanol from biomass fermentation were introduced. They were developed based on an idea that is not known by the

conventional solution-diffusion model in the permeation and separation of materials through the membrane. In addition, the chemical and physical structure of the polymer membrane are take into consideration, plus chemical and physical control of the permeants to obtain ethanol/water selective membranes with high permeability and high selectivity in the concentration of bio-ethanol. This approach can lead to a practical use of a membrane separation technology, which is different from the conventional mechanism of permeation and separation through dense polymer membranes.

In this review, the following academic significances, originalities, and far-reaching effects were proposed.

I. Academic significances
   1) Proposal of new membrane separation techniques
   2) Proposal of a control method of the physical structure of porous polymer membranes by the freeze-dray method
   3) Clarification of the relationship between the structure of porous polymer membranes and the permeation and separation characteristics in TDED
   4) Analysis of the mechanism for the permeation and separation through porous polymer membranes in TDEV
   5) Analysis of the detail settings of the permeation conditions during the membrane permeation in stable long-term continuous operation

II. Originalities
   1) Concentration of ethanol in bioethanol by a new evapomeation and TDEV process instead of pervaporation
   2) Application of porous polymer membranes to TDEV
   3) Development of high permeation rate [1 kg/(m^{2}h)] and high ethanol/water selectivity (more than 85 wt % ethanol) from dilute aqueous ethanol solutions
   4) Production of absolute ethanol by a series membrane separation techniques[27,28] using both the ethanol and water selective membranes in TDEV
   5) Application of porous polymer membrane on the head of a distillation tower

III. Far reaching effects
   1) Proposal of importance of polymer science in the construction of strictly structural controlling porous polymer membranes: control of distribution in molecular weight
   2) Control technique of pore size and porosity of porous polymer membranes by the freeze-dry method: possibility of preparation of membranes for the treatment of the waste fluids and gas separation membranes
   3) Contribution to the help of energy politics with production of fuel ethanol by saving of consumption energy in comparison to the distillation
   4) Contribution to the prevention of global warming by reduction of CO$_2$
   5) Large industrial far-reaching effects by applying of porous polymer membranes on the head of the existing distillation tower

In the near future, we hope that bio-ethanol produced from the core and stem of corn, squeezed lees of sugar corn, cut back

branches, fallen leaves and so on, can be concentrated by membrane separation techniques and contribute as one of the new renewable energy sources.

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