

Design of Polymer Membrane with Permselectivity for Water-Ethanol Mixture. II. Preparation of Crosslinked Poly(methyl Acrylate) Membrane with Diethylene Triamine and Its Permselectivity

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Synopsis

In order to permeate water from a water-ethanol mixture by pervaporation on the basis of the difference in solubility between two components toward a polymer membrane, polymer membrane having polar group, poly(methyl acrylate) (PMA) membrane crosslinked with diethylene triamine (DETA) was prepared. The permselectivity of the membrane was investigated with attention to the feed composition of water-ethanol mixture and the effect of introduction of DETA into the membrane. It is found that water was permeated through PMA-DETA crosslinked membrane preferentially in all ranges of feed composition, the highest permselectivity being observed at 25% ethanol aqueous solution. Moreover, the pervaporation rate of water was found to depend on the ratio of DETA introduction into the membrane. When the ratio of introduction into the membrane was 0.144, water was permeated through the membrane from 25% ethanol aqueous solution at a rate of 1.26×10^{-1} g m/m² h. These results can be explained by high diffusivity of the membrane due to the low glass transition temperature of PMA and permeation of water through polar DETA moiety in the membrane.

INTRODUCTION

Recently, a method has been found for ethanol production by the fermentation of starch, sugar, and cellulose. This method requires a separation process, since ethanol is obtained in a 5–10% aqueous solution. An enormous amount of energy which consists of above 60% cost of production is consumed by the distillation generally used for the separation of ethanol, and this has prompted the development of a different separation process. For continuous and economical operation, a separation process using a polymer membrane has been proposed.¹ This pervaporation method does not require isolation of the permeate and can be applied to various organic liquid mixtures.² Actually, when polymer membrane is applied for ethanol separation process from ethanol aqueous solution obtained by the fermentation, it is proposed that the combined use of distillation and membrane separation process is effective. For example, according to Mehta, the effective process to prepare anhydrous ethanol from its aqueous solution was as follows: first, 8% ethanol aqueous solution is concentrated to 30% by membrane separation technique and 30–95% by distillation, and then 95–99.5% by membrane separation again.³ Therefore, the design of membranes with high permeation rate and selectivity is necessary for each stage of ethanol concentration.

Separation of a water-ethanol mixture using various polymer membranes by pervaporation has been reported.⁴⁻⁶ However, this separation technique has not as yet been put to practical use because of the delay in the development of a membrane with high permselectivity including durability during the operation.

Generally, permeation of materials in the dense membrane is the solution-diffusion mechanism.⁷ Therefore, the selectivity of a liquid mixture through the polymer membrane is a function of the difference in solubility between the components of the mixture. From these points of view, we have been investigating the design of the polymer membrane with permselectivity for liquid mixtures.⁸⁻¹¹ Already, the membrane with permselectivity for ethanol from water-ethanol mixture has been designed.¹¹

In this article, in order to permeate water from water-ethanol mixture, a polymer membrane having moderate polarity and moderate swelling by water, with DETA introduced into PMA as a crosslinked moiety, was prepared. In this way, PMA achieves high diffusivity because of low glass transition temperature, and DETA in a polar molecule used as the cross-linked agent. Pervaporation of the water-ethanol mixture through this membrane was carried out, and the effects of solubility and diffusivity in the membrane on permselectivity were studied.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile(AIBN), benzene, toluene, *N,N*-dimethylformamide(DMF), ethanol, 1-propanol, and methanol were purified by conventional methods. Methyl acrylate (MA) was distilled and the fraction of bp 80°C/760 mm Hg was used. DETA was distilled under reduced pressure in a nitrogen atmosphere and the fraction of bp 75°C/5 mm Hg was used. All other reagents and solvents were of extra pure grade.

Polymerization of Methyl Acrylate

MA was polymerized in benzene for 0.5 h at 60°C by using AIBN as an initiator. After the reaction mixture was cooled it was poured into an excess of methanol. The precipitation of PMA was filtered off and dried *in vacuo*. The molecular weight of PMA was 7.1×10^5 by viscosity measurement in benzene at 30°C. Table I shows the polymerization condition of MA.

TABLE I
Preparation of PMA

[MA] (mol/L)	[AIBN] (mol/L)	Temp (°C)	Time (h)	Conversion (%)	$[\eta]^a$ (dl/g)	\bar{M}_w^b
2.0	5×10^{-3}	60	0.5	32.4	1.66	7.10×10^5

^a In benzene at 30°C.

^b $[\eta] = 3.56 \times 10^{-5} \bar{M}_w^{0.798}$

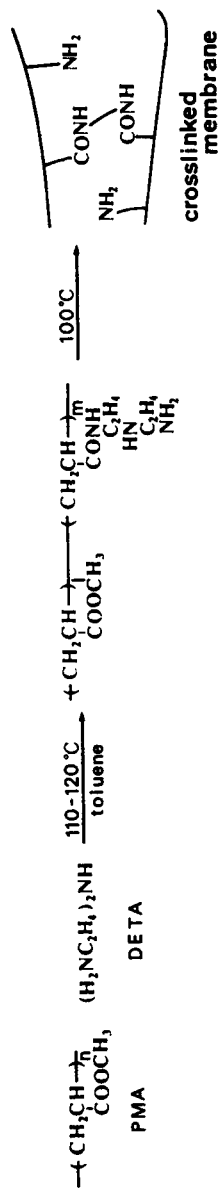


Fig. 1. Preparation of PMA-DETA crosslinked membrane.

Preparation of PMA-DETA Crosslinked Membrane

PMA was dissolved in toluene and 30 times larger amount of DETA than MA unit mole was added to the solution. The solution refluxed at 110–120°C for a given of time to exchange a part of methyl ester in the PMA side chain to primary amino group of DETA. The reaction mixture was poured into an excess of diethyl ether to remove unreacted DETA. The precipitated polymer was dissolved in DMF and casted on a Teflon plate. After the solvent was evaporated at 40°C for 24 h to prepare the polymer membrane, it was heated at 100°C for 20 h to proceed the crosslinking reaction. Figure 1 shows the scheme of the synthesis of PMA-DETA crosslinked membrane.

This reaction was confirmed by production of methanol and observation of characteristics IR bands of amide and amino groups. Table II shows the result of the synthesis of PMA-DETA crosslinked membrane. The ratio of DETA introduction can be controlled by the reaction time at reflux stage.

Pervaporation Experiment

The apparatus used for measuring the pervaporation rate through the membrane is shown in Figure 2, and a cross section showing the details of the pervaporation cell is given in Figure 3. The cell was stainless steel. The upper compartment had a capacity of about 80 mL, and the membrane area in contact with the feed solution was about 5.7 cm². The membrane was supported by filter paper resting on a sintered stainless disk. The feed solution was introduced into the upper stirrer throughout the experiment. The lower compartment was evacuated to less than 2 mm Hg, and the permeate was collected in a trap cooled by liquid nitrogen. The composition and flux of the permeate were determined by gas chromatography (Shimadzu GC-3BT type). 1-Propanol served as the internal standard for the determination of the permeated water and ethanol. All of these procedures were repeated until a steady-state permeability had been obtained at 25°C.

The permeability of a membrane was measured with respect to pervaporation rate and separation factor. Since the permeate flux is inversely proportional to membrane thickness, the permeation rate P is defined as

$$P = \frac{w \cdot \theta}{a \cdot t} \quad (1)$$

TABLE II
Preparation of PMA-DETA Crosslinked Membrane

Membrane	Reaction time (h)	Ratio of DETA introduction
PMA-DETA (0.054)	0.1	0.054
PMA-DETA (0.110)	0.4	0.110
PMA-DETA (0.144)	0.5	0.144
PMA-DETA (0.178)	0.6	0.178
PMA-DETA (0.240)	1.0	0.240

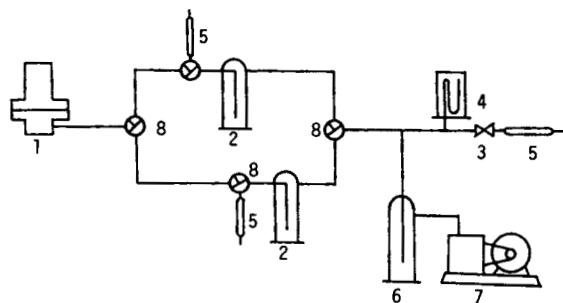


Fig. 2. Experimental system for pervaporation experiments: (1) pervaporation cell; (2) traps; (3) stopcocks; (4) manometer; (5) leaks; (6) trap; (7) vacuum pump; (8) three way cocks.

where w , θ , α , and t denote the permeate flux, the membrane thickness, the membrane area, and time, respectively. The separation factor α is defined as

$$\alpha = \frac{P_A/P_B}{F_A/F_B}, \quad A = \text{water}, B = \text{ethanol} \quad (2)$$

where P_A/P_B and F_A/F_B denote the concentration ratio of permeate and the feed solution, respectively.

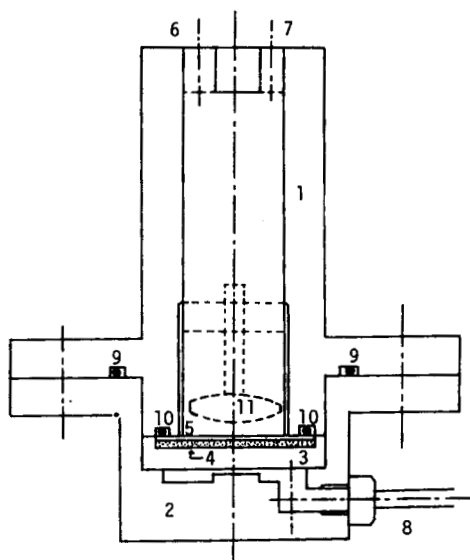


Fig. 3. A pervaporation cell for pervaporation experiments: (1) upper compartment; (2) lower compartment; (3) steel disk supporter; (4) sintered stainless disk; (5) polymer membrane; (6) thermometer holder; (7) feed solution inlet; (8) vapor outlet joint; (9) O-ring G-60; (10) O-ring G-35; (11) stirrer.

Sorption and Desorption Experiments

Swelling Ratio. A piece of membrane was immersed in a water-ethanol mixture solvent at room temperature. When the sorption reached equilibrium, the membrane was rapidly removed from the mixture solvent, blotted to remove the surface solvent and placed on a electronic reading balance. The first reading was 40 s following removal of the membrane from the mixture, and four to five readings were made at 10 s intervals. The weight of solvent-swollen membrane was obtained by extrapolating the initial portion of the experimental curve to zero time. The swelling ratio S is defined as

$$S = \frac{W_s - W_d}{W_d} \quad (3)$$

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

Solvent Composition in the Membrane. Desorption experiment was carried out as follows. The solvent-swollen membrane was immersed in methanol to extract the solvent in the membrane. The concentrations of both water and ethanol in the methanol were determined by gas chromatography, and ethanol volume fraction was calculated in the swollen membrane.

RESULTS AND DISCUSSION

The Influence of Feed Composition on Permselectivity

Figure 4 shows the relation between pervaporation rate, equilibrium swelling ratio, and ethanol composition in feed solvent using PMA-DETA (0.178) membrane. The pervaporation rate increased with increasing ethanol composition in feed solvent until it was about 0.7. The tendency of pervaporation rate was similarly to that of equilibrium swelling ratio.

Figure 5 shows the relation between the solvent composition in permeate, that in membrane, and that in feed solvent. The solvent composition in the membrane was rich. Therefore, the selectivity of a mixture through the

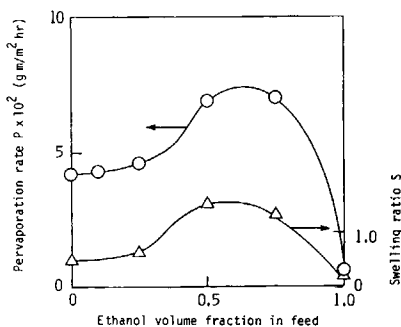


Fig. 4. Relation between pervaporation rate, swelling ratio, and ethanol volume fraction in feed using PMA-DETA (0.178) membrane at 25°C.

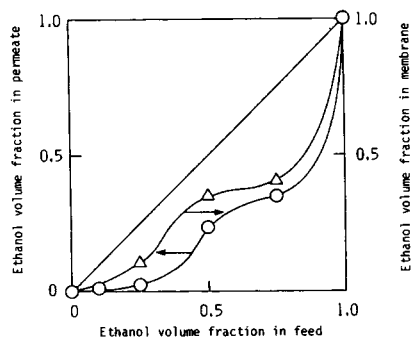


Fig. 5. Relation between the solvent composition in permeate, in membrane and ethanol volume fraction in feed using PMA-DETA (0.178) membrane at 25°C.

polymer membrane appeared in the solution process of the solvent into the membrane. According to these results, both permeability and selectivity of the membrane can be estimated by the solution of solvent into the membrane. That is, permeability is governed by the equilibrium swelling ratio and selectivity results from the solvent composition in the membrane.

Figure 6 shows the relation between permselectivity of PMA-DETA (0.178) membrane and the ethanol composition of feed solvent. All ranges of composition, water permeated preferentially from the feed solvent.

These results mentioned above lead to conclusion that the influence of ethanol composition on the permeation rate and selectivity can be explained as follows: The polarity of PMA-DETA (0.178) membrane seems to be similar that of 50% ethanol aqueous solution. Therefore, the water-ethanol mixture with this composition tend to enter the membrane. In other words, the swelling of the membrane was remarkable. The permeation characteristics strongly depend on the swelling ratio of the membrane. It is considered that the mobility of polymer chain was increased by swelling and the diffusion rate of the solvent increased particularly in the permeation side of the membrane. Consequently, the feed composition dependence of the pervaporation rate was similarly to that of the equilibrium swelling ratio. On the other hand, the separation factor decreased in the vicinity of 50% ethanol aqueous solution. This phenomenon can be explained by the plas-

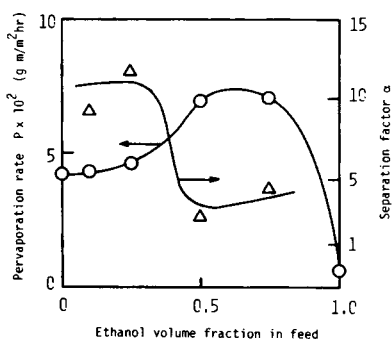


Fig. 6. Relation between permselectivity of PMA-DETA (0.178) membrane and the composition of feed mixture at 25°C.

ticizing effect.¹¹ When the swelling ratio of the membrane in the mixture was large, ethanol permeated the membrane in spite of its low affinity toward the membrane. That is, excessive swelling due to the selective solvent (water) causes a nonselective solvent (ethanol) to permeate through the membrane and lowers the selectivity.

In this way, PMA-DETA crosslinked membrane had high permselectivity to water-ethanol mixture, particularly it was useful for the concentration of ethanol from its aqueous solution with low ethanol composition.

The Influence of DETA Introduction of Permselectivity

In this section, the pervaporation experiments were carried out using 25% ethanol aqueous solution as feed solvent, because this composition was found to give the best results for separation of the water-ethanol mixture in the previous section.

Figure 7 shows the relation between the permselectivity and DETA introduction. A maximum pervaporation rate was observed where the ratio of DETA introduction was about 0.15, and selectivity was superior at 0.05–0.10. The appearance of this selectivity appeared to be caused by selective solution of water into the membrane. This result indicated that the solution of water into the membrane increased with increasing the DETA introduction ratio; thus a high pervaporation rate was obtained. However, when the ratio of DETA introduction was higher (above 0.15), the pervaporation rate became low. It was considered that the interaction between water and polar group of the polymer membrane was too strong, so that the diffusivity in the membrane was suppressed. Consequently, it is necessary to introduce DETA moiety into the polymer membrane moderately in order to acquire high permselectivity.

The Mechanism of Permeation through PMA-DETA Crosslinked Membrane

It is known that the value of $P \times \alpha$ is used for the evaluation of performance of permselective membrane.

Figure 8 shows the relation between the value of $P \times \alpha$ and the ratio of DETA introduction, when 25 and 50% ethanol aqueous solutions were ap-

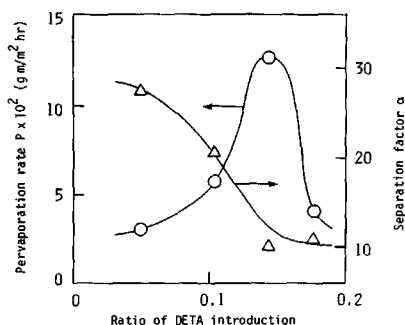


Fig. 7. Relation between permselectivity of membrane and ratio of DETA introduction in ethanol 25 vol % aqueous solution system at 25°C.

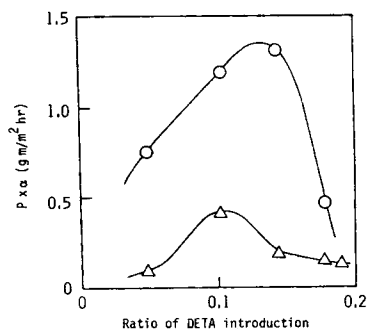


Fig. 8. Relation between $P \times \alpha$ and ratio of DETA introduction in water-ethanol mixture system at 25°C: (○) ethanol 25% aqueous solution; (△) ethanol 50% aqueous solution.

plied as feed solvent. It can be seen from the figure that the permselectivity of the membrane for 25% ethanol aqueous solution was superior to that for 50% solution. Moreover, in order to obtain high permselectivity, effective ratio of DETA introduction to the membrane for both feed solvents was in vicinity of 0.10 to 0.15.

Table III shows the pervaporation characteristics of PMA-DETA cross-linked membrane. The value of pervaporation rate was corrected for membrane thickness. Therefore, actual permeation amount was 12.6 kg; using 10 μm in thickness and 1 m^2 in area membrane per hour in the case of the highest permeation rate (1.26×10^{-1} g m/m² h).

Thus, as mentioned in this paper, high permselectivity was achieved. It is due to using rubbery polymer as PMA that has high diffusivity. Further, it is expected that permeability of the membrane may be closely relate to the structure of crosslinking, as illustrated in Figure 9. The left side is the conventional crosslinked membrane, whose polymer segments have affinity toward selective solvent, and crosslinking is formed by conventional agents or irradiation.⁸ It has disadvantages as follows: When the solvent permeates through the membrane, the distance of crosslinked points is spread out by solvent; then selectivity is decreased; when the degree of crosslinking is increased to prevent this effect, the pervaporation rate decreases. On the other hand, in the case of PMA-DETA crosslinked membrane, the permeate pathway is around the crosslinked points, so that polymer chains spread very little. Consequently, the PMA-DETA crosslinked membrane has high permselectivity for water-ethanol mixture.

TABLE III
Characteristics Pervaporation through PMA-DETA Crosslinked Membrane in Water-Ethanol System at 25°C

Membrane	Ethanol volume fraction in feed	Pervaporation rate (g m/m ² h)	Separation factor α
PMA-DETA (0.110)	0.5	6.87×10^{-2}	5.8
PMA-DETA (0.178)	0.5	6.90×10^{-2}	2.7
PMA-DETA (0.110)	0.25	5.54×10^{-2}	21.0
PMA-DETA (0.144)	0.25	1.26×10^{-1}	10.0
PMA-DETA (0.178)	0.25	3.94×10^{-2}	11.7

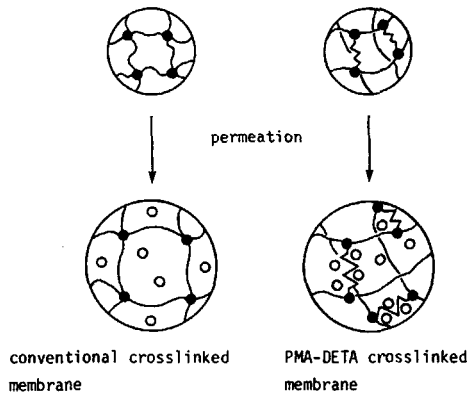


Fig. 9. Schematic representation of permeation mechanism for crosslinked membrane. (●) Crosslinking point; (w) DETA; (○) solvent.

In short, for the design of membrane with high permselectivity, it is important to consider not only chemical structure of polymer, but also the way of crosslinking and the crosslinked structure of the membrane.

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