Polymer Membrane as a Reaction Field IV. Separation of Water-Ethanol Mixture through Poly(methyl methacrylate-co-styrene) Membranes

Masakazu YOSHIKAWA*, Takashi YUKOSHI, Kohei SANUI, Naoya OGATA

Department of Chemistry, Faculty of Science and Technology, Sophia
University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan.

* To whom correspondence should be addressed. Present address:

Department of Chemical Engineering, Faculty of Engineering,
Kyoto University, Kyoto 606, Japan

and Takeo SHIMIDZU

Division of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Kyoto 606, Japan.

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Membrane polarity value, $E_T(25^\circ\text{C})$, was an effective index in order to prepare membrane materials for water-ethanol separation by pervaporation technique. Hydrophobic synthetic polymer membranes, poly(methyl methacrylate-co-styrene) membranes, having hydrogen-bonding site (ester group) as a fixed carrier, showed wide separation properties toward water-ethanol mixture. Separation properties changed from the water permeable membrane to the ethanol permeable one in accord with compositions of membrane materials, that is, chemical compositions of poly(methyl methacrylate-co-styrene).

Key words: Pervaporation, Permselectivity, Separation of water-ethanol mixture, Water permeable membrane, Ethanol permeable membrane, Hydrogen-bonding interaction, Carrier mechanism, Michaelis-Menten type profile

Introduction

We have reported that membrane polarity¹⁾ in terms of Dimroth's solvent polarity value ($E_T(25^\circ\text{C})$) is one of the possible parameters to explain membrane performance, such as selectivities of metal ions through common polymer membranes by piezodialysis²⁾, the transport mechanism and transport selectivities of halogen ions^{3, 4)}, or organic acids⁵⁾, and the separation

of water-ethanol mixture by pervaporation method⁶⁻⁸⁾.

Till now we have been studying on selective separation of aqueous ethanol solution through synthetic polymer membranes by making use of hydrogen-bonding interaction by pervaporation technique^{6, 7, 9-12)}. Selective separation of aqueous ethanol solution has been attracting attention, since the formation of ethanol via fermentation of biomasses will be in near future an important industrial process, which relates to the energy problem. Most of novel membranes reported by our research group permeated water preferentially^{6, 7, 9-12)}. Especially, poly{1-(2-methylpropenoxy) suc-

* 反応場としての合成高分子膜 (第4報). ポリ (メタクリル酸
メチル-スチレン) 膜による水-エタノール混合液の分離.

** 吉川正和, 湯越 隆, 讃井浩平, 緒方直哉: 上智大学理工学部
化学科, 〒102 東京都千代田区紀尾井町 7-1;
清水剛夫: 京都大学大学院工学研究科分子工学専攻, 〒606
京都市左京区吉田本町

cinimide-co-acrylonitrile} membrane gave a high separation factor, which reached over 2000 for water¹¹⁾.

There are two ways to separate aqueous ethanol solution. One way is that water is selectively permeated (removed) through membranes as we reported, while the other one is that ethanol is separated through membranes as reported by other researchers¹³⁻¹⁹⁾. Our previously reported results were classified in the former way. In the present article, we describe the separation of aqueous ethanol solution by the latter one.

From the relationship between the separation factor for water and the membrane polarity value (Figure 3)⁸⁾, we deduced following idea: membranes having membrane polarity value of around 30 kcal mol⁻¹ or less than that value will make it possible to permeate ethanol preferentially instead of water. Based on this idea, ester group (methyl methacrylate), which was expected to have less hydrogen-bonding ability than imide moiety or carboxyl group, was selected as a fixed carrier for permeated substrates. Styrene was used as a membrane matrix, because polystyrene has a low membrane polarity value of 31.7 kcal mol⁻¹¹¹⁾. As a result, we prepared poly (methyl methacrylate-co-styrene) membranes, and the separation ability of water-ethanol mixture was investigated by pervaporation technique. The possibility of molecular design to obtain membrane materials which

selectively permeate ethanol from aqueous ethanol solution is also described.

Experimental

Materials

Methyl methacrylate (5), styrene (6), 2,2'-azobis(2-methylpropionitrile) (AIBN), N,N-dimethylformamide (DMF), toluene, and ethanol were purified by conventional methods. Dioxane and methanol were used as received without further purification. Water distilled once was used in the present study.

Poly(methyl methacrylate-co-styrene) (1-4) were prepared by usual bulk copolymerization of 5 and 6 initiated by AIBN at 62°C. The obtained polymers were reprecipitated in dioxane/methanol. The results are summarized in Table 1.

All membranes were obtained by casting from toluene solution (ca. 100g dm⁻³). The solution was poured onto a glass plate with an applicator (casting thickness, 0.254mm), and the solvent was allowed to evaporate at 40°C overnight.

	m	n
1	0.034	0.966
2	0.079	0.921
3	0.116	0.884
4	0.180	0.820

Table 1 Results of copolymerization^{a)}

Polymer	Monomer		AIBN	Time	Yield	Mol fraction of 5 in		η_{sp}/C^b
	5/g	6/g				Monomer	Polymer	
			g	h	g			dm ³ g ⁻¹
1	0.53	49.52	0.40	40	47.22	0.011	0.034	0.063
2	2.42	47.43	0.40	40	48.39	0.050	0.079	0.060
3	3.29	30.52	0.40	40	31.92	0.101	0.116	0.054
4	4.86	28.89	0.40	40	28.08	0.149	0.180	0.058

a) Polymerization temp., 62°C.

b) Reduced viscosity was measured at $C = 1.0 \text{ gdm}^{-3}$ -DMF at 30°C.

Membranes were removed spontaneously from glass plate by immersing glass plates with membranes in water. The thickness of the membrane was 18-22 μ m.

Pervaporation

The apparatus for pervaporation was the same as that in a previous paper¹⁰⁾. The flux was obtained by weighing the trapped permeate. The separation factor, α , was calculated by determining the composition of the feed liquid mixtures and the permeates. The composition analysis was carried out on a Shimadzu GC-8A Gas Chromatograph equipped with a 1-m-long column packed with Porapak Q. The separation factor, α , is defined as

$$\alpha = (Y_{\text{Water}}/Y_{\text{Ethanol}})/(X_{\text{Water}}/X_{\text{Ethanol}})$$

where Y_i 's are weight fractions of permeates and X_i 's are those of feeds, respectively.

Spectroscopic Measurement

IR spectra of membranes, which were immersed in water or ethanol solution at 15°C for 1 week, were taken at ca. 20°C on a HITACHI 260-50 Infrared Spectrophotometer.

Determination of Membrane Polarity Value, E_T (25°C)

E_T (25°C) values (Dimroth's solvent polarity values) of membranes 1-4 were measured as described previously, using 1-octadecyl-3, 3-dimethyl-6'-nitrospiro (indoline-2, 2'-2H-benzopyran) as the indicator¹¹⁾. A 250W high-pressure mercury lamp was used as a light source. Absorption spectra were measured with a Shimadzu UV-240 UV-Visible recording spectrophotometer.

Measurement of Degree of Swelling

A piece of membrane after drying to constant weight (W_d) was immersed in the liquid of various water-ethanol mixtures at 15°C. When the sorption equilibrium was reached, the piece was weighed rapidly after blotting free surface liquid.

The degree of swelling for membranes was defined by

$$\text{Degree of Swelling} = \frac{W_s - W_d}{W_d} \times 100$$

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

Results and Discussion

Membrane Polarity Values, E_T (25°C)

Membrane polarity values, E_T (25°C), for the present membranes are summarized in Table 2 together with wave-length of the absorption maximum of the indicator. These four membranes were less polar than poly (methyl methacrylate) (homopolymer of 5), of which E_T (25°C) value was 42.5 kcal mol⁻¹¹¹⁾ and gave nearly the same value of polystyrene (homopolymer of 6), whose E_T (25°C) value was 31.7 kcal mol⁻¹¹¹⁾. Membrane polarity values increased with the increase of 5 content in the membrane. These results were on our consideration. Since the increase of 5 content in the membrane led to the increase in the concentration of polar moiety (ester group) in the membrane. Further, these results might be explained by making use of E_T (25°C) values for homopolymers of 5 and 6.

Separation of Water-Ethanol Mixtures through Membranes 1-4

Fig.1 shows results of the pervaporation experiments for membranes 1-4, where the weight fractions of water in permeate are plotted as a function of water in feed. Fig.2 gives the separation factor (α), total fluxes, and degree of swelling plotted against the weight fraction of water in feed. Membranes 1 and 2 preferentially

Table 2 $\lambda_{\text{max}}^{\text{Vis}}$ and membrane polarity values (E_T (25°C)) of synthetic polymer membranes

Polymer Membrane	$\lambda_{\text{max}}^{\text{Vis}}$ nm	E_T (25°C) kcal mol ⁻¹
1	605	31.0
2	603	31.7
3	602	32.1
4	601	32.5

Fig.1

Effect of feed composition on the separation of water-ethanol through membranes 1-4.

(Operating temp., 15°C ; down-stream pressure, 400 Pa (ca. 3.0 torr).)

permeated water in the most part of feed fraction except the low water feed fraction region, where the weight fraction of water in feed was less than around 0.08. Slightly more ethanol was permeated through membranes 1 and 2 than water at the low water fraction region, where the weight fraction of water in feed was less than around 0.08.

Separation factors for pervaporation experiments through membranes 1 and 2 at the point where the weight fraction of water in feed was around 0.5 (in the case of membrane 1, that was at 0.425) are plotted against their membrane polarity values together with previously reported results⁸⁾ and they are shown in Fig.3. Separation factors for membranes 1 and 2 gave same tendencies as previously reported⁸⁾. These two plots in Fig.3, however, deviated from the solid line. One of the plausible reason for the present deviation was as follows: membranes 1 and 2 showed observable swelling as shown in Fig.2,

although membranes used for the study⁸⁾ of the correlation between separation factor for water and the membrane polarity value did not show the swelling. As a result, the separation factor, selectivity toward water deviated from the solid line.

In contrast with the results of pervaporation experiments through membranes 1 and 2, membranes 3 and 4 selectively permeated ethanol, not water. Comparing membranes 3 with 4, of which 5 content was higher than that of membrane 3, membrane 4 more preferentially permeated ethanol than membrane 3. Separation factors for membranes 3 and 4 at the point where the weight fraction of water in feed was around 0.5 are also plotted against their polarity values in Fig.3. These two points also deviated from the previously reported solid line. One of reasons for these deviations from the solid line was presumably due to the swelling of the membrane by water-ethanol mixtures.

Fig. 2

Effect of feed composition on separation factor (α), flux, and degree of swelling in water-ethanol pervaporation through membranes 1-4. (Operating temp. 15°C; down-stream pressure, 400 Pa (ca. 3.0 torr).)

Permeation Mechanism

In order to study the permeation mechanism of water and ethanol through present membranes, we at first separated the observed fluxes into their respective water and ethanol components, so that each component-flux could be plotted against its feed concentration. These separated fluxes are shown in Fig. 4. Relationship between water flux through membranes 1 and 2 and its feed concentration, and those between ethanol flux through membrane 4 and its feed concentration seemed to give a Michaelis-Menten type profile as pre-

viously reported⁹⁻¹²⁾ although membranes were swollen. On the other hand, other relationships gave complicated profiles because of the swelling of the membrane. Fig. 4 led to the conclusion that the permeation of water through membranes 1 and 2, and that of ethanol through membrane 4 were carried out by a carrier-mediated mechanism. In the present paper, however, a carrier (ester group in 5 unit) was immobilized in the membrane. As for other permeations, we could not derive the precise permeation mechanism.

Secondly, we investigated the selective hydrogen-bonding interaction between permeating

Fig. 3 Relationship between separation factor (α) and membrane polarity value ($E_T(25^\circ\text{C})$).

($\circ$, pervaporation data cited from ref. 8; $\bullet$, present data; operating temp., 15°C ; down-stream pressure, 333-430 Pa (2.5-3.2 torr); weight fraction of water in feed, ~ 0.5)

substrates (water and ethanol) and fixed carrier (ester group in 5 unit) by spectroscopic approach as previously reported^{6, 10}. The magnitude of hydrogen-bonding between ester group (5 unit) in the membrane, and water or ethanol were studied qualitatively by IR. The IR stretching

bands of carbonyl ($-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$) of membranes 1-4 were 1735cm^{-1} . On the other hand, those of membranes 1-4 immersed in water or ethanol were 1733cm^{-1} . This result suggested that the hydrogen-bonding ability of the ester group with water and ethanol were nearly equivalent and that both water and ethanol may interact ester group in membranes 1-4 equivalently, in other words, indiscriminately.

From relationships between flux and its feed concentration and selectivity toward water or ethanol, it is deduced that ester group in membranes 1 and 2 interact with water more preferentially than ethanol, and that in membrane 4 with ethanol more preferentially than water. The difference in conclusions deduced from IR data and permeation data were presumably attributed to the difference in temperature of IR measurement and permeation

Fig. 4 Effect of water and ethanol concentrations on their fluxes in water-ethanol pervaporation through membranes 1-4.

($\circ$, membrane 1; $\bullet$, membrane 2; $\circ$, membrane 3; $\bullet$, membrane 4; operating temp., 15°C ; down-stream pressure, 400 Pa (ca. 3.0 torr).)

experiment.

Although the swelling of membranes made it difficult to deduce precise permeation mechanism, permeation of water through membranes 1 and 2, and that of ethanol through membrane 4 were concluded to be carried out by a carrier mechanism by making use of ester group (5 unit) in the membrane as a fixed carrier for

water (in the case of membranes 1 and 2), or for ethanol (in the case of membrane 4). That is, water, which interacts with a fixed carrier in the membranes 1 and 2 by hydrogen-bonding interaction more preferentially than ethanol, was incorporated into the membrane with high selectivity. As a result, water was permeated preferentially compared with ethanol. On the contrary, ethanol, which interacts with a fixed carrier in membrane 4 with selectivity, was incorporated into the membrane selectively, and ethanol was permeated more preferentially than water. As for other permeation mechanisms, such as permeation of water through membranes 3 and 4, and that of ethanol through membranes 1, 2, and 3, it is impossible to deduce precise permeation mechanisms.

It is necessary for membranes to have a cross-linking structure in order to give high selectivity toward both ethanol and water. However, in this article, we made it clear that hydrophobic membranes containing hydrogen-bonding site as a fixed carrier was able to permeate ethanol more preferentially than water by making use of membrane polarity value, E_T (25°C), as an index.

Conclusion

Poly (methyl methacrylate-co-styrene) membranes showed a wide range of permselectivities toward separation of water-ethanol mixtures by pervaporation method. Permselectivities were dependent on the chemical composition of poly (methyl methacrylate-co-styrene). Membrane performance changed from the water permeable membrane to the ethanol permeable membrane with increase in the fraction of methyl methacrylate in the membrane. Membrane polarity value, E_T (25°C), which was

evaluated by making use of 1-octadecyl-3, 3-dimethyl-6'-nitrospiro(indoline-2, 2'-2H-benzopyran) as the indicator, was effective to prepare membrane materials for water-ethanol separation.

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