Pervaporation of Ethanol-Water Mixture through Composite Membranes Composed of Styrene-Fluoroalkyl Acrylate Graft Copolymers and Cross-linked Polydimethylsiloxane Membrane[1]

INTRODUCTION

Recently, an ethanol production by fermentation of biomass, such as, starch, sugar, and cellulose has received increasing attention. As this method produces only about 10 wt% aqueous ethanol solution, concentration of the ethanol is inevitable. In general, distillation method is used for the purpose. The method, however, suffers from high energy cost, as well as azeotrope formation. As a continuous and economical method, a pervaporation process using various polymer membranes has been reported.[2-7] In most cases, the process is applied to selective water removal through the membrane. However, it is more practical to separate ethanol by its selective permeation through the membrane since it is a minor component in the fermentation product.

In pervaporation, the permselectivity of a polymer membrane depends on the differences of the solubility of each component into the membrane and/or its diffusivity in the membrane.[8] At the selective permeation of ethanol, it is especially very important to enhance the solubility of ethanol over water by designing a polymer membrane because diffusivity of water is higher than ethanol. Itoh et al. devised a liquid-polymer hybrid membrane using carbon tetrachloride as a liquid membrane component to enhance the solubility difference between ethanol and water.[9] Since the liquid membrane layer dissolves ethanol selectively and the diffusivity of the carbon tetrachloride in the polymer membrane layer is lower than that of ethanol, ethanol was completely separated from its aqueous solution. In polymer membrane case, however, excessive enhancement of the affinity of the polymer membrane for ethanol may lead to the decrease of the selectivity owing to the membrane swelling in a high ethanol composition region in feed. In fact, though a cross-linked polydimethylsiloxane (PDMS) membrane is well known as an ethanol permselective membrane, the selectivity for ethanol diminishes, especially when the composition of ethanol in feed exceeds 70 wt%. At the concentration range, considerable swelling of the membrane was observed owing to its high affinity for ethanol. Therefore, increased selectivity can be expected by modification of the surface of PDMS membrane by another polymeric material which can enhance the solubility difference between ethanol and water, and also resist the membrane swelling by ethanol.

In this communication, we describe the preparation of a composite membrane composed of styrene (St)–fluoroalkyl acrylate (FAA) graft copolymer and PDMS membrane, as well as the selectivity of the membrane for ethanol.

EXPERIMENTAL

St-2-(4-nitrophenylcarbonyloxy)ethylmethacrylate copolymer, which was used as a backbone polymer of the graft copolymer, was synthesized by a polymer reaction between St-2-hydroxyethyl methacrylate copolymer and 4-nitrobenzoyl chloride in N,N-dimethylformamide using triethylamine as a hydrogen chloride trapping agent. The mole fraction of the 4-nitrophenyl group in the backbone polymer was 0.125.

As FAA monomer, 2,2,2-trifluoroethyl acrylate (TFEA), 2,2,3,3,3-pentafluoropropyl acrylate (PFPA), 2,2,3,3,4,4,4-heptafluorobutyl acylate (HFBA), 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate (NFHA), and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (HdFDA) were used.

A St-FAA graft copolymer was synthesized as follows. FAA monomer was polymerized in the presence of the backbone polymer in ethyl acetate using 2,2,'-azobisisobutyronitrile as an initiator. The radicals of the growing poly(FAA) segments were terminated at the 4-nitrophenyl group.[10] The graft copolymer was purified by fractional precipitation with an ethyl acetate-diethyl ether system repeatedly, and finally the graft copolymer was precipitated into excess of methanol. Thus, unbound poly(FAA) was removed from the product of the graft copolymeriza-

tion. The mole fraction of FAA moiety in the graft copolymer was determined by elemental analysis. Moreover, it was proved that the graft copolymers used in this study have a microphase-separated structure because of the existence of two glass transition points corresponding to the St and FAA segments. All St-FAA graft copolymers obtained did not swell in both water and ethanol.

A cross-linked PDMS membrane was prepared by casting a 4 wt% toluene solution of oligodimethylsiloxane having crosslinkable acetoxysilyl groups on a Teflon plate.

The composite membrane was prepared by casting the St-FAA graft copolymer of its 5 wt% ethyl acetate solution on the PDMS membrane under spinning the membrane. The membrane was then dried under reduced pressure for two days. The membrane thickness of the composite membrane was 120 μm, where the thickness of the PDMS layer was 100 μm and that of the St-FAA copolymer layer was 20 μm.

Pervaporation of aqueous ethanol solutions through the composite membrane was carried out by a usual method using a stainless steel cell at 30°C described previously.[2,4] The feed solution (i.e., an aqueous ethanol solution) was circulated on the upper side of the membrane, and the pressure of the permeation side was kept at about 1 mmHg. The St-FAA graft copolymer layer was in contact with the feed solution and the permeation area of the composite membranes was 9.6 cm^2. Composition and flux of the permeated solution were determined by means of gas chromatograph connected directly to the pervaporation cell, in order to avoid the effect of moisture. The pervaporation rate, P in g $\cdot$ m $\cdot$ m^{-2} $\cdot$ h^{-1}, was calculated by correcting the flux for the thickness of the membrane. The separation factor, α, which was a measure of the perferential permeation component A, was defined as the concentration ratio Y_A/Y_B in the permeate divided by the concentration ratio X_A/X_B in the feed. A and B indicate ethanol and water, respectively.

RESULTS AND DISCUSSION

Table I shows the typical pervaporation results of 8 wt% aqueous ethanol solution using the composite membranes obtained. The separation factor, α, was larger than 1.0 in every composite membrane tested, which indicated that ethanol permeated preferentially through the composite membranes. In particular, the composition of ethanol in permeate exceeded 70 wt% when membranes coated with the St-FAA graft copolymer having long perfluoroalkyl chain such as NFHA and HdFDA, were used. On the contrary, the separation factor of the original PDMS membrane was ca. 11 at the same concentration of the feed solution.[3] Another known ethanol permselective membrane [i.e., poly[1-(trimethylsilyl)-1-propyne](PTMSP)] membrane also shows similar low selectivity.[4] Thus, only less than 50 wt% aqueous ethanol solution was obtained as permeate through these two membranes.

The pervaporation rate of these composite membranes was in the order of 10^{-3} g $\cdot$ m $\cdot$ m^{-2} $\cdot$ h^{-1}, which is the same level of that of PDMS and PTMSP membranes.

TABLE I
Pervaporation Result of 8 wt% Aqueous Ethanol Solution through the
Composite Membrane of St-FAA Graft Copolymer and PDMS Membrane at 30°C

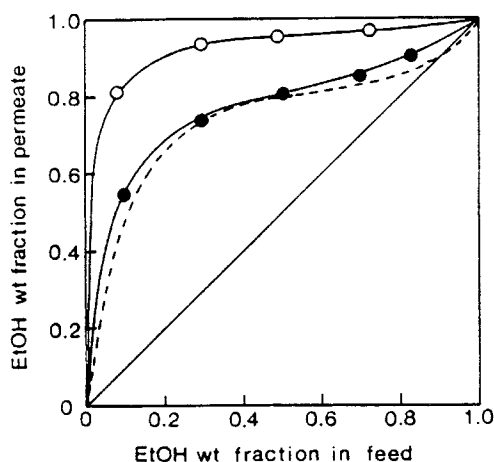| Code	FAA	FAA mole fraction in graft copolymer	$P \times 10^3$ (g $\cdot$ m/m$^2 \cdot$ h)	α	EtOH composition in permeate (wt%)
F-1	TFEA	0.505	1.14	16.3	58.6
F-2	PFPA	0.347	1.00	16.3	58.6
F-3	HFBA	0.669	0.89	17.4	60.2
F-4	NFHA	0.606	1.41	28.4	71.2
F-5	NFHA	0.381	1.62	24.7	68.2
F-6	HdFDA	0.283	1.69	30.5	72.6
F-7	HdFDA	0.124	0.60	45.9	80.0
PDMS	—	—	2.51	10.8	48.4
PTMSP[a]	—	—	1.15	11.2	49.3

[a]from Ref. 4.

Fig. 1. Permeation composition curves of ethanol-water mixture through (○) the composite membrane, F-7, and (●) PDMS membrane at 30°C, with (---) vapor-liquid equilibrium curve at 760 mmHg.

Figure 1 shows the permeation composition curves of the aqueous ethanol solution on F-7 membrane and PDMS membrane. The vapor-liquid equilibrium curve in ethanol-water system at 760 mmHg is also shown in Figure 1. The vapor-liquid equilibrium curve indicates the existence of an azeotropic point at the ethanol concentration of 95.6 wt%. On the other hand, the permeation curves through PDMS membrane and the composite membrane showed no azeotropic point. Thus, the concentration of ethanol can be accomplished by pervaporation using these membranes over all the range of ethanol composition in feed. Moreover, the composition of ethanol permeated through the composite membrane was much higher than that through the PDMS membrane. The high selectivity observed in the composite membranes is attributable to the St-FAA graft copolymer layer faced to the feed solution.

Figure 2 shows the relation between the compositions of ethanol in feed and the separation factor for ethanol or the pervaporation rate on F-7 membrane and the PDMS membrane. The separation factor decreased with increasing the composition of ethanol in both membranes. However, the separation factor for ethanol on the composite membrane is larger than that on
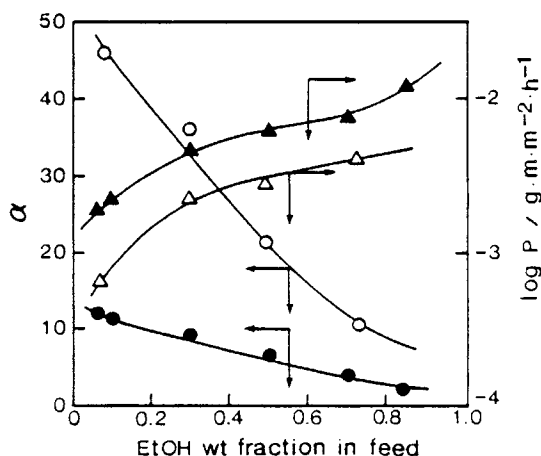

Fig. 2. Effect of feed composition on the separation factor for ethanol α and the pervaporation rate P in ethanol-water mixture for the pervaporation through (○, △) the composite membrane, F-7, and (●, ▲) PDMS membrane at 30°C.

PDMS membrane over all ranges of the ethanol composition in feed. For example, though the separation factor on PDMS membrane at 70 wt% aqueous ethanol solution in feed was only 4.1, that of the composite membrane was 10.1 even when 72 wt% ethanol was applied as a feed solution. A similar tendency was observed in other composite membrane cases. The pervaporation rate increased with increasing the ethanol composition on both membranes.

In order to evaluate the affinity of the membrane for liquid components, the contact angle by the liquid on the surface of the membrane was measured.[11] On the surface of St-HdFDA graft copolymer, the contact angle by water was 115°, and that by ethanol was 54°. On PDMS membrane surface, the contact angle by water was 108° and that by ethanol was below 25°. This fact indicates that the hydrophobicity of the surface of PDMS membrane was almost the same level of that of the St-HdFDA graft copolymer. However, the affinity of PDMS membrane for ethanol was higher than that of St-HdFDA graft copolymer. Thus, for PDMS membrane case since the membrane was swollen by ethanol owing to its high affinity for ethanol, water molecules permeated easily through the swollen region and thus, the selectivity of the membrane for ethanol diminished. When the surface of PDMS membrane was modified by casting the St-FAA graft copolymer, relatively low affinity of the graft copolymer for ethanol effectively suppressed the membrane swelling and its hydrophobicity resisted the dissolution of water molecules. Thus, the composite membranes composed of the St-FAA graft copolymer and PDMS membrane can show high selectivity for ethanol even at high ethanol concentration region in feed.

More detailed study is now underway and the results will be reported elsewhere.

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