

## Permselectivity of Liquid-Polymer Hybrid Membrane Composed of Carbon Tetrachloride and 2-Hydroxyethyl Acrylate-Acrylonitrile Graft Copolymer for Ethanol-Water Mixture

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**ABSTRACT:** A membrane with selective permeability for ethanol was designed for the separation of ethanol from its aqueous solution by pervaporation on the basis of the difference in solubility between two components of the membrane. A liquid membrane was introduced to extend this difference and ethanol in the liquid membrane was isolated by the polymer membrane; that is, a liquid-polymer hybrid membrane was formed. Carbon tetrachloride was used as a liquid membrane, and 2-hydroxyethyl acrylate (HEA) (branch)-acrylonitrile (AN) (backbone) graft copolymer membrane was used as a polymer membrane. The effect of the microphase separated structure of the graft copolymer membrane on permselectivity was studied. The microdomain of the AN moiety displayed more dispersion and a smaller microdomain with decreasing chain length of the backbone polymer. It was found that the plasticizing effect was suppressed effectively by the microphase separated structure and the permselectivity of the graft copolymer membrane for ethanol was higher. When pervaporation of the ethanol-water mixture was carried out using the liquid-polymer hybrid membrane, ethanol completely permeated the liquid-polymer hybrid membrane.

**KEY WORDS** Pervaporation / Ethanol-Water Mixture / Membrane / Graft Copolymer / 2-Hydroxyethyl Acrylate / Acrylonitrile / Microphase Separated Structure / Carbon Tetrachloride / Separation / Solubility /

Recently, a method has been found for ethanol production by the fermentation of starch, sugar, and cellulose.<sup>1</sup> This method requires a separation process, since ethanol is obtained in about a 5% aqueous solution. An enormous amount of energy is consumed by the distillation generally used for the separation of ethanol and this has prompted the development of a difference separation process. For a continuous and economical operation, a separation process using a polymer membrane has been found. This pervaporation method does not require isolation of the permeate and can be applied to various organic liquid mixtures.<sup>2</sup> Separation of an ethanol-water mixture using various polymer membranes by pervaporation has been reported. These generally involve water permeation through the membrane.<sup>3,4</sup> However, it is more practical to per-

meate ethanol through the membrane since it is a minor component in the mixture produced by biomass.

Permselectivity of the polymer membrane for the solvent takes place by two steps in the permeation process, *i.e.*, dissolution and diffusion of the membrane. Therefore, the selectivity of a liquid mixture through the polymer membrane is a function of the difference in solubility and diffusivity of the solvents.<sup>5</sup> However, in the case of ethanol permeation from an ethanol-water mixture, even if the solubility of ethanol toward the membrane is practical, the permselectivity of ethanol is not enhanced because of the poor diffusivity of ethanol owing to its molecular size. If a component with low diffusivity such as ethanol in an ethanol-water system is permeated selectively, it is necessary to design a

membrane which may improve the diffusivity of ethanol, and consequently a hybrid membrane was designed. A liquid membrane improves diffusivity and the difference in the solubility of the components can be used effectively for permselectivity. The component dissolved in the liquid membrane is isolated by the polymer membrane. Thus, separation of ethanol from the aqueous solution takes place in two steps: ethanol dissolves selectively into the liquid membrane from the aqueous solution and ethanol in the liquid membrane is isolated by the polymer membrane. Since separation of ethanol-water system is changed to the separation of the ethanol-liquid membrane component system using the polymer membrane, it is easy to design the polymer membrane since its permselectivity is not influenced by diffusivity owing to the molecular size of ethanol and water.

In a previous paper, it was found that polymer membranes having microdomain structures and continuous domains function as permeation pathways for selective components of the mixture and that dispersed domains function to prevent excessive swelling of the membrane by the selective component. Such polymer membranes can be used to bring about the complete separation of a mixture with a high permeation rate. Actually, a 2-hydroxyethyl methacrylate-methyl acrylate graft copolymer membrane showed permselectivity for a benzene-cyclohexane azeotropic mixture because of its microdomain structure.<sup>6</sup>

This paper describes a liquid-polymer hybrid membrane to separate ethanol from an aqueous solution and investigates the effects of the microdomain structure of the polymer membrane on permselectivity. Carbon tetrachloride was used as the liquid membrane, and 2-hydroxyethyl acrylate (HEA) (branch)-acrylonitrile (AN) (backbone) graft copolymer, as the polymer membrane. Poly(HEA) has affinity toward ethanol and poly(AN) does not have affinity toward all components.

## EXPERIMENTAL

### Materials

2,2'-Azobisisobutyronitrile (AIBN), AN, 1-butanethiol, *N,N*-dimethylformamide (DMF), carbon tetrachloride, and 1-propanol were purified by conventional methods. HEA was distilled under reduced pressure in a nitrogen atmosphere and the

fraction of bp 55°C/2.5 mmHg was used. All other reagents and solvent were of extra grade.

### Synthesis of Backbone Polymer; HEA-AN Random Copolymer Having *p*-Nitrophenyl Group

An HEA-AN random copolymer was synthesized by ordinary radical copolymerization using AIBN as the initiator. A copolymer of shorter length was synthesized by the addition of 1-butanethiol as a chain transfer agent. The copolymer was dissolved in a mixture of DMF and pyridine, and an excess of *p*-nitrobenzoyl chloride was added to the mixture. The reaction was continued for 48 h at 0–20°C. The reaction mixture was poured into an excess of water to precipitate the polymer. The polymer was dissolved in DMF again and added dropwise to methanol for purification. After repeating this operation twice, the precipitated copolymer was filtered off and dried *in vacuo*. In this manner an HEA-AN random copolymer having a *p*-nitrophenyl (PNP) moiety as a backbone polymer was obtained. The composition of the PNP moiety in the backbone polymer was determined on the basis of the absorption coefficient of ethyl *p*-nitrobenzoate at 330 nm in DMF, ( $\epsilon = 4.98 \times 10^3$  l mol<sup>-1</sup> cm<sup>-1</sup>). Table I shows the backbone polymers prepared.

### Synthesis of an HEA-AN Graft Copolymer and Preparation of the Polymer Membrane

An HEA-AN graft copolymer was synthesized as follows. HEA monomer was polymerized using AIBN as the initiator in the presence of a backbone polymer. The radicals of the growing poly(HEA) segments were terminated at the PNP group.<sup>7</sup> The graft copolymer was purified by fractional precipitation with a methanol-diethyl ether system repeatedly, and finally the graft copolymer was precipitated into ethanol. Thus, unbonded poly(HEA) was removed from the reactant of the graft copolymerization.

The membrane was prepared by casting a 5% DMF solution of the copolymer onto a teflon plate and by evaporating the solvent at 40°C for 48 h. The membrane was then dried under reduced pressure for two days.

### Electron Microscope Observation of the Polymer Surface

The DMF solution of the copolymer was made to

flow over the carbon coated collodion membrane, and a thin film was prepared by evaporating the solvent at 40°C. After drying under reduced pressure, the film was fixed by osmium tetroxide vapor for 24 h. The microdomain structure was observed with an electron microscope (Hitachi HU-11 Type).

#### Pervaporation Experiment

The apparatus for pervaporation was the same as that in a previous paper.<sup>6</sup> 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 solvents. The pervaporation rate and separation factor were defined in a previous paper as,

$$P = w \cdot \theta / a \cdot t$$

where  $w$ ,  $\theta$ ,  $a$  and  $t$  denote the permeate flux, the membrane thickness, the membrane area and time, respectively.<sup>6</sup>

Pervaporation using a liquid-polymer hybrid membrane was carried out as follows. After carbon tetrachloride as the liquid membrane was put on the HEA-AN graft copolymer membrane, ethanol-water as a feed solvent was injected into the liquid membrane and then pervaporation was started.

#### Sorption Experiment

The method of sorption of the polymer membrane was the same as that in a previous paper.<sup>6</sup> The swelling ratio of solvent in the polymer membrane  $S$

was defined as,

$$S = (W_s - W_d) / W_d$$

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

Ethanol-water (1:1 by volume) mixture was gently poured into carbon tetrachloride. To determine the solubility of ethanol and water in the liquid membrane, the composition of carbon tetrachloride at 1.2 cm below the interface between the mixture and carbon tetrachloride layer was analyzed by gas chromatography.

## RESULTS AND DISCUSSION

#### Synthesis of HEA-AN Graft Copolymers and Microphase Separated Structure

The intrinsic viscosity of an S type backbone polymer was lower than that of L type as shown in Table I, due to the addition of the chain transfer agent, when HEA-AN random copolymer was synthesized as the backbone polymer. This indicates that the chain length of the S type backbone polymer was shorter.

Table II shows the results of the synthesis of the HEA-AN graft copolymer. The L type backbone polymer was used for L-1 to L-5 (L-series) and the S type for S-1 to S-3 (S-series). The intrinsic viscosity of the graft copolymer was higher than that of the backbone polymer in DMF at 30°C and characteristic IR bands of both polymers were observed, indicating that the HEA (branch)-AN (backbone) graft copolymer was synthesized. The HEA mole

Table I. Synthesis of backbone polymer

Code	HEA mole fraction in monomer	[S]/[M] <sup>a</sup>	Time h	HEA mole fraction in copolymer <sup>b</sup>	[NBC]/[OH] <sup>c</sup>	PNP mole fraction in backbone polymer <sup>d</sup>	Introduction degree %	$[\eta]^e$ dl g <sup>-1</sup>
L	0.05	0	2.0	0.057	15	0.053	93	1.12
S	0.05	0.006	3.5	0.053	27	0.047	88	0.44

[M] = 3.0 mol l<sup>-1</sup> in DMF, [AIBN] = 5.0 × 10<sup>-3</sup> mol l<sup>-1</sup>.

<sup>a</sup> S; chain transfer agent, 1-butanethiol.

<sup>b</sup> Determined by elemental analysis.

<sup>c</sup> NBC, *p*-nitrobenzoyl chloride.

<sup>d</sup> Determined by absorption coefficient of ethyl *p*-nitrobenzoate at 330 nm in DMF solvent,  $\epsilon = 4.98 \times 10^3$  l mol<sup>-1</sup> cm<sup>-1</sup>.

<sup>e</sup> In DMF at 30°C.

**Table II.** Synthesis of HEA-AN graft copolymer

Code	Concentration of PNP	Concentration of HEA	[S]/[M] <sup>a</sup> × 10 <sup>3</sup>	Time	HEA mole fraction of graft copolymer <sup>b</sup>
	(mol <sup>-1</sup> ) × 10 <sup>3</sup>	mol <sup>-1</sup>		h	
L-1	10.0	1.5	6.7	1.0	0.175
L-2	10.0	2.0	5.0	0.6	0.194
L-3	5.0	2.0	2.5	1.1	0.260
L-4	10.0	1.0	10.0	3.0	0.291
L-5	7.0	2.0	3.5	0.4	0.475
S-1	2.7	1.0	2.7	0.9	0.340
S-2	10.0	2.0	5.0	1.0	0.530
S-3	5.4	2.0	2.7	0.8	0.776

[AIBN] =  $5.0 \times 10^{-3}$  mol<sup>-1</sup>.

<sup>a</sup> S, PNP group.

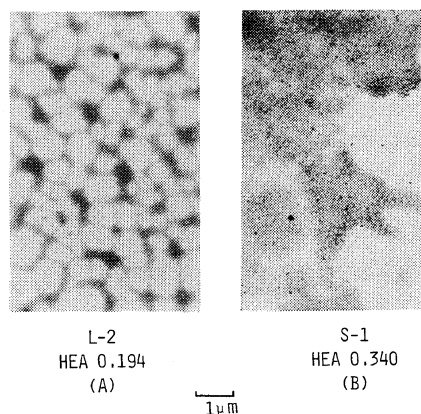
<sup>b</sup> Determined by elemental analysis.

fraction in the graft copolymer could be controlled by adjusting the concentration of both the HEA monomer and the backbone polymer and polymerization time.<sup>7</sup>

Figure 1 shows typical electron micrographs of the surface of the HEA-AN graft copolymer membrane. The dark portions correspond to the HEA domains stained by osmium tetroxide and the bright portions are AN domains. Because of the strong cohesive force of AN segments, the AN domains were spherical (island phase) in shape in spite of their high concentration. The AN domains were spherical in all the graft copolymer membranes examined and those of membrane (B) showed greater dispersion and were smaller than those of membrane (A). These differences in the microphase separated structures may be due to the chain length of the AN segments since the backbone polymer was shorter. It may be concluded that the microphase separating the structure of the graft copolymer can be controlled by adjustment of both component composition and chain length.

#### *Permeability of HEA-AN Graft Copolymer Membrane in Ethanol-Carbon Tetrachloride System*

Figure 2 shows the relation between the swelling ratio in an ethanol-carbon tetrachloride mixture (1:1 by volume) at 25°C and the composition of a graft copolymer membrane. The swelling ratio increased monotonously with increasing composition



**Figure 1.** Electron micrographs of an HEA-AN graft copolymer film cast from a 1.5% DMF solution.

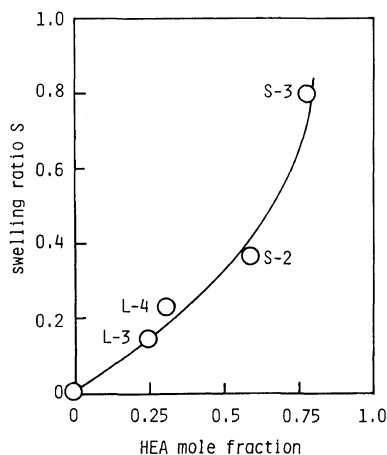
of HEA in the membrane. That is, the affinity of the membrane for the mixture increased with increasing HEA composition.

Table III shows the results of pervaporation of the ethanol-carbon tetrachloride mixture through the HEA-AN graft copolymer membrane. Figure 3 shows the relation between the pervaporation rate and composition of HEA in the graft copolymer membrane. The pervaporation rate for ethanol increased monotonously with increasing composition of HEA, which is consistent with the swelling ratio. No permeation of carbon tetrachloride could be detected and complete separation was realized up to

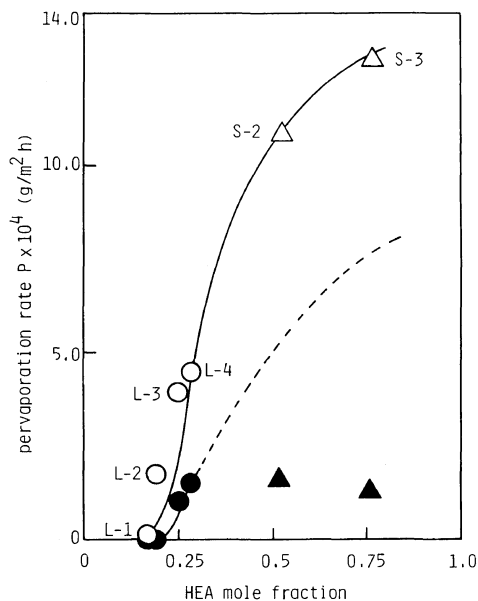
Permselectivity of Membrane for Ethanol-Water Mixture

**Table III.** Characteristics of pervaporation through membrane in ethanol-carbon tetrachloride (1:1 by volume) mixture at 25°C

Membrane	HEA mole fraction in copolymer	Thickness μm	Pervaporation rate/g m <sup>-2</sup> h <sup>-1</sup>		Separation factor α
			Ethanol (P <sub>E</sub> )	CCl <sub>4</sub> (P <sub>C</sub> )	
L-1	0.175	13.4	5.57 × 10 <sup>-6</sup>	0	∞
L-2	0.194	19.6	1.71 × 10 <sup>-4</sup>	0	∞
L-3	0.260	15.9	3.94 × 10 <sup>-4</sup>	1.11 × 10 <sup>-4</sup>	8.0
L-4	0.291	10.1	4.47 × 10 <sup>-4</sup>	1.48 × 10 <sup>-4</sup>	6.1
S-2	0.530	31.1	1.08 × 10 <sup>-3</sup>	1.70 × 10 <sup>-4</sup>	12.8
S-3	0.776	93.0	1.29 × 10 <sup>-3</sup>	1.29 × 10 <sup>-4</sup>	27.5



**Figure 2.** Swelling ratio of the membranes of an HEA-AN graft copolymer in an ethanol-carbon tetrachloride (1:1 by volume) mixture with an HEA mole fraction in the membrane at 25°C.

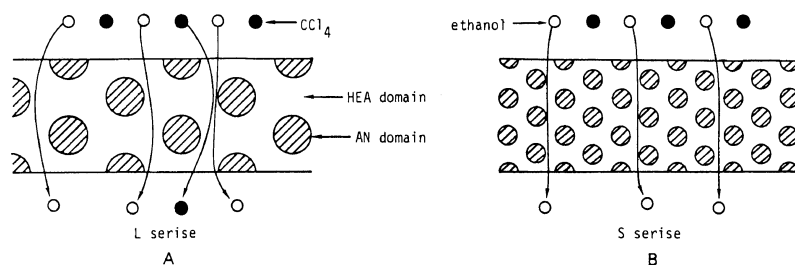


**Figure 3.** Pervaporation rate *P* vs. HEA mole fraction for the membranes of an HEA-AN graft copolymer in an ethanol-carbon tetrachloride system at 25°C. (○, ●), L series; (Δ, ▲), S series; open plot, ethanol; closed plot, carbon tetrachloride.

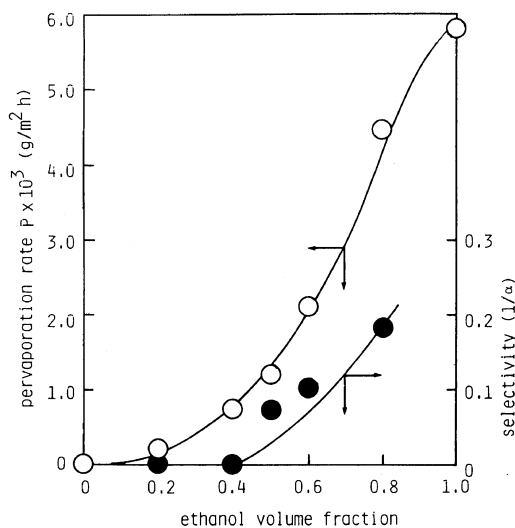
an HEA mole fraction of about 0.2. On the other hand, when the HEA mole fraction exceeded 0.2, carbon tetrachloride permeated through the membrane. When the swelling ratio of the membrane of the mixture was large, the mobility of polymer segments increased and consequently, carbon tetrachloride started permeating the membrane in spite of its low affinity toward the membrane; this behavior is the so-called "plasticizing effect."<sup>8</sup> However, when using a membrane of the S series, the pervaporation rate of carbon tetrachloride was lower than the value anticipated from the membrane of the L series, and the selectivity was high in spite of the high HEA concentration.

It is expected that a great change in the per-

meability of the membrane may be closely related to the morphology of the microdomain structure, as illustrated in Figure 4. AN domains for the S series (B) were more dispersed and smaller in domain size than those of (A), as shown in Figure 1. In the case of (A), it is considered that the plasticizing effect in the central part of the HEA domain occurs by excessive swelling of the membrane of the mixture, and thus carbon tetrachloride permeates easily through the membrane. On the other hand, since



**Figure 4.** Schematic representation of the mechanism for pervaporation through the HEA-AN graft copolymer membrane.



**Figure 5.** Pervaporation rate and selectivity ( $1/\alpha$ ) vs. the ethanol volume fraction in an ethanol-carbon tetrachloride system using an HEA-AN graft copolymer membrane (S-2 HEA mole fraction 0.530) at 25°C.  $1/\alpha = (P_C/P_E)/(F_C/F_E)$ .  $P_E$ ,  $P_C$ , pervaporation rate ethanol and carbon tetrachloride, respectively,  $F_E$ ,  $F_C$ , weight fraction of each component in the feed.

the plasticizing effect was depressed effectively by suppressing the mobility of the HEA segments in the dispersed AN domains throughout the membrane in the case of (B), permeation of carbon tetrachloride is considered to occur with difficulty. Therefore, control of the microphase separated structure as well as composition of the membrane is an important factor in the permselectivity of the membrane when a graft copolymer membrane with microdomains of each component is utilized for the pervaporation.

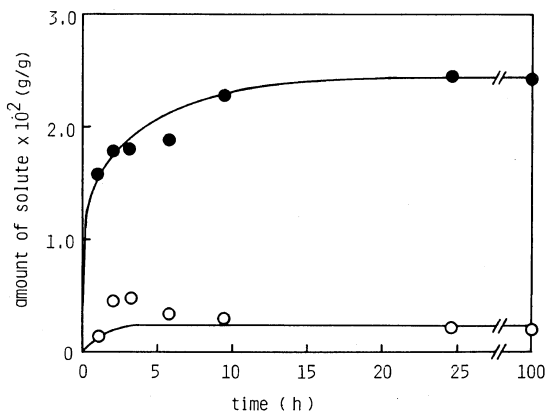
Figure 5 shows the relation between the perm-

**Table IV.** Concentration of ethanol and water containing in carbon tetrachloride

Volume ratio of $\text{CCl}_4^a$	Concentration in $\text{CCl}_4$ / vol%		Solubility ratio $\alpha_1^b$
	Ethanol ( $C_E$ )	Water ( $C_W$ )	
0.12	44.1	4.4	10.0
0.20	4.32	0.20	21.4
0.33	3.84	0.17	22.4

<sup>a</sup> Ethanol: water = 1:1 by volume.

<sup>b</sup> Solubility ratio  $\alpha_1 = C_E/C_W$ .



**Figure 6.** Time dependence of the amount of solute in carbon tetrachloride at 25°C. (●), ethanol; (○), water.

selectivity of an S-2 membrane and the composition of the ethanol-carbon tetrachloride mixture. The pervaporation rate increased monotonously with increasing composition of ethanol in the feed. Permeation of carbon tetrachloride could not be detected up to an ethanol volume fraction of 0.4; thus, complete separation was realized. When

the composition of ethanol in the feed mixture was high, this membrane swelled excessively in the mixture and permeation of carbon tetrachloride, due to the plasticizing effect, was found to be induced.

#### Solubility and Diffusivity in Liquid Membrane

Table IV shows the solubility of ethanol and water in carbon tetrachloride, a liquid membrane component. Ethanol was found to dissolve preferentially in carbon tetrachloride. Moreover, the concentration of ethanol in carbon tetrachloride could be controlled by changing the amount of carbon tetrachloride; that is, the concentration of ethanol in the liquid membrane could be regulated when using the liquid-polymer hybrid membrane for the separation of the ethanol-water mixture.

Figure 6 represents the sorption of each component in carbon tetrachloride. Both components were diffused in carbon tetrachloride and the composition reached an equilibrium state in about 10 h. It is generally known that the diffusion rate of a solute in a liquid is rapid, 100–1000 times more than that in a solid.<sup>9</sup> Even through a liquid membrane is much thicker than a polymer membrane in a liquid-polymer hybrid membrane system, the diffusion of the solute in the liquid membrane is not the rate-determining step. Therefore, the composition of the liquid membrane remains constant during pervaporation. The liquid membrane enhances the difference in the solubility between ethanol and water. Consequently, it is considered that the polymer membrane must be designed for an effective separation of an ethanol-liquid membrane component mixture, such as that of ethanol carbon tetrachloride. When using a graft copolymer membrane of the S-2 type for the separation of ethanol-liquid membrane components, the most practical composition of the liquid membrane is a volume

fraction of 0.6 (Figure 5).

#### Permselectivity of the Liquid-Polymer Hybrid Membrane in Ethanol-Water Mixture

Table V shows the results of the pervaporation of an ethanol-water mixture using the liquid-polymer hybrid membrane. Since the concentration of ethanol in the liquid membrane was low, as shown in Table IV, the swelling ratio of the graft copolymer membranes, S-2, S-3, was small and no plasticizing effect was induced. Carbon tetrachloride as a liquid membrane component did not permeate the polymer membrane. Moreover, since the difference in solubility between ethanol and water was enhanced by the liquid membrane, ethanol permeated preferentially. In particular, a complete separation of the ethanol-water mixture was achieved using the S-3 membrane as a polymer membrane under the experimental conditions mentioned in Table V.

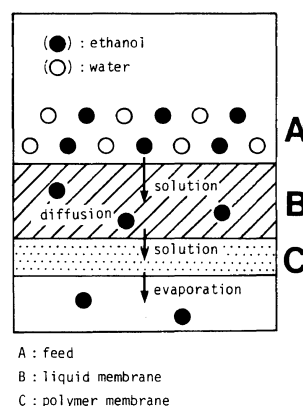


Figure 7. Schematic representation of the separation process for an ethanol-water mixture in a liquid-polymer hybrid membrane system.

Table V. Characteristics pervaporation through liquid-polymer hybrid membrane composed of carbon tetrachloride and HEA-AN graft copolymer in ethanol water (1:1 by volume) mixture at 25°C

Polymer membrane	HEA mole fraction in copolymer	Volume ratio of liquid membrane	Pervaporation rate/gm <sup>-2</sup> h <sup>-1</sup>			Separation factor $\alpha$
			Ethanol	Water	CCl <sub>4</sub>	
S-2	0.530	0.20	$9.57 \times 10^{-7}$	$5.37 \times 10^{-7}$	0	2.24
S-2	0.530	0.33	$4.23 \times 10^{-7}$	$1.72 \times 10^{-7}$	0	3.12
S-3	0.776	0.33	$6.62 \times 10^{-7}$	0	0	$\infty$

Figure 7 illustrates the mechanism for permeation through the liquid-polymer hybrid membrane. The separation process is considered to be as follows. (1) At the interface between A and B, ethanol dissolves into B selectively. (2) Ethanol molecules diffuse into the liquid membrane (B) rapidly and become situated at the interface between B and C. (3) At this interface, C, ethanol dissolves into C selectively. (4) Ethanol molecules diffuse in the domains in the graft copolymer membrane and are vaporized. According to this process, ethanol is separated selectively from the ethanol-water mixture. This separation process differs from the method reported by McCandless, *et al.* with respect to the fundamental mechanism since the extracting agent to increase the permselectivity is not permeated.<sup>10</sup>

A combination of liquid and polymer membranes facilitates the design of a permselective membrane and also, the membrane performs a greater number of functions. This separation technique is apparently used in preference to other liquid mixture system.

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