

Separation of Organic Solvent from Dilute Aqueous Solutions and from Organic Solvent Mixtures through Crosslinked Acrylate Copolymer Membranes by Pervaporation

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ABSTRACT: The composite membranes of acrylate polymers and porous substrate were prepared. The separation of the organic solvent–water mixtures and the organic solvent–organic solvent mixtures through these membranes by pervaporation was investigated. The acrylate copolymer membrane showed the organic solvent permselectivity for the separation of the organic solvent–water mixture, especially for the chlorinated hydrocarbon–water mixture separation. The high organic solvent permselectivity should be governed by solubility selectivity. The influence of the ester residue of acrylate on the phenol–water mixture separation was observed. The copolymerization of the macromonomers containing the polystyrene, poly(methyl methacrylate), and polydimethylsiloxane chain had a small effect on the separation of the chlorinated hydrocarbon–water mixture. High flux and low selectivity of organic solvent were observed in the case of the organic solvent mixture separation through the *n*-butylacrylate membrane. The difference of permeability of organic solvent was observed for the acrylate copolymer which has various structures of ester residue. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1483–1494, 1998

Key words: pervaporation; acrylate copolymer; organic solvent mixture

INTRODUCTION

Separation of liquid mixture by pervaporation has been considered a useful method, and a hydrophilic water-permselective membrane from a water–organic solvent mixture (for example, a

water–ethanol mixture) has been practically available for an industrial use.¹

If the organic solvent in a water–solvent mixture is present in low concentration and its boiling point is higher than that of water, pervaporation with a hydrophobic membrane is also an effective method for reducing the amount of organics.^{2–8}

In recent years, membranes for the separation of organic solvent from dilute aqueous solutions and from organic solvent–organic solvent mixtures have been investigated.^{2,4–6,9–13} We have also reported an organic solvent-permselective

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membrane for dilute organic solvent aqueous solutions.^{14–16} Such membrane is an acrylate copolymer membrane, and was selected by the following method.

First, polyacrylates exist in the rubbery state at pervaporation operating temperatures (usually from room temperature to 100°C) because they have low glass transition temperatures (T_g). Given the rubbery nature of the membrane, high permeability would be expected.

Second, it is possible to obtain acrylate monomers which have ester residues, and to change the affinity of polyacrylate membrane for the organic solvent.

Third, the polyacrylate is generally soluble in the organic solvent (for example, ethyl acetate or toluene), and its membrane can easily be prepared by the coating method.

A previous work investigated the separation of chlorinated hydrocarbon–water mixture through crosslinked poly(*n*-butyl acrylate-*co*-acrylic acid [poly(BA-*co*-AA)]) composite membrane with porous substrate. The poly(BA-*co*-AA) membrane showed high chlorinated hydrocarbon permselectivity. From results of sorption and pervaporation measurement, it is considered that the high permselectivity was obtained by high solubility selectivity, and that the diffusivity selectivity was not favorable for the chlorinated hydrocarbons. Furthermore, the poly(BA-*co*-AA) membrane preferentially permeated ethyl acetate and ethanol from aqueous solutions.

In this study, the following items are investigated for the further examination of the organic solvent mixture separation through the polyacrylate membranes:

1. For the organic solvent aqueous solutions:
 - sorption and pervaporation of chlorinated hydrocarbons and ethanol and ethylacetate aqueous solutions;
 - pervaporation of trichloroethylene (trichloroethylene) and tetrachloroethylene (perylene) aqueous solutions;
 - influence of copolymerization with methacrylate monomer (macromonomer) which has polystyrene, poly(methyl methacrylate), and polydimethylsiloxane chain on the pervaporation and sorption of the 1,1,2-trichloroethane–water mixture separation; and
 - influence of side chain of acrylate on pervaporation of phenol aqueous solution.

2. For the organic solvent–organic solvent mixture:
 - pervaporation and swelling measurement of organic solvent mixtures;
 - influence of crosslinking agent content on the separation of hexane–heptane mixture; and
 - influence of acrylate and methacrylate side chain on the separation of hexane–heptane mixture.

EXPERIMENTAL

Synthesis of Acrylate and Methacrylate Copolymer

Acrylate and methacrylate copolymers were synthesized by solution polymerization with 2,2'-azobis(isobutyronitrile) or 2,2'-azobis(2,4-dimethylvaleronitrile) as an initiator. Composition and polymerization conditions of acrylate and methacrylate copolymers are summarized in Table I.

The acrylate monomers (methyl acrylate, ethyl acrylate, BA, lauryl acrylate, *tert*-BA, and cyclohexyl acrylate), the methacrylate monomer [lauryl methacrylate (LaMA)], and AA were purified by a vacuum distillation, and the macromonomers (MM1: polystyrene type; MM2: poly(methyl methacrylate) type; and MM3: polydimethylsiloxane type; structure is shown in Fig. 1) and other reagents were used without further purification.

The copolymer with 90% BA content and 10% AA content is represented as poly(BA-*co*-AA) (90 : 10).

Preparation of Membrane

An acrylate and methacrylate copolymer solution after polymerization was diluted by toluene at 25 wt %. A crosslinking agent (TGXDA; structure is shown in Fig. 1) was added to the polymer solution. The solution was cast on an exfoliation-treated poly(ethylene terephthalate) (PET) film and then dried at 100°C for 1 min. (One side of the PET film was coated by silicone compounds as exfoliation-treated material and then cured by heat. This layer stuck to the PET film so that it did not exfoliate from the PET film with the (meth)acrylate membrane at preparation of the composite membrane.) A polypropylene porous sheet, Celgard® 2500 (Daicel Chemical Industries, Ltd., Osaka, Japan), was covered on the acrylate copolymer membrane, and after removal of the PET film, the porous sheet was covered on the other side of the membrane. Thus, a sand-

Table I Polymerization Conditions of Acrylate and Methacrylate Copolymers

Monomer (Weight fraction)	Solvent (Weight fraction)	Monomer Concentration (wt %)	Temperature (°C)	Time (h)	Initiator (mol %)
MA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	24	AIBN, ^a 0.10
EA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	24	AIBN, 0.10
BA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	24	AIBN, 0.10
<i>tert</i> -BA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	8	AIBN, 0.10
CHA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	8	AIBN, 0.10
LA : AA = 90 : 10	Ethyl acetate	40	55	24	ADMVN, ^b 0.10
LaMA : AA = 90 : 10	Ethyl acetate : Toluene = 90 : 10	40	70	24	AIBN, 0.10
BA : AA : MM1 = 70 : 10 : 20	Ethyl acetate	30	70	8	AIBN, 0.05
BA : AA : MM1 = 40 : 10 : 50	Ethyl acetate	30	70	8	AIBN, 0.05
BA : AA : MM2 = 70 : 10 : 20	Ethyl acetate	30	70	8	AIBN, 0.05
BA : AA : MM2 = 40 : 10 : 50	Ethyl acetate	30	70	8	AIBN, 0.05
BA : AA : MM3 = 70 : 10 : 20	Ethyl acetate	30	70	8	AIBN, 0.05
BA : AA : MM3 = 40 : 10 : 50	Ethyl acetate	30	70	8	AIBN, 0.05

MA, methyl acrylate; EA, ethyl acrylate; CHA, cyclohexyl acrylate; LA, lauryl acrylate; LaMA, lauryl methacrylate.

^a AIBN; 2,2'-Azobis(isobutyronitrile).

^b ADMVN; 2,2'-Azobis(2,4-dimethylvaleronitrile).

wich-type composite membrane was prepared. Figure 2 shows the membrane preparation method.

The poly(BA-*co*-AA) (90 : 10) membrane of which the crosslinking agent content was 0.05 (the ratio of the epoxy group of TGXDA to that of the carboxyl group of the copolymer) is represented as poly(BA-*co*-AA) (90 : 10, 0.05).

Pervaporation Measurement

The pervaporation measurement was carried out under vacuum (below 10 mmHg) on the downstream side of the membrane, and the upstream pressure was maintained at atmospheric pressure. A schematic diagram of the pervaporation apparatus is shown in Figure 3. The effective membrane area was 10.21 cm². In the case of the organic solvent–water mixture separation, 1000 cm³ of feed solution was circulated with a microtube pump to reduce the in-

fluence on the concentration decrease by the high organic solvent permselectivity and the low organic solvent concentration in the feed solution. For the separation of the organic solvent mixtures, 60 cm³ of feed solution was supplied to the upper compartment of the pervaporation cell without circulation because the decrease in the concentration change was small.

The permeate vapor was collected in a cold trap with liquid nitrogen. The concentrations of organic solvents and water in the feed and permeate solution were determined by gas chromatographic analysis, and the flux was determined by measuring the weight of the collected sample. For the organic solvent–water mixture separation, the concentration of organics in the permeate solution was high, so that the permeate separated into two phases. The gas chromatographic measurement was therefore carried out by adding 2-propanol to make a uniform solution. The flux

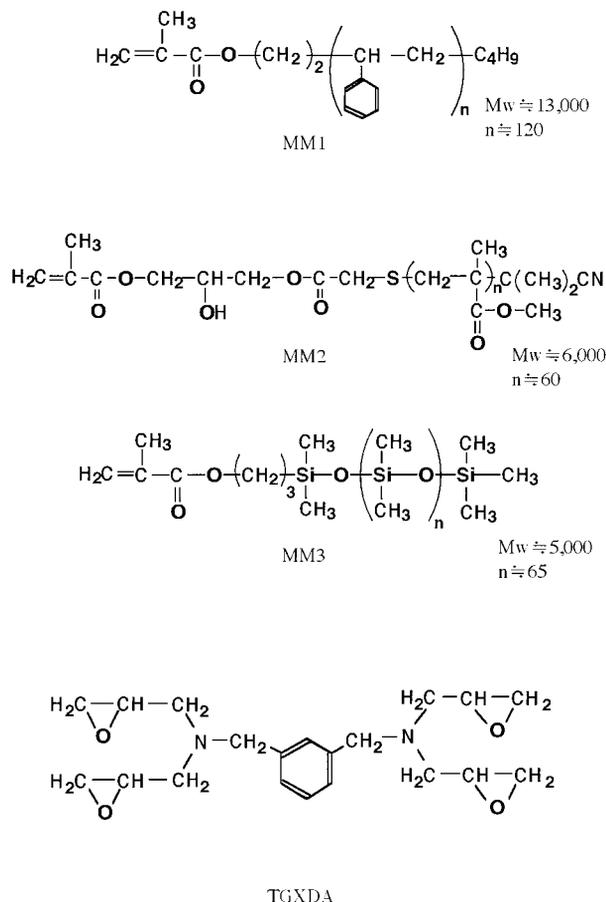


Figure 1 Structure of macromonomers and crosslinking agent.

and the separation factor, α_P , were calculated by the following equations:

$$\text{Flux (g m}^{-2} \text{ h}^{-1}) = \frac{Q}{At} \quad (1)$$

$$\alpha_{P(ij)} = \frac{C_{i2}/C_{j2}}{C_{i1}/C_{j1}} \quad (2)$$

(See Nomenclature section for definitions of terms.)

Sorption and Degree of Swelling Measurement

The swelling measurement was carried out as follows. The membrane pieces, the swollen weight of which was previously measured (W_w), were immersed in the organic solvent–water mixture or the organic solvent mixture for 48 h at the same temperature of pervaporation measurement. The solution on the membrane surface was

wiped off and the weight of the dried membrane was measured (W_D).

The membrane pieces were then frozen in a glass vessel under vacuum. The glass vessel was heated and the vaporized absorbate was collected in the cold trap with liquid nitrogen. The concentrations of organic solvent and water were determined in the same way as the pervaporation measurement.

The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{W_w - W_D}{W_D} \times 100 \quad (3)$$

The separation factor of partition, α_K , was calculated from eq. (4).

$$\alpha_{K(ij)} = \frac{K_i}{K_j} = \frac{C_{i3}/C_{i1}}{C_{j3}/C_{j1}} \quad (4)$$

For the pervaporation, the permeability coefficient represents the product of the partition coefficient and the diffusion coefficient. Therefore, it is considered that the separation factor of permeation, α_P , is also expressed as the product of α_K and that of diffusion, α_D , as follows^{9,17}:

$$\alpha_{P(ij)} = \alpha_{K(ij)}\alpha_{D(ij)} \quad (5)$$

RESULTS AND DISCUSSION

Organic Solvent–Water Mixtures

Sorption and Pervaporation Measurement for Various Organic Solvent–Water Mixtures

The results of the pervaporation measurement and the sorption measurement for the poly(BA-co-AA) (90 : 10, 0.05) membrane and α_D , calculated by eq. (5), are summarized in Table II.

Comparison of α_P with α_K showed α_K to be larger than α_P , and $\alpha_D < 1$. Because $\alpha_D < 1$, its diffusivity selectivity was preferable to that of the water. It is considered that this can be attributed to the difference between the molecular size of the organic solvent and that of the water. On the other hand, $\alpha_K > 1$ and its solubility selectivity was therefore preferable to that of the organic solvents. As a result of the pervaporation measurement, the poly(BA-co-AA) membrane showed the organic solvents' permselectivity. Consequently, it is considered that the organic solvents

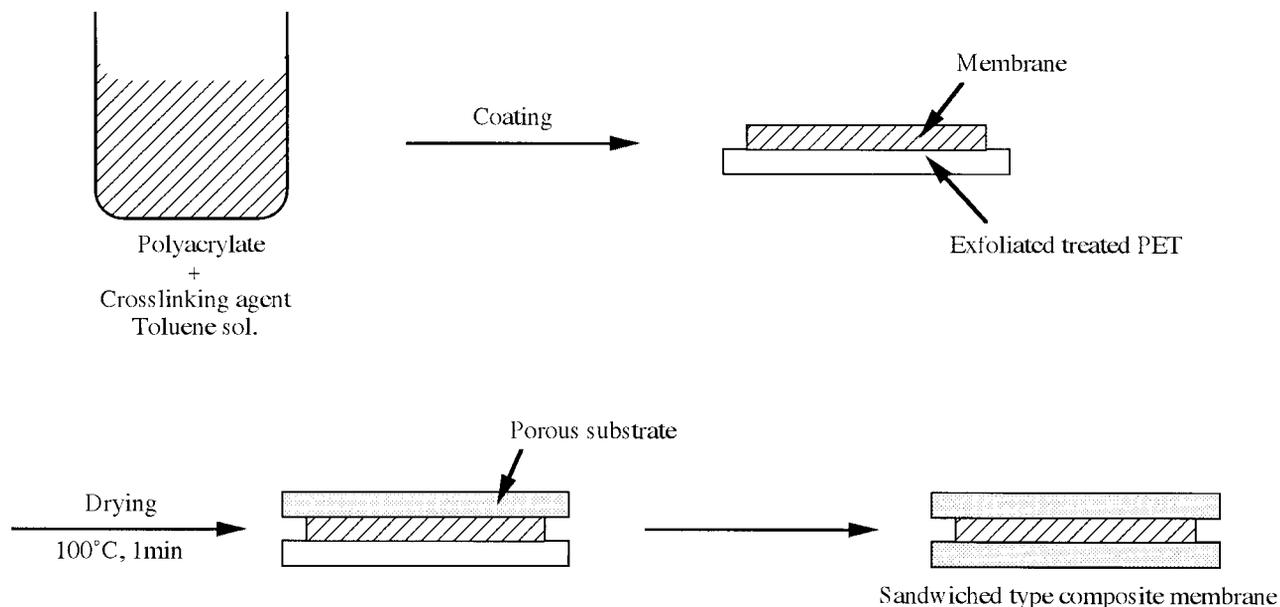


Figure 2 Membrane preparation method.

permselectivity was governed by the solubility selectivity. The organic solvent, with which solubility for the membrane was low, therefore showed the low permselectivity.

Comparison of the chlorinated hydrocarbon showed that the diffusivity selectivity decreased with increasing molecular size. It seems that this is due to increase in the diffusion resistance.

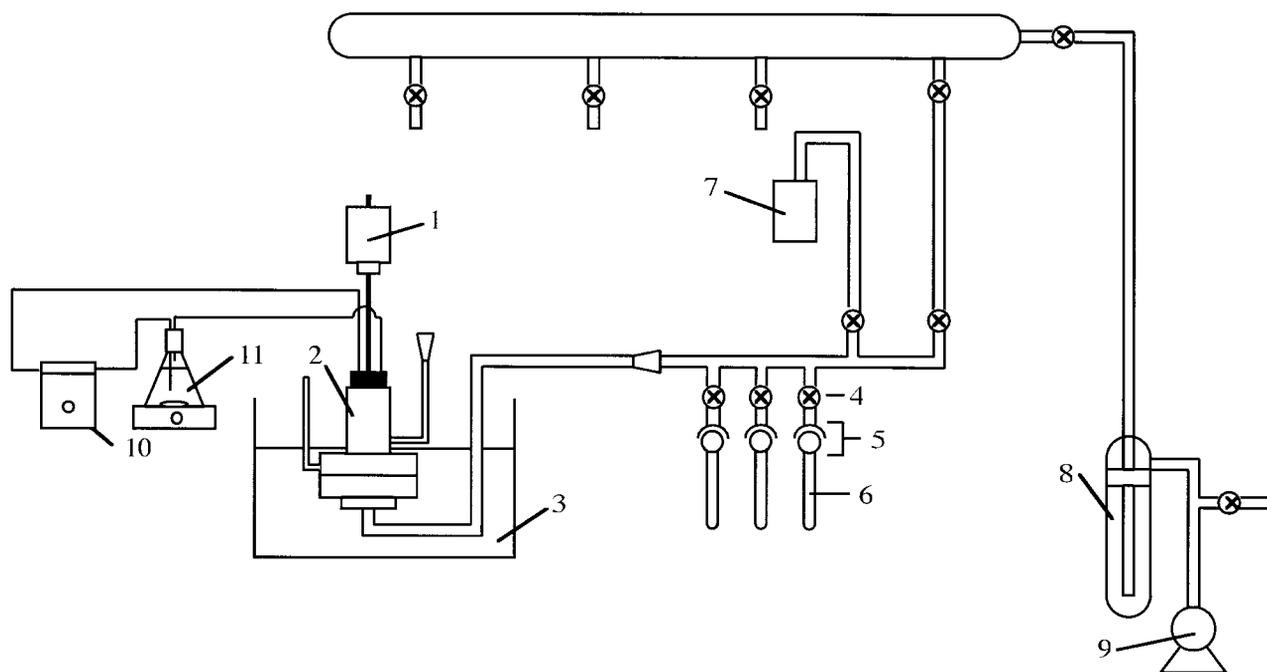


Figure 3 Pervaporation apparatus: 1, stirring motor; 2, pervaporation cell; 3, constant-temperature water bath; 4, greaseless cock; 5, ball joint; 6, cold trap for collecting sample; 7, vacuum gauge; 8, cold trap; 9, vacuum pump; 10, micro tube pump; 11, feed solution.

Table II Pervaporation and Sorption Data of Organic Solvent–Water Mixtures for Poly(BA-co-AA) (90 : 10, 0.05) Membrane at 25°C

Organic Solvent	Pervaporation			Sorption			
	Organic Solvent in Feed (wt %)	α_P^a	Flux ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Organic Solvent in Feed (wt %)	Organic in Membrane (wt %)	α_K^a	α_D^a
Chloroform	0.155	467	15.8	0.225	54.88	539	0.866
1,2-Dichloroethane	0.175	320	24.1	0.200	54.32	593	0.539
1,1,2-Trichloroethane	0.202	708	36.3	0.200	68.83	1103	0.642
Trichloroethylene	0.0529	804	21.3	0.0521	51.94	2075	0.387
Tetrachloroethylene	0.00652	905	15.1	0.00719	21.18	3737	0.242
Ethyl acetate	0.162	29.1	14.3	0.224	9.995	49.4	0.589
Ethanol	4.97	2.32	16.6	4.99	18.31	4.27	0.543

^a Organic solvent/water.

The relationship between the solubility of the chlorinated hydrocarbons for the water and the α_P is shown in Figure 4.^{18,19} The α_P decreased with increasing the solubility of the chlorinated hydrocarbons for the water. It is considered that the hydrophilicity became large because of the increase in the solubility for the water. Therefore, it seems that the affinity of the chlorinated hydrocarbons for the membrane decreased, and its selectivity also decreased.

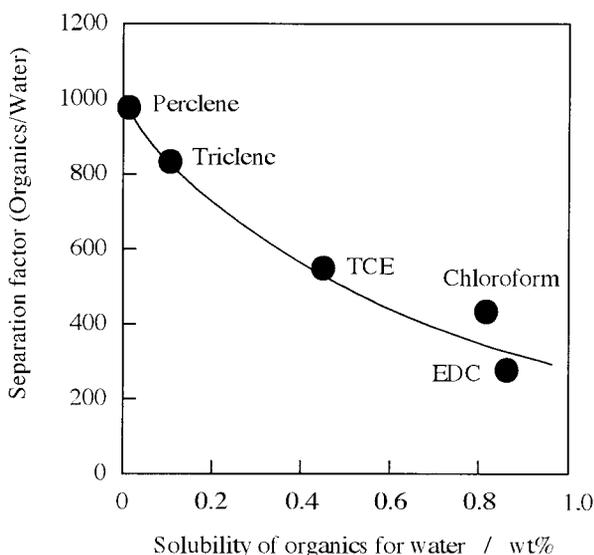


Figure 4 Relationship between solubility of the chlorinated hydrocarbons for the water and the separation factor of permeation for the poly(BA-co-AA) (90 : 10, 0.05) membrane at 25°C (organic solvent concentration in the feed solution: 0.015 wt %).

Pervaporation of Triclene–Water and Perclene–Water Mixtures

The effect of the feed solution triclene concentration on the pervaporation separation for poly(BA-co-AA) (90 : 10, 0.05) membrane is shown in Figure 5.

The triclene concentration in the permeate solution increased from 11.8 to 43.3 wt % with increasing triclene concentration in the feed solution. The total flux and the triclene partial flux increased from 16.7 to 28.0 $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and from 1.96 to 12.1 $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, respectively, whereas the water flux was relatively constant.

The effect of the feed solution perclene concentration on the pervaporation separation is shown in Figure 6. The perclene in the permeate solution increased from 2.9 to 8.3 wt %. The change in the total flux and the water partial flux was small, and the perclene partial flux increased with increasing perclene concentration in the feed solution.

The flux of pervaporation is expressed as follows^{20,21}:

$$J_i = -D_i \frac{dC_i}{dx} \quad (6)$$

$$D_i = D_{0i} \exp(\gamma_i C_i) \quad (7)$$

The integration of eq. (7), taking into account eq. (6), gives

$$J_i = \frac{D_{0i}}{\gamma_i l} [\exp(\gamma_i C_{i1}) - \exp(\gamma_i C_{i2})] \quad (8)$$

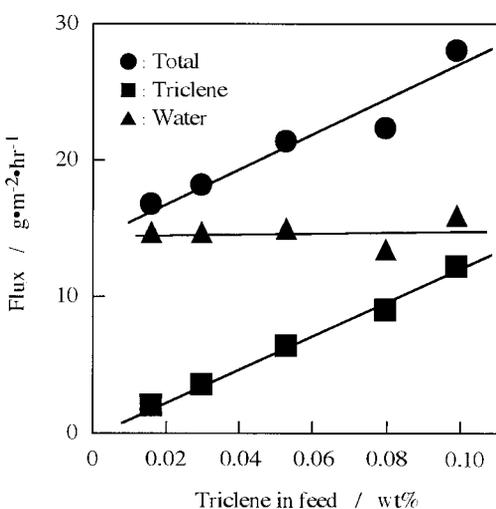
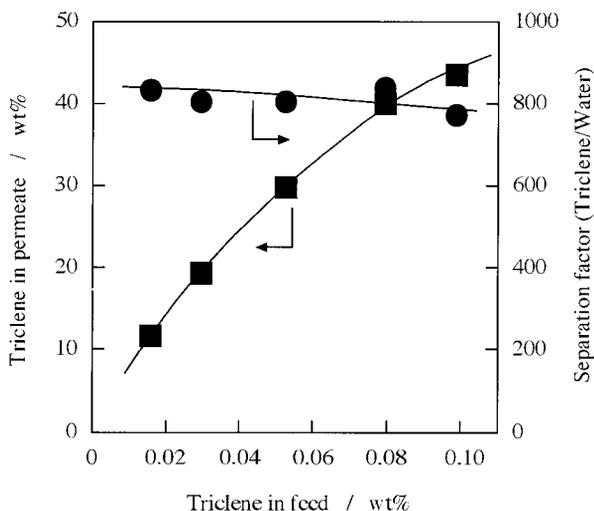


Figure 5 Effect of the trichloroethylene concentration in the feed solution on the pervaporation for poly(BA-co-AA) (90 : 10, 0.05) membrane at 25°C.

In this study, the concentration C_{i2} is nearly equal to zero because the downstream side of the membrane is maintained at very low pressure. With that assumption, eq. (8) can be rewritten as

$$J_i = \frac{D_{0i}}{\gamma_i l} [\exp(\gamma_i C_{i1}) - 1] \quad (9)$$

The volume of polymer which sorbed a unit amount of solvent, γ , is called a plasticization parameter, and it is considered that γ becomes larger with increasing affinity of the organic solvent for the membrane. For the trichloroethylene and perchloroethylene separation, these solvents show high affinity for the polyacrylate, and that of water is low. The γ values of trichloroethylene and perchloroethylene are

consequently large, and a change of exponential term concerning the concentration also becomes large. Therefore, the concentration dependence of the organic solvent partial flux was observed. The γ value of the water should be small because of water's low affinity for the membrane, so the influence of concentration on the water partial flux was small.

Influence of Macromonomer

The influence of macromonomer copolymerization on the separation and sorption is summarized in Table III.

The flux of each membrane was nearly equal in the low macromonomer-containing region. In the

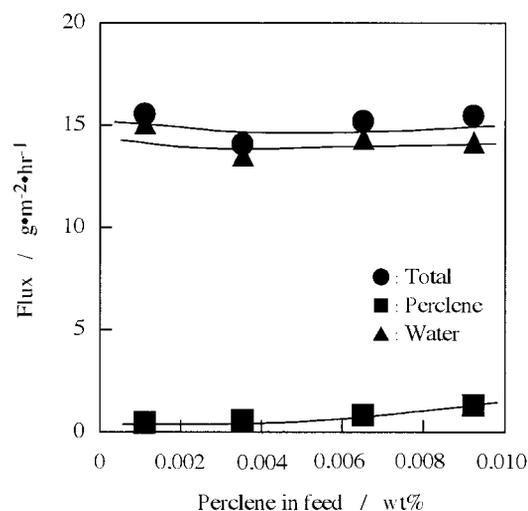
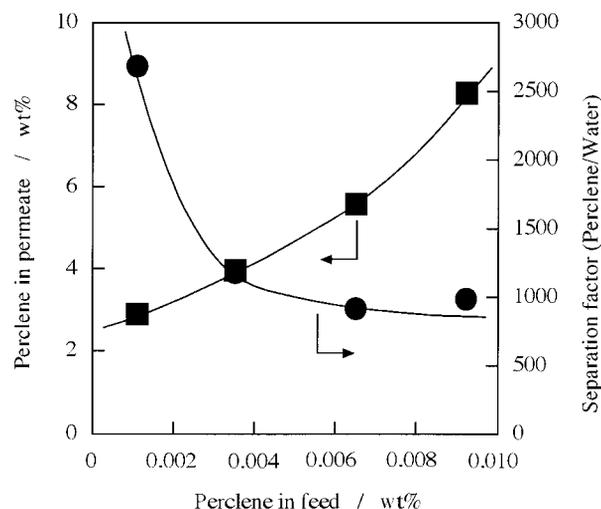


Figure 6 Effect of the perchloroethylene concentration in the feed solution on the pervaporation for poly(BA-co-AA) (90 : 10, 0.05) membrane at 25°C.

Table III Pervaporation and Sorption Data of 1,1,2-Trichloroethane (TCE)–Water Mixture Through Acrylate Copolymer Membranes at 25°C

Membrane	Pervaporation			Sorption			
	TCE in Feed (wt %)	α_P^a	Flux ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	TCE in Feed (wt %)	TCE in Membrane (wt %)	α_K^a	α_D^a
BA-co-AA-co-MM1 (7 : 1 : 2)	0.205	698	32.4	0.218	35.82	256	2.73
BA-co-AA-co-MM2 (7 : 1 : 2)	0.202	758	26.0	0.218	34.95	250	3.03
BA-co-AA-co-MM3 (7 : 1 : 2)	0.209	448	33.3	0.218	53.65	530	0.845
BA-co-AA-co-MM1 (4 : 1 : 5)	0.210	338	7.80	0.209	41.11	334	1.01
BA-co-AA-co-MM2 (4 : 1 : 5)	0.200	446	7.57	0.209	34.75	255	1.75
BA-co-AA-co-MM3 (4 : 1 : 5)	0.205	686	45.6	0.209	52.95	538	1.28
BA-co-AA (90 : 10, 0.05)	0.202	708	36.3	0.200	68.83	1103	0.642

^a TCE/water.

high macromonomer-containing region the flux decreased, except in the copolymer containing MM3. The MM1 has the poly(methyl methacrylate) chain, and the MM2 has the polystyrene chain. The diffusivity of these chains should be smaller than that of the poly(BA-co-AA). Therefore, it is considered that the flux of the copolymer containing the MM1 and the MM2 decreased with increase in the macromonomer content. The MM3 has the polydimethylsiloxane chain. The diffusivity of polydimethylsiloxane is high, and it shows the organic solvent permselectivity for the organic solvent–water mixture separation.^{22–24} It seems that the flux increased with increase in the MM3 content of the copolymer.

The sorption measurements demonstrate that there is no effect from the macromonomer content, and that the α_K values of the copolymers were smaller than that of the poly(BA-co-AA). The α_K of the copolymer containing MM3 was larger than that of the other copolymers. This result should be attributed to the affinity of the polydimethylsiloxane chain for the organic solvents.

In this case, the diffusivity selectivity slightly contributed to the 1,1,2 trichloroethane (TCE) permselectivity because α_P was larger than α_K .

Influence of the Acrylate Side Chain

The influence of the side chain of the acrylate on the phenol–water mixture separation is shown in Figure 7.

The α_P increased from 2.92 to 19.2 with increase in the carbon number of the ester residue. The flux and the water partial flux decreased

from 343 to 37.4 $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and from 331 to 31.0 $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, respectively. On the other hand, the phenol partial flux changed slightly and had maximum value.

For a copolymer containing the acrylate which has a short hydrocarbon chain, it is anticipated that the hydrophilicity is larger than that of one having the long hydrocarbon chain, and the diffusion resistance of the membrane is small. In contrast, the hydrophobicity increases for the copolymer having a long hydrocarbon chain, and the diffusion resistance becomes large because of the bulky side chain. Therefore, it is considered that the water partial flux decreased drastically because of the increase in hydrophobicity and the diffusion resistance. The phenol partial flux should increase with increased hydrophobicity. The diffusion resistance of phenol also increased with increase in the carbon number of the ester residue. Consequently, it is considered that the phenol partial flux changed slightly, and had a maximum value.

Organic Solvent Mixtures

Pervaporation and Swelling Measurement of Organic Solvent Mixtures

The influence of the feed solution hexane concentration on the pervaporation separation is shown in Figure 8. The poly(BA-co-AA) membrane showed the hexane permselectivity. The total flux increased with increase in the hexane concentration in the feed solution.

The influence of the immersion liquid hexane concentration on the degree of swelling is shown

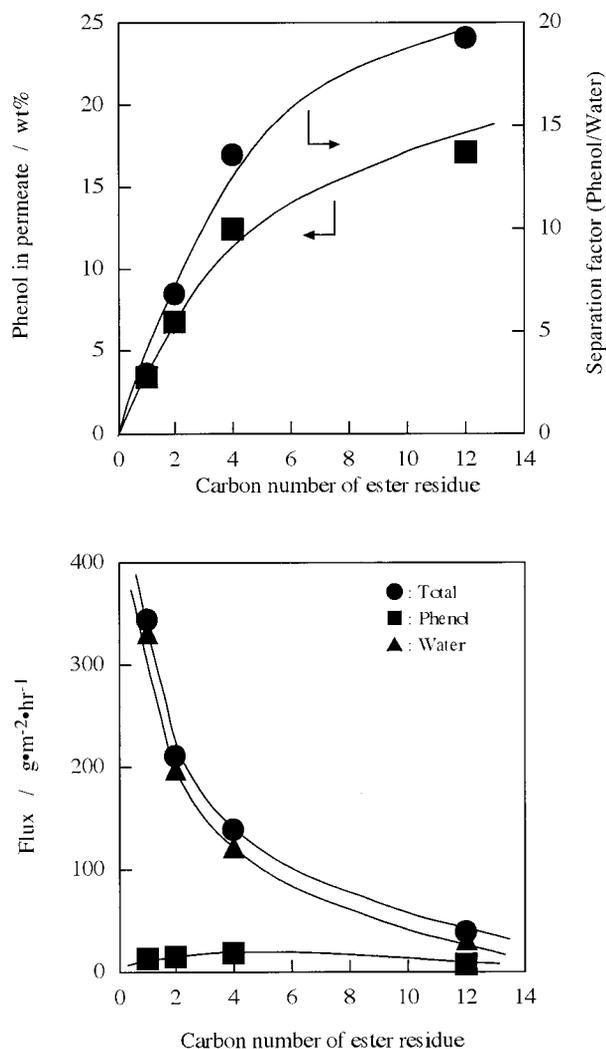


Figure 7 Influence of the acrylate side chain on the pervaporation of phenol–water mixture at 50°C (1 wt % phenol in the feed solution).

in Figure 9. The degree of swelling decreased from 22.1 to 15.0 with increasing hexane concentration in the immersion liquid.

From the swelling measurement, it seems that the affinity of hexane for the poly(BA-co-AA) membrane was smaller than that of heptane. The solubility selectivity was consequently anticipated to be favorable for the heptane, whereas the hexane permselectivity was observed for all compositions of the feed solution. Therefore, the diffusivity selectivity was favorable for the hexane. The difference in diffusivity should be attributed to the difference of molecular size between hexane and heptane.²⁵ It is considered that the diffusivity selectivity of hexane for the poly(BA-co-AA) membrane was larger than the solubility selectivity of

heptane for that membrane, and the poly(BA-co-AA) membrane showed the hexane permselectivity.

The results of pervaporation measurement for the various organic solvent mixtures (hexane–heptane, hexane–ethanol, hexane–methanol, benzene–cyclohexane and benzene–ethanol) through poly(BA-co-AA) membranes are summarized in Table IV.

The poly(BA-co-AA) membrane preferentially permeated hexane from hexane–heptane and hexane–alcohol mixtures, and permeated benzene from benzene–cyclohexane and benzene–ethanol mixtures. Though the poly(BA-co-AA) membrane showed high permselectivity for the separation of organic solvent–water mixtures, the permselectivity of that membrane was low in the case of organic solvent mixtures separation.

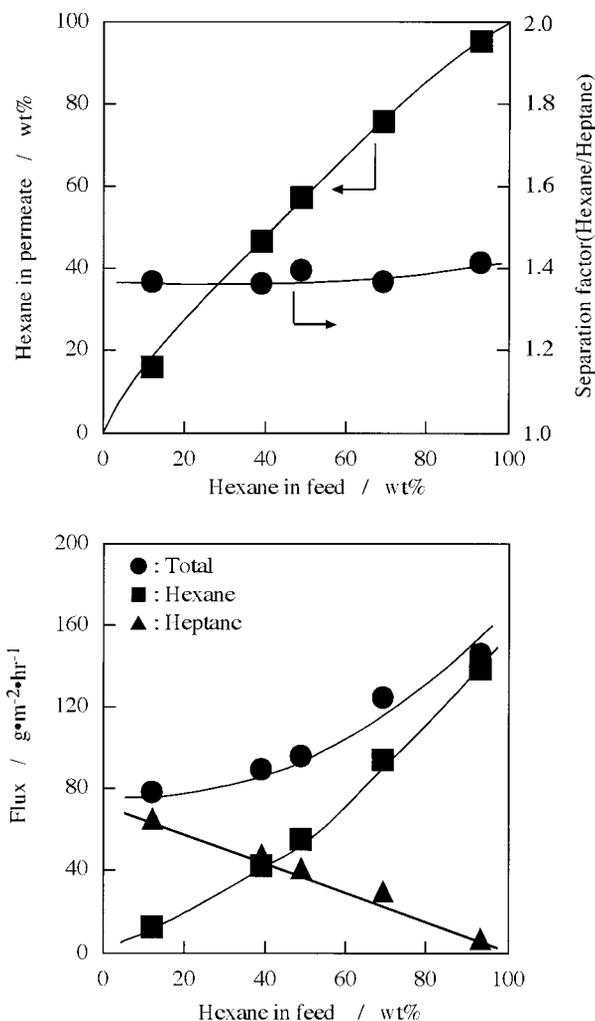


Figure 8 Influence of the hexane concentration in the feed solution on the pervaporation of hexane–heptane mixture for poly(BA-co-AA) (90 : 10, 0.05) membrane at 25°C.

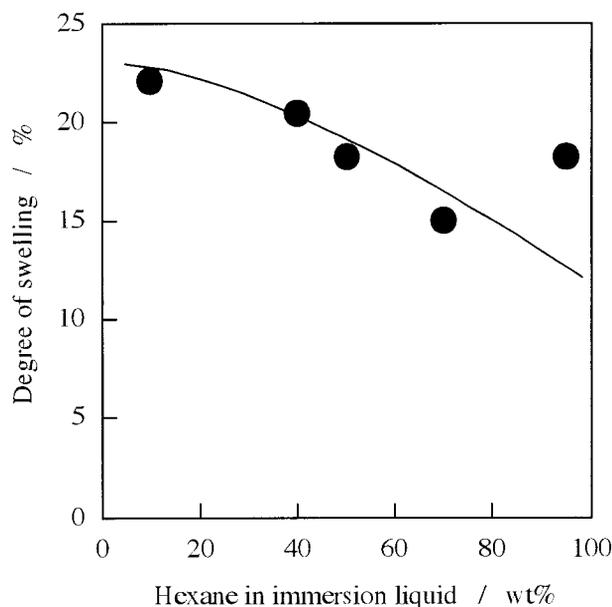


Figure 9 Influence of the hexane concentration in the immersion liquid on the swelling for poly(BA-co-AA) (90 : 10, 0.05) membrane at 25°C.

Influence of Crosslinking Agent Content

Figure 10 shows the influence of the crosslinking agent content on the pervaporation separation.

The flux (total, hexane, and heptane) slightly decreased with increase in the crosslinking agent content. The hexane concentration in the permeate solution and the separation factor also decreased.

The flexibility of the polymer chain was reduced by increasing the crosslinking agent content (increasing the crosslinking density) and diffusion resistance became large. Therefore, it is considered that the flux (total, hexane, and heptane) decreased. Because of the increase in crosslinking density, it seems that the difference

in diffusivity from hexane and heptane became small. The hexane in the permeate solution and the separation factor should consequently decrease.

Influence of Acrylate Side Chain

The acrylate copolymers which have the difference structure of the ester residue were synthesized, and the results of the pervaporation and the swelling measurement are summarized in Table V.

The flux decreased as the acrylate side chain became bulky, whereas the difference of the hexane selectivity was small. We believe that the flux decreased with increase in the diffusion resistance because the hydrocarbon group of the ester residue became bulky.

The molecular size of hexane is smaller than that of heptane, so the diffusion resistance of hexane should also be smaller than that of heptane.²⁵ It is assumed that the diffusion of heptane is more affected by the increase in bulkiness of the ester residue. On the other hand, the influence on the hexane should be small. Therefore, α_P was slightly increased with increasing the bulkiness of ester residue.

For the poly(LaMA-co-AA) membrane, α_P was the same value as other polyacrylate membranes and the flux was maximized. The T_g of the poly(LaMA) is the lowest in the polymethacrylate series.²⁶ The flexibility of the molecular chain contributes to the permeability. It seems that the polymer chain which has a low T_g is more flexible than the polymer having a high T_g at the same temperature. Therefore, the low T_g of poly(LaMA) should contribute to the permeability. The result of swelling measurement for the poly(LaMA-co-AA) membrane was very high. The flexibility of its molecular chain is therefore larger than other

Table IV Pervaporation and Degree of Swelling of Organic Solvent Mixtures for Poly(BA-co-AA) (90 : 10) Membrane at 25°C

Organic Solvent		A in Feed (wt %)	A in Permeate (wt %)	α_P (A/B)	Flux ($g \cdot m^{-2} \cdot h^{-1}$)	Degree of Swelling (%)	TGXDA Content
A	B						
Hexane	Heptane	48.8	57.1	1.39	96.0	18.21	0.05
Hexane	Ethanol	48.4	52.1	1.16	164	788.5	0.05
Hexane	Methanol	36.1	36.8	1.04	319	419.6	0.05
Hexane	Heptane	46.7	52.7	1.27	86.1	—	1.0
Benzene	Cyclohexane	44.0	51.4	1.34	638	—	1.0
Benzene	Ethanol	48.6	52.6	1.17	389	—	1.0

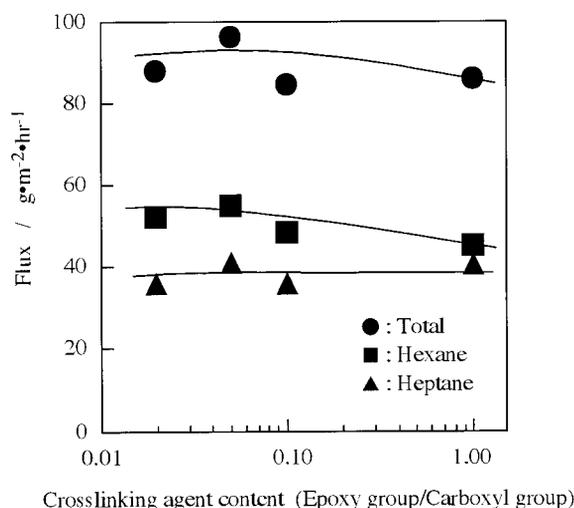
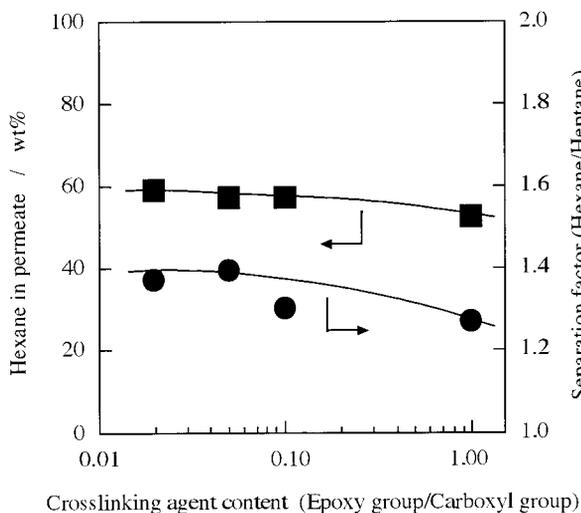


Figure 10 Influence of the crosslinking agent content on the pervaporation of the hexane–heptane mixture for poly(BA-co-AA) (90 : 10) membranes at 25°C.

membranes. Consequently, we believe that the poly(LaMA-co-AA) membrane shows the high flux.

CONCLUSIONS

Organic Solvent–Water Mixtures Separation

- The polyacrylate membrane showed organic solvent permselectivity, and the chlorinated hydrocarbon permselectivity was especially high. We propose that the organic solvent permselectivity was governed by the solubility selectivity.

- The diffusivity selectivity for TCE was slightly increased by the introduction of macromonomer (MM1: polystyrene type; MM2: poly(methyl methacrylate) type; and MM3: polydimethylsiloxane type), and the solubility selectivity was decreased. Therefore, the permselectivities of these membranes were nearly equal to that of the poly(BA-co-AA) membrane, and the introduction of macromonomer into the poly(BA-co-AA) for the separation had little effect.
- As the side chain of acrylate was lengthened, the selectivity increased and the flux decreased. It seems that the hydrophobicity and the diffusion resistance increased with increase in the hydrocarbon side chain length.

Organic Solvent Mixtures Separation

- Compared with the separation of organic solvent–water mixtures, the permselectivity of the polyacrylate and polymethacrylate copolymer membranes for the organic solvent mixture separation was low.
- The flux and separation factor decreased slightly with increased crosslinking agent content in the poly(BA-co-AA) membrane. We propose that the diffusion resistance increased with increasing crosslinking density.
- The separation factor increased slightly and the flux decreased with increase in the bulkiness of the acrylate side chain.

NOMENCLATURE

A	effective membrane area
C	concentration
K	partition coefficient
D	diffusion coefficient
D_0	diffusion coefficient at zero concentration
J	flux
l	membrane thickness
Q	weight of permeate liquid
t	measurement time
W_D	dried membrane weight
W_W	swollen membrane weight
x	distance along the direction of permeation
α_P	separation factor of permeation
α_D	separation factor of diffusion
α_K	separation factor of partition
γ	volume of polymer which sorbed a unit amount of solvent (plasticization parameter)

Table V Pervaporation of Hexane–Heptane Mixture Through Poly(acrylate-co-AA) (90 : 10, 0.05) and Poly(methacrylate-co-AA) (90 : 10, 0.05) Membranes at 25°C

Membrane	Hexane in Feed (wt %)	Hexane in Permeate (wt %)	α_P^a	Flux ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Degree of Swelling (%)	Thickness (μm)
Poly(BA-co-AA)	48.8	57.1	1.39	96.0	18.2	97.6
Poly(<i>tert</i> -BA-co-AA)	50.8	59.9	1.45	27.2	15.7	147
Poly(CHA-co-AA)	49.0	59.8	1.55	6.55	2.08	63.0
Poly(LaMA-co-AA)	48.9	56.0	1.33	316	296	512

CHA, cyclohexyl acrylate; LaMA, lauryl methacrylate.
^a (Hexane/heptane).

Subscripts

- i* component *i*
- j* component *j*
- 1 quantities concerning the bulk feed solution
- 2 quantities concerning the downstream side of the membrane
- 3 quantities concerning the membrane interior

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