Pervaporation Separation of 1,1,2-Trichloroethane–Water Mixture Through Crosslinked Acrylate Copolymer Composite Membranes

MASARU HOSHI,¹ TAKANORI SAITOH,² CHIKAKO YOSHIOKA,³ AKON HIGUCHI,^{3,*} TSUTOMU NAKAGAWA³

¹ Laboratory of Healthcare Products, LINTEC Corporation, Nishikicho, Warabi, Saitama 335-0005, Japan

² Research & Development Division, LINTEC Corporation, Nishikicho, Warabi, Saitama 335-0005, Japan

³ Department of Industrial Chemistry, Meiji University, Higashimita, Tama-ku, Kawasaki, Kanagawa 214-0033, Japan

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ABSTRACT: The separation of a chlorinated hydrocarbon from a dilute aqueous solution through a crosslinked acrylate copolymer-porous substrate composite membrane by pervaporation was investigated. Poly(*n*-butyl acrylate-*co*-acrylic acid) and poly(*n*-butyl acrylate-*co*-2-hydroxyethyl acrylate) were synthesized and composite membranes were prepared, which were made from the crosslinked polymer and a porous substrate. Pervaporation measurement was carried out for a dilute aqueous solution of 1,1,2trichloroethane at 25°C and under a vacuum on the permeate side (below 10 mmHg). The separation factor, overall flux, 1,1,2-trichloroethane concentration in the membrane, and the degree of swelling decreased with increase in the acrylic acid or 2-hydroxyethyl acrylate content of the acrylate copolymer. The influence of the crosslinking agent content on the pervaporation performance was small, and the separation factor and the overall flux showed a convex curve. The structure of the crosslinking agent had no effect on the separation. The influence of the pore size of the substrate and the thickness of the polymer layer on the separation of 1,1,2-trichloroethane was observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 983–994, 1999

Key words: pervaporation; polyacrylate; 1,1,2-trichloroethane; permselective membrane; porous substrate; crosslinking agent

INTRODUCTION

The separation of a liquid mixture by pervaporation has been investigated as a useful method. Thus far, water permselective membranes for water–organic solvent mixtures have been developed and have been submitted to practical use.^{1–3} In recent years, organic solvent permselective membranes have been studied as the next step. These are membranes which separate an organic solvent from a dilute aqueous solution. Membranes which have high permselectivity for specific organics have been obtained.³⁻¹² These membranes consist of hydrophobic polymers and have a high affinity for specific organic solvents which are separated from the aqueous solution. In general, the molecular size of the organic solvent is bigger than that of water. The membrane materials are therefore rubbery polymers at the operating temperature to decrease the diffusion resistance of the organic solvent.

We have reported that crosslinked polyacrylate and polymethacrylate membranes have high

Correspondence to: T. Nakagawa.

^{*} Present address: Department of Industrial Chemistry, Seikei University, Kichijojikitamachi, Musashino, Tokyo 180-0001, Japan.

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permselectivity for chlorinated hydrocarbons and esters for the separation of these organic solvents from dilute aqueous solutions.^{13–15} In the previous work using polyacrylate or polymethacrylate, copolymer membranes of acrylic acid (AA), methacrylic acid (MA), and methyl methacrylate (MMA) were employed for water-permselective membranes.^{16–20} The polyacrylate and the polymethacrylate polymers, which contain a short hydrocarbon chain of an ester residue or a hydrophilic functional group, show water permselectivity and have a high glass transition temperature (T_g) . When the hydrocarbon chain of the ester residue becomes long, the T_g of polyacrylate and polymethacrylate is below the ordinary temperature.²¹ The polyacrylate and the polymethacrylate in a rubbery state show adhesiveness and their mechanical strength is low. Therefore, these polymers have scarcely been studied as materials for separation membranes. However, these polymers have high affinity for specific organic solvents. In the case of the separation of an organic solvent from a dilute aqueous solution, the rubbery polymer is favorable for the organic solvent in terms of the diffusivity. It is considered that these polymers are excellent as materials for organic solvent permselective membranes. To utilize these polymers for an organic solvent permselective membrane, we reduced the above disadvantages by crosslinking of these polymers and making a composite membrane with a porous substrate. The crosslinking of the polymer was carried out by the reaction of a multifunctional compound with the polymer which copolymerizes with a monomer containing a functional group, for example, AA or 2-hydroxyethyl acrylate (HEA). The AA and the HEA have hydrophilic functional groups, a carboxyl group and a hydroxyl group. These functional groups were consumed by reacting with the crosslinking agent. Because not all the functional groups were consumed, their influence on the organic solvent permselectivity was presumed. It was anticipated that the difference in the crosslinking density, the number of functional groups, and the structure of the crosslinking agent would affect the permselectivity.

In previous work, it was confirmed that the hydrophobicity of the porous substrate influenced the permselectivity.^{13,14} Consequently, it was expected that there would be an influence of the porous substrate on the permselectivity. For the separation of phenol in a polyurethane membrane, the dependence of the polyurethane layer

thickness on the permselectivity was observed.²² In this study, the effects of the AA or the HEA content of the *n*-butyl acrylate (BA) copolymer, the thickness of the acrylate layer, the crosslinking agent, and the porous substrate were investigated to show the influence of these factors on the separation of an 1,1,2-trichloroethane (TCE)–water mixture.

EXPERIMENTAL

Synthesis of Poly(BA-co-AA) and Poly(BA-co-HEA)

Poly(BA-co-AA) and poly(BA-co-HEA) were prepared by solution polymerization. Acrylate monomers (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), azobisisobutyronitrile (AIBN, Wako Pure Chemical Industry, Ltd., Osaka, Japan) as the initiator, and a mixture of toluene and ethyl acetate as the solvent were stirred in a 500-cm³ flask equipped with a condenser and a calcium dichloride drying tube. The reactor was purged with dried nitrogen. After stirring for 30 min, the mixture was heated at 70°C using a temperaturecontrolled water bath. The polymerization reaction was then carried out at the same temperature for 8 h. The AIBN concentration was 0.05 mol % of the acrylate monomers, and the solvent mixture ratio was 9:1 (ethyl acetate : toluene). The AA content of poly(BA-co-AA) was 0, 3, 5, 10, and 15 wt % and the HEA content of poly(BA-co-HEA) was 2, 5, 8, and 10 wt %. The BA, AA, and HEA were purified by vacuum-distillation, while the other reagents were used without further purification.

The molecular weight of the acrylate copolymer was measured by size-exclusion chromatography (SEC standard, polystyrene). The glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC sample weight, 5–8 mg; rate, 10°C/min).

Membrane Preparation

A crosslinking agent (TGXDA, TMPTDI, or Al $(acac)_3$; structures are shown in Fig. 1) was added to a toluene solution containing 25 wt % of the acrylate copolymer. The solution was cast onto an exfoliation-treated poly(ethylene terephthalate) (PET) film and then dried at 80°C for 5 min. A porous substrate was placed on the acrylate copolymer membrane and the PET film was displaced by the porous substrate. Thus, a sandwich-



Figure 1 Structure of crosslinking agent.

type composite membrane was prepared. The membrane preparation is shown in Figure 2. The cross section of the composite membrane was observed with a scanning electron microscope (SEM).

The membrane of which the AA content was 10% and the crosslinking agent (e.g., TGXDA)

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

Pervaporation Measurement

A schematic diagram of the pervaporation measurement apparatus is shown in Figure 3. A permeation cell was assembled from two half-cells of stainless steel and fastened together by bolted clamps. An O-ring was used between the pervaporation cell's upper compartment and the membrane. The membrane was supported on a sintered stainless-steel plate with holes, and the effective membrane area was 10.21 cm^2 . The feed liquid was circulated using a microtube pump through a stainless tube in the constant temperature water bath at 25°C, and the amount of the feed liquid was 1000 cm³. The downstream pressure was kept below 10 mmHg, and the upstream pressure was maintained at atmospheric pressure. The permeate vapor was collected in a cold trap surrounded by liquid nitrogen.

The experimental procedure was as follows: The pervaporation cell, after inserting the membrane, was placed in a constant temperature water bath maintained at 25°C. The downstream side of the membrane was under a vacuum, and the feed liquid was circulated. After reaching a steady-state condition (more than 12 h later), the permeate vapor was collected for 3 h. The TCE concentration in the feed liquid was measured by gas chromatographic analysis at the start and at the end of the pervaporation measurement. The concentration of TCE and water in the permeate liquid and the flux were determined by gas chro-



Figure 2 Preparation of the composite membrane.



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) microtube pump; (11) feed solution.

matographic analysis and by measuring the weight of the collected sample, respectively. The concentration of TCE in the permeate liquid was high, so that the permeant separated into two phases. The gas chromatographic analysis was then carried out by adding 2-propanol to make a uniform solution.

For each condition, the above pervaporation measurement was conducted three times, and the flux and the concentration of TCE and water in the permeate liquid were confirmed to be constant. The flux was calculated using the following equation:

Flux (g m⁻² h⁻¹) =
$$\frac{Q}{A t}$$
 (1)

The separation factor of pervaporation, α_P , is expressed as follows.

$$\alpha_{P(i|j)} = \frac{C_{i2}/C_{j2}}{C_{i1}/C_{j1}}$$
(2)

Degree of Swelling and Sorption Measurement

The acrylate copolymer membrane piece, the weight of which was previously measured, was immersed in the aqueous TCE solution (50 cm^3) for 48 h at 25°C. The solution on the membrane surface was wiped off, and the weight of the membrane was measured. The degree of swelling was calculated as follows:

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

The concentration of the absorbate was measured with the apparatus shown in Figure 4.



Figure 4 Desorption apparatus: (1) glass vessel; (2) cold trap for collecting sample; (3) ball joint; (4) greaseless cock; (5) glass cock; (6) drying tube with CaCl₂; (7) to vacuum line.



Figure 5 Cross-sectional view of poly(BA-*co*-AA) (90 : 10, TGXDA 0.05)–porous polypropylene (PP) substrate composite membrane by SEM.

After weighing the swollen membrane for the degree of swelling measurement, the membrane piece was frozen in a glass vessel with liquid nitrogen. The glass vessel and a cold trap were under a vacuum, and then the glass vessel was heated (at 70–80°C) after removing the liquid nitrogen. The absorbate was vaporized and collected in the cold trap with liquid nitrogen. After 30 min, the pressure of the glass apparatus was made atmospheric by opening a leak cock attached to a calcium dichloride drying tube. The concentration of TCE and water were determined by measuring the collected liquid in the same way as the pervaporation. The separation factor of partition, $\alpha_{K(i/i)}$, can be written as

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

RESULTS AND DISCUSSION

Membrane Preparation

The weight-average molecular weight of the acrylate copolymer was from 3.12×10^5 to 4.87×10^5 . The T_g of poly(BA-co-AA) (90 : 10) and poly(BA-co-HEA) (90 : 10) was -34.0 and -44.7° C, respectively.

A BA homopolymer membrane which had sufficient strength to be used for the separation was not obtained. On the other hand, the crosslinked copolymer membranes had adequate strength, so that the composite membranes were prepared.

A cross-sectional view of the poly(BA-co-AA) (90:10, TGXDA 0.05)-polypropylene porous substrate (Celgard[®] 2500) composite membrane by SEM is shown in Figure 5. The acrylate copolymer did not intrude into the pores.

Influence of AA or HEA Content in Copolymers

The influence of the AA content in the poly(BAco-AA) on the separation of a TCE–water mixture is shown in Figure 6. The TGXDA content of the poly(BA-co-AA) membranes was the same as the poly(BA-co-AA) (90 : 10). The TCE concentration in the permeate solution decreased from 60.4 to 53.5 wt %, and the overall flux decreased from 45.9 to 37.0 g m⁻² h⁻¹ with increasing the AA content in the acrylate copolymer. To decrease the TCE concentration in the permeate solution, the separation factor was decreased from 776 to 592.

Figure 7 shows the influence of the AA content in the acrylate copolymer on the sorption and the degree of swelling. The TCE concentration in the membrane and the degree of swelling decreased from 91.1 to 61.0 wt % and from 19.4 to 13.2% with increasing AA content in the copolymer. The AA has a hydrophilic carboxyl group. When the AA in the poly(BA-co-AA) increased, the water affinity of the membrane became higher. Therefore, the TCE affinity of the membrane was reduced, and it is considered that the TCE concentration in the membrane decreased. The separation of TCE through the polyacrylate membrane is governed by the solubility selectivity.^{13–15} Because the TCE affinity of the membrane became lower, namely, the TCE solubility in the membrane decreased, the TCE concentration in the permeate solution decreased. The degree of swelling also decreased due to the decrease in the amount of TCE in the membrane.

The influence of the HEA content in the poly (BA-co-HEA) is shown in Figure 8. The TGXDA



Figure 6 Influence of AA content on the TCE–water mixture separation through poly(BA-*co*-AA) membrane. Each point represents the mean of three determinations. Pervaporation conditions: feed solution, 0.2 wt % TCE aq.; temperature, 25°C; downstream pressure, under 10 mmHg.

content of the poly(BA-co-HEA) membranes was the same as that of the poly(BA-co-HEA) (90:10). The permeated TCE decreased from 58.4 to 53.0 wt % with increasing HEA content in the copolymer, and the overall flux slightly decreased from 53.4 to $51.1~{\rm g}~{\rm m}^{-2}~{\rm h}^{-1}.$ The result of the sorption and the degree of swelling are shown in Figure 9. The concentration of TCE in the membrane decreased from 77.4 to 65.0 wt %, and the degree of swelling also decreased from 29.4 to 21.8% with increasing HEA content in the membrane. It is considered that the decrease in these values with increasing HEA in the acrylate copolymer is explained by the increase in hydrophilicity in the same manner as that of the poly(BA-co-AA) membrane.

The apparent mean diffusion coefficient of the TCE and the water (D_{TCE} and D_{water}) can be calculated using eqs. (5), (6) and (7)²²:

$$P_i = D_i K_i \tag{5}$$

$$J_i = \frac{P_i}{l} C_{i1} \tag{6}$$

$$K_j = \frac{C_{i3}}{C_{i1}}$$
 (7)

Figures 10 and 11 show the relationship between the AA or the HEA content in the acrylate copolymer and the $D_{\rm TCE}$ and the $D_{\rm water}$. Each value decreased with increase in the functional monomer content. The increase in carboxyl groups of the copolymer can contribute to an increase in hydrogen bonding. The mobility of the polymer chains was reduced in order to increase the hydrogen bonds and to decrease the degree of swelling.^{1,23} Therefore, it seems that the diffusion resistance increased and a decrease in the flux resulted.

Even though the D_{water} was greater than the D_{TCE} , the partial flux of TCE was greater than that of water. In general, the permeability is represented by the products of the diffusivity and the solubility.^{24,25} As a result of the sorption measurement, the affinity of TCE for the acrylate



Figure 7 Influence of AA content on the sorption and the degree of swelling for poly(BA-*co*-AA) membrane in 0.2 wt % TCE aqueous solution at 25°C. Each point represents the mean of three determinations.



Figure 8 Influence of HEA content on the TCE–water mixture separation through poly(BA-co-HEA) membrane. Each point represents the mean of three determinations. Pervaporation conditions: feed solution, 0.2 wt % TCE aq.; temperature, 25°C; downstream pressure, under 10 mmHg.

copolymer was very high. Although the diffusivity was favorable for water, the permeability of TCE was greater than that of water due to the contribution of high TCE solubility.

Comparison of the results of the pervaporation and the sorption for the acrylate copolymer containing AA with that containing HEA shows that the former had a larger TCE concentration in the permeate solution than had the latter. The latter was larger than the former in the flux (total and partial flux) and the degree of swelling. On the other hand, the TCE concentration in both membranes was nearly equal.

It seems that the influence of the hydrophilic functional monomer on the TCE solubility for the



Figure 9 Influence of HEA content on the sorption and the degree of swelling for poly(BA-*co*-HEA) membrane in 0.2 wt % TCE aqueous solution at 25°C. Each point represents the mean of three determinations.

polyacrylate membrane was very small as a result of the sorption measurement. Therefore, a difference in the diffusivity between the poly(BA-co-AA) and poly(BA-co-HEA) was suggested. This should be supported by Figures 10 and 11.

The D_{TCE} of poly(BA-co-AA) and poly(BA-co-HEA) was nearly equal, and the D_{water} of poly (BA-co-HEA) was greater than that of poly(BA-co-



Figure 10 Influence of AA content on the apparent mean diffusion coefficient for poly(BA-*co*-AA) membrane at 25°C. Each point is calculated by the mean of three determinations.



Figure 11 Influence of HEA content on the apparent mean diffusion coefficient for poly(BA-co-HEA) membrane at 25°C. Each point is calculated by the mean of three determinations.

AA) without the copolymer containing 3% AA. Because the acidity of the carboxyl group is higher than that of the hydroxyl group, the hydrogen-bond intensity of the carboxyl group is larger than that of the hydroxyl group.

The degree of swelling of poly(BA-co-HEA) should become greater than that of poly(BA-co-AA) due to the decrease in the interaction between polymer chains. Consequently, it is considered that the polymer chains of poly(BA-co-HEA) become more flexible than those of poly(BA-co-AA). With increasing flexibility, the diffusion resistance of the membrane becomes small.^{1,23} It seems that the flux of the poly(BA-co-HEA) was greater than that of the poly(BA-co-AA).

The change in intermolecular space with the molecular chain flexibility should influence the diffusivity of water (molecular size is small) and should have little influence on that of TCE (molecular size is large). Therefore, it is considered that the difference in the $D_{\rm water}$ and that of TCE was small.

Membrane Thickness

The influence of the membrane thickness on the separation of the TCE–water mixture through the poly(BA-co-AA) (90 : 10, TGXDA 0.05) membrane is shown in Figure 12. The overall and partial fluxes were plotted as a function of the reciprocal of the thickness. The membrane thickness was measured before the pervaporation measurement.

The flux decreased from 46.2 to 27.3 g m⁻² h⁻¹ with increasing membrane thickness. The TCE concentration in the permeate solution increased from 54.6 to 62.7 wt %, and the separation factor also increased from 613 to 833. A linear relationship existed between the flux and the reciprocal membrane thickness. It is considered that the flux obeyed Fick's law. The flux (overall and partial) did not become zero when the membrane thickness was extrapolated to infinity. The membrane swelled gradationally, and the membrane



Figure 12 Effect of membrane thickness on the separation of TCE through poly(BAco-AA) membrane. Each point represents the mean of three determinations. Pervaporation conditions: feed solution, 0.2 wt % TCE aq.; temperature, 25° C; downstream pressure, under 10 mmHg.

thickness was greater than that of the dried membrane under pervaporation conditions. It is anticipated that the swollen membrane thickness was not increased proportionally to the increase in the dried membrane thickness. The measurement of the membrane thickness under pervaporation conditions was very difficult, and the fluxes were plotted using the dried membrane thickness for the sake of convenience. Therefore, it is considered that the plots of fluxes did not pass through the origin of the coordinates due to the difference between the dried membrane thickness and that of the swollen membrane under pervaporation conditions.

Under the steady-state condition of pervaporation with moderate swelling taking place in the membrane, the concentration of the penetrants is high on the upstream side of the membrane and gradually decreased toward the downstream side of the membrane. There is, then, a remarkable decrease on the downstream side of the membrane.^{24,26,27} The degree of swelling should be considered in the same manner as in the concentration of the penetrants.

The solubility of TCE in the membrane was very high as a result of the sorption measurement, so that the concentration gradient of phenol in the highly swollen region was very small. There should be a concentration gradient of water in the entire membrane, and that was greater than the TCE because the solubility of water was low.

It is presumed that the difference in the concentration of TCE around the downstream side between the thin membrane and the thick membrane was relatively small, and the concentration of water around the downstream side in the thin membrane was greater than that of the thick membrane because of the concentration profile of TCE and water in the membrane. Consequently, it seems that the decrease in the TCE partial flux with increasing membrane thickness was smaller than that of water. The TCE selectivity should be increased due to the behavior of the TCE and water partial flux.

Porous Substrate

The dependence of the pore size of the porous PTFE substrate on the separation of the TCE– water mixture through the poly(BA-co-AA) (90 : 10, TGXDA 0.05) membrane is shown in Figure 13. The TCE concentration in the permeate solution decreased from 60.3 to 42.3 wt %, and the



Figure 13 Pore size of porous PTFE substrate dependence on the separation of TCE–water mixture through poly(BA-co-AA) membrane. Each point represents the mean of three determinations. Pervaporation conditions: feed solution, 0.2 wt % TCE aq.; temperature, 25°C; downstream pressure, under 10 mmHg.

permeation rate increased from 0.883×10^{-3} to 1.70×10^{-3} g m m⁻² h⁻¹ with increasing pore size of the porous substrate. The permeation rate of TCE increased slightly, whereas that of water changed remarkably. The resistance of vapor permeation in the permeate side decreased with enlargement of the pore size. The influence of the hydrophobicity of the porous substrate on the water should be decreased with increasing pore size. Consequently, it is considered that the permeation rate, especially that of water, increased, and the TCE selectivity was decreased. The increase in the porosity of the porous PTFE substrate with increasing pore size should also contribute to the increase in the permeation rate.

	Specifica	tion of Porous	s Substrate		Per	vaporation Data	
Substrate	Pore Size (μm)	Porosity (%)	Thickness of Substrate (µm)	TCE in Feed (wt %)	$\alpha_P~({\rm TCE/Water})$	Permeation Rate $(\times 10^{-3} \text{ g m} \text{m}^{-2} \text{ h}^{-1})$	Thickness of BA–AA Layer (μm)
Porous PP	0.075 imes 0.25	45	25	0.195	708	2.23	61.4
Porous PE-1	1.0 (max)	28	50	0.199	552	1.27	46.0
Porous PE-2	0.7 (max)	30	35	0.197	648	1.45	73.0
Porous PE-3	0.8 (max)	30	50	0.206	642	2.12	69.0
Porous PTFE-1	0.45	60 - 70	80	0.202	776	0.883	32.0
Porous PTFE-2	1.0	70–80	80	0.195	465	1.26	32.1
Porous PTFE-3	2.0	70–80	80	0.195	375	1.70	67.0
Cellulose acetate	0.2	66	125	0.195	122	2.65	70.0
Nonsubstrate	I		I	0.201	646	2.26	52.4

The separation of the TCE–water mixture with the poly(BA-co-AA) (90 : 10, TGXDA 0.05) and the various porous substrate composite membranes is summarized in Table I. The specifications of the porous substrate are also summarized. The obvious relationship between the permeation rate and the specifications of the porous substrate was not observed without the porous PTFE substrate.

The selectivity for TCE of the membranes using hydrophobic PP, PE, and PTFE substrates and of the nonsubstrate membrane was higher than that of the membrane using hydrophilic cellulose acetate. It seems that concentration polarization occurred on the surface of the feed side of the membrane. For the hydrophobic substrate, the TCE concentration on the surface of the feed side should become higher than the TCE concentration of the feed solution due to concentration polarization.^{13,14} The concentration polarization in the hydrophilic substrate should be lower than that of the hydrophobic substrate. Therefore, it is considered that the membrane selectivity for TCE using the hydrophobic substrate was higher than that of the membrane using the hydrophilic substrate. For the nonsubstrate membrane, the concentration polarization is favorable for TCE because of the high affinity of the poly(BA-co-AA) for TCE. The TCE selectivity of the nonsubstrate membrane was therefore similar to that of the membrane using the hydrophobic substrate membranes.

Crosslinking Agent

The influence of the amount of the crosslinking agent in the poly(BA-co-AA) on the separation of the TCE-water mixture is shown in Figure 14. The TCE concentration in the permeate solution and the water partial flux were nearly constant. The overall and TCE partial flux slightly changed and showed a convex curve. In the case of a low proportion of the crosslinking agent, the flexibility of the polymer chains was reduced by the hydrogen bonding of the carboxyl group which did not react with the crosslinking agent. With a high proportion of the crosslinking agent, the flexibility was also reduced by the crosslinked structure.^{1,23} The diffusion resistance became large in the presence of low and high proportions of the crosslinking agent. Therefore, it is considered that the flux showed a convex curve. The molecular size of water is smaller than that of TCE, and the diffusion resistance of the water is also smaller than that of TCE. Consequently, the TCE



Crosslinker content (Epoxy group/Carboxyl group)

Figure 14 Influence of amount of crosslinking agent on the separation of TCE-water mixture through poly (BA-co-AA) membrane. Each point represents the mean of three determinations. Pervaporation conditions: feed solution, 0.2 wt % TCE aq.; temperature, 25°C; downstream pressure, under 10 mmHg. partial flux became slightly decreased at the low and high crosslinking agent concentrations, and the water partial flux was relatively constant. The TCE in the permeate solution showed a slight convex curve due to the behavior of the TCE and the water partial flux.

The influence of the various crosslinking agents on the separation and the sorption is summarized in Table II. As a result of the pervaporation and the sorption, a significant difference between each crosslinking agent was not observed. It is considered that the influence of the crosslinking agent on the diffusivity and the solubility was very small. Therefore, little effect on the membrane structure was observed when using each of the crosslinking agents.

CONCLUSIONS

- The TCE permselectivity, the flux (total and partial), the TCE concentration in the membrane, and the degree of swelling decreased with increasing AA or HEA content in the copolymers.
- The TCE permselectivity increased, and the flux decreased with increasing membrane thickness.
- The water partial flux increased with the magnification of the pore size of the substrate, whereas the increase in the TCE partial flux was smaller than that of the water. Consequently, the TCE permselectivity decreased and the total flux increased.
- A difference in the TCE permselectivity between the hydrophobic porous substrate and the hydrophilic porous substrate was ob-

Table II Effect of the Various Crosslinking Agents on the Separation of TCE–Water Mixture Through Poly(BA-co-AA) Membranes at 25°C

	Pervaporation				Sorption		
Crosslinking Agent	TCE in Feed Solution (wt %)	$(\overset{\alpha_P}{\text{(TCE/Water)}})$	$Flux \\ (g \ m^{-2} \ h^{-1})$	Thickness (µm)	TCE in Immersed Solution (wt %)	TCE in Membrane (wt %)	α_K (TCE/Water)
TGXDA TMPTDI Al(acac) ₃	$0.202 \\ 0.207 \\ 0.201$	708 692 682	$36.3 \\ 42.0 \\ 40.2$	$61.4 \\ 49.4 \\ 55.4$	0.200 0.202 0.203	68.8 73.9 72.7	1100 1399 1309

Each value represents the mean for three determinations.

served. On the other hand, the difference for the hydrophobic substrate was small.

- The TCE permselectivity, the total flux, and the TCE partial flux showed a slight convex curve with increasing crosslinking agent content.
- No influence of the structure of the crosslinking agent on the permselectivity was observed.

NOMENCLATURE

A	effective membrane area				
C	concentration				
D	diffusion coefficient				
J	flux per unit time and per unit area				
Κ	partition coefficient				
l	membrane thickness				
Ρ	permeability coefficient				
Q	weight of permeate liquid				
t	measurement time				
W_D	dried membrane weight				
W_W^-	swollen membrane weight				
α_P	separation factor				
α_K	separation factor of partition				
subscript <i>i</i>	component <i>i</i>				
subscript j	component j				
subscript 1	quantities concerning the bulk feed solution				
subscript 2	quantities concerning the down- stream side of the membrane				
subscript 3	quantities concerning the mem- brane interior				

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