

# Charged Polyacrylonitrile Membranes Having Amphiphilic Quaternized Ammonium Groups for Ultrafiltration

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**ABSTRACT:** Four types of positively charged polyacrylonitriles having quaternized *N,N*-dimethylaminoethyl methacrylate (DAMA) were synthesized and were used to prepare ultrafiltration membranes by a phase-inversion method. The effect of aliphatic ethyl, octyl, and stearyl groups and the benzyl group, which covalently bind to the quaternary ammonium group, on filtration properties was studied by ultrafiltration under an applied pressure of 760 mmH<sub>2</sub>O. Water permeability through the resultant membranes increased as the aliphatic chain length on the quaternary ammonium group increased. For a copolymer membrane having a benzyl group on the quaternary ammonium group, water permeability was lower than that for the ethyl type of copolymer membrane. The membrane permeability and pore size for the molecular size-exclusion effect were studied at various NaCl concentrations in the 0–0.15 *M* region. The membranes having octyl and stearyl groups showed stable filtration behavior by increase of the NaCl concentration, while the membranes having an ethyl group and a benzyl group on the quaternary ammonium group showed a change of the water permeability due to a pore-size increase for the membrane by NaCl addition. Measurements of membrane potential indicated the shielding of positively charged sites of the membranes by salt addition. Further, the copolymer membranes showed a separation ability for water/2-butanol of low water content. The separation ability was attributed to the chemical structure of the membranes having different interaction characteristics with the mixture components.  
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**Key words:** charged membrane; amphiphilic polyacrylonitrile; ultrafiltration; quaternized ammonium salt

## INTRODUCTION

A charged ultrafiltration (UF) membrane has unique filtration behavior in the separation of a protein mixture<sup>1,2</sup> and a charged macromolecule with a noncharged macromolecule of similar molecular weight<sup>3</sup> and in a concentration of salt<sup>4–6</sup> and electrocoating paint rinsing water.<sup>7</sup> We reported previously that the UF behavior of charged

membranes is influenced by the salt concentration of the feed solution.<sup>8</sup> This is due to the electrostatic effect of salt on fixed charges in the membrane.<sup>8,9</sup> In our studies on a series of charged UF membranes having amphiphilic counterions,<sup>10</sup> the separation of dextran and a dextran sulfate mixture was performed with a high permeate rate and a high separation efficiency. It was found that the amphiphilic nature of the counterions in the membrane strongly contributes to the efficient separation. Then, positively charged polyacrylonitrile (PAN) membranes with amphiphilic quaternized ammonium groups were developed and used to investigate the effect of the hydrophobic alkyl group on the UF properties.<sup>11</sup> In the present study

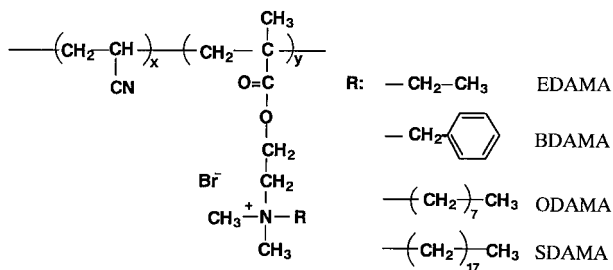
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Scheme 1

on a series of amphiphilic-charged membranes, novel PAN copolymers having quaternized DAMA (Scheme 1) groups were synthesized and used to prepare UF membranes. The filtration properties of UF membranes having different aliphatic and benzyl groups on the quaternized ammonium group were examined at various salt concentrations. Further, the role of the amphiphilic nature of these PAN membranes is discussed in the separation processes of water/alcohol mixtures.

## EXPERIMENTAL

### Reagents

*N,N*-Dimethylaminoethyl methacrylate (DAMA) (Kasei, Tokyo) was used for the synthesis of each quaternized ammonium salt monomer by the reaction with alkyl halide such as ethyl bromide, octyl bromide, stearyl bromide, and benzyl chloride. Acrylonitrile (AN) and dimethyl sulfoxide (DMSO) were distilled under reduced pressure before use in the presence of hydroquinone (HQ). Dextrans having a molecular weight (MW) of  $1 \times 10^4$ ,  $4 \times 10^4$ ,  $7 \times 10^4$ ,  $5 \times 10^5$ , and  $2 \times 10^6$  were products of Pharmacia (Uppsala, Sweden) and used without further purification. All other reagents were of reagent grade.

### Synthesis of Quaternized DAMA Monomers

Four types of quaternized DAMA monomers were prepared in the presence of HQ by the reaction of DAMA with each kind of alkyl halide, according to the method reported previously.<sup>11</sup> As an example, the reaction of DAMA with ethyl bromide was carried out as follows: DAMA (15 g, 95.5 mmol), ethyl bromide (11 g, 101 mmol), HQ (0.1 g), and acetone (200 mL) were mixed in a 500-mL flask for 24 h at room temperature. The white solid of the quaternized DAMA derivative precipitated in the flask was filtered. The resultant monomer,

quaternized *N,N*-dimethylethyl ammonium bromide (EDAMA), was recrystallized with ethyl acetate. A white monomer was obtained in 85.2% yield. The preparation of the DAMA derivative quaternized by benzyl chloride (BDAMA) was carried out similarly to the above procedure. An acetone solution (200 mL) of DAMA (15 g, 95.5 mmol), benzyl chloride (13 g, 103 mmol), and HQ (0.1 g) was used for the quaternization reaction. For quaternized DAMA derivatives having octyl (ODAMA) and stearyl (SDAMA) groups, the preparation followed was the Nagai method.<sup>12</sup> Each kind of monomer obtained was kept in a refrigerator until copolymerization with AN.

### Copolymerization of AN and Quaternized DAMA

Copolymerizations of AN with quaternized DAMA derivatives were carried out in a DMSO (318 g) solution by radical polymerization in a nitrogen atmosphere at 60°C for 5 h. The initiator used, AIBN, was of 0.5 mol % concentration in the total monomer. Details of the copolymerization condition were similar to those reported previously.<sup>11</sup> Table I shows the properties of the copolymers obtained by the copolymerization of AN and quaternized DAMA derivatives (Scheme 1), where the intrinsic viscosities of resultant copolymers were estimated by extrapolating the linear plot of  $\eta_{sp}/C$  versus concentration,  $C$ . Here, the viscosity was measured using an Ubbelohde viscometer. To overcome the intermolecular interaction, the copolymers were dissolved in *N,N*-dimethylformamide containing 0.5 mol/L LiCl. The copolymer concentration was in the range of 0.5 to 1.5 g/100 mL. The molar fraction,  $y$ , of the quaternized DAMA units in the resultant copolymer was determined with a <sup>1</sup>H-NMR spectrometer (JNM-GX270) using DMSO-*d*<sub>6</sub> as the solvent. The NMR spectrum for the EDAMA copolymer has the following characteristic peaks:  $\text{---CH}_3$  (d, 3H): 0.7–0.8 ppm;  $\text{---CH}_2$  (t, 2H): 1.2–1.4 ppm;  $\text{---}(\text{CH}_2\text{---CH})\text{---}$  (m, 2H): 1.6–1.7 ppm;  $\text{---CH}_2\text{---N}^+$  (t, 2H): 1.7–1.8 ppm;  $\text{---CH}_2\text{---C(=O)O---R}$  (m, 2H): 2.2–2.4 ppm. For the copolymer having the benzyl group, the spectrum has following resonance peaks for the benzene ring:  $\text{---C}_6\text{H}_4\text{---CH}_2\text{---}$  (d, 4H): 7.7 ppm, and  $\text{---CH}_2\text{---phe}$  (m, 2H): 2.6 ppm, overlapped with peaks for DMSO protons. For copolymers having octyl or stearyl groups, the spectra have strong resonance peaks at 1.2–1.4 ppm for  $\text{---}(\text{CH}_2)_7\text{---}$  (m, 14H) or  $\text{---}(\text{CH}_2)_{17}\text{---}$  (m, 34H), respectively.

For further characterization of the resultant

**Table I** Properties of PAN Copolymers Obtained by Radical Polymerization of AN and DAMA Derivatives Having Quaternary Ammonium Groups

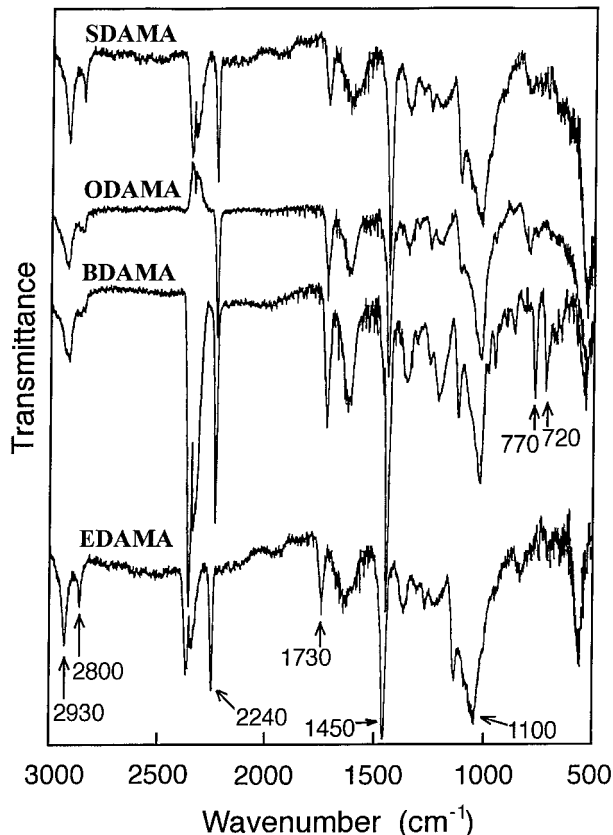
Copolymer	Comonomer	(g)	AN (g)	Yield (%)	Comonomer Mol Fraction, $y^a$	Viscosity <sup>b</sup> (cP)	Intrinsic Viscosity (cm <sup>3</sup> /g)
P(AN-co-EDAMA)	EDAMA	9.29	90.7	86.8	0.02	510	1.04
P(AN-co-BDAMA)	BDAMA	12.1	90.2	88.5	0.025	510	1.09
P(AN-co-ODAMA)	ODAMA	17.1	90.2	89.8	0.028	380	0.75
P(AN-co-SDAMA)	SDAMA	9.84	90.1	89.0	0.012	1200	1.72

<sup>a</sup> Comonomer fraction,  $y$ , was measured by <sup>1</sup>H-NMR. In Scheme 1,  $x + y = 1$ .

<sup>b</sup> Viscosity of cast solution for 10 wt % polymer solution was measured by B-shaped viscometer (Model BL, Tokimec Inc.) using No. 6 rotator at 12 rpm rotating rate.

copolymers, FTIR spectra were measured by the attenuated total reflection (ATR-IR) technique with a Shimadzu FTIR8100 spectrometer. Here, the FTIR-ATR spectra of the membranes were obtained by placing the membrane films at a 45° angle to the incident light. Figure 1 shows the FTIR-ATR spectra of the copolymer membranes. For AN segments in the copolymer, the characteristic absorption due to CH stretching and CH

bending appear near 2930 and 1450 cm<sup>-1</sup>, respectively. Also, the spectra have sharp peaks due to the CN stretching at 2240 cm<sup>-1</sup>. For quaternized DAMA segments, the spectra have an IR peak for the ester carbonyl group (C=O) at 2800 and 1730 cm<sup>-1</sup>. In the spectra, there is also characteristic peak for the quaternary ammonium group at about 1100 cm<sup>-1</sup>. For the BDAMA copolymer, the spectrum has a characteristic peak for aromatic CH bending at 770 and 720 cm<sup>-1</sup>. In the spectra, there are no signals of the vinyl group of the quaternized DAMA derivatives and AN. From these data, it was confirmed that the copolymerizations proceeded successfully without monomer decomposition.



**Figure 1** FTIR-ATR spectra of the four types of amphiphilic copolymer membranes.

#### Membrane Preparation and Permeation Experiments

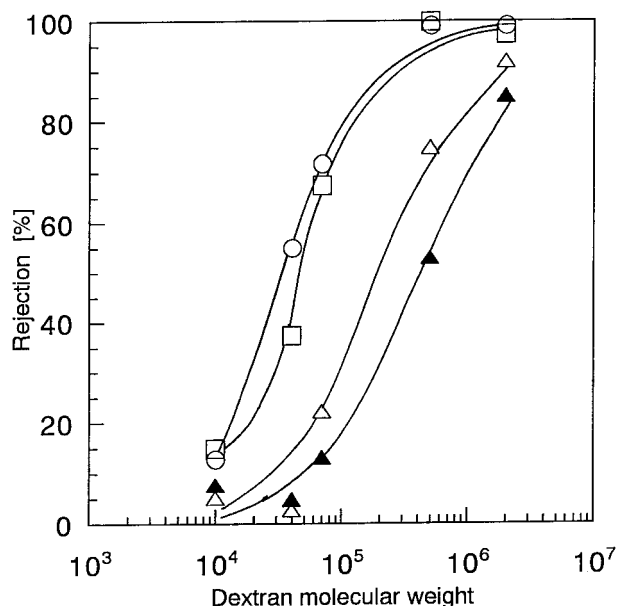
Membranes of the resultant copolymers were prepared by the phase-inversion method according to a previous report.<sup>11</sup> The copolymer was dissolved in DMSO overnight at 50°C to obtain a 10 wt % solution. The solution was spread onto a glass plate (120 × 250 mm<sup>2</sup>) with a pair of 100- $\mu$ m-thick controlling spacers on it. Then, the glass plate was immediately immersed into a coagulation water bath at 30°C. To coagulate the membranes completely, the membrane was kept in a water bath overnight. The membrane obtained was washed with excess water to remove the DMSO. Before the filtration experiments, the membrane sheet was cut into disks having a diameter of 43 mm for setup in a filtration cell (Amicon Co. Ltd., Type 8050). Filtration experiments were carried out under 760 mmH<sub>2</sub>O pressure at 25°C and a stirring speed of 200 rpm. For the measurements of the molecular size-exclusion property of the membranes, a dextran solution

was used in a 0.1 wt % concentration. The dextran concentrations in the feed and permeate solutions were analyzed with a gel permeation chromatograph (GPC; Toyo Soda Co. Ltd., CCPE-II RI8000 with 30-cm column of TSEgel G5000 PW). Dextran rejection was calculated from the area of the GPC curves. The rejection,  $R$ , is defined as  $R(\%) = (1 - A_p/A_f) \times 100$ , where  $A_p$  and  $A_f$  denote the area of the GPC curves for the permeate and feed samples, respectively. For salt rejection, electrical conductivity of the feed and permeate solution was measured with a Horiba B-173 conductivity meter (Horida, Ltd., Tokyo, Japan). The membrane potential was measured according to ref. 13 using a Horiba F-21 pH meter (Horida Ltd). Analysis of the water and 2-butanol was performed with gas chromatography (Shimadzu GC-3BT with 30-cm column of PEG 6000).

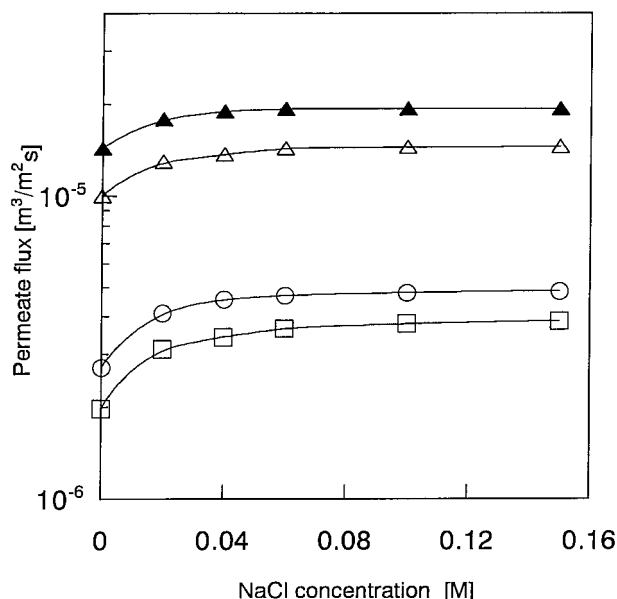
## RESULTS AND DISCUSSION

### Properties of Ultrafiltration Membranes at Various Salt Concentrations

Under 760 mmH<sub>2</sub>O of applied pressure, water was permeated through the resultant membranes. Four kinds of positively charged membranes made of copolymers having EDAMA, BDAMA, ODAMA, and SDAMA groups have a water per-



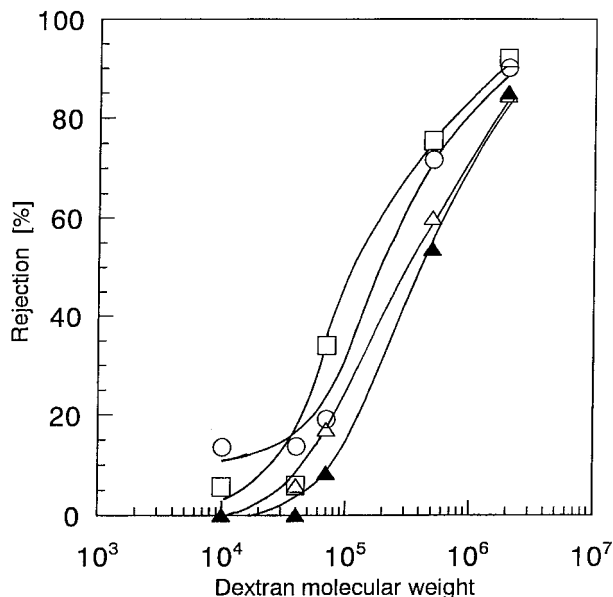
**Figure 2** MWCO curves of the amphiphilic copolymer membranes at  $[\text{NaCl}] = 0\text{M}$ : (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.



**Figure 3** Volume flux of NaCl solutions through the amphiphilic copolymer membranes: (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.

meability of  $2.2 \times 10^{-6}$ ,  $2.0 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$ , and  $1.4 \times 10^{-5} \text{ m}^3/(\text{m}^2 \text{ s})$ , respectively. It is noted that copolymer membranes having long alkyl chains of octyl and stearyl groups show a high water permeability relative to that of the copolymer membranes having ethyl and benzyl groups. The slow water permeability through the EDAMA and BDAMA membranes may be due to the expanded positively charged segments in the membranes as reported previously.<sup>8,9</sup> Figure 2 shows the membrane rejection curves for different MW dextrans. The MW cutoff (MWCO) curves of EDAMA and BDAMA copolymer membranes show similar behavior with each other. As the aliphatic chain length of the quaternary ammonium group increases, the curves shift toward the high MW side of the dextran solutes. The results for the MWCO curves show that both the BDAMA and EDAMA copolymer membranes have a small pore size relative to the ODAMA and SDAMA copolymer membranes. The results for the high permeation flux and low dextran rejection of the ODAMA and SDAMA membranes may be due to the hydrophobicity of the aliphatic groups which influence the phase-inversion processes of the copolymer in a water-coagulation medium.

It is known that the filtration properties of charged membranes are influenced by the salt concentration of the feed solution.<sup>5,8,9</sup> Thus, we examined the salt effect on the UF properties of

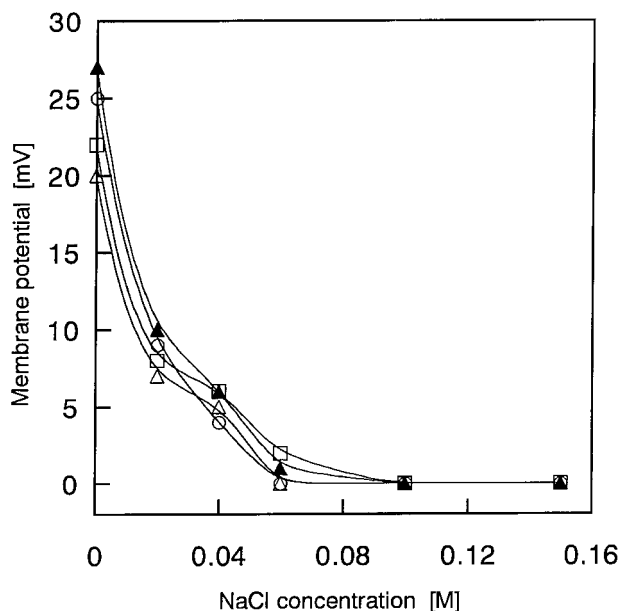


**Figure 4** MWCO curves of the amphiphilic copolymer membranes at  $[\text{NaCl}] = 0.15\text{M}$ : (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.

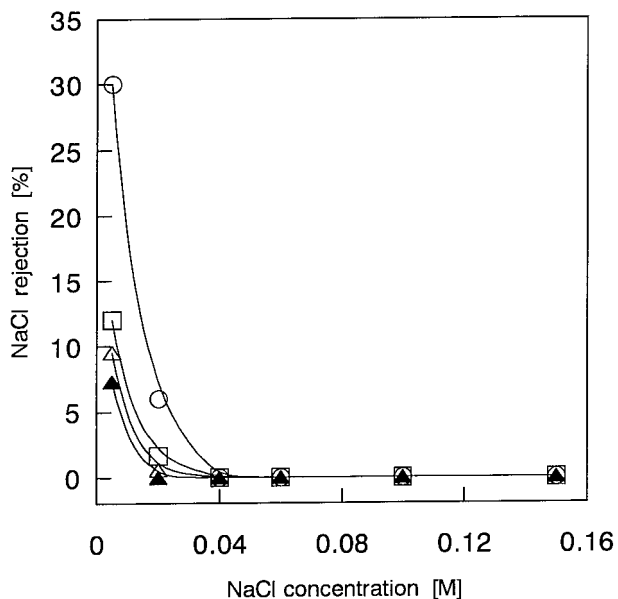
the resultant membranes. Figure 3 shows the permeate flux of the membrane measured under different NaCl concentrations in the 0–0.15M region. For all of these membranes, the permeate flux of the salt solution increases with increase in the NaCl concentration in the range of 0–0.04M and then approaches a constant value at a higher concentration than 0.04M. When the NaCl concentration is higher than 0.06M, those values for the EDAMA, BDAMA, ODAMA, and SDAMA copolymer membranes approach  $5 \times 10^{-6}$ ,  $4 \times 10^{-6}$ ,  $1 \times 10^{-5}$ , and  $2 \times 10^{-5} \text{ m}^3/(\text{m}^2 \text{ s})$ , respectively. Figure 4 shows the MWCO curves of the copolymer membrane measured using different MW dextran solutions containing  $[\text{NaCl}] = 0.15\text{M}$ . In comparison with the rejection curves in Figure 2, the rejection curve for each membrane in Figure 4 shifts toward the higher MW side of dextran by the addition of salt. This indicates that the pore size of the copolymer membranes increases in the presence of NaCl. Since the salt effect upon the filtration properties of the charged membrane is related to the electrostatic characteristics, the membrane potential ( $\phi$ ) value of the copolymer membranes was further estimated at various salt concentrations as shown in Figure 5. The  $\phi$  value of each membrane decreases drastically as NaCl concentration increased in the 0–0.02 M region. This suggests that the positively charged sites in the copolymer membrane were shielded by the

salt ions such as the  $\text{Cl}^-$  ion. The  $\phi$  value becomes zero at a higher concentration than 0.06M. This tendency corresponds well to the filtration behavior shown in Figure 3. The data of the membrane potential suggest that the resultant membrane behaves as a nonionic membrane at high NaCl concentration. Because the electrostatic repulsion between the positively charged segments was weakened by the salt addition, the charged segments tend to retain a compact conformation in the presence of salt. Under the salt-free condition, the charged chains in the membrane are in an expanded conformation due to electrostatic repulsion between positively charged segments.<sup>8</sup> Consequently, the conformation change of the charged segments in the absence and presence of salt is responsible for the changes in pore size and permeate flux of the membrane.

It is very interesting to study the salt rejection under such a low applied pressure because the reverse osmosis process needs very high pressure. We examined salt rejection in the present membranes. Figure 6 shows the NaCl rejection measured at different NaCl concentrations. The salt rejection decreased with increasing salt concentration. Particularly, the decrease is significant in the 0–0.02M region. At higher than 0.04M concentration, charge segments may be shielded completely by salt ions and the membrane behaves as



**Figure 5** Membrane potentials of the amphiphilic copolymer membranes measured at various NaCl solutions: (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.



**Figure 6** NaCl rejections by the each kind of copolymer membranes measured at different concentrations of NaCl solution: (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.

a noncharged membrane. At 0.005M NaCl concentration, the EDAMA membrane shows the highest rejection to NaCl. This may be due to the membrane property such as the smallest pore size resulting in the long residence time of the solute solution in the membrane.

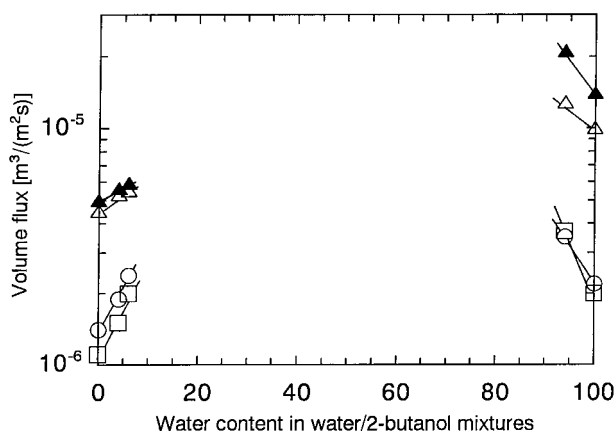
#### Separation Ability of Membrane for 2-Butanol/Water Mixtures

It is well known that the UF membrane cannot directly separate small molecules such as organic solvent from a water/organics mixture, because the UF membrane has a very big pore size relative to the size of the organic molecule. An amphiphilic UF membrane has both hydrophobic sites and hydrophilic sites and, hence, different permeability behavior is expected for the organic solvent/water system. As reported<sup>9,10</sup> and mentioned above, the aliphatic hydrophobic groups are influenced by the ultrafiltration properties of the charged membrane having the amphiphilic quaternary ammonium group. If water is replaced by alcohol, the membrane properties significantly change,<sup>14</sup> because the destruction of the hydrophobic interaction between the aliphatic hydrophobic groups coagulated in the membrane occurs.<sup>15</sup>

In the present study, the aliphatic chain effect of the amphiphilic UF membranes on the separa-

tion ability for the water/2-butanol mixture was examined. Figure 7 shows the volume flux of the copolymer membrane for water/2-butanol mixtures at 760 mmH<sub>2</sub>O applied pressure. It is known that the immiscible region for water/2-butanol mixtures is represented between about 10 and 90 wt % of water content.<sup>16</sup> Therefore, the filtration experiments were carried out in both water concentration regions of 0–10 and 90–100 wt %. There is a tendency that the permeate flux of the membrane increases when the water content increases in the 0–10 wt % concentration region. As listed in Table II, the water or 2-butanol content in the membrane suggests that the resultant membrane swells well in water relative to 2-butanol. Apparently, this indicates that the charged segments such as quaternized ammonium groups behave as absorption sites for the water molecules. Hence, in Figure 7, increase of the permeate flux may be due to water absorption to the charged sites of the membranes. Here, the alcohol is a poor solvent for PAN membrane materials, which are shrunk in the solvent. Therefore, the PAN membrane structure is dense in the poor solvent, which has lower dielectric content, 16.5, than that of water, and the relative slow permeation resulted in the alcohol solvent.

In Table II, the separation factors,  $\alpha_{w/b}$ , for a low water content mixture (water: 6 wt %) and a high water content mixture (94%) are listed. The value of  $\alpha_{w/b}$  for the water/2-butanol mixture is defined as the ratio of  $(W_{\text{water}}/W_{\text{2-butanol}})_p$  to  $(W_{\text{water}}/W_{\text{2-butanol}})_f$ , where  $W_{\text{water}}$  and  $W_{\text{2-butanol}}$  represent the weight percentage of the water and 2-butanol components, respectively. The subscripts,



**Figure 7** Membrane permeate flux for different compositions of water/2-butanol mixtures: (○) EDAMA; (□) BDAMA; (△) ODAMA; (▲) SDAMA.

**Table II** Properties of Copolymer Membranes for Water/2-Butanol Mixtures

Membrane	Volume Flux [m <sup>3</sup> /(m <sup>2</sup> s)]		Separation Factor $\alpha_{w/b}$		Membrane Content <sup>a</sup> (wt %)	
	6 wt %	94 wt %	6 wt %	94 wt %	Water	2-Butanol
EDAMA	$2.4 \times 10^{-6}$	$3.4 \times 10^{-6}$	1.1	1.0	93.8	88.2
BDAMA	$2.0 \times 10^{-6}$	$3.7 \times 10^{-6}$	2.1	1.0	94.6	91.2
ODAMA	$5.5 \times 10^{-6}$	$12.8 \times 10^{-6}$	1.7	1.0	92.9	88.7
SDAMA	$5.9 \times 10^{-6}$	$21.1 \times 10^{-6}$	1.8	1.0	92.9	88.9

<sup>a</sup> Membrane content was obtained by the weight measuring of the dry membrane and wet membrane.

$f$  and  $p$  denote the “feed” and “permeate,” respectively. We found that each membrane shows a separation ability of water from the low water content of the water/2-butanol mixture. However, the EDAMA membrane, which contains no amphiphilic group, has no separation ability in both high and low water content mixtures. On the other hand, for the BDAMA copolymer membrane, the value of  $\alpha_{w/b}$  is 2.1 in the low water content mixture. The membranes having octyl and stearyl groups also show relatively higher  $\alpha_{w/b}$  values than that for the EDAMA membrane in a 6 wt % water-content mixture, indicating that the presence of amphiphiles in the membrane gives effective results for the separation. Since the amphiphilic membrane has both nonpolar aliphatic chain sites and polar ionic sites, water molecules may be strongly absorbed to the charged sites of the membrane material, and alcohol molecules, to nonpolar sites such as the aliphatic hydrophobic chain or benzyl groups. So, in the low water-content region, at first, water molecules may absorb to the membrane to create carrier-mediated transfer sites.<sup>17,18</sup> Then, the membrane supports the permeated water molecules by a carrier-mediated transfer mechanism. In the low dielectric alcohol medium, as a result, water permeates through the membrane more quickly than does 2-butanol. On the other hand, in the high water-concentration region at higher than 90 wt %, the values of  $\alpha_{w/b}$  in Table II represent that the water and the alcohol permeate similarly through the membrane. Hence, the carrier mediation for only water molecules is not effective in the excess water medium. It is noted in Figure 7 that the value of the permeated flux for each membrane decreases as the water content increases. This is apparently due to the pore size decrease by electrostatic repulsion of the charged segments in the membrane.<sup>8,9</sup> So, in the water-excess medium, most of the alcohol molecules can be soluble in

the water medium and may permeate through the membrane together with the water molecules.

For the present amphiphilic membranes, it was found that the hydrophobic sites of the membrane have influence on the water/alcohol separation in a limited composition such an alcohol-excess medium. These results for the separation of the water/alcohol mixture suggest the development of new types of membranes for alcohol purification using porous UF membranes.

## CONCLUSIONS

Positively charged UF membranes with an amphiphilic group were prepared by using copolymers of AN and quaternized DAMA derivatives. For UF membranes with different quaternized ammonium groups, the filtration properties of the water and dextran solution were examined in the absence and presence of NaCl. The membrane permeability increases with increase of the aliphatic chain length of the alkyl group on the quaternary ammonium salt group. All the membranes had higher permeability and smaller rejection for dextrans when NaCl was added in the solution, which was confirmed by the measurement of the membrane potential for each membrane and that the salt effect is due to the shielding of charged groups in the membrane. In addition, it was found that the amphiphilicity of these UF membrane contributes to their separation ability for a water/2-butanol mixture of low water content.

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