

Transport Properties of Anion-Exchange Membranes Having a Hydrophobic Layer on Their Surface in Electrodialysis

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After a hydrophobic layer having cationic charge had been formed on a strongly basic anion-exchange membrane by coating cationic polysoap solutions on the membrane surface or by reacting tertiary amines having hydrophobic groups with chloromethyl groups of the cross-linked membrane, the transport numbers of various anions, sulfate, bromide, nitrate, fluoride, and iodide ions, relative to chloride ions in electrodialysis, were evaluated. The layer formed on the desalting side of the membrane enhanced the permeation of bromide, iodide, and nitrate ions and depressed that of sulfate and fluoride ions with increasing hydrophobicity of the layer without a remarkable increase in electrical resistance and any decrease in the current efficiency of the membrane. On the other hand, the polysoap layer on the concentrated side gave a similar change to the transport numbers of the anions, but caused the current efficiency to decrease. The anion-exchange membranes reacted with the hydrophobic tertiary amines with one surface of the membrane showed a similar change in the transport numbers of the anions relative to chloride ions without any decrease in the current efficiency. From an analysis of the ionic ratio in the membrane just after electrodialysis, the uptake of less hydrated anions was enhanced, and strongly hydrated anions were difficult to ion exchange with the membrane by the formation of the hydrophobic layer on the membrane surface. This is closely related to the hydration energy of anions in water.

Introduction

Today, various kinds of separation membranes have been studied and utilized industrially in various fields. The purpose of membrane research is to prepare the membranes to efficiently separate a specific component from their mixture. Ion-exchange membranes are one of the most advanced separation membranes, which have been widely used in various industries.¹ Their electrochemical properties have been vastly improved in recent years: the transport number of counterions becomes almost unity in any concentration of solutions. However, ion-exchange membranes cannot separate ions with the same sign and same valence.

Many trials to prepare the ion-exchange membranes having permselectivity for a specific ion have been carried out because of an academic interest and industrial requirements. Those in the cation-exchange membranes increase the cross-linkage of the membrane,² form highly cross-linked layer on the membrane surface,³ introduce specific cation-exchange groups into the membrane,⁴ form a cationic charged layer on the membrane surface,⁵ etc. Anion-exchange membranes having similar properties were also reported: the increase in the cross-linkage of the membrane,⁶ the formation of highly cross-linked layers on the membrane surface,⁷ partial decomposition of quaternary ammonium groups or inactivation of the groups on the membrane surface,⁸ the formation of an anionic charged layer on the membrane surface,⁹ the control of hydrophilicity of the membrane,¹⁰ the formation of layers having weakly basic anion-exchange groups on the membrane surface,¹¹ etc. In the initial stage, monovalent anion and cation permselective ion-exchange membranes were studied to avoid the precipitation of calcium sulfate and calcium carbonate in concentrated solution during

electrodialysis. In recent years, the concentration of nitrate ions in groundwater has greatly increased, which is a serious problem.¹² Nitrate ion permselective anion exchange membranes have been required to remove the ions from water.¹³ At the same time, harmful ions are contained in groundwater in some countries, such as fluoride ions in China.¹⁴ It is necessary to develop ion-exchange membranes having permselectivity for respective ions.

In this work, a hydrophobic layer, cationic polysoaps layer, poly(*N*-alkyl-4-vinylpyridinium bromide), or a layer in which quaternary ammonium groups with hydrophobic groups are covalently bonded, was formed on the surface of the anion-exchange membrane with benzyl trimethylammonium groups to control the hydrophilicity of the membrane surface. The effect of the hydrophobic layer on the permselectivity between two anions in electrodialysis was then examined and analyzed.

Experimental Section

Materials. a. Chemicals. Vinyl monomers for membrane preparation, chloromethylstyrene, obtained from Seimi Chemical Co., Ltd., and divinylbenzene (the purity of divinylbenzene is 55%: a mixture of *m*-, *p*-divinylbenzene, ethylvinylbenzenes, and diethylbenzenes), from Sankyo Kasei Kogyo Co., Ltd., were used without further purification. Acrylonitrile–butadiene rubber (NBR) was obtained from Japan Synthetic Rubber Co., Ltd. Sodium chloride, sodium sulfate, sodium nitrate, sodium bromide, sodium fluoride, and sodium iodide for the measurement of permselectivity between two anions, solvents such as nitromethane, ethyl ether, *n*-butyl alcohol, ethyl alcohol, acetone, *n*-butyl ether and other reagents such as benzoyl peroxide (an initiator to polymerize vinyl monomers), trimethylamine, tri-

TABLE 1: Characteristics of Anion Exchange Membranes Prepared in This Work

	AEM ^a (symmetric)	C ₄ -AEM ^b (asymmetric)	C ₈ -AEM ^c (asymmetric)	C ₁₂ -AEM ^d (asymmetric)	DMBA-AEM ^e (asymmetric)
electrical ^f resistance	1.30	1.86	1.95	1.99	3.03
transport ^g number	>0.98	>0.99	>0.99	>0.99	>0.99
ion exchange ^h capacity	2.25	2.01	1.95	1.96	1.88
water content ⁱ	0.31	0.29	0.29	0.29	0.23
thickness (μm)	135	131	126	130	126

^a Anion exchange groups: benzyl trimethylammonium groups. ^b Anion exchange membrane with benzyl trimethylammonium groups having a thin layer of benzyl tri-*n*-butylammonium groups. ^c Anion exchange membrane with benzyl trimethylammonium groups having a thin layer of benzyl tri-*n*-octylammonium groups. ^d Anion exchange membrane with benzyl trimethylammonium groups having a thin layer of benzyl tri-*n*-dodecylammonium groups. ^e Anion exchange membrane with benzyl trimethylammonium groups having a thin layer of benzyl tri-*N,N*-dimethylbenzylammonium groups. ^f $\Omega \text{ cm}^2$, measured with 1000 Hz AC at 25.0 °C after equilibration with 0.500 N sodium chloride solution. ^g Measured by electroanalysis of 0.50 N sodium chloride solution at 10 mA/cm² for 60 min at 25.0 °C. ^h Mequiv/g-Cl⁻ form dry membrane. ⁱ grams of H₂O/g Cl⁻ form dry membrane after equilibration with 0.50 N sodium chloride solution.

n-butylamine, tri-*n*-octylamine, tri-*n*-dodecylamine, *N,N*-dimethylbenzylamine, hydrochloric acid (35%), ammonia solution (29%), etc., obtained from Ishizu Chemical Co., Ltd., and Wako Pure Chemical Industries Ltd., were of reagent grade and used without further purification. The reagents for cationic polysoaps, *n*-octyl bromide, *n*-dodecyl bromide and *n*-hexadecyl bromide, obtained from Ishizu Chemical Co., Ltd., and Wako Pure Chemical Industries, Ltd., were of reagent grade and used without further purification. 4-Vinylpyridine, kindly supplied by Koei Chemical Co., Ltd., was used after reduced-pressure distillation (1–2 mm Hg). Deionized water was used in all experiments.

b. Preparation of Anion-Exchange Membranes. The copolymer membrane (a precursor of anion-exchange membranes) was prepared by copolymerizing chloromethylstyrene and divinylbenzene in the presence of acrylonitrile–butadiene rubber and woven backing fabric, which was made of poly(vinyl chloride), Tevion cloth, Teijin Co., Ltd. Chloromethylstyrene (82 wt %) and *m*-, *p*-divinylbenzene (10 wt %) were mixed, and 5 wt % of acrylonitrile–butadiene rubber was dissolved in the vinyl monomer mixture to give mechanical strength to the membrane. After 3 wt % of benzoyl peroxide had been added to the mixture, the obtained pasty material was coated on the woven fabric and polymerized at 80 °C for 16 h under nitrogen atmosphere after covering with a polyester film on both sides. An anion-exchange membrane with benzyl trimethylammonium groups was prepared according to the same method as previously reported.⁶ Anion-exchange membranes with a layer in which quaternary ammonium groups with hydrophobic chains were covalently bonded were prepared as follows: after the copolymer membrane had been installed in a two-compartment reactor made of stainless steel (SUS 304. Capacity of each compartment: 500 cm³. Membrane area for the reaction: 8.0 cm × 15.0 cm.), one compartment was filled with a 1:1 mixed solution of bulky tertiary amine, tri-*n*-butylamine, tri-*n*-octylamine, tri-*n*-dodecylamine or *N,N*-dimethylbenzylamine, and *n*-butyl ether and heated at 60 °C for 48 h (other compartment was empty). The opposite compartment was then filled with 1.0 N trimethylamine water (75%) and acetone (25%) mixed solution (for 24 h at 25.0 °C). After the obtained membranes had been completely washed with ethyl alcohol and then with 1.0 N hydrochloric acid solution, the membranes were equilibrated alternately with 1.0 N hydrochloric acid solution and 0.5 N ammonia solution several times and then stored in 0.50 N sodium chloride solution. The characteristics of the prepared anion-exchange membranes are shown in Table 1. Before use, the anion-exchange membranes were equilibrated with the solutions to be used in the measurement.

c. Preparation of Cationic Polysoaps. After 10.0 parts of the distilled 4-vinylpyridine and 0.2 part of benzoyl peroxide

had been dissolved in 90.0 parts of ethyl alcohol, the solution was heated at 80 °C for 6 h while stirring. The obtained viscous solution was poured into pure water to obtain poly(4-vinylpyridine). The polymer was dried and then dissolved in ethyl alcohol. The solution was again poured into pure water to purify the polymer, and this procedure was repeated three times. The relationship of the reduced viscosity to the molecular weight of poly(4-vinylpyridine), reported by Bergkowitz et al., was used ($[\eta] = 2.5 \times 10^{-4} \text{M}^{0.68}$)¹⁵ to estimate the molecular weight, which was about 10 000. After the purified poly(4-vinylpyridine) had been dissolved in nitromethane as 10% solution, 2 equiv of the respective alkyl bromide to the pyridine unit of the polymer were added to the solution. The mixture was heated at 80 °C for 45 h with stirring. The alkylated poly(4-vinylpyridine) precipitated with increasing reaction time. After the reaction, an excess amount of ethyl ether was added to the reaction mixture to completely precipitate poly(*N*-alkyl-4-vinylpyridinium bromide). The obtained polymers were washed with ethyl ether using a Soxhlet extractor to completely remove unreacted alkyl bromide. The polymers were then dried under reduced pressure and stored in a desiccator.

From elemental analysis of the polymers, the ratio of *N*-alkyl pyridinium groups to total pyridine groups of the polymer was 91.0% in poly(*N*-octyl-4-vinylpyridinium bromide) (poly-4VP-C₈), 89.4% in poly(*N*-dodecyl-4-vinylpyridinium bromide) (poly-4VP-C₁₂) and 92.6% in poly(*N*-hexadecyl 4-vinylpyridinium bromide) (poly-4VP-C₁₆).

d. Formation of a Polysoap Layer on a Surface of the Anion-Exchange Membrane with Benzyl Trimethylammonium Groups. After the anion-exchange membrane had been dried at room temperature (relative humidity: 60%) and fixed on a horizontal glass plate with adhesive tape, a 10% polysoap *n*-butyl alcohol solution was coated on the surface of the membrane and dried at room temperature. The thickness of the polysoap layer was controlled by the number of coatings and measured with a micrometer. The anion-exchange membrane with the layer was equilibrated with the solutions to be used in the measurement.

Measurements

a. Measurements of Basic Properties of Anion-Exchange Membranes. Electrical resistance of the membranes was measured at 1000 Hz AC (Hewlett-Packard LCR meter 4263A), at 25.0 °C using a two-compartment cell with platinum black electrodes after equilibration with 0.500 N sodium chloride solution. The transport number of the anion-exchange membrane was evaluated by electroanalysis of 0.50 N sodium chloride solution at 25.0 °C at the current density of 10 mA/cm² for 60 min. The ion-exchange capacity and water content of the

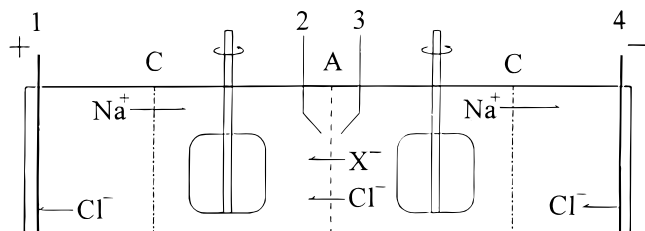


Figure 1. Apparatus for measurement of transport properties of the anion exchange membrane. C: cation exchange membrane. A: anion exchange membrane to be measured. X^- : SO_4^{2-} , Br^- , NO_3^- , F^- , I^- . 1,4: Ag-AgCl electrodes for current supply. 2,3: Ag-AgCl probe electrodes. Effective membrane area: 10 cm^2 ; Capacity of each compartment: 100 cm^3 .

membranes were measured according to conventional methods (based on dry membrane weight).

b. Apparatus. The same four-compartment cell with two kinds of silver-silver chloride electrodes as used in a previous work (Figure 1) was used to measure the electrodialytic transport properties of the anion-exchange membrane.¹⁰ The two kinds of electrodes were plate electrodes for current supply ($4.0 \text{ cm} \times 10.0 \text{ cm}$ size which were bent in a wavelike shape) and wire electrodes for the measurement of the voltage drop across the membrane during electrodialysis, which were placed 2 mm apart from the membrane surfaces. The effective membrane area was 10 cm^2 ($2 \text{ cm} \times 5 \text{ cm}$), and the capacity of each compartment was 100 cm^3 . The sodium chloride solution was used as an anolyte and a catholyte, which were separated by cation-exchange membranes (NEOSEPTA CM-2, made by Tokuyama Corp.; the transport number of sodium ions in the membrane is greater than 0.99 in the electrodialysis of 0.50 N sodium chloride solution at the current density of 20 mA/cm^2 ; the electrical resistance is $2.8 \Omega \text{ cm}^2$) from the middle compartments. The two middle compartments were filled with a 1:1 mixed salt solution. The amount of current passing through the membrane was measured with a coulometer, Nikko Digital Coulometer NDCM-4, Nikko Keisoku, Ltd. The voltage drop across the membrane measured with the probe electrodes was recorded on an X-t recorder, Toa Electronics Co., EPR-2T.

c. Evaluation of Transport Properties of Anion-Exchange Membranes with a Hydrophobic Layer. The measured transport properties of the anion-exchange membranes with a hydrophobic layer were the transport numbers of fluoride, bromide, iodide, sulfate, and nitrate ions relative to chloride ions, the current efficiency, and the voltage drop across the membrane. The transport number of anions A relative to chloride ions was defined as follows:

$$P_{\text{Cl}}^{\text{A}} = \frac{t_{\text{A}}/t_{\text{Cl}}}{C_{\text{A}}/C_{\text{Cl}}}$$

where t_{A} and t_{Cl} are the transport numbers of anion A and the chloride ions in the membrane, and C_{A} and C_{Cl} are the average concentrations of anion A and the chloride ions before and after electrodialysis. P_{Cl}^{A} is the permeated equivalent of anion A through the membrane when 1 equivalent of chloride ions permeates through the membrane (because a 1:1 mixed salt solution as equivalent was used).

d. Procedure. After an anion-exchange membrane with a hydrophobic layer had been placed in the middle of the cell, the two middle compartments were filled with 100 cm^3 of the 1:1 mixed salt solution (sodium sulfate and sodium chloride, sodium nitrate and sodium chloride, sodium fluoride and sodium chloride, sodium bromide and sodium chloride, or sodium iodide

or sodium chloride. Concentration of sodium ions: 0.500 N), and both anolyte and catholyte were filled with 100 cm^3 of 0.500 N sodium chloride solution. The hydrophobic layer on the membrane surface was usually faced to the desalting side of the membrane (cathode side), and electrodialysis was carried out under vigorous agitation ($1500 \pm 100 \text{ rpm}$ with stirrers) at the current density of 10 mA/cm^2 for 60 min at 25.0°C . After electrodialysis, the solutions of the middle compartments were analyzed by the Mohr method (for Cl^-), conventional chelate back titration (for SO_4^{2-}), or ion chromatography (TOSOH CCPD, IC-8010, Chromatocorder 21). The transport number of anion A relative to the chloride ions was calculated from the change in the concentration of each anion, and the current efficiency was calculated from the change in the concentrations of anions in each compartment to the electricity measured with a coulometer. To further examine the effect of the hydrophobic layer on the transport properties of the anion-exchange membranes, the same measurement was also carried out facing the layer to the concentrated side of the membrane (anode side).

e. Determination of the Ratio of Sulfate or Nitrate Ions to Chloride Ions in the Membrane Phase Just after Electrodialysis. Because the anion-exchange membrane with a hydrophobic layer is asymmetric, the ionic composition in the membrane during electrodialysis is expected to be different depending on the direction of the current. To estimate the ratio of anions (sulfate or nitrate) to chloride ions during electrodialysis, the ionic ratio in the membrane phase just after electrodialysis was determined. After the anion-exchange membranes with a hydrophobic layer had been installed in the four-compartment cell facing the layer to the desalting side or the concentrated side, electrodialysis was carried out under the same conditions as the measurement of the transport properties (10 mA/cm^2 , 60 min, 25.0°C). After electrodialysis had been stopped, the membrane was instantaneously removed from the cell (within 10 s) without washing and wiped with filter paper. The membrane area through which the current was passed ($2.0 \text{ cm} \times 5.0 \text{ cm}$) was cut from the membrane and immersed in 0.02 N sodium nitrate solution to elute anions from the membrane. The concentrations of chloride and sulfate ions or chloride ions in the eluent were determined. The amount of nitrate ions was calculated by subtracting the amount of chloride ions from the ion-exchange capacity of the membrane. The ratio of anions in the membrane during electrodialysis was estimated using the following equation:

$$K_{\text{Cl}}^{\text{A}} = \frac{C_{\text{A}}^{\text{M}}/C_{\text{Cl}}^{\text{M}}}{C_{\text{A}}^{\text{S}}/C_{\text{Cl}}^{\text{S}}}$$

where C_{A}^{M} and C_{Cl}^{M} are equivalents of sulfate or nitrate ions and chloride ions in the membrane, and C_{A}^{S} and C_{Cl}^{S} are average concentrations of sulfate or nitrate ions and chloride ions in the solution during electrodialysis.

Results and Discussion

a. The Change in Transport Numbers of Various Anions Relative to Chloride Ions by the Formation of a Cationic Polysoap Layer on the Anion-Exchange Membrane. The transport number of anions A relative to the chloride ions is a product of the ion-exchange equilibrium constant of anions A to chloride ions and the ratio of the mobility of anions A to that of chloride ions.¹⁶ To change the ion-exchange equilibrium constant of specific ions with the membrane in electrodialysis, a cationic polysoap layer was formed on the membrane surface of the desalting side. When bulky amines react with the

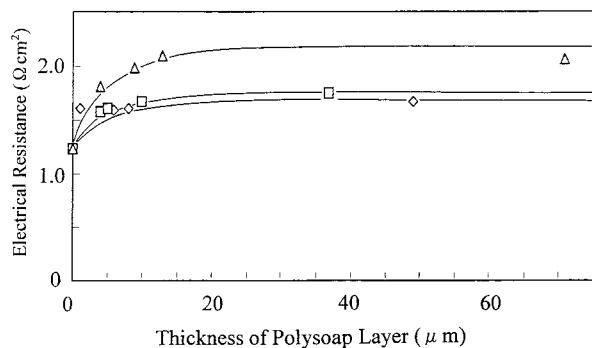


Figure 2. Effect of thickness of a cationic polysoap layer on electrical resistance of the anion exchange membrane. \diamond : poly-4VP-C₈. \square : poly-4VP-C₁₂. \triangle : poly-4VP-C₁₆. A layer of cationic polysoap [poly(*N*-alkyl 4-vinylpyridinium bromide)] was formed by coating a 10% *n*-butyl alcohol solution on a membrane surface and evaporating the solvent. Electrical resistance was measured with 1000 Hz AC at 25.0 °C after equilibration with 0.500 N sodium chloride solution.

chloromethyl groups of the cross-linked membranes to decrease the hydrophilicity of the membrane, the reaction becomes difficult with increasing molecular weight of the amines; therefore, the ion-exchange capacity was extremely low and the electrical resistance of the membranes was very high.¹⁰ It is expected that the formation of a thin, hydrophobic layer on the surface of the anion-exchange membranes changes the ion exchange equilibrium constant of specific ions with the membrane in electrodialysis. Thus, the permselectivity between the anions is thought to change in electrodialysis.

The hydrophilicity of compounds is defined by the HLB value (hydrophilic lipophilic balance): $HLB = \Sigma(\text{hydrophilic groups numbers}) - \Sigma(\text{hydrophobic groups numbers}) + 7$.¹⁷ The HLB value of the vinyl benzyl trimethylammonium groups (unit of anion-exchange groups of the membrane) was calculated to be 10.70. To make the membrane surface less hydrophilic than this, a layer of cationic polysoaps, which are insoluble in water, was formed on the surface of the membrane. The HLB values of *N*-octyl-, *N*-dodecyl- and *N*-hexadecyl(4-vinylpyridinium) groups (unit of the polysoaps) were 9.28, 7.38, and 5.48, respectively. These groups are less hydrophilic than the anion-exchange groups of the membrane.

Figure 2 shows the change in the electrical resistance of the anion-exchange membrane by the formation of a polysoap layer. The electrical resistance increased with increasing thickness of the layer and attained a constant value for thickness greater than 20 μm . The fact that the electrical resistance of the membrane attained a constant value can be explained as follows: because the charge density of the anion-exchange membrane is high and the membrane surface is strongly hydrophilic, the cationic charges in the polysoap layer might be located on the membrane surface and the region of the smaller charge density might be formed in the layer because of the aggregation of the alkyl groups of the polysoap. This region is thought to cause the increase in the electrical resistance of the membrane. It was reported that the soluble cationic polysoaps form an intramolecular micelle in water: long alkyl groups aggregate inside and positive charge is located on the outside of the micelles.¹⁸ However, because the cationic charges are distributed more homogeneously in the layer with increasing thickness of the layer, the electrical resistance would be expected to attain almost constant value. Because the layer is not cross-linked by covalent bonds, the electrical resistance should be low compared with that of the anion-exchange membrane. The voltage drop across the membrane during electrodialysis, which was measured with probe electrodes, was almost the same as that without the layer.

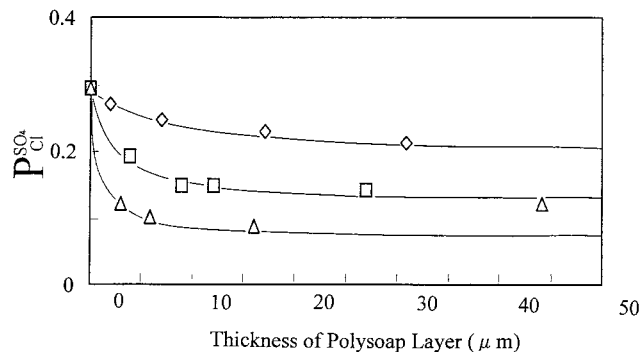


Figure 3. Effect of thickness of a polysoap layer on transport number of sulfate ions relative to chloride ions. \diamond : poly-4VP-C₈. \square : poly-4VP-C₁₂. \triangle : poly-4VP-C₁₆. A 0.25 N sodium sulfate and 0.25 N sodium chloride mixed solution was electrodialyzed at 10 mA/cm² at 25.0 °C.

TABLE 2: Gibbs Hydration Energy of Anions in Water and Stokes Radius²⁰

anion species	$-\Delta G_h^0$ (kJ/mol)	r_s (Å)
I ⁻	257	1.20
NO ₃ ⁻	270	1.29
Br ⁻	303	1.18
Cl ⁻	317	1.21
F ⁻	434	1.66
SO ₄ ²⁻	1000	2.31

ΔG_h^0 : Gibbs hydration energy. r_s : Stokes radius.

On the other hand, the electrical resistance increased with increasing carbon number of the alkyl groups bonded to the pyridinium groups. The aggregation number of micelles was reported to increase with increasing carbon number of the alkyl groups of surface-active agents.¹⁹ Alkyl chains in the polysoap layer are thought to aggregate more tightly with increasing carbon number of the chains, which caused the difficulty in the permeation of anions through the layer. After all, the polysoap layer on the membrane surface did not cause a remarkable increase in the electrical resistance of the membrane.

Figure 3 shows the relationship of the transport number of sulfate ions relative to chloride ions to the thickness of the polysoap layer when the layer faced the desalting side of the membrane. Apparently, the permeation of the sulfate ions relative to chloride ions decreased steeply with increasing thickness of the layer until about 10 μm thickness and then gradually decreased. Especially, the layer of poly(*N*-hexadecyl-4-vinylpyridinium bromide) decreased the $P_{\text{Cl}^{SO_4}}$ until one-third of that of the anion-exchange membrane. It is apparent from the Gibbs hydration energies of chloride and sulfate ions (Table 2) that sulfate ions are strongly hydrated compared with chloride ions and larger than the chloride ions.²⁰ Because the polysoap layer changed the membrane surface to less hydrophilic, the ion exchange of sulfate ions with the membrane is thought to become difficult, which caused the permeation of sulfate ions to decrease. Table 3 shows the ionic ratio just after electrodialysis in the anion-exchange membrane with a 9- μm -thick layer of poly(*N*-dodecyl-4-vinylpyridinium bromide) and in the membrane without the layer. Apparently, the ratio of sulfate ions to chloride ions in the membrane with the layer was lower than that of the membrane without the layer. The polysoap layer disturbs the ion-exchange of the sulfate ions with the membrane. In this case, the polysoap layer stably adhered to the membrane surface during the electrodialysis. This might be due to the partially ionic cross-linkage of the pyridinium groups of the polysoap with the divalent anions (sulfate), though

TABLE 3: Ratio of Sulfate or Nitrate Ions to Chloride Ions in the Anion-Exchange Membrane during Electrodialysis with and without a Polysoap, Poly-4VP-C₁₂, Layer^a

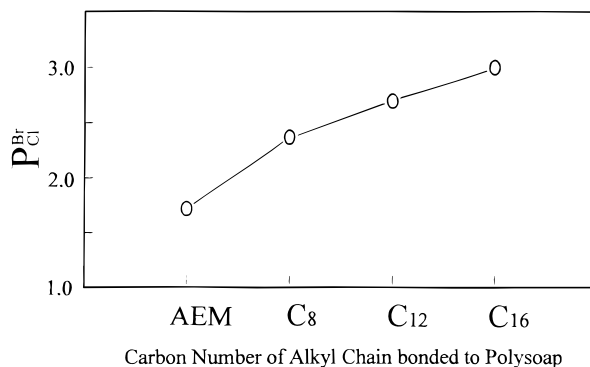
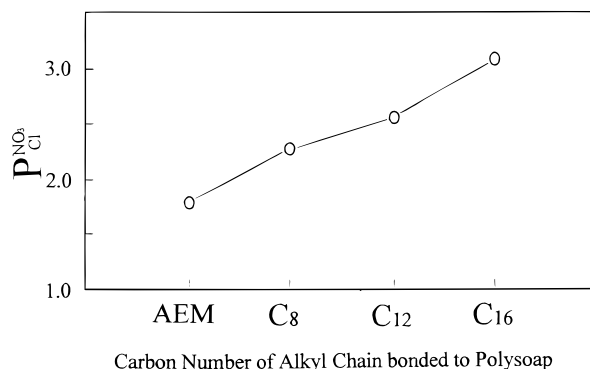
	without a polysoap	direction of current	
		polysoap layer facing the desalting side	polysoap layer facing the concentrated side
$K_{\text{Cl}}^{\text{SO}_4}$	0.290	0.230	0.298
$K_{\text{Cl}}^{\text{NO}_3}$	3.45	4.24	3.37

^a After electrodialysis of a 1:1 mixed salt solution of 0.25 N sodium sulfate and 0.25 N sodium chloride or 0.25 N sodium nitrate and 0.25 N sodium chloride had been carried out at 10 mA/cm² at 25.0 °C for 60 min, the ratio of sulfate ions to chloride ions or nitrate ions to chloride ions in the membrane phase was determined after removing the membrane instantaneously (within 10 s) from the cell.

the layer was partially detached from the membrane surface during electrodialysis in the measurements of other mixed salt solutions.

The permeation of the sulfate ions also remarkably decreased when the layer faced the concentrated side of the membrane, and $P_{\text{Cl}}^{\text{SO}_4}$ attained a value of 0.02 [9- μm -thick layer of poly-(*N*-dodecyl-4-vinylpyridinium bromide)], which was maintained during four repetitions of electrodialysis. Originally, sulfate ions were difficult to permeate through the anion-exchange membrane compared with chloride ions ($P_{\text{Cl}}^{\text{SO}_4}$ without the layer: 0.3 in Figure 3). Thus, the ratio of sulfate ions to chloride ions at the interface between the anion-exchange membrane and the polysoap layer on the concentrated side should be lower than that of the bulk solution. The polysoap layer was also a barrier for the sulfate ions. Thus, the permeation of sulfate ions is thought to be more depressed compared to the membrane with the layer on the desalting side. However, the current efficiency of the anion-exchange membrane with the layer on the concentrated side was about 50% (the current efficiency was greater than 99% when the layer faced the desalting side of the membrane). The decrease in the current efficiency is thought to be due to the following reasons: (1) because about 90% of the pyridine groups of the polysoap were alkylated with bulky alkyl halide and the polymer aggregates by hydrophobic bonds in the layer, the pyridinium groups of the polymer might be sterically difficult to completely ion-exchange with divalent anions; (2) sulfate ions were accumulated in the membrane phase over the ion-exchange capacity due to a blocking layer for the sulfate ions. Thus, the negative charge originating from the sulfate ions might exist in the layer (amphoteric). In fact, from Table 3, the ratio of sulfate ions to chloride ions in the membrane just after electrodialysis was to be calculated as 1.00 vs 0.79 vs 1.03 for the membrane without the layer, that with the layer on the desalting side, and that on the concentrated side, respectively. The sulfate ions were accumulated in the membrane phase when the layer faced the concentrated side. Thus, the remaining negative charge should act as cation exchangeable groups.

Similarly, the change in $P_{\text{Cl}}^{\text{Br}}$ with the carbon number of the alkyl groups bonded to pyridinium groups of the polysoaps (an asymptote was adopted because the $P_{\text{Cl}}^{\text{Br}}$ approached a constant value with increasing thickness of the layer similar to Figure 3) is shown in Figure 4 when the layer faced the desalting side of the membrane. The $P_{\text{Cl}}^{\text{Br}}$ increased with increasing carbon number of the alkyl groups bonded to the pyridinium groups. Because the hydrophilicity of the layer decreases with increasing carbon number of the alkyl groups of the polymer, the affinity of less-hydrated bromide ions than chloride ions (Table 2) to the membrane is thought to increase. Although the bromide

**Figure 4.** Relationship of $P_{\text{Cl}}^{\text{Br}}$ to carbon number of alkyl group of poly(*N*-alkyl-4-vinylpyridinium bromide). AEM: without a layer. C₈: poly-4VP-C₈. C₁₂: poly-4VP-C₁₂. C₁₆: poly-4VP-C₁₆. A 0.25 N sodium bromide and 0.25 N sodium chloride mixed solution was electrodialyzed at 10 mA/cm² at 25.0 °C.**Figure 5.** Relationship of $P_{\text{Cl}}^{\text{NO}_3}$ to carbon number of alkyl group of poly(*N*-alkyl-4-vinylpyridinium bromide). AEM: without a layer. C₈: poly-4VP-C₈. C₁₂: poly-4VP-C₁₂. C₁₆: poly-4VP-C₁₆. A 0.25 N sodium nitrate and 0.25 N sodium chloride mixed solution was electrodialyzed at 10 mA/cm² at 25.0 °C.

ions generally more selectively permeate through the anion-exchange membrane having quaternary ammonium groups than the chloride ions,²¹ the permeation of bromide ions is enhanced by the formation of the less-hydrophilic layer.

Nitrate ions are less hydrated compared with chloride ions as shown in Table 2. Figure 5 shows that the permeation of nitrate ions increased with increasing carbon number of the alkyl groups bonded to the pyridinium groups of the polysoaps, which is similar to the bromide-chloride system. $P_{\text{Cl}}^{\text{NO}_3}$ of the membrane with poly(*N*-hexadecyl-pyridinium bromide) layer attained almost twice the value compared with the membrane without the polysoap layer. In general, nitrate ions permeate more selectively through the anion-exchange membranes having quaternary ammonium groups than chloride ions in spite of the larger ions as shown in Table 2. This is because of the strong affinity of the nitrate ions to the anion-exchange membrane. Table 3 shows the ionic ratio just after electrodialysis in the membrane without the layer: that with the layer on the desalting side and that on the concentrated side [thickness of poly(*N*-dodecyl-4-vinylpyridinium bromide): 10 μm]. When the layer faced the desalting side of the membrane, the $K_{\text{Cl}}^{\text{NO}_3}$ was high, which means that the layer selectively took nitrate ions in the membrane phase. This is why the permeation of nitrate ions through the membrane was enhanced by the layer. When the same layer faced the concentrated side of the membrane, $P_{\text{Cl}}^{\text{NO}_3}$ attained 3.17, which was higher than that of the membrane with the layer on the desalting side. Because the $K_{\text{Cl}}^{\text{NO}_3}$ of the membrane without the layer was 3.45 (Table 3), the ratio of nitrate ions to chloride ions in the membrane phase is higher

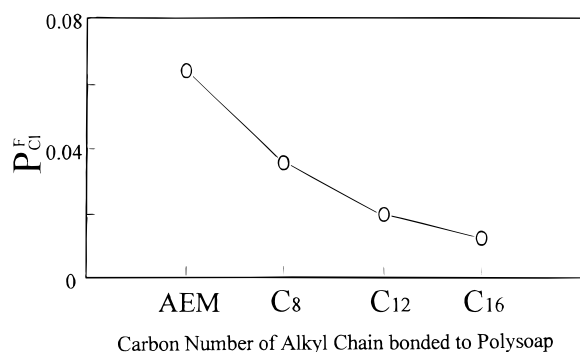


Figure 6. Relationship of P_{Cl}^F to carbon number of alkyl group of poly(*N*-alkyl-4-vinylpyridinium bromide). AEM: without a layer. C₈: poly-4VP-C₈. C₁₂: poly-4VP-C₁₂. C₁₆: poly-4VP-C₁₆. A 0.25 N sodium fluoride and 0.25 N sodium chloride mixed solution was electrodialed at 10 mA/cm² at 25.0 °C.

TABLE 4: Transport Number of Iodide Ions Relative to Chloride Ions of Anion-Exchange Membrane by the Formation of a Polysoap, Poly(*N*-alkyl 4-vinylpyridinium bromide), Layer Having Different Alkyl Chain Length^a

chain length of alkyl groups	C ₈ ^b	C ₁₂ ^c	C ₁₆ ^d	without polysoap layer
P _{Cl} ^f	28.2	35.5	28.5	4.56

^a A 0.25 N sodium iodide and 0.25 N sodium chloride mixed salt solution was electrodialed at 10 mA/cm² at 25.0 °C for 60 min. ^b C₈: octyl-. ^c C₁₂: dodecyl-. ^d C₁₆: hexadecyl-. ^f Benzyl groups: benzyl *N,N*-dimethylbenzylammonium groups.

than that in the solution. The nitrate ions, which migrated through the anion-exchange membrane to the polysoap layer on the concentrated side, are thought to selectively ion exchange with the layer on the concentrated side due to strong affinity with the polysoap layer. However, the current efficiency of the membrane with the layer on the concentrated side was 88%, though that of the membrane with the layer on the desalting side was greater than 99%. Because the layer is not covalently cross-linked, the layer could not completely reject the permeation of sodium ions unlike the cross-linked membrane (the concentration of sodium ions was high: 0.50 N).

Similarly, Figure 6 shows the change in P_{Cl}^F with the carbon number of the alkyl chains bonded to the pyridinium groups of the polymer (the layer faced the desalting side of the membrane). In general, fluoride ions are difficult to permeate through the anion-exchange membranes because fluoride ions are strongly hydrated as shown in Table 2. The permeation of fluoride ions was depressed by the formation of the layer, especially, with the increasing carbon number of the alkyl groups bonded to the pyridinium groups. The change in the P_{Cl}^F with the carbon number of the alkyl groups is similar to that of the sulfate–chloride mixed solution.

Table 4 shows the transport number of iodide ions relative to chloride ions in the membranes with the respective polysoap layer. The P_{Cl}^I increased from 4.56 to more than 30 by the formation of the polysoap layer (poly-4VP-C₁₂). Although the layer was unstable in the sodium iodide and sodium chloride mixed solution (gradually detached from the membrane during electrodialed), a very thin layer, several micrometers, was effective on the increase in the P_{Cl}^I . Because it is apparent from the Gibbs hydration energy (Table 2) that iodide ions are less hydrated, iodide ions would be selectively adsorbed on the polysoap layer and permeate through the membrane. On the other hand, it is well-known that iodide forms a charge-transfer complex with pyridine.²² Though it could not be confirmed in this research, the pyridine groups of the polysoap layer might form the charge-transfer complex with a small amount of iodide

TABLE 5: Change in Transport Number of Nitrate Ions Relative to Chloride Ions with Species of Hydrophobic Groups Bonded Covalently to a Surface of the Anion-Exchange Membrane^a

species of hydrophobic groups	without Reaction ^b	<i>n</i> -Butyl Groups ^c	<i>n</i> -Octyl Groups ^d	<i>n</i> -Dodecyl Groups ^e	Benzyl Groups ^f
P _{Cl} ^{NO₃}	1.78	1.98	2.16	2.65	3.59

^a Electrolysis of a 1:1 mixed salt solution of 0.25 N sodium nitrate and 0.25 N sodium chloride was carried out at 10 mA/cm² at 25.0 °C for 60 min facing the layer reacted with hydrophobic amine to the desalting side. ^b Without reaction: benzyl trimethylammonium groups. ^c Butyl groups: benzyl tri-*n*-butylammonium groups. ^d *n*-Octyl groups: Benzyl tri-*n*-octylammonium groups. ^e *n*-Dodecyl groups: benzyl tri-*n*-dodecylammonium groups. ^f Benzyl groups: benzyl *N,N*-dimethylbenzylammonium groups.

formed by the oxidation of iodide ions (air or light) and enhance the selective permeation of iodide ions.

b. Properties of Anion-Exchange Membranes with a Hydrophobic Layer Bonded Covalently to the Membrane Surface. Although a cationic polysoap layer on the anion-exchange membrane remarkably changed the permselectivity between anions without an increase in the electrical resistance of the membrane, the polysoap layer was detached from the membrane in some cases. It is desirable to form a hydrophobic layer on the membrane surface by a covalent bond. The characteristics of anion exchange membranes with a hydrophobic layer bonded covalently to the membrane surface are shown in Table 1. The electrical resistance of the anion-exchange membranes slightly increased with increasing carbon number of the alkyl chains (from butyl to dodecyl), and the resistance of the membrane with the *N,N*-dimethylbenzylamine layer was relatively high. The ion-exchange capacity of the membranes was about 10–16% lower than that of the membrane with benzyl trimethylammonium groups. The water content of the membranes with the hydrophobic layer was also lower than that of the membrane with benzyl trimethylammonium groups. Because the reaction to introduce benzyl trimethylammonium groups was sufficiently carried out in all membranes, the bulky and hydrophobic ammonium groups are thought to disturb the reaction of trimethylamine with the chloromethyl groups of the membrane. Table 5 shows the change in the transport number of the nitrate ions relative to the chloride ions with species of amines when electrodialed was carried out facing the layer with which the hydrophobic amines reacted to the desalting side. The $P_{Cl}^{NO_3}$ apparently increased with increasing carbon number of the alkyl groups bonded to the ammonium groups, though these bulky amines are thought to be sterically difficult to react with the chloromethyl groups of the inner part of the cross-linked membrane. On the basis of the degree of volume swelling,²³ the mean effective pore size of a copolymer of styrene and divinylbenzene is calculated to be 5.3 Å when the content of divinylbenzene is 10%.²⁴ On the other hand, the bond distance of C–C and C–N is 1.54 and 1.48 Å, respectively.²⁵ Because the bond angle is 110°, the length of the base of a trigonal pyramid (tri-*n*-butylamine, tri-*n*-octylamine, and tri-*n*-dodecylamine) is approximately 10, 20, and 30 Å, respectively. Apparently, these amines should react with the chloromethyl groups below 10 Å thickness on the membrane surface even if *n*-butyl ether (solvent) swells the copolymer membrane. In fact, the amount of the tertiary amines bonded to the membrane was too low to determine by conventional method to measure the ion-exchange capacity. Furthermore, after the membranes had been equilibrated with aqueous 1.0 N hydrogen bromide solution, the distribution of the bromide ions was

TABLE 6: Change in Transport Numbers of Various Anions Relative to Chloride Ions in Electrodialysis with a Direction of a Layer (Anion-Exchange Membrane with a Layer of Benzyl *N,N*-dimethylbenzylammonium Groups)^a

	ionic species:A	SO ₄ ²⁻	F ⁻	NO ₃ ⁻	Br ⁻
P _{Cl} ^A	without the layer	0.300	0.067	1.79	1.72
P _{Cl} ^A	a layer faced desalting side	0.040	0.048	3.59	2.44
	a layer faced concentrated side	0.136	0.066	2.36	2.05

^a Electrodialysis of a 1:1 mixed salt solutions of 0.25 N various sodium salt and 0.25 N sodium chloride was carried out at 10 mA/cm² at 25.0 °C for 60 min facing the layer reacted with benzyl *N,N*-dimethylbenzylammonium groups to the desalting side or the layer to the concentrated side.

analyzed by EPMA (electron probe microanalysis: a JEOL JXA-8621M instrument) concerning a cross-section of the membrane. A trace amount of bromide ions was detected on the membrane surface with the layer. From the molecular size, the *N,N*-dimethylbenzylamine can react with the chloromethyl groups of the inner part of the membrane.

The $P_{Cl}^{NO_3}$ of the membrane with a layer of *N,N*-dimethylbenzylamine exhibited the highest value though its HLB value is not the lowest among the amines used. This is due to a significant introduction of the hydrophobic amine on the membrane surface (water content of the membrane was also the lowest).

Table 6 shows the change in the transport numbers of anions relative to chloride ions when electrodialysis was carried out from the respective directions using the same membrane reacted with *N,N*-dimethylbenzylamine: facing the layer to the desalting side and then facing the layer to the concentrated side, together with those of the membrane reacted with only trimethylamine. The transport numbers of nitrate and bromide ions relative to chloride ions increased and those of the sulfate and fluoride ions decreased compared with the membrane without the layer in both cases. Especially, the transport numbers of the nitrate and bromide ions were high, and those of the sulfate and fluoride ions were low when the layer faced the desalting side, compared with the values facing the layer to the concentrated side. The hydrophobic layer of the desalting side significantly affected the change in the transport numbers of anions relative to chloride ions (though the transport numbers of the sulfate and nitrate ions relative to the chloride ions changed remarkably when the polysoap layer faced the concentrated side). The difference in the transport properties between the membrane having a layer covalently bonded and the membrane with the coated layer is thought to be due to the thickness of the layer and the existence of cross-linkage in the layer. In fact, the current efficiency of these membranes was greater than 99% when the layer was faced to both the desalting side and the concentrated side. The cross-linkage provides high fixed ion concentration to the layer.

Conclusions

The permselectivity of specific ions in the anion-exchange membranes in electrodialysis is governed by the difference in the mobility of each anion in the membrane phase and the affinity of the anions to the membrane. To change the affinity of the anions to the membrane, a hydrophobic layer, cationic polysoap layer or a layer having bulky quaternary ammonium groups, was formed on a membrane surface. Although the permeation of strongly hydrated anions compared with chloride ions was depressed and that of less-hydrated anions was enhanced by the cationic polysoap layer on the desalting side

or concentrated side, the layer on the concentrated side caused the current efficiency to decrease. The hydrophobic layer bonded covalently to the membrane surface gave a similar change in the permselectivity without a decrease in the current efficiency and an increase in electrical resistance. The permselectivity between two anions can be remarkably changed by controlling the affinity of the anions to the membrane on the membrane surface.

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