Modification of Transport Properties of Ion Exchange Membrane. XI. Electrodialytic Properties of Cation Exchange Membranes Having Polyethyleneimine Layer Fixed by Acid–Amide Bonding

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Synopsis

For the purpose of preparing the monovalent cation permselective membrane for electrodialysis, the membrane having $-SO_2Cl$ groups reacted with the polyethyleneimine to form a cationic polyelectrolyte layer on the membrane surface by using the acid–amide bonding. Reaction conditions, i.e., reaction temperature, concentration of the polyethyleneimine solution and the addition of tertiary amines to the polyethyleneimine solution, were all examined in detail. As a result, all the different kinds of polyethyleneimines were effective in obtaining the monovalent cation permselective membrane if the correct reaction conditions were selected. The durability of the monovalent cation permselectivity was evaluated in a continuous electrodialytic concentration of sea water. The monovalent cation permselectivity decreased gradually during the electrodialysis in the cation exchange membrane with the polyethyleneimine layer. Therefore, the cation exchange membrane with the cationic polyelectrolyte layer was further treated with crosslinking reagents, i.e., formaldehyde–hydrochloric acid, epichlorohydrin, etc. or other alkylating reagents. The monovalent cation permselectivity of the treated membranes was almost constant for two months. The crosslinking reaction of polyethyleneimine was more effective than alkylation in maintaining the high permselectivity constantly.

INTRODUCTION

As reported previously, when a cation exchange membrane has a thin cationic charged layer on the membrane surface, it shows specific permselectivity: The lower valent cations permeate more selectively than the higher ones, and the larger hydrated cations also permeate more selectively than the smaller hydrated ones.[1-8] Although the cationic charged layer formed by immersing the membrane into the cationic polyelectrolyte solution is effective on the specific permselectivity, it is desirable to form the cationic polyelectrolyte layer on the cation exchange membrane with a stable chemical bond from the viewpoint of durability for the specific permselectivity. It has been reported that the specific permselectivity of the cation exchange membrane was maintained in a long-term continuous electrodialysis when polyamino compounds of low molecular weight were reacted with the $-SO_2Cl$ groups on the membrane surface to form an acid–amide bonding.[9] However, the electric resistance of the membrane increased while the current efficiency decreased using this treatment. It is sug-

gested that the increase in the electric resistance and the decrease in current efficiency are due to the reaction of the low molecular weight polyamino compounds in the inner part of the membrane. In the previous paper, polyethyleneimines having high molecular weights were used in the reaction to yield cation exchange membrane with the excellent specific permselectivity, low electric resistance, and a high value of the current efficiency.[10]

In order to prepare cation exchange membranes with specific permselectivity in electrodialysis and with enough durability, in this work the reaction conditions and additional reactions were examined in detail by using the polyethyleneimines described in a previous paper.[10] The durability of the specific permselectivity of the resulting cation exchange membranes was evaluated in a long-term continuous electrodialytic tests using sea water.

EXPERIMENTAL

Materials

Membrane

In order to form the cationic polyelectrolyte layer on the cation exchange membrane by acid–amide bonding, chlorosulfonyl groups ($-SO_2Cl$) were introduced into the base membrane, which was mainly composed of a styrene-divinylbenzene copolymer and a PVC fabric. The base membrane was made by using the "paste method"[11-14] and the composition of the base membrane was the same as that of NEOSEPTA CL-25T, which is sulfonic acid type cation exchange membrane.

Reagents

Chlorosulfonic acid and carbon tetrachloride were of reagent grade obtained from Wako Pure Chemicals Industries Ltd. Table I shows the characteristics of the polyethyleneimines which were used in this work. In some of the reactions

TABLE I
Characteristics of Polyethyleneimines Used

Maker	Grade[a]	η_{sp}/C (1.0%)[b]	MW[c] (calcd)	MW[d]
Sogo Pharmaceutical Co. Ltd.	Everamine 210T (50%)	0.125	1920	5000
Dow Chemical Co.	Montrek 600 (33%)	0.494	7600	40,000–60,000
Chemirad Corp.	Low mol. weight (50%)	0.126	1940	2000–6000

[a] All polyethyleneimines were supplied as an aqueous solution. Number in the parenthesis shows concentration of them when they were supplied.

[b] Reduced viscosity was measured using a 1.0% aqueous solution at 25.0°C.

[c] Calculated by equation $\eta_{sp}/C = 2.8 \times 10^{-4} M_w$ (C = mol/L, 1.0 aqueous solution, at 25.0°C) proposed by Jones et al.[19]

[d] Molecular weight shown officially by each producer.

for the acid–amide bond formation, additives, such as triethanolamine, trimethylamine, and pyridine, were used in order to remove the hydrochloric acid which was generated from the reaction. These were obtained from Wako Pure Chemicals Industries Ltd.

In order to improve the durability of the specific permselectivity, the cation exchange membranes on which the polyethyleneimine layer had been formed reacted further with methyl iodide, propylene oxide, formaldehyde, and epichlorohydrin. The reagents for this purpose were also obtained from the Tokyo Kasei Kogyo Co., Ltd.

Reactions

The $-SO_2Cl$ groups were introduced into the base membrane by using a 1 : 2 mixture (wt ratio) of carbon tetrachloride and chlorosulfonic acid (reaction period 4 h; temperature 10°C).[9]

In the reaction of the $-SO_2Cl$-substituted membrane with the polyethyleneimines, pure water was used as a solvent. Thus, after reaction, the $-SO_2Cl$ membrane was immersed in an aqueous solution of polyethyleneimine under stirring, the membrane was washed with pure water and then immersed in an aqueous 2.5 N sodium hydroxide solution for 8 h to hydrolyze the $-SO_2Cl$ groups which remained in the interior of the membrane.

In order to form acid–amide bonding between the $-SO_2Cl$ groups of the membrane and the polyethyleneimines effectively, additives such as triethanolamine, trimethylamine, or pyridine were added to the polyethyleneimine solution.

The polyethyleneimine layer on the membrane surface was alkylated and/or crosslinked by usage of several adequate reagents to improve the durability of the monovalent cation permselectivity.

1. The reaction with formaldehyde: The cation exchange membrane with the polyethyleneimine layer was immersed into a solution of 2 parts of the aqueous 36% formaldehyde solution and 1 part of the aqueous 35% hydrochloric acid solution for 24 h at room temperature.

2. The reaction with propylene oxide: the cation exchange membrane with the polyethyleneimine layer was immersed in a 20% methanol solution of propylene oxide for 20 h at room temperature.

3. The reaction with epichlorohydrin: the cation exchange membrane with the polyethyleneimine layer was immersed in a 20% methanol solution of epichlorohydrin for 20 h at room temperature.

4. The reaction with methyl iodide: the cation exchange membrane with the polyethyleneimine layer was immersed in a 43% methanol solution of methyl iodide for 24 h at room temperature.

Before measurements, all of the cation exchange membranes with the polyethyleneimine layer were alternately equilibrated several times in the aqueous 1.0 N hydrochloric acid and in the aqueous 0.5 N sodium chloride solution and then were equilibrated in the salt solution to be used for the measurements.

TABLE II
Typical Composition of Sea Water[a] Used in This Work

Ionic species	Eq. (1)	$(A^+$ or $M^+/$ total A^- or $M^+)$
Cl^-	0.523	0.903
HCO_3^-, CO_3^{2-} [b]	0.0023	0.004
SO_4^{2-}	0.054	0.093
Na^+	0.443	0.764
K^+	0.0095	0.016
Ca^{2+}	0.0198	0.034
Mg^{2+}	0.108	0.186

[a] pH of sea water was about 8.2.

[b] Alkalinity of sea water (sea water was titrated with 0.1 N hydrochloric acid until methyl orange changed to red).

Measurements

The electrochemical properties of the resulting cation exchange membranes, i.e., monovalent cation permselectivity, current efficiency, electric resistance of the membrane, and transport number calculated from the membrane potential, were measured.

The monovalent cation permselectivity was evaluated by two methods: (1) batchwise electrodialysis of sea water by two compartment cell to estimate the degree of the monovalent cation permselectivity; (2) continuous electrodialytic concentration of sea water to evaluate the durability of the monovalent cation permselectivity. In the case of the two compartment cell, the same apparatus as reported in the previous paper was used together with the same electrodialyzer having two compartments (the effective membrane area was 2×5 cm^2 and the capacity of each compartment was 120 cm^3).[15] The electrodialysis was carried out at a current density of 20 mA/cm^2 for 60 min at 25.0°C under vigorous agitation (1700 rpm). On the other hand, the durability of the monovalent cation permselectivity was evaluated by a long-term continuous electrodialysis of sea water by using the multicompartment electrodialyzer, which was the modified filter press type reported in the paper[16] (the effective membrane area was 4×25 cm^2). A number of the compartments for the concentrated solution and compartments for sea water were formed by placing an alternating series of cation exchange membranes and anion exchange membranes between an anode (Pt electrode on Ti plate) compartment and a cathode (stainless steel plate) compartment. The anion exchange membrane used was NEO-SEPTA AVS-4T made by Tokuyama Soda Co., Ltd., which was permselective for chloride ions. The electrodialysis was continuously carried out at the current density of 20 mA/cm^2 at 30°C. The linear flow velocity of sea water to the membrane surface was 6.0 cm/s. The concentrated solution was sampled periodically after the composition of the concentrated solution had attained an equilibrium. The concentrated solution was composed of transported ions, osmotic water, and electrosmotic water, which permeated through the cation exchange membrane and the anion exchange membrane.

The sea water used in this work was obtained from Tokuyama Bay and the contents of main ions are shown in Table II. The sea water was treated with a mesh filter and a sand filter in order to remove particulate materials before use. Especially, in the case of the measurement by the two compartment cell, the treated sea water was further filtered with filter paper immediately before use. The pH of the sea water used was about 8.2.

As a measure of the monovalent cation permselectivity of the cation exchange membrane, the purity of brine was defined. In the case of measurement by the two compartment cell, the purity of brine was calculated from the following equation:

$$\text{purity of brine } (\%) = \frac{t_{\text{Na}} + t_{\text{K}}}{t^+} \times 100$$

where t_{Na} and t_{K} are the transport numbers of sodium ions and potassium ions in the membrane and t^+ is the transport number of total cations in the membrane. t^+ was calculated from the change in chloride ions in each compartment because Ag–AgCl electrodes were used in the cell. The sum of the concentration of sodium ions and that of potassium ions in each compartment was calculated by subtracting the concentrations of calcium ions and magnesium ions from those of the total cations. The concentrations of calcium ions and magnesium ions were analyzed by the conventional chelate titration method. Chloride ions were analyzed by Mohr method and sulfate ions were analyzed by the chelate back titration method using EDTA and barium chloride. The concentrations of HCO_3^- and CO_3^{2-} were determined by titration with 0.1 N hydrochloric acid until methyl orange changed to red.

In the case of the continuous electrodialytic concentration of sea water, the purity of brine was conventionally determined as follows:

$$\text{purity of brine } (\%) = \frac{[\text{Na}^+] + [\text{K}^+]}{[\text{A}^+]} \times 100$$

where $[\text{Na}^+]$ and $[\text{K}^+]$ are the concentrations of sodium ions and potassium ions in the sampled concentrated solution and $[\text{A}^-]$ is the concentration of total cations in the concentrated solution. The current efficiency of the two compartment cell was calculated from the change of the concentrations of the cations in each of the compartment and the amount of the electricity as measured with the aid of digital coulometer. In the case of the multicompartment filter press type electrodialyzer, the current efficiency was calculated from the amount of total cations in the concentrated solution obtained for a given period and the amount of electricity which passed for the same period (measured with a digital coulometer).

The electric resistance of the membrane was measured with 1000 cycle AC at 25.0°C after the membrane had been equilibrated with 0.500 N sodium chloride solution. The membrane potential was also measured in some of the membrane samples. The membrane was placed between a 0.500 N sodium chloride solution and a 2.500 N sodium chloride solution and the membrane potential was measured with the aid of calomel electrodes and a digital volt-meter with
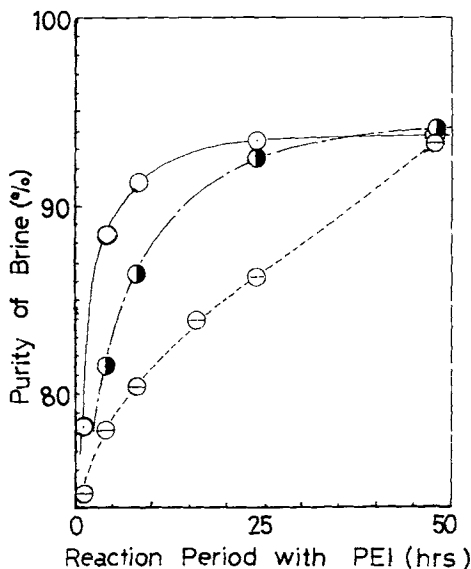
Fig. 1.   Increase in purity of brine with reaction period and temperature: (○) Chemirad low
MW at 20°C; (⊖) Everamine 210T at 20°C; (◑) Everamine 210T at 50°C. The reaction was carried
out by immersing the —SO$_2$Cl membrane into the aqueous 5% polyethyleneimine solution and
then into the hydrolysis solution.

a high impedance (10 MΩ). The transport number of sodium ions was calculated
by the reported equation.[17]

RESULTS AND DISCUSSION

Examination of the Reaction Conditions of —SO$_2$Cl
Membrane with Polyethyleneimines

In the previous paper, various species of polyethyleneimines were used to
form the cationic polyelectrolyte layer on the cation exchange membrane by
using an acid–amide bonding.[10] Electrochemical properties of the resulting
membranes changed according to the polyethyleneimine species. In this work,
three different types of polyethyleneimine were selected from the point of view
of the reactivity and the electrochemical properties of the membranes.

Though polyethyleneimine, Everamine 210T and Chemirad low MW, showed
almost the same value of the reduced viscosity, Chemirad low MW allowed the
membrane to achieve higher value of purity of brine more easily than Everamine
210T. Namely, Chemirad low MW was more reactive to —SO$_2$Cl membrane
than Everamine 210T was. It is thought that this is due to the difference in
the branching of the polyethyleneimines[18] (the aqueous 1.0% solution of Ev-
eramine 210T was slightly cloudy). Because the highly branching polyethyl-
eneimines have the advantage in being able to react with only the surface
portion of the membrane, it is expected that the resulting cation exchange
membranes will have a relatively low electric resistance with a high value of
monovalent cation permselectivity. In order to make the —SO$_2$Cl membrane

react with the branching polyethyleneimine such as Everamine 210T, the temperature of the reaction solution was changed. Figure 1 shows the effect of the reaction temperature on the purity of brine. Everamine 210T showed a high value of the purity of brine when the reaction was carried out at 50°C. Another factor to accelerate the reaction was the increase in the concentration of the polyethyleneimine solution. Figure 2 shows the relationship between the purity of brine and the concentration of the polyethyleneimine solution. Everamine 210T was more dependent on the concentration than Chemirad low MW. In any case, all kinds of polyethyleneimines were effective in increasing in the purity of brine through the acid–amide bond formation, if the suitable reaction conditions were selected according to the species.

Addition of Tertiary Amines to the Polyethyleneimine Solution

Although any species of polyethyleneimines were effective on increasing the purity of brine as mentioned before, the reaction temperature at 50°C was not adequate for the cation exchange membrane because the membrane contained PVC fabric which gives mechanical strength to the membrane. And the aqueous polyethyleneimine solution more than 10% was too viscous to react with the membrane. On the other hand, although a very small amount of polyethyleneimine molecules in the reaction solution was consumed by the reaction to form an acid–amide bonding with the $-SO_2Cl$ groups of the membrane, the value in the purity of brine was dependent on the concentration of the polyethyleneimine. After the introduction of the $-SO_2Cl$ groups into the base membrane, the adsorbed acids in the membrane could not be removed completely by washing with pure water. Hydrochloric acid is generated by the reaction of the acid–
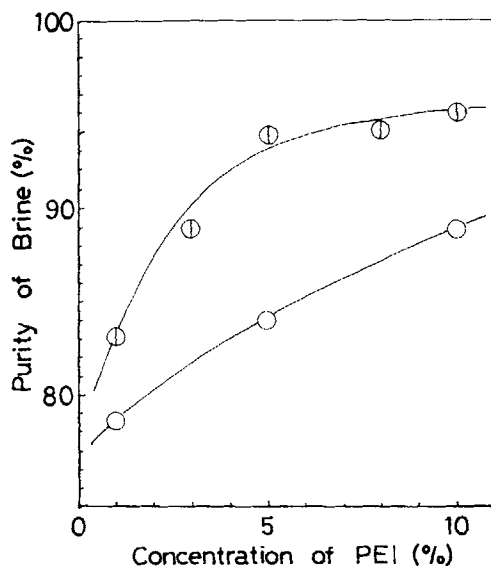

Fig. 2.   Effect of concentration of polyethyleneimines on purity of brine: (○) Everamine 210T; (⦿) Chemirad low MW. The reaction was carried out at room temperature for 19 h by immersing the $-SO_2Cl$ membrane into the aqueous polyethyleneimine solution of a given concentration and then into the hydrolysis solution.

TABLE III
Effect of Additives to Polyethyleneimine Solution on the Membrane Properties[a]

Run no.	Reaction solution	Concn (%)	Purity of brine (%)	R (Ω cm^2)[b]
1	Everamine 210T	10	88.8	4.3
2	Everamine 210T	10	94.5	9.6
	Triethanolamine	10		
3	Everamine 210T	10	90.5	6.6
	Triethanolamine	3		
4	Chemirad low MW	5	93.0	7.4
5	Chemirad low MW	5	96.0	16.5
	Triethanolamine	10		
6	Chemirad low MW	5	95.0	6.7
	Triethanolamine	3		

[a] After the —SO$_2$Cl membranes had been immersed into an aqueous reaction solution for 18 h at room temperature, the membranes with polyethylenimine layer were immersed into the aqueous 2.5 N sodium hydroxide solution for 8 h.

[b] The electric resistance of the membranes was measured by 1000 cycle AC after the membranes had been equilibrated with 0.5 N sodium chloride solution.

amide bond formation. The protonated primary and secondary amines do not react with the —SO$_2$Cl of the membrane and make the conformation of the polyethyleneimine molecules change in the solution. In order to catch the acids, chemicals, which do not react with the —SO$_2$Cl groups of the membrane, were added in the polyethyleneimine solution. The amines having tertiary amino groups are suitable for this purpose. Pyridine, triethanolamine, and trimethylamine were examined. Pyridine and trimethylamine deteriorated the membrane because of an abnormal irreversible swelling of the membrane. Table III shows the transport properties of the membranes when the triethanolamine was added to the aqueous polyethyleneimine solutions. The purity of brine was improved by addition of this tertiary amine in comparison with the membrane without triethanolamine.

Because triethanolamine has alcohol groups, this alcohol groups might react with the —SO$_2$Cl groups of the membrane and give the amphoteric properties to the cation exchange membrane. In order to confirm this possibility, the —SO$_2$Cl membranes were immersed into the aqueous 10% triethanolamine

TABLE IV
Transport Properties of the Membranes Reacted with Triethanolamine and Diethanolamine[a]

Reagent	Current efficiency (%)	Purity of brine (%)	R (Ω cm^2)
Triethanolamine	99.5	75.7	4.0
Diethanolamine	77.8	88.5	78

[a] After the —SO$_2$Cl membranes had been immersed into the aqueous 10% solution of each compound for 16 h at room temperature, the membranes were immersed into the aqueous 2.5 N sodium hydroxide solution.

solution and the aqueous 10% diethanolamine solution. Table IV shows the properties of both membranes. Although diethanolamine gave a high electric resistance and a low current efficiency to the membrane due to the acid–amide bond formation, triethanolamine did not have any effect on the membrane properties. Even though the ester bond was formed between triethanolamine and the $-SO_2Cl$ groups of the membrane, the hydrolysis of the ester bond occurs during the hydrolysis reaction by aqueous sodium hydroxide solution (the hydrolysis of the ester bond was confirmed by the measurement of IR spectrum of the membrane before and after immersing the $-SO_3CH_3$ membrane into the aqueous sodium hydroxide solution).[9] Because the purpose of this work is to prepare the monovalent cation permselective membrane with high durability, the continuous electrodialytic concentration of sea water was carried out to evaluate the durability. Figure 3 shows the change in the purity of brine of the continuous electrodialytic concentration of sea water. The purity of brine decreased gradually during the long term continuous electrodialysis. (In the case of the cation exchange membrane which the polyethyleneimine adsorbed or ion-exchanged with, the purity of brine decreased from 98% to about 73% after 2–3 weeks while under the same electrodialytic conditions. When the pH of sea water was maintained between 6.0 and 6.5, the purity of brine of the membrane which the polyethyleneimine adsorbed or ion-exchanged with decreased from 98% to 88% after 6 months.)

The Aklylation or (and) Crosslinking of the Polyethyleneimine Layer

The purity of brine in the cation exchange membranes on which the polyethyleneimine layer had been formed by acid–amide bonding decreased gradually
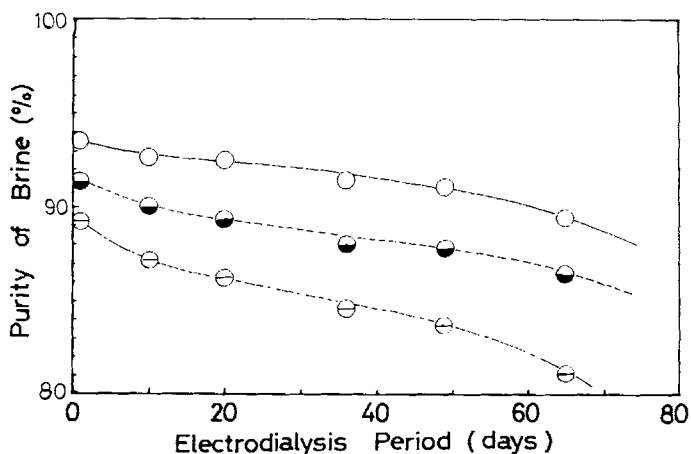

Fig. 3.   Change in purity of brine in continuous electrodialytic concentration of sea water: ($\bigcirc$) mixed solution of Everamine 210T (15%) and triethanolamine (10%); ($\ominus$) mixed solution of Chemirad low molecular weight (3%) and triethanolamine (10%); ($\ominus$) mixed solution of Everamine 210T (5%) and triethanolamine (10%). (i) The $-SO_2Cl$ membrane was immersed into the aqueous mixed solution of each polyethyleneimine and triethanolamine and then into the hydrolysis solution. (ii) pH of sea water used was about 8.2.

in a long-term continuous electrodialysis of sea water. The expected reasons for why the purity of brine decreased are as follows: (1) the polyethyleneimine molecules delaminate from the membrane surface as a result of the decomposition of the acid–amide bond during electrodialysis; (2) the dissociation of the weakly basic anion-exchangable groups on the membrane surface is depressed during electrodialysis because the pH of the sea water used was about 8.2. One method to protect the polyethyleneimine molecules from the delamination is to form a crosslinking between the polyethyleneimine molecules on the membrane surface. On the other hand, alkylation of weakly basic anion-exchangable groups in the polymer should be made to protect against the decrease in the dissociation of the polyethyleneimine layer in sea water. The cation exchange membrane with the polyethyleneimine layer was treated with methyl iodide, formaldehyde, propylene oxide, and epichlorohydrin to prove these deductions.

Figure 4 shows the relationships between the purity of brine and the electric resistance of the membrane when the membranes with the polyethyleneimine layer reacted with formaldehyde–hydrochloric acid or epichlorohydrin. Though there were some deviations, the cation exchange membranes having the reaction with formaldehyde–hydrochloric acid or epichlorohydrin showed a high value of purity in the brine with a low electric resistance in comparison to the membranes without the additional reaction. It is thought that the polyethyleneimine layer would become a tight and dense structure and the weakly basic groups changed into the strongly basic groups. Therefore, the electrostatic repulsion force against multivalent cations should become stronger on the membrane surface.
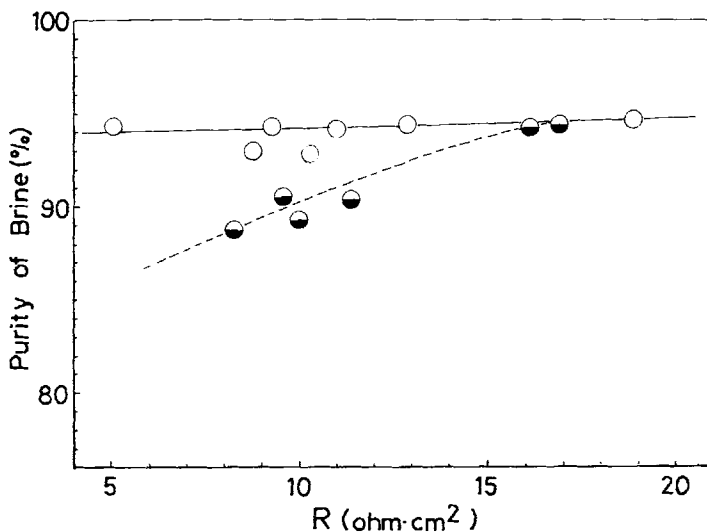

Fig. 4. Relationship between purity of brine and electric resistance of cation exchange membranes with polyethyleneimine layer: (◓) the $-SO_2Cl$ membrane was immersed into the aqueous mixed solution of polyethyleneimine and triethanolamine of various concentration and then into the hydrolysis solution; (○) the cation exchange membrane with polyethyleneimine layer reacted with formaldehyde–hydrochloric acid or epichlorohydrin. Polyethyleneimines used were Chemirad low MW, Everamine 210T, and Montrek 600.

Figure 5 shows the relationships between the electric resistance of the membrane and the transport number calculated from the membrane potential. In general, when the polyethyleneimine reacted with the $-SO_2Cl$ membrane under severe conditions, the cation exchange membrane showed the properties of both the bipolar ion exchange membranes and the amphoteric, i.e., the cation exchange membrane had the high electric resistance and the low current efficiency in the electrodialysis.[10] However, the membranes treated with crosslinking reagents show lower electric resistance than the membranes without the crosslinking reactions at the same transport number. As the transport number corresponds to the current efficiency in the electrodialysis, it is desirable that the amphoteric properties of the membrane were eliminated through the reaction with the crosslinking reagents.

Figure 6 shows the effect of species of the crosslinking reagents on the relationship between the purity of brine and the transport number. When the cation exchange membranes with the polyethyleneimine layer were treated with formaldehyde–hydrochloric acid or epichlorohydrin, the membranes showed less dependance of the purity of brine on the transport number as compared with the membranes without the crosslinking reactions. It is expected from these results that the cation exchange membranes treated with formaldehyde–hydrochloric acid or epichlorohydrin will show a high value of the purity of brine and also a high current efficiency in the electrodialysis. However, the cation exchange membranes treated with propylene oxide showed an abnormal behavior: The transport number decreased markedly when the purity of brine increased. At the same time, the electric resistance of all the membranes treated with propylene oxide was high (more than 15 Ω cm^2 when measured with 0.500
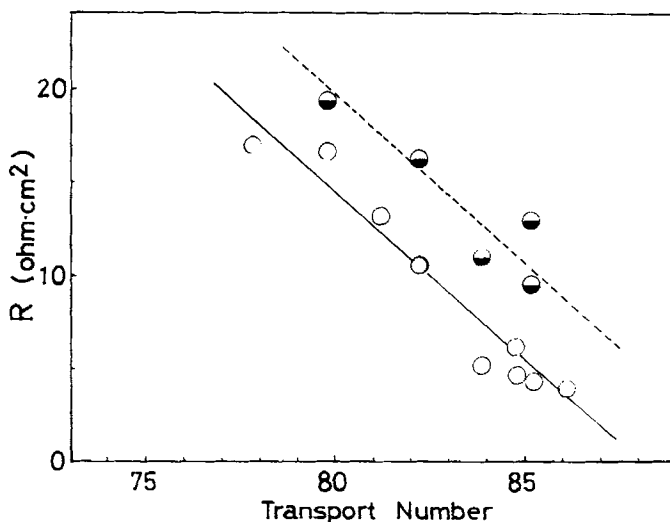

Fig. 5. Relationship between electric resistance and transport number of cation exchange membranes having polyethyleneimine layer with or without crosslinking reaction: (◖) the -SO$_2$Cl membrane was immersed into the aqueous mixed solution of polyethyleneimine and triethanolamine of various concentration and then into the hydrolysis solution; (○) The cation exchange membrane with polyethyleneimine layer reacted with formaldehyde-hydrochloric acid or epichlorohydrin. Polyethyleneimines used were Chemirad Low MW, Everamine 210T and Montrek 600.
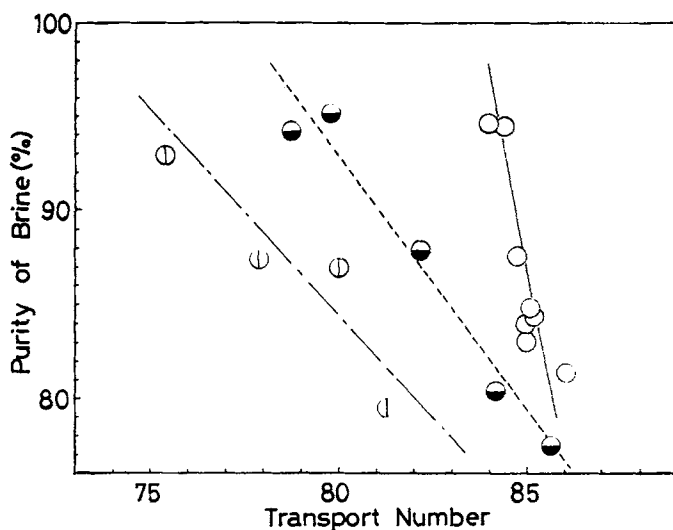
Fig. 6. Effect of crosslinking reaction on relationship between purity of brine and transport number: (◒) without crosslinking reaction; (○) immersed into formaldehyde–hydrochloric acid or epichlorohydrin; (◐) immersed into propylene oxide solution. (i) After the —SO₂Cl membrane had been immersed into the aqueous mixed solution of polyethyleneimine and triethanolamine of various concentration and then into the hydrolysis solution, crosslinking reaction was carried out by immersing the membrane into the solution of each crosslinking reagent. (ii) Polyethyleneimines used were Chemirad low MW, Everamine 210T, and Montrek 600.

N sodium chloride solution). It is thought that the propylene oxide would react easily with amino groups in the polyethyleneimine layer and give more hydrophobic properties to the layer, through which cations would not be able to permeate easily.

Figure 7 shows the durability in the purity of brine by using the cation exchange membranes with the polyethyleneimine layer which was treated with the crosslinking reagents or the alkylating in a long-term continuous electrodialytic concentration of sea water. Two kinds of polyethyleneimines and two kinds of reagents were compared (the polyethyleneimine layer was formed in the presence of triethanolamine). Figure 7 means that the durability in the purity of brine was mainly dependent on the species of polyethyleneimines used, and that the crosslinking reaction (reacted with formaldehyde–hydrochloric acid) was more effective than the alkylation of the amino groups (reacted with methyl iodide) on the durability of the purity of brine.

If the suitable polyethyleneimine species, which was dependent on the composition of the base membrane, were selected for the reaction of the acid–amide bond formation and a crosslinkage was formed on the polyethyleneimine layer, the high value of the purity of brine can be maintained in a long-term continuous electrodialytic concentration of sea water.

CONCLUSION

In order to give monovalent cation permselectivity to the cation exchange membrane permanently, polyethyleneimines reacted with the membranes hav-
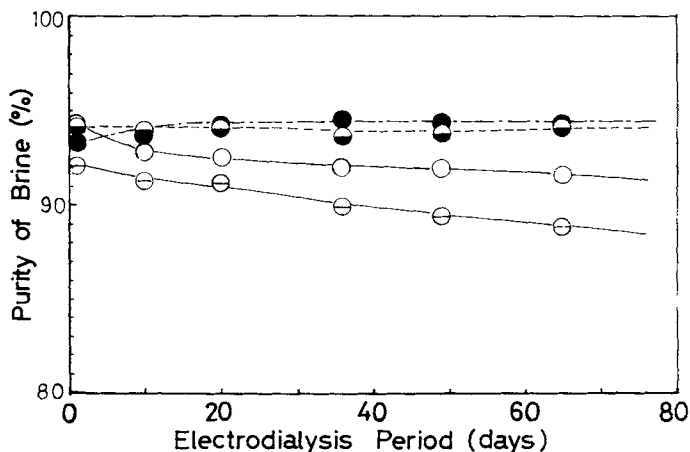
Fig. 7. Change of purity of brine in continuous electrodialytic concentration of sea water: (●) after the —SO₂Cl membrane had been immersed into the aqueous mixed 5% Chemirad low MW and 10% triethanolamine solution for 18 h and then into the hydrolysis solution, the membrane reacted with formaldehyde–hydrochloric acid; (◐) after the —SO₂Cl membrane had been immersed into the aqueous mixed 5% Chemirad low MW and 10% triethanolamine solution for 18 h and then into the hydrolysis solution, the membrane reacted with methyl iodide; (○) after the —SO₂Cl membrane had been immersed into the aqueous mixed 10% Everamine 210T and 10% triethanolamine solution for 18 h and then into the hydrolysis solution, the membrane reacted with formaldehyde–hydrochloric acid; (⊖) after the —SO₂Cl membrane had been immersed into the aqueous mixed 10% Everamine 210T and 10% triethanolamine for 18 h and then into the hydrolysis solution, the membrane reacted with methyl iodide.

ing the —SO₂Cl groups to form acid–amide bonding on the membrane surface and then the remaining —SO₂Cl groups were hydrolyzed by a sodium hydroxide solution. The reaction conditions with the polyethyleneimines, such as the reaction temperature, the concentration of the polyethyleneimine solution, and the addition of tertiary amines to the polyethyleneimine solution, were examined for the purpose of preparing cation exchange membranes with a high value of the purity of brine. The purity of brine was improved by the addition of triethanolamine to the polyethyleneimine solution, with the result being that the purity of brine was maintained at 85% or higher for more than 2 months in a continuous electrolytic concentration of sea water (the pH of sea water was about 8.2). However, the purity of brine decreased gradually during the electrodialysis.

The cation exchange membranes with the polyethyleneimine layer reacted further with the crosslinking reagents or alkylating reagents. The cation exchange membranes treated with formaldehyde–hydrochloric acid or methyl iodide showed a constant value in the purity of brine at more than 90% for 2 months in the continuous electrolytic concentration of sea water with a pH of 8.2.

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