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Modification of Transport Properties of Ion-Exchange Membranes. XIV. Introduction of $-\text{SO}_2\text{Cl}$ Groups with $\text{ClSO}_3\text{H}-\text{H}_2\text{SO}_4$ Mixture into Membrane and Formation of Acid-Amide Bonding Between Polyethyleneimines and $-\text{SO}_2\text{Cl}$ Groups

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MODIFICATION OF TRANSPORT PROPERTIES OF ION-EXCHANGE MEMBRANES. XIV. INTRODUCTION OF —SO₂Cl GROUPS WITH ClSO₃H—H₂SO₄ MIXTURE INTO MEMBRANE AND FORMATION OF ACID-AMIDE BONDING BETWEEN POLYETHYLENEIMINES AND —SO₂Cl GROUPS

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ABSTRACT

Sulfonyl chloride groups and sulfonic acid groups were introduced into a membranous copolymer of styrene and divinylbenzene by the reaction of ClSO₃H—H₂SO₄. The formation ratio of sulfonyl chloride groups versus sulfonic acid groups increased with increasing reaction time and the concentration of ClSO₃H in the mixture. Sulfonyl chloride groups were stable for 1 week in pure water at low temperature, and the surface of the chlorosulfonated membranes reacted with polyethyleneimines. However, a higher content of sulfonyl chloride groups resulted in a higher electrical resistance of the membranes whereas a lower content of the groups resulted in excellent permselectivity for monovalent cations versus the multivalent ones and a low electrical resistance of the membranes.

INTRODUCTION

Ion-exchange membranes have been widely used in various industries: the electro-dialytic concentration of seawater to produce edible salt, diffusion dialysis to recover acid from waste acid solution, electrolysis of sodium chloride solution, etc. Especially in the case of seawater concentration, monovalent ion permselectivity of the membrane against multivalent ones and low electrical resistance of the membranes are required to save energy and to avoid scaling problems associated with alkali earth metal compounds such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

It was reported that cetyldimethylbenzylammonium cation reduces the rate of $\text{Na}^+ - \text{Na}^+$ exchange between the Na^+ form of a styrene-based sulfonic-acid-type cation exchanger and an aqueous solution of a sodium salt [1]. A composite membrane in which a cation- and an anion-exchange membrane were stuck together performed monovalent ions permselectivity versus multivalent ones [2]. In order to prepare an excellent monovalent cation permselective membrane, various methods concerning the surface modification of a cation-exchange membrane were studied [3]. One method was to adsorb or ion-exchange cationic polyelectrolytes such as polyethyleneimines and poly-*N*-methyl-4-vinylpyridinium chloride on the surface of the cation-exchange membranes [4-12]. Polyethyleneimines were absorbed or ion exchanged with the sulfonic acid groups on the membrane surface. However, monovalent cation permselectivity was gradually lost during long-term electro-dialysis. Therefore, it is desired to form a stable chemical bonding between the cationic polyelectrolyte and a cation-exchange membrane.

The second method was the formation of acid-amide bonding between sulfonyl chloride groups and polyethyleneimines on the surface of the membranes [13-16]. These membranes exhibited high monovalent cation permselectivity and also higher electrical resistance of membranes. In this case sulfonyl chloride groups were introduced by the reaction of chlorosulfonic acid and carbon tetrachloride with the precursor membranes which were composed of the copolymer of styrene and divinylbenzene. Since the reaction of a higher concentration of chlorosulfonic acid with the membranous copolymer is severe, the polymer matrix of the membrane might partially decompose. Further, it was difficult to maintain the purity of the chlorosulfonic acid at higher levels because chlorosulfonic acid is liable to decompose to sulfuric acid under high air humidity.

The third method was to utilize precursor membranes composed of the styrene sulfonyl chloride and divinylbenzene copolymer [17]. Although these membranes showed excellent permselectivity, styrene sulfonyl chloride was an expensive compound to produce.

Therefore, we tried to introduce sulfonyl chloride groups into the precursor for cation-exchange membranes using moderate reaction conditions, that is, by use of a mixture of a lower concentration of chlorosulfonic acid in sulfuric acid. Since sulfonyl chloride groups are functionally active, it was postulated that there was a sufficient concentration of sulfonyl chloride groups in the membranes to form acid-amide bonding with the polyethyleneimines and produce excellent monovalent permselective membranes. In this work the relationship between the sulfonyl chloride groups content in the membranes and the electrochemical properties of the resultant membranes were studied in detail.

EXPERIMENTAL

Materials

Membrane

The precursor membrane for the cation-exchange membrane was synthesized by the "paste method," that is, copolymerization of styrene and divinylbenzene in the presence of polyvinyl chloride powder using a cloth support material [18-22]. The precursor membranes were provided by the Tokuyama Corporation. The membrane thickness was about 0.11 mm.

Reagents

Chlorosulfonic acid, sulfuric acid, sodium hydroxide, sodium chloride, and calcium chloride were reagent grade. They were obtained from Wako Pure Chemical Industries Co. Table 1 shows the characteristics of the polyethyleneimines used in this work.

Reaction

The precursor membranes ($7 \times 40 \text{ cm}^2$, 2 sheets) were reacted with about a 500-g mixture of chlorosulfonic acid and sulfuric acid at room temperature for 30-60 minutes. After chlorosulfonation, the membranes were successively washed with concentrated sulfuric acid, 80% sulfuric acid, 40% sulfuric acid, and pure water without the generation of heat. The membranes were then stored in pure water at about 4°C.

Surface Modification of the Membrane

In order to form a cationic polyelectrolyte layer on the surface of the membrane, membranes containing sulfonyl chloride groups were immersed in an aqueous 10% polyethyleneimine solution at room temperature.

Hydrolysis

After the precursor membranes had been treated with an aqueous polyethyleneimines solution, the membranes were immersed in an aqueous 1 or 2.5 N NaOH

TABLE 1. Characteristics of Polyethyleneimines

Maker	Grade ^a	η_{sp}/C (1.0%) ^b	MW ^c	MW ^d
Sogo Pharmaceutical Co.	Everamine 210T (50%)	0.125	1,920	5,000

^aPolyethyleneimines were supplied as an aqueous solution. The number in parentheses shows the concentration when they were supplied.

^bReduced viscosity was measured in a 1.0% aqueous solution at 25.0°C.

^cCalculated by $\eta_{sp}/C = 2.8 \times 10^{-4} \text{ MW}$ ($C = \text{mol/L}$, 1.0% aqueous solution, 25.0°C), proposed by G. D. Jones et al.

^dMolecular weight supplied by maker.

solution to hydrolyze any remaining sulfonyl chloride groups at room temperature. The conditions of the hydrolysis reaction were examined to obtain a membrane with a low electrical resistance.

Measurements

The content of sulfonic acid groups ($-\text{SO}_3\text{H}$) and sulfonyl chloride groups ($-\text{SO}_2\text{Cl}$) in the precursor membrane were measured as follows. There were two types of functional groups in the membrane after chlorosulfonation, that is, sulfonyl chloride groups and sulfonic acid groups. Although hydrogen ions of the sulfonic acid groups ion-exchange with other cations such as sodium ions, sulfonyl chloride groups are not ion-exchange sites.

The precursor membranes ($5 \times 5 \text{ cm}^2$, 2 sheets) were washed several times with pure water at room temperature until the water remained neutral. The membranes were then immersed in 100 mL of an aqueous 3 N NaCl solution, and the amount of sulfonic acid groups was estimated from the concentration of H^+ ions exchanged by Na^+ ions which were measured by an acid-base titration. In order to measure the amount of sulfonyl chloride groups remaining in the membrane, the membranes were washed several times with pure water and the sulfonyl chloride groups in the membranes were then hydrolyzed into sulfonic acid groups with 100 mL of an aqueous 0.1 N NaOH solution for 1 week at room temperature. The amount of chloride ions which were the by-product of the hydrolysis reaction was measured by Mohr's method using silver nitrate. The content of sulfonylchloride groups in the membrane was estimated from the amount of chloride ions. The ion-exchange capacity of the membrane was measured by conventional methods. The content of sulfonyl chloride groups in the membrane is defined as

$$\begin{aligned} & [-\text{SO}_2\text{Cl}] / ([-\text{SO}_2\text{Cl}] + [-\text{SO}_3\text{H}]) \\ & = ([\text{ion-exchange capacity}] - [-\text{SO}_3\text{H}]) / [\text{ion-exchange capacity}] (\%) \end{aligned}$$

where $[-\text{SO}_2\text{Cl}]$ is the sulfonyl chloride groups in the membrane (meq/dry membrane) and $[-\text{SO}_3\text{H}]$ is the sulfonic acid groups in the membrane (meq/dry membrane).

The electrochemical properties of the resulting cation-exchange membranes, i.e., electrical resistance of the membrane and monovalent cation permselectivity, were measured. The electrical resistance of the membranes was measured with a 1000 cycle AC signal at 25°C after the membrane had been equilibrated with 0.500 N sodium chloride solution.

The monovalent cation permselectivity was evaluated using measurement of the relative transport number of calcium ions to sodium ions. Cation-exchange membranes which had been modified by polyethyleneimines were used in the electro dialysis. A membrane was placed in the two-compartment cell, and both compartments were filled with a mixed salt solution composed of 0.25 N sodium chloride and 0.25 N calcium chloride (the effective membrane area was $2 \times 5 \text{ cm}^2$). The electro dialysis was carried out at a current density of 20 mA/cm^2 for 60 minutes at 25°C with vigorous stirring at $1500 \pm 100 \text{ rpm}$. The relative transport number of calcium ions to sodium ions is defined as follows:

$$P_{\text{Na}}^{\text{Ca}} = (t_{\text{Ca}}/t_{\text{Na}})/(C_{\text{Ca}}/C_{\text{Na}})$$

where t_{Ca} and t_{Na} are the transport numbers of calcium and sodium ions, respectively, in the membrane, and C_{Ca} and C_{Na} are the concentrations of calcium and sodium ions, respectively, in the solution before electro dialysis.

RESULTS AND DISCUSSION

Introduction of Sulfonyl Chloride Groups in the Precursor Membrane

The precursor membranes were reacted with a mixture of chlorosulfonic acid and sulfuric acid at room temperature for 30–60 minutes. The total amount of ion-exchange groups (sulfonic acid groups) and precursor ion-exchange groups (sulfonyl chloride ones) was introduced within 30 minutes with 40–98% of the chlorosulfonic acid in sulfuric acid at room temperature. It was thought that the sulfonyl chloride groups are not formed by the reaction of a lower concentration mixture of chlorosulfonic acid and a higher concentration of sulfuric acid, and also that sulfonyl chloride groups are easily decomposed into sulfonic acid groups in water at room temperature. However, it was found that sulfonyl chloride groups were comparatively stable during measurement of the content and electrical resistance of the membranes. These results will be discussed later.

The sulfonyl chloride groups content in the membranes increased with the reaction time as shown in Fig. 1. The sulfonic acid groups were initially introduced into the copolymer of styrene and divinylbenzene, and then the sulfonic acid groups

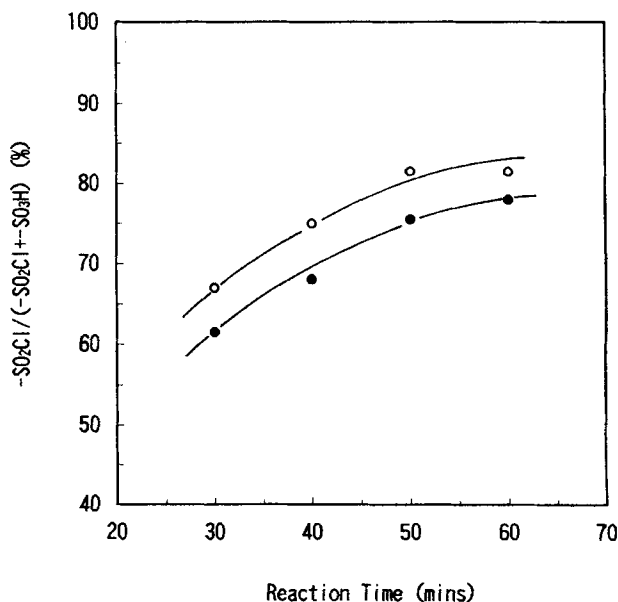
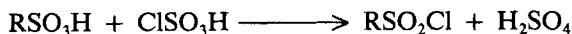


FIG. 1. Effect of reaction time on the content of sulfonyl chloride groups in membranes: (○) $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4) = 64.3\%$; (●) $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4) = 55.6\%$ at room temperature.

were converted into sulfonyl chloride groups as shown in Scheme 1 [23]. However, a long chlorosulfonation time produced membranes with inferior properties, e.g., destruction of the membrane matrix accompanied by brown coloration. Therefore, an appropriate reaction time should be selected from the viewpoint of the electrochemical and mechanical properties of the membranes. The proper reaction period was 30-60 minutes.



SCHEME 1.

Since the ion-exchange groups, that is, the sulfonic acid groups, decreased with the formation of sulfonyl chloride groups, the electrical resistance of the membranes increased with increasing reaction time of the chlorosulfonation as shown in Fig. 2.

After the precursor membranes reacted with a 38-95% concentration of chlorosulfonic acid in sulfuric acid at room temperature for 1 hour, the content of sulfonyl chloride groups was measured. Figure 3 shows the relationship between $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H})$ in the precursor membranes and the concentration

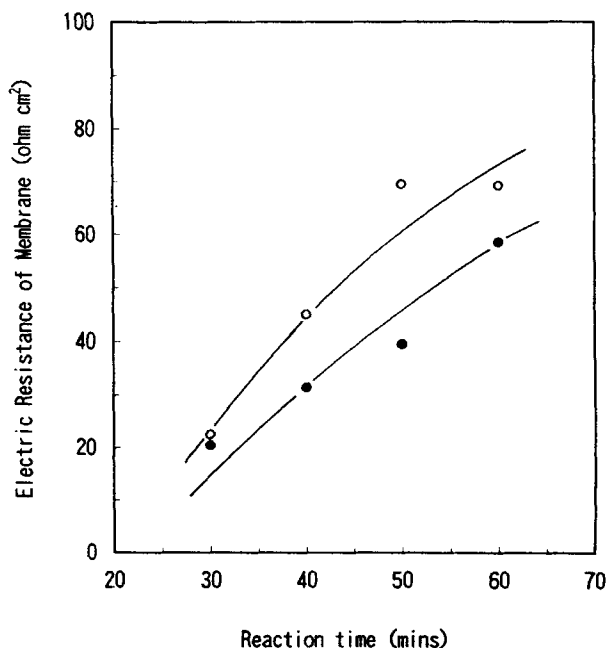


FIG. 2. Effect of reaction time on electric resistance of cation-exchange membranes: (○) $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4) = 64.3\%$; (●) $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4) = 55.6\%$ at room temperature.

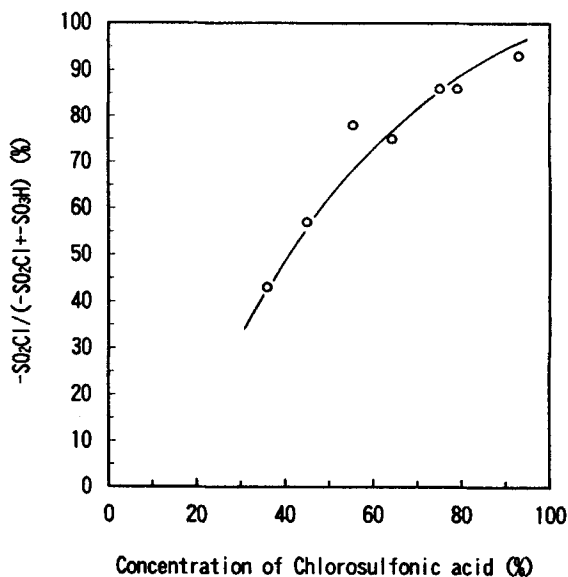


FIG. 3. Relationship between $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H})$ in membranes and concentration of chlorosulfonic acid: $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4)$.

of chlorosulfonic acid. The content of sulfonyl chloride groups increased with an increase in the concentration of chlorosulfonic acid, which was almost proportional to the concentration of chlorosulfonic acid.

Figure 4 shows the relationship between the electrical resistance of the membranes and $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H})$ in the membranes. Electrical resistance of the membranes increased with increasing content of $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H})$. Therefore, the proportion of sulfonyl chloride groups in the membranes could be estimated from measurement of the electrical resistance of the membranes.

Stability of Sulfonyl Chloride Groups in the Precursor Membrane

In order to fix the cationic polyelectrolyte layer on the surface of the cation-exchange membrane, the content of sulfonyl chloride groups in the membranes is an important factor, especially to prepare acid-amide bonding with the polyethyleneimines. Therefore, the stability of the sulfonyl chloride groups was essential to produce excellent membranes. After chlorosulfonation had been carried out using 94.2% chlorosulfonic acid in sulfuric acid, the stability of the sulfonyl chloride groups was examined by immersing the chlorosulfonated membranes in various solutions at room temperature, i.e., an aqueous 1 N HCl, 1 N H_2SO_4 and 0.5 N NaCl solutions. The results are shown in Fig. 5. The electrical resistance of the membranes gradually decreased with increasing immersion time. Sulfonyl chloride groups decomposed into sulfonic acid groups and hydrogen chloride. Although there was no large difference in the electrical resistance of the membranes among these aqueous acids or salt solutions at room temperature, the membrane maintained almost the initial electrical resistance at 4°C in pure water for 6 days.

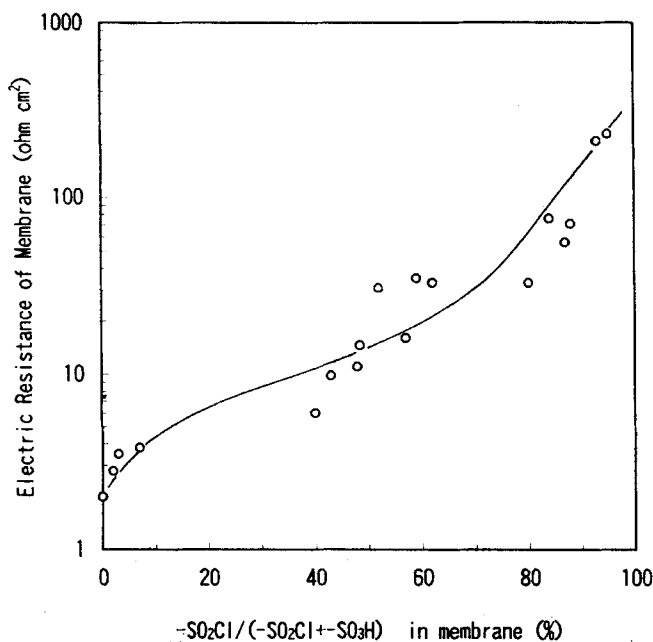


FIG. 4. Relationship between $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H})$ in membranes and electric resistance of the membranes.

Figure 6 shows the ratios of the content of sulfonylchloride groups and sulfonic acid groups versus the ion-exchange capacity of the membrane while the membrane was stored at 4°C in pure water. Chlorosulfonation was carried out using 54.2% chlorosulfonic acid in sulfuric acid. The content of sulfonyl chloride groups was estimated by measuring the amount of chloride ion after the sulfonyl chloride groups in the membrane were hydrolyzed with an aqueous 0.1 N NaOH solution. It was found that the content of sulfonyl chloride groups in the membrane slightly decreased from 76 to 62% over 7 days. These results agree with the small decrease in electrical resistance of a membrane stored at 4°C in pure water as shown in Fig. 5. The sum of sulfonyl chloride groups and sulfonic acid groups in the chlorosulfonated membrane was nearly equal to the ion-exchange capacity of the membrane. Therefore, it was determined that sulfonyl chloride groups in the membrane are considerably stable at 4°C in pure water for 7 days. Thus, chlorosulfonated membranes were stored at 4°C in pure water.

Hydrolysis

Hydrolysis conditions were examined before the chlorosulfated membranes were treated with the polyethyleneimines. The membranes were immersed in an aqueous NaOH solution to hydrolyze any remaining sulfonyl chloride groups. When the sulfonyl chloride groups were completely converted into sulfonic acid groups, the electrical resistance of the membranes was about 2 ohm·cm². The

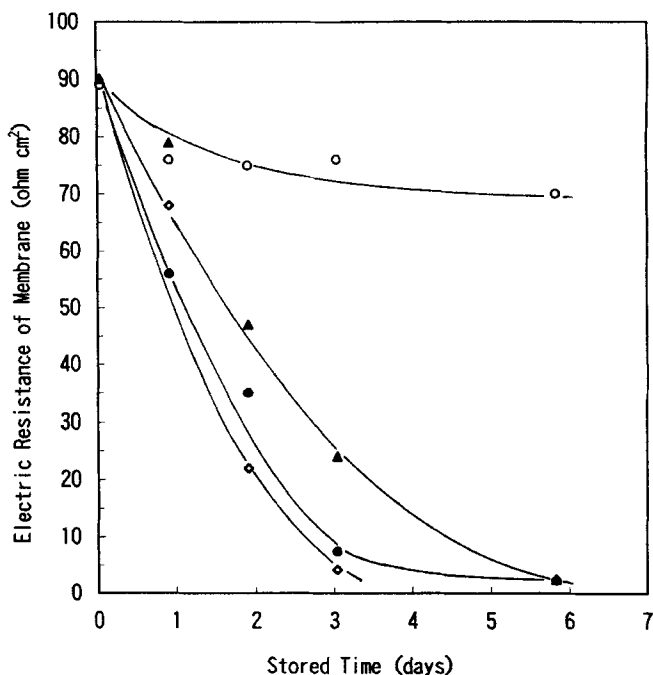


FIG. 5. Stability of sulfonyl chloride groups of membranes in various media: (○) pure water at 4°C; (▲) 1 N HCl; (●) 1 N H₂SO₄; (◇) 0.5 N NaCl at room temperature. Chlorosulfonation reaction conditions were ClSO₃H/(ClSO₃H + H₂SO₄) = 94.2% for 1 hour at room temperature.

hydrolysis reaction conditions were examined under 1 NaOH and 2.5 NaOH at room temperature for 1–4 hours. When the membranes reacted with higher chlorosulfonic acid concentrations (99.5 and 79.3%), the hydrolysis reaction needed 4 hours under an aqueous 1 N NaOH solution as shown in Fig. 7(a). On the other hand, in lower concentrations of chlorosulfonic acid solution (52.6 and 36.2%) the hydrolysis reaction were easily performed within 2 hours in an aqueous 1 N NaOH solution. In the case of an aqueous 2.5 N NaOH solution, the highly chlorosulfonated membranes were easily hydrolyzed into sulfonic acid groups within 2 hours as shown in Fig. 7(b). Thus, the chlorosulfonated membranes were hydrolyzed under an aqueous 2.5 N NaOH solution for 2 hours at room temperature.

The Reaction of Sulfonyl Chloride Groups with Polyethyleneimines

In order to prepare monovalent permselective cation-exchange membranes, polyethyleneimines were fixed on the surface of the membranes by acid–amide bonding between the sulfonyl chloride groups and polyethyleneimines. The appropriate content of the sulfonyl chloride groups in the membranes was investigated after measuring the electrochemical properties of the membranes. An aqueous 10% polyethyleneimine 210T solution was reacted with chlorosulfonated membranes in

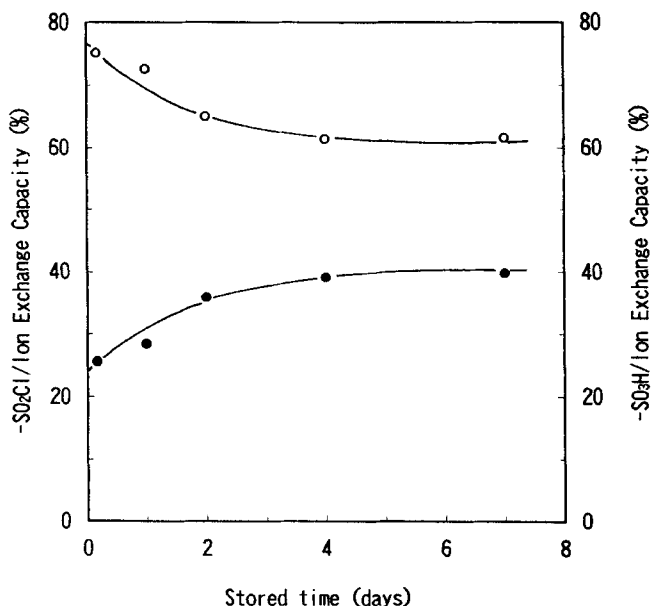


FIG. 6. Stability of sulfonyl chloride groups and sulfonic acid groups in the chlorosulfonated membrane at 4°C in pure water: (○) $-\text{SO}_2\text{Cl}/(\text{ion-exchange capacity})$; (●) $-\text{SO}_3\text{H}/(\text{ion-exchange capacity})$. Chlorosulfonation reaction conditions were $\text{ClSO}_3\text{H}/(\text{ClSO}_3\text{H} + \text{H}_2\text{SO}_4) = 54.2\%$ for 1 hour at room temperature.

which the sulfonyl chloride groups were 51 and 91%. Membranes containing 51% of the sulfonyl chloride groups exhibited a low membrane electrical resistance of about $4 \text{ ohm} \cdot \text{cm}^2$ as shown in Fig. 8. The electrical resistance of the membranes did not increase with the reaction time. On the contrary, in the 91% chlorosulfonated membranes, the electrical resistance of the membranes increased with an increase in the reaction time. The greater the sulfonyl chloride group content in the membranes, the more was the acid—amine bonding between the sulfonyl chloride groups and polyethyleneimines. The electrical resistance of the membranes then increased with an increase in the reaction time, and the ion-exchange capacity of the membranes decreased.

Permselectivity ($P_{\text{Na}}^{\text{Ca}}$) of the membranes was determined as the relative transport number between calcium ions and sodium ions. Cation-exchange membranes with sulfonic acid groups exhibit about a 2.4 permselectivity ($P_{\text{Na}}^{\text{Ca}}$). The relationship between permselectivity and the proportion of sulfonyl chloride groups in the membranes was investigated. Membranes which contained 91% of the sulfonyl chloride groups needed 3 days for the polyethyleneimine 210T reaction period to reach a high permselectivity at room temperature, as shown in Fig. 9. However, membranes which contained 51% sulfonyl chloride groups showed a high permselectivity value, 0.2, after 1 day of reaction. The higher the sulfonyl chloride group concentration in a membrane, the longer the reaction time required. It is thought that since a large portion of the primary and secondary amines in polyethyleneimines react with sulfo-

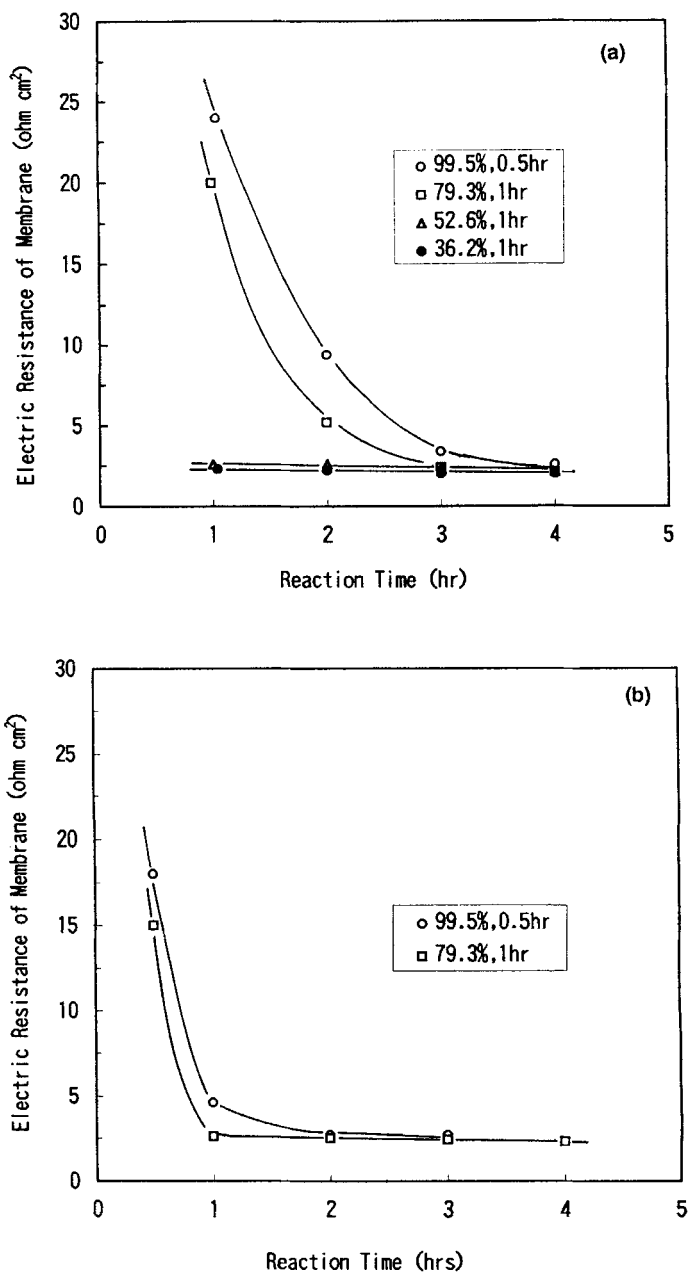


FIG. 7. Hydrolysis of chlorosulfonated membranes by (a) an aqueous 1 N NaOH solution and (b) an aqueous 2.5 N NaOH solution.

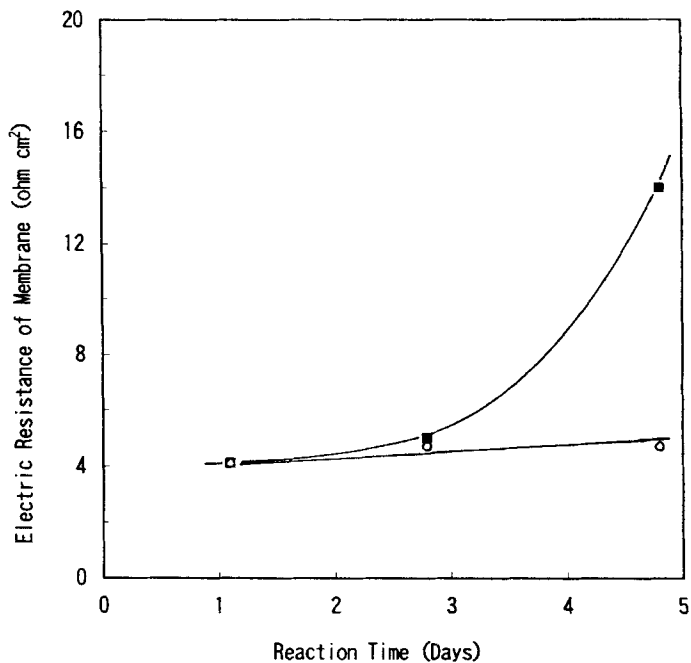


FIG. 8. Effect of reaction time of 10% polyethyleneimine with chlorosulfonated membranes on electric resistance of membrane: (○) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 51\%$; (■) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 91\%$.

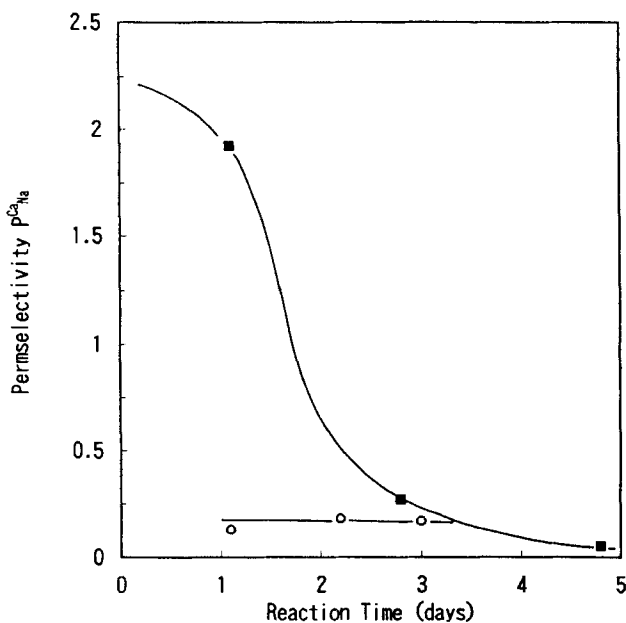


FIG. 9. Effect of reaction time of 10% polyethyleneimine with chlorosulfonated membranes on monovalent cation permselectivity: (○) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 51\%$; (■) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 91\%$.

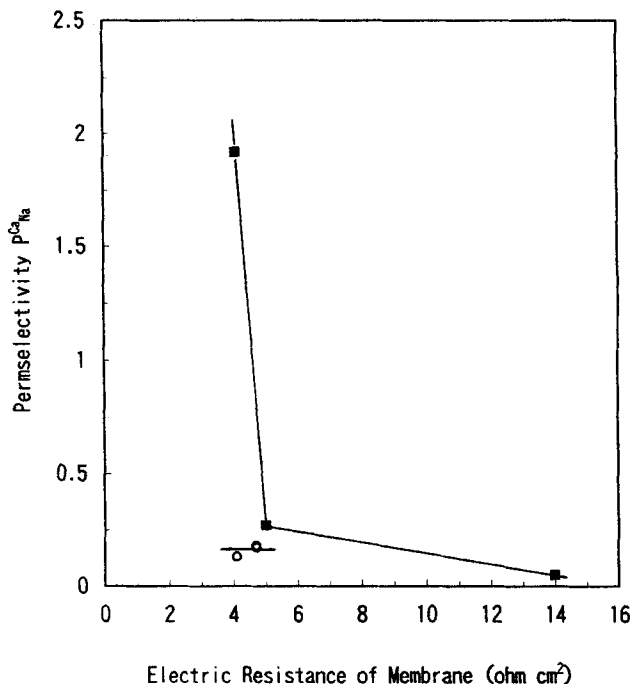


FIG. 10. Relationship between monovalent cation permselectivity and electric resistance of membrane: (○) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 51\%$; (■) $-\text{SO}_2\text{Cl}/(-\text{SO}_2\text{Cl} + -\text{SO}_3\text{H}) = 91\%$.

nyl chloride groups to form acid—amide bonding, a few amino groups remained on the surface of the membranes. Therefore, the formation of a thick acid—amide layer is required to obtain high permselectivity on the surface of membranes, and that causes a decrease in the ion-exchange capacity and a higher electrical resistance of the membranes.

Figure 10 shows the relationship between permselectivity ($P_{\text{Na}}^{\text{Ca}}$) and electrical resistance of membranes. When the content of sulfonyl chloride groups in the membranes is high, the electrical resistance of the resulting membrane is high at the same permselectivity value.

In order to prepare high performance membranes, a smaller chlorosulfonic acid concentration was suitable in order to obtain a higher permselectivity ($P_{\text{Na}}^{\text{Ca}}$) and a lower electrical resistance of the membranes. It is easy to control the concentration of chlorosulfonic acid in sulfuric acid in the lower concentration range.

CONCLUSIONS

1. Sulfonyl chloride groups were introduced into the precursor membranes by the reaction of a mixture of chlorosulfonic acid and sulfuric acid. The content of sulfonyl chloride groups was almost proportional to the chlorosulfonic acid

concentration. Sulfonyl chloride groups increase with an increase in reaction time. The sulfonyl chloride groups are stable in pure water at 4°C for about 1 week.

2. Chlorosulfonated membranes react with polyethyleneimines and form a cationic polyelectrolyte layer by means of acid–amide bonding. A higher content of sulfonyl chloride groups results in a higher electrical resistance of the membranes. High performance ion-exchange membranes (that is, membranes with higher permselectivities and lower electrical resistance) are obtained from a comparatively lower concentration of chlorosulfonic acid in sulfuric acid. The value of permselectivity (P_{Na}^{Ca}) is about 0.2.

REFERENCE

- [1] H. Small, *J. Am. Chem. Soc.*, **90**, 2217 (1968).
- [2] E. Glueckauf and G. P. Kitt, *J. Appl. Chem.*, **6**, 511 (1956).
- [3] T. Sata, *J. Membrane Sci.*, **93**, 117 (1994).
- [4] T. Sata, *J. Colloid Interface Sci.*, **44**, 393 (1973).
- [5] T. Sata, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1063 (1978).
- [6] T. Sata and R. Izuo, *Kolloid-Z. Z. Polym.*, **256**, 757 (1978).
- [7] T. Sata and Y. Mizutani, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1199 (1979).
- [8] T. Sata, R. Yamane, and Y. Mizutani, *Ibid.*, **17**, 2071 (1979).
- [9] Y. Tanaka and M. Seno, *J. Membrane Sci.*, **8**, 115 (1981).
- [10] K. Shimazaki, H. Ihara, and Y. Mizutani, *J. Appl. Polym. Sci.*, **34**, 1093 (1987).
- [11] N. Ohmura, Y. Kagiya, and Y. Mizutani, *Ibid.*, **34**, 1173 (1987).
- [12] A. Chapotot, V. Lopez, A. Lindheimer, N. Aouad, and C. Gavach, *Desalination*, **101**, 141 (1995).
- [13] T. Sata, R. Izuo, and K. Takata, *J. Membrane Sci.*, **45**, 197 (1989).
- [14] T. Sata and R. Izuo, *J. Angew. Makromol. Chem.*, **171**, 101 (1989).
- [15] T. Sata and R. Izuo, *J. Appl. Polym. Sci.*, **41**, 2349 (1990).
- [16] T. Sata and R. Izuo, *J. Membrane Sci.*, **45**, 209 (1989).
- [17] K. Takata, H. Ihara, and T. Sata, Unpublished Work.
- [18] Y. Mizutani, R. Yamane, H. Ihara, and H. Motomura, *Bull. Chem. Soc. Jpn.*, **36**, 361 (1963).
- [19] Y. Mizutani, R. Yamane, and H. Motomura, *Ibid.*, **38**, 689 (1965).
- [20] Y. Mizutani, W. Tesima, and S. Akiyama, Jpn. Pat. Appl. Publ. 38-003592 (1963).
- [21] Y. Mizutani, R. Yamane, and H. Motomura, Jpn. Pat. Appl. Publ. 39-027861 (1964).
- [22] Y. Mizutani, W. Tesima, S. Akiyama, R. Yamane, and H. Ihara, US Patent 3,451,951 (1969).
- [23] E. E. Gilbert, *Sulfonation and Related Reactions*, Interscience, New York, 1965, p. 84.

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