The Preparation of Divalent Cation Non-permselective Cation Exchange Membrane by Coating with Vinylon Film[1)]

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The preparation of non-permselective membrane for the divalent cation was attempted by coating it with thin vinylon film on one side of a commercial cation-exchange membrane. When the coating surface of the cation-exchange membrane was set on the concentration-compartment side (cathode side), the permselectivity coefficient of the calcium ion to the sodium ion was equal to that of untreated cation-exchange membrane and no effect of the selective treatment was recognized. However, when the coating sufrace was directed to the desalting-compartment side (anode side), an effect of the selective treatment was observed; in this case, the permeability of the calcium ion was more depressed, corresponding with the formalation degree of the selective–treatment membrane; for example, the permselectivity of the calcium ion for the membrane which was formalated for 180 min at 30°C decreased about one half compared with the untreated membrane. The electric resistance of the cation-exchange membrane increased upon the coating with the vinylon film, and especially the resistance of the calcium ionic-form membrane indicated a remarkable increase.

In the concentration of sea-water by electrodialysis through an ion-exchange membrane, the preparation of a non-permselectivity membrane for the divalent cation is one of the important subjects in connection with the increase in the current efficiency of sodium chloride and the prevention of scaling. At present, with regard to the procedure of increasing the non-permselectivity for the divalent cation, several papers have been published as to either the synthesis of new kinds of base membranes[2)] or the addition of surfactants as selective improvement agents to sea water during electrodialysis.[3)]

The present authors[4–6)] studied the mechanism of the permselectivity between same-charge ions across the cation-exchange membrane and recognized that the divalent cation show a large permselectivity in spite of their small mobility in a cation-exchange membrane because they have a much larger separation factor than the sodium ion in the ion-exchange equilibria. Also, as has been described in a previous paper,[7)] the permselectivity between ions of the same charge across a vinylon membrane is predominantly effected by the mobility ratio of both ions in the membrane, regardless of the total concentration or of the composition ratio in the original solution. On the other hand, the ion-transport numbers for membranes with a very low ion-exchange capacity approximate to a neutral membrane have been reported by Kumins and London.[8)] and other workers,[9)] but these membranes can not be used as practical as diaphrams in an electrodialysis concentration because the transport number decreases remarkably in a highly concentrated solution.

In this paper, vinylon-coated ion-exchange membranes were prepared by the following method. A thin film of polyvinyl alcohol (PVA) was smeared on the surface of one side of a commercial cation-exchange membrane, and then it was formalated under various conditions. Then the permselectivities of the calcium ion to the sodium ion across these selective-treatment membranes were measured, and the mechanism was discussed.

Experimental

Selective Treatment of Cation-exchange Membrane. A commercial cation-exchange membrane (exchange capacity, 1.79 meq/g dry; water content, 33.5%; membrane thickness, 0.16 mm) was used as the base membrane; a 10% aqueous solution of polyvinyl alcohol (polymerization degree 2400—2500) was smeared on one side of this membrane and it was dried in an air bath at room temperature for 24 hours. The dried membrane was then formalated under various conditions of time and temperature in a solution composed of concentrated H_2SO_4 200 g/*l*, Na_2SO_4 200 g/*l* and 135 g/*l* of 37% formalin, and it was washed in deionized water. These formalated membranes were used for the experiments.

The symbols of all the selective-treatment membranes and the formalation conditions are listed in Table 1.

Apparatus and Procedure of Electrodialysis. The cation-exchange membrane and anion-exchange membrane used in this experiment were strongly acidic and basic membranes. The electrodialysis apparatus was a cell with eight compartments separated by a cation-exchange membrane and an anion-exchange membrane, each with an area of 13×4 cm^2; the selective-treatment membrane was placed between the 5th compartment and the 6th compartment (Fig. 1).

In this cell, a mixed solution of a 0.35N-NaCl solution and a 0.03 N-$CaCl_2$ solution, as the original solution (20 *l*), was circulated in order from the 4th through the 6th to 2nd compartment at about 500 m*l*/min. at 30±1°C, and the 3rd, 5th, and 7th compartments were filled with a 0.1N-$NaNO_3$ solution. The left- and the right-side compartments, separated by a cation-exchange membrane, were cathode and anode compartments respectively, and in both electrode compartments a 0.3 N-Na_2SO_4 solution was circulated. The electrodialysis was carried out at a constant quantity of elec-

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1) Presented at the Local Meeting of the Chemical Society of Japan, Nagoya, October, 1970.

2) For example, R. Yamane, Y. Mizutani, H. Motomura, and R. Izuno, *Denki Kagaku,* **32,** 277 (1964).

3) For example, T. Sata, *Kolloid-Z. Polym.,* **243,** 157 (1971); A. Kuzuyama, S. Nagata, and S. Saito, the 20th Annual Meeting of the Science of Sea Water Society of Japan, Abstract, p. 3 (1969).

4) R. Dohno, T. Azumi, and S. Takashima, *Nippon Kagaku Zasshi,* **89,** 245 (1968).

5) R. Dohno, T. Azumi, and S. Takashima, *ibid.,* **91,** 131 (1970).

6) R. Dohno, T. Azumi, and S. Takashima, *ibid.,* **92,** 136 (1971).

7) R. Dohno, T. Azumi, and S. Takashima, *ibid.,* **91,** 1133 (1970).

8) C. A. Kumins and A. London, *J. Polym. Sci.,* **46,** 395 (1960).

9) T. M. Ellison and H. G. Spencer, *Polym. Lett.* **1,** 707 (1963).

TABLE 1. FORMALATION CONDITION AND MEMBRANE SYMBOL

Symbol of membrane		A-60	A-120	A-180	B-50	B-70	D-60	D-120	C-M
Formalation condition	Temp. (°C)	30	30	30	50	70	40	40	untreatment membrane
	Time (min)	60	120	180	120	120	60	120	

TABLE 2. T^{Ca}_{Na} FOR TREATMENT AND UNTREATMENT MEMBRANES

Current density (A/dm²)		0.42	0.83	1.67	2.50	3.33
Untreatment membrane (Cation membrane)		2.88	2.04	1.60	1.42	1.33
Treatment membrane[a]	Cathode side	2.86	1.98	1.58	1.37	1.30
	Anode side	2.32	1.62	1.23	0.95	0.95

[a] A-60

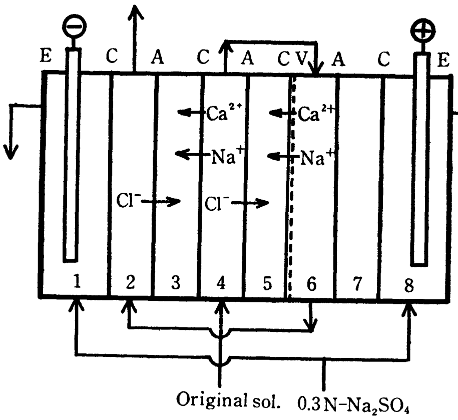

Fig. 1. Schematic diagram of electrodialysis cell.
C: cation exchange membrane
A: anion exchange membrane
CV: selective treatment membrane
E: carbon electrode

tricity by alternating the current density and the time respectively, and then the transfer eqivalents of the calcium ion and the sodium ion were determined from the concentrations of these ions in the 3rd and 5th compartments respectively. From these values, the permselectivity coefficients of the calcium ion to the sodium ion were calculated by means of Eq. (1):

$$T^{Ca}_{Na} = (E_{Ca}/E_{Na})/(C_{Ca}/C_{Na}) \qquad (1)$$

where E is the transfer equivalent and where C is the concentrantion in the original solution. The analysis of the chloride ion and the calcium ion was done by Mohr's method and the EDTA method, while the sodium ion was determined by calculation.

Membrane Resistance. The untreated membrane (*i. e.*, the cation-exchange membrane) and the selective-treatment membranes were equilibrated with a $0.5N$-NaCl or $0.5N$-$CaCl_2$ solution for 50-hr. A cell with two compartments equipped with platinized platinum electrodes was used for the measurement, and the resistances were measured by means of a 1000-cycle AC bridge (Yokogawa Electric Works Ltd. BV-Z-103 B) at 30±0.5°C. The membrane resistance was obtained as the difference between the reading with the membrane and without the membrane.

Results and Discussion

Direction of Treatment Surface. The permselectivity coefficients in each case of the treatment surface of a cation-exchange membrane placed in the direction of the concentration-compartment side and in that of the desalting-compartment side are shown in Table 2.

When the selective-treatment surface was directed at the concentration-compartment side, the permselectivity coefficients were equal to that of the untreated membrane; that is, no effect of selective treatment was recognized. However, when it was directed to the desalting-compartment side, the values of the permselectivity coefficients decreased in comparison with

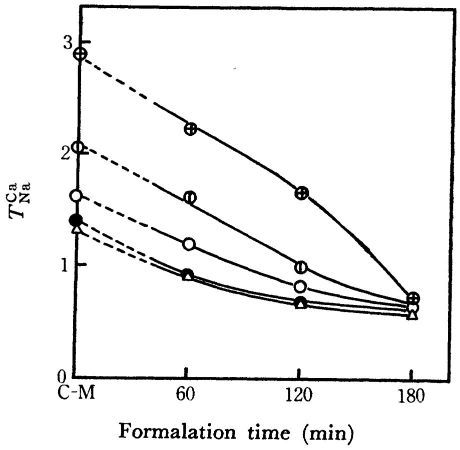

Fig. 2. Effect of formalation time on permselectivity coefficient.
Current density (A/dm²);
⊕: 0.42, ⦶: 0.83, ○: 1.67, ●: 2.50, △: 3.33

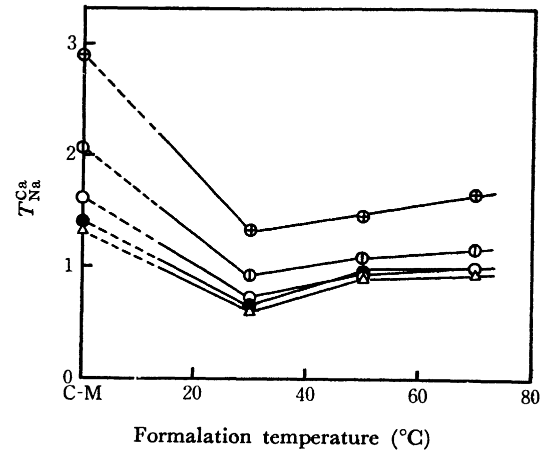

Fig. 3. Effect of formalation temperature on permselectivity coefficient.
Current density (A/dm²);
⊕: 0.42, ⦶: 0.83, ○: 1.67, ●: 2.50, △: 3.33

that of the untreated membrane. From these results, it can be concluded that the permselectivity of the calcium ion varies with the direction of the treated surface. Therefore, in the subsequent experiments, the permselectivities were measured for the treated surface directed to the desalting-compartment side.

Change of Permselectivity with the Formalation Conditions. Figures 2 and 3 show the change in the permselectivity coefficients due to the formalation conditions at each current density.

The permselectivity coefficients of the treated membrane decrease with an increase in the formalation time. It is presumed that the transfer of the calcium ion, which possesses a larger hydration radius,[10] was more depressed than that of the sodium ion because the vinylon phase came to have a fine structure upon formalation.[11] However, when the formalation time is over a certain length, the permselectivity coefficient does not decrease, because the transfer of the sodium ion is depressed as well as that of the calcium ion. For example, the permselectivity of the calcium ion to the sodium ion across the A–180 membrane is nearly equal to that of the A–120 membrane, but these values were about half that of the untreated membrane. On the other hand, at a constant formalation time, the permselectivity coefficient appears to have a tendency to increase somewhat with a rise in the formalation temperature (Fig. 3).

Membrane Resistance. The effective resistance of the treatment membrane in a calcium ionic form and in a sodium ionic form *vs.* the formalation time and the temperature are shown in Figs. 4 and 5 respectively.

In all cases, the resistance of the calcium ionic-form membrane was larger than that of the sodium ionic-form membrane. The resistance of both ionic-form membranes increased with an increase in the formalation time and temperature; the resistance of the calcium ionic-form membrane indicated an especially remarkable increase. This suggests that the transfer of the calcium ion is depressed by the vinylon-film coat on the cation-exchange membrane. Also, the degree of the increase in resistance due to the formalation conditions is greater with the formalation temperature than with the formalation time.

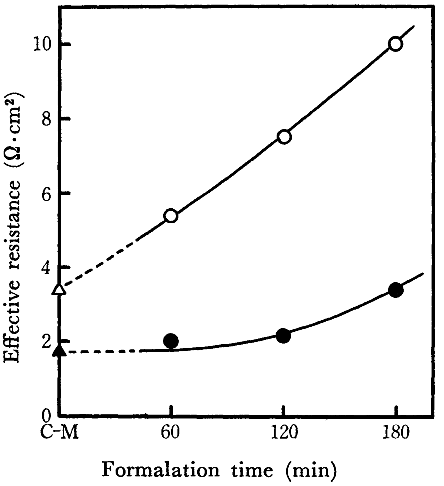

Fig. 4. Change of resistance by formalation time. (Formalation temperature: 30°C)
○: 0.50 N-CaCl$_2$ ●: 0.50 N-NaCl, △▲: C-M

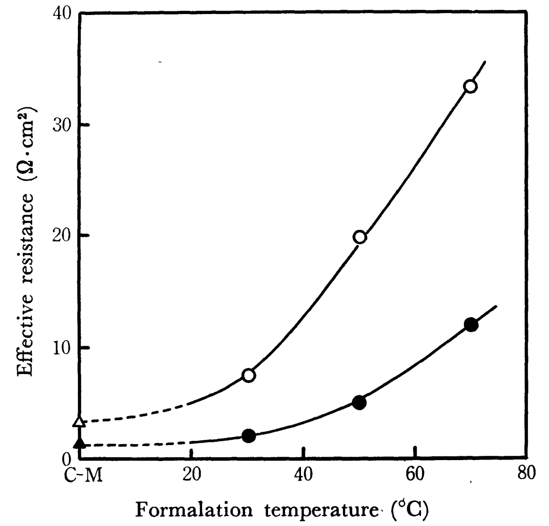

Fig. 5. Change of resistance by formalation temperature. (Formalation time: 120 min.)
○: 0.50 N-CaCl$_2$, ●: 0.50 N-NaCl, △▲: C-M

It can be considered that, at low temperatures, the formalation proceeds with the increase of time until the PVA phase, because the formalation reaction does not proceed very fast; a fine structure will thus be formed. However, at high temperatures, a layer of a higher formalation degree will be formed on the surface of the PVA phase in even a short reaction time and the formalation can not succeed until within this phase.

Mechanism of Permselectivity for Treatment Membrane. The permselectivity between the same-charge ions across an ion-exchange membrane is split into two terms, the mobility term and the concentration term, as is shown by Eq.(2);

$$T_{A}^{B} = (\bar{U}_{B}/\bar{U}_{A})S_{A}^{B} \tag{2}$$

where $\bar{U}$ is the mobility in the ion-exchange membrane and S_{A}^{B} is the separation factor of the B ion to the A ion the cation-exchange membrane which is defined by Eq. (3);

$$S_{A}^{B} = (\bar{C}_{B}/\bar{C}_{A})/(C_{B}/C_{A}) \tag{3}$$

where $\bar{C}$ is the concentration in the ion-exchange membrane and C is the concentration in the solution.

Usually, the mobility ratio and the separation factor of the calcium ion to the sodium ion for the cation-exchange membrane are established experimentally as follows:

$$(\bar{U}_{Ca}/\bar{U}_{Na})<1,\ S_{Na}^{Ca}>1$$

The permeability of the calcium ion is larger than the sodium ion because the effect of S_{Na}^{Ca} is larger than the $(\bar{U}_{Ca}/\bar{U}_{Na})$ term. *i. e.*, $T_{Na}^{Ca}>1$. Thus, it is possible that the permselectivity of the calcium ion de-

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[10] T. Yamabe and M. Seno, "Ion Kokan Jushimaku," Gihodo, Tokyo, Japan (1964), p. 47.

[11] N. Takahashi and K. Onozata, *Kogyo Kagaku Zasshi*, **63**, 1540 (1960).

pressed by a decrease in the concentration of the calcium ion in the cation-exchange membrane, *i. e.* $S_{Na}^{Ca}<1$.

On the other hand, the permselectivity for the vinylon membrane is given by Eq. (4) as well as for the cation-exchange membrane:

$$V_{Na}^{Ca} = (\bar{U}'_{Ca}/\bar{U}'_{Na})S'^{Ca}_{Na} \qquad (4)$$

where $\bar{U}'$ is the mobility in the vinylon membrane and where S'^{Ca}_{Na} indicates the selective adsorption of the calcium ion to the sodium ion for the vinylon membrane, as defined by Eq. (5):

$$S'^{Ca}_{Na} = (\bar{C}'_{Ca}/\bar{C}'_{Na})/(C_{Ca}/C_{Na}) \qquad (5)$$

where $\bar{C}'$ is the concentration in the vinylon membrane and where C is in accordance with that in Eq.(3).

Table 3 shows the values of S'^{Ca}_{Na} measured for the vinylon membrane formalated under various conditions. These values indicate that $S'^{Ca}_{Na} \doteqdot 1$ within the experimental error; that is, the concentartion ratio of the calcium ion to the sodium ion in the vinylon membrane is equal to that of the original solution. Also, $(\bar{U}'_{Ca}/\bar{U}'_{Na})<1$ is deduced from Figs. 4 and 5. Accordingly, $V_{Na}^{Ca}<1$. That is to say, the permselectivity for the vinylon membrane is primarily ruled by the mobility ratio of both ions in the vinylon phase, and this ratio is closely related to the fine structure of vinylon.

TABLE 3. S'^{Ca}_{Na} OF VINYLON MEMBRANE

Symbol of membrane	A-60	A-120	D-60	D-120
S'^{Ca}_{Na}	1.3	1.0	0.8	1.0

Now, in the case of the treatment membrane obtained by combining a cation-exchange membrane and vinylon film, the value of V_{Na}^{Ca} indicates the ratio of the transfer equivalent of the calcium ion to the sodium ion which is supplied to the cation-exchange membrane across the vinylon film coated on the desalting-compartment side. Since V_{Na}^{Ca} is smaller than that of the original solution, the concentration ratio of the calcium ion to the sodium ion in the cation-exchange membrane phase will decrease compared with the untreated membrane. Consequently, the permselectivity of the calcium ion across the treatment membrane decreases. However, when the treatment surface was directed to the concentration-compartment side, the concentration ratio of the two ions in the cation-exchange membrane phase become the same value as that of the untreated membrane because the cation exchange membrane directly contacts the original solution. Accordingly, no change in the permselectivity of the treatment membrane was observed.

On the other hand, the transport number of cations in the vinylon phase will be nearly equal to that in the original solution because the vinylon has no ion-exchange group, and the concentration polarization on the interface between the vinylon film and the original solution is negligibly small. Thus the deficiency of calcium ions and the accumulation of sodium ions will occur at the interface between the cation-exchange membrane and the vinylon film because $T_{Na}^{Ca}>1$ and $V_{Na}^{Ca}<1$. The value of $\bar{C}_{Ca}/\bar{C}_{Na}$ in the cation-exchange membrane decreases with an increase in the current density, and approaches $(\bar{U}'_{Ca}/\bar{U}'_{Na})S_{Na}^{Ca}$. That is, the permselectivity coefficient at infinity of a current density for the treatment membrane is equal to the mobility ratio $(\bar{U}'_{Ca}/\bar{U}'_{Na})$ of both ions in the vinylon phase by reason of $S'^{Ca}_{Na} \doteqdot 1$.

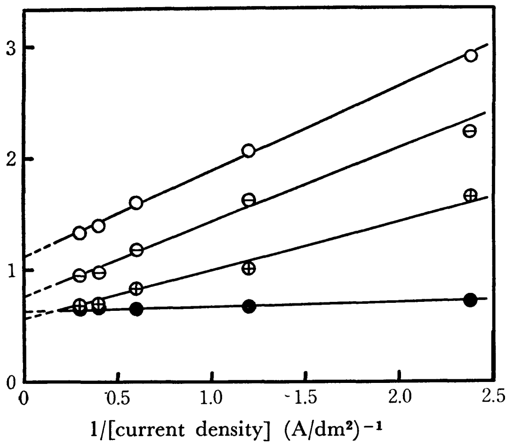

Fig. 6. Relationship between permselectivity and reciprocal of current density.
(Effect of formalation time)
○: C-M, ⊖: A-60, ⊕: A-120, ●: A-180

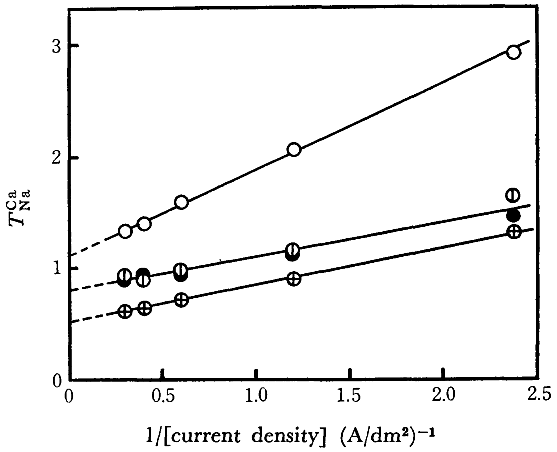

Fig. 7. Relationship between permselectivity and reciprocal of current density.
(Effect of formalation temperature)
○: C-M, ⊕: A-120, ●: B-50, ⦶: B-70

TABLE 4. MOBILITY RATIO IN VINYLON PHASE

Symbol of membrane	A-60	A-120	A-180	B-50	B-70
$\bar{U}'_{Ca}/\bar{U}'_{Na}$	0.77	0.52	0.66	0.80	0.80

The relationship between the permselectivity and the reciprocal of the current density is shown in Figs. 6 and 7, while Table 4 shows the value of the permselectivity coefficient (*i. e.*, $\bar{U}'_{Ca}/\bar{U}'_{Na}$) obtained by an extrapolation to infinity of the current density in these figures.

For the untreated membrane the extrapolating value is 1.15; this value is consistent with the mobility ratio of both ions in a free solution, but for the other membranes, which are formalated under various conditions, the values of $\bar{U}'_{\mathrm{Ca}}/\bar{U}'_{\mathrm{Na}}$ are smaller than that in solution; these results indicate that the mobility of the calcium ion to the sodium ion in the vinylon phase is depressed, as can be expected from Figs. 4 and 5.

From the above experimental results, it can be considered that the permeability of the divalent cation can be depressed by coating the desalting side of the cation-exchange membrane with vinylon film. However, in this case the electric resistance of the membrane increases; this problem may be resolved to a certain extent by making the vinylon-phase coat as thin as possible.