Studies on Ion Exchange Membranes. VII. Permselectivity of Improved Cation Exchange Membranes for NaCl-CaCl₂ System*

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Introduction

In the preceding paper¹⁾, we reported on the improvement of permselectivity of phenolic cation exchange membrane. The cation exchange membranes were improved as follows: on the base membranes of smaller phenol content, the cation exchange resins of the larger phenol content were fixed as thin film not so as to increase the electric resistance so much. These membranes were superior to the membranes with no thin film part in the electrochemical properties.

In this report, to elucidate the behaviour of bivalent cations in the electrophoretic concentration of sea water using these membranes, permselectivities of Ca²⁺ in NaCl-CaCl₂ system were investigated. As the result, we recognized that permselectivities of Ca²⁺ in NaCl-CaCl₂ system were decreased with the increase of current densities and were changed by the direction of current passing through these membranes.

Experimental

Membrane The membranes were prepared by condensation of phenol, m-phenolsulfonate (m.p. s.s.) and formaline with sodium hydroxide as a catalyst, following to the procedures described in the preceding report¹⁾. The compositions of materials are shown in Table 1.

Table 1 The Composition of Materials (mole ratio)

Membrane No.	2	3	4	2-3	2-4
Phenol/m.p.s.s.	2.0	3.0	4.0	2.0-3.0	2.0-4.0
Formaldehyde/Phenol+m.p.s.s.	2.7	2.7	2.7	2.7	2.7

Measurement The characteristic data were obtained for these membranes with the usual method²⁾. Water content, exchange capacity, fixed ion concentration, specific conductivity and transport number were measured. The transport numbers were calculated from the concentration changes of the solution at both sides of a membrane, originated from current flowing through the membrane.

Results and Discussion

In Table 2, the transport numbers of the improved membranes are shown, measured in the solution of the constant composition, i.e., C_{Cl}=0.5 N and equivalent fraction of Ca²⁺=25%. The relative transport number P_{Ca} were calculated from the following equation:

$$P_{Ca} = (t_{Ca}/t_{Na}) / (C_{Ca}/C_{Na}),$$

t : transport number in the membrane,

c : ionic concentration in the solution.

In Fig. 1, P_{Ca} of the improved membranes are compared with those of the membranes with no thin film part. P_{Ca} of the improved membranes were placed between P_{Ca} of the membranes having the phenol content corresponding to the thin film part and the base membrane part.

* The original written in Japanese can be seen in Denki-Kagaku 29, 544 (1961).

Table 2 The Relative Transport Number

Current density [A/dm ²] Transport number Current direction Membrane		0.45				1.0				2.0			
		<i>t</i> _{Na}	<i>t</i> _{Ca}	<i>t</i> _{Cl}	<i>P</i> _{Ca}	<i>t</i> _{Na}	<i>t</i> _{Ca}	<i>t</i> _{Cl}	<i>P</i> _{Ca}	<i>t</i> _{Na}	<i>t</i> _{Ca}	<i>t</i> _{Cl}	<i>P</i> _{Ca}
2-3	⇌	63.4	35.4	1.2	1.86	64.9	34.1	1.2	1.76	67.4	30.1	2.5	1.49
	⇌	64.8	34.4	0.8	1.78	64.4	32.6	3.0	1.69	69.3	27.2	3.5	1.31
2-4	⇌	—	—	—	—	64.8	33.8	1.4	1.59	67.5	31.1	1.4	1.37
	⇌	67.5	31.2	1.3	1.39	66.5	28.0	5.5	1.27	72.0	24.3	1.7	1.02

Composition of solution : *C*_{Cl}=0.5 [N]
Equivalent fraction of Ca²⁺=25 [%]
Current direction : ⇌ The thin film part was faced to anode side
⇌ The base membrane part was faced to anode side

Fig. 1 Relative transport number

face is most dominant to the ionic composition in the membrane. Thus, when the cations transfer from the smaller phenol content part to the larger one, Ca²⁺ is accumulated in the membrane, and in the reverse case, Ca²⁺ is diminished. These considerations were confirmed by the measurement of equivalent fractions of Ca²⁺ in the membranes under current flowing for NaCl-CaCl₂ system, as shown in Table 3.

As mentioned above, the relations between *P*_{Ca} and current direction are attributed to the changes of ionic compositions in the membranes by the current direction.

Table 3 Equivalent Fraction of Ca²⁺ in the Membrane Under Current

Current density [A/dm ²] Current direction Membrane		0	1	2	3
2-4	⇌	83.0	52.1	48.8	48.2
	⇌	83.0	54.7	51.8	50.2

Composition of solution : *C*_{Cl}=0.5 [N]
Equivalent fraction of Ca²⁺=25 [%]

Of the improved membranes, *P*_{Ca} were changed with the current direction. When the current were passed from the larger phenol content part to the smaller phenol content part, *P*_{Ca} were smaller. The larger the differences of phenol content between the two parts were, the larger the changes of *P*_{Ca} by the current direction were.

It is known that the transport numbers of Ca²⁺ in the membranes for NaCl-CaCl₂ system are decreased with the increase of phenol contents of the membranes. Therefore, in the improved membranes, the concentration polarizations are established, not only at the membrane/solution interfaces, but also at the thin film part/base membrane part interface, due to the difference of phenol content between the two parts. It is expected that the concentration polarization at the thin film part/base membrane part inter-

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Literature:

- 1) Y. Onoue, Y. Mizutani, R. Yamane, W. Teshima, S. Akiyama, *Denki-Kagaku* **29**, 468 (1961), This Journal **29**, E 226 (1961).
- 2) Y. Onoue, Y. Mizutani, R. Yamane, *Denki-Kagaku* **27**, 482 (1959).

Studies on Ion Exchange Membranes. VIII. On the Anion Exchange Membranes Using Dimethyl (2-oxybenzyl) Amine*

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1. Introduction

There are many reports¹⁾ about the anion exchange membranes and resins prepared by polycondensation. In these exchangers amine groups are usually used as the ion exchange sites in the form of polymer chain unit but not in the form of side chain. For example, the preparation of the anion exchange membranes using tetraethylene pentamine was already reported^{2), 3)}.

Usually, amine groups are sensitive to oxidation. So, if amine groups were used in the form of polymer chain unit, not only the losses of ion exchange sites, but also the scissions of the polymer chains could be induced by the oxidative attack. On the other hand, if amine groups were used in the form of side chain, the losses of ion exchange sites could be occurred, but the scissions of polymer chains could be hardly induced under the same conditions. It would be anticipated that the latter should be more stable than the former for the oxidative attack.

From the viewpoints described above, the anion exchange membranes using dimethyl (2-oxybenzyl) amine were prepared and their electrochemical properties and stabilities were measured.

2. Experimental

(1) **Dimethyl (2-oxybenzyl) Amine [DMBA]** Dimethyl (2-oxybenzyl) amine was prepared by Mannich's reaction.

(2) **Preparation of Membranes** The materials (DMBA, phenol, 37% formaline and H_2SO_4 - CH_3COOH) with the appropriate molar ratio were mixed under cooling and stirring, and the mixtures of the materials were stirred for 1 hour at 50-60°C. Thus, the viscous resinous solutions were obtained. These solutions were laminated with glass clothes and cured at 60-70°C for 8 hours.

The ion exchange sites of the prepared membranes were tertiary amine groups (TA membranes). TA membranes were quaternized with CH_3I - CH_3OH (1 : 1 in volume) at room temperature (QA membranes).

(3) **Measurement** Water content, exchange capacity, specific conductivity and membrane potential were measured by the preceding methods²⁾. Specific conductivities were measured in 0.5 N NaCl at 25°C. Transport numbers were calculated from the membrane potential by Nernst's equation, which was measured with 0.5 N NaCl and 2.5 N NaCl at 25°C.

* The original written in Japanese can be seen in *Denki-Kagaku* **29**, 653 (1961).