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Electrochemical Polarization Characteristics and Ion Transport through Ion Exchange Membranes in Sodium Chloride Solution

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Abstract

The polarization behavior and transport property of cation and anion exchange membranes (CMV, AMV) in diluted NaCl aqueous solutions were investigated by potentiostatic and galvanostatic techniques, and the application of these membranes to desalination was discussed. Both potentiostatic and galvanostatic I-V curves gave the same limiting current densities, which were coincident with the current densities at which the pH values of bulk solution began to increase or decrease in galvanostatic pH-I curves. The diffusion constants of Cl^- and NaCl through CMV were determined by using radioisotope ^{36}Cl to be $\bar{D}_{\text{Cl}^-} = 5 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1}$ and $\bar{D}_{\text{NaCl}} < 10^{-9} \text{ cm}^2 \cdot \text{sec}^{-1}$. The transport numbers of Na^+ , Cl^- and H^+ ions for CMV were estimated by measuring the flow of ^{36}Cl and the increase of solution pH. Furthermore, the concentration difference between the two interfacial solutions of both sides of CMV was calculated from the Cl^- transport through the membrane.

1. Introduction

Ion exchange membranes and reverse osmosis membranes have been used for production of fresh water from sea water or salt water. It is known that the ion exchange membrane method is more advantageous than the reverse osmosis membrane method in the case of small plants for obtaining drinking water on islets or ships, because of the simplicity of instrument and the easiness of operation: Recently, a few electrodialysis instruments for desalination¹⁾ using ion exchange membranes have been produced for experimental plants in our land. In the ion exchange membrane method, the selection of the electrodialysis condition is important, particularly, in the case of diluted solutions.

In this paper, a new method to determine a suitable current density for electrodialysis is described. The relationship between the polarization behavior and the ion transport phenomena is also discussed for systems of ion exchange membranes and diluted sodium chloride aqueous solutions with a view to contributing to the estimation of the efficiency for desalination.

2. Experimental

2-1. Membrane

The ion exchange membrane used here was Selemion CMV-10 and AMV-4

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(Asahi Glass Co., Ltd.). Both membranes were cut to obtain an area of 2 cm² from the original sheets and kept in 0.01 M sodium chloride after washing by water. The characteristics of the membranes, i.e., the thickness, the specific resistance, the ionic concentration, the self-diffusion constant of chloride ion, and the salt diffusion constant of sodium chloride are summarized in Table 1.

TABLE 1 Characteristics of the membranes*

membrane	concentration of fixed-ion mg·equiv·cm ⁻³	concentration of co-ion mg·equiv·cm ⁻³	thickness cm	specific resistance $\Omega \cdot \text{cm}$	self-diffusion constant of Cl ⁻ cm ² ·sec ⁻¹	salt diffusion constant cm ² ·sec ⁻¹
CMV	1.5	1.37×10 ^{-4**}	0.13×10 ⁻²	190~230	5×10 ⁻⁸	<1×10 ⁻⁹
AMV	1.5	10 ⁻⁴	0.14×10 ⁻²	280~320	1×10 ^{-8***}	<1×10 ⁻⁹

* Selenion membranes of Asahi Glass Co., Ltd.

** Measured by ³⁶Cl concentration in the wet membrane which is in equilibrium with 0.01 M NaCl aqueous solution containing ³⁶Cl.

*** The self diffusion of Cl⁻ for anion exchange membrane is controlled by the diffusion across the membrane-solution interface, whereas it is controlled by the diffusion through the membrane itself for cation exchange membrane.

2-2. Polarization Behavior

The electro dialysis cell used for measurements of the potentiostatic polarization behavior is shown in Fig. 1. It consists of five compartments made of Pyrex glass with each compartment separated by the same type of ion exchange membrane namely CMV or AMV, (M₁~M₄). The cathode, which is a platinum electrode immersed in 0.1 M NaCl filled in to a cylindrical vessel made of CMV, is inserted into compartment (A). Similarly, the anode covered by AMV is inserted into compartment (E). Four Luggin capillaries, (C₁~C₄), are placed in the cell,

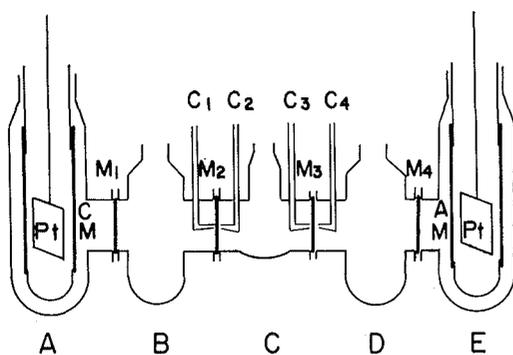


Fig. 1. Cell for measurement of potentiostatic I-V curve.

A~E: Compartments of cell.

C₁~C₄: Luggin capillaries connected to calomel electrodes.

M₁~M₄: Ion exchange membranes.

CM: Cation exchange membrane (CMV).

AM: Anion exchange membrane (AMV).

each being connected via a saturated calomel electrode to a membrane-potentiostat; this new type of potentiostat, constructed in the author's laboratory, makes it possible to control the potential difference across a membrane.

In the cation exchange membrane (CMV) system, the steady current flowing between the two platinum electrodes was measured while holding the potential difference constant between capillaries C₁ and C₂. The concentration of sodium chloride in this system was kept at 0.1 M in compartment (A), (D), and (E), and was changed from 0.01 M to 0.04 M

in compartment (B) and (C). In the case of the anion exchange membrane (AMV) system, the potential difference between capillaries C_3 and C_4 was controlled instead of that between C_1 and C_2 .

The electro dialysis cell used for measurements of the galvanostatic polarization behavior or the amount of transported ions also consist of five compartments of the same type as those shown Fig. 1. In this cell, however, the Luggin capillaries can be removed from the cell, when necessary for measuring the pH change or the chloride ion transport. The temperature of the cell was controlled by an air bath between 20° and 21°C.

2-3. pH Change

The pH value in compartment (C), which contained 15 ml of the solution, was measured by a pH-meter (Beckmann, type SS-2) after a given amount of coulomb had passed at constant current density. The concentration of each compartment was the same as that used for the measurement of polarization behavior. The pH measurements were carried out under the stagnant condition of solutions.

2-4. Chloride Ion Transport through Membrane

The self-diffusion constant of chloride ion through the membranes was determined by using a radioisotope of ^{36}Cl which is made to flow in the system of 0.01 M NaCl (^{36}Cl)-membrane-0.01 M NaCl. The same measurement was made in the system of 0.01 M NaCl (^{36}Cl)-membrane-water to determine the salt-diffusion constant of NaCl.

The amount of transported chloride ion through CMV at constant current densities was also measured by ^{36}Cl flow in 0.01 M NaCl solution. 1.0 ml of the sample was withdrawn by using a holepipet at the time when a given amount of coulomb (1.0 coulomb) had been transported through the membrane. The amount of ^{36}Cl was counted by a liquid scintillation counter (Aloca Co., Ltd.), in which a solution mixture of PPO (20 mg), POPOP (0.25 mg), naphthalene (600 mg), and dioxane (5 ml) was used as a liquid scintillator. The efficiency of the counting was about 80%, independent of the ^{36}Cl concentration examined.

3. Results and Discussion

3-1. Polarization Behavior

The current density which flows through CMV at potentiostatic polarization in 0.01 M NaCl is shown as a function of time in Fig. 2. The current density decreases rapidly in the initial period of time and then reaches a steady value which depends on the potential difference applied. The same behavior was also observed with AMV. Fig. 3 and Fig. 4 show respectively the potentiostatic polarization curves (the relation between the potential difference and the steady state current density) for CMV and those for AMV in NaCl solutions of various concentrations. It may be seen that the polarization curve consists of two parts, a linear and a non-linear part of the curve. The linear part which appears at

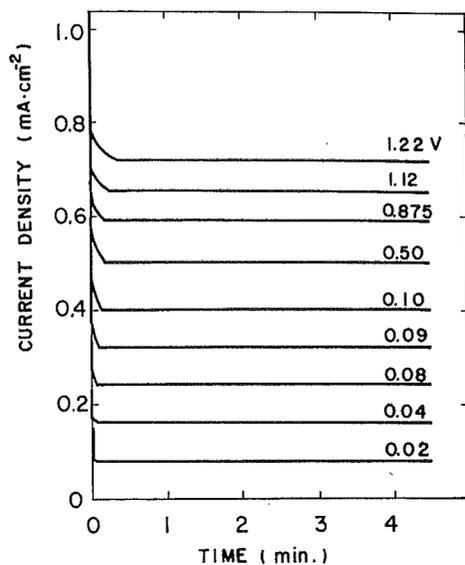


Fig. 2. Variation of current density with time in potentiostatic polarization of CMV in 0.01 M NaCl.

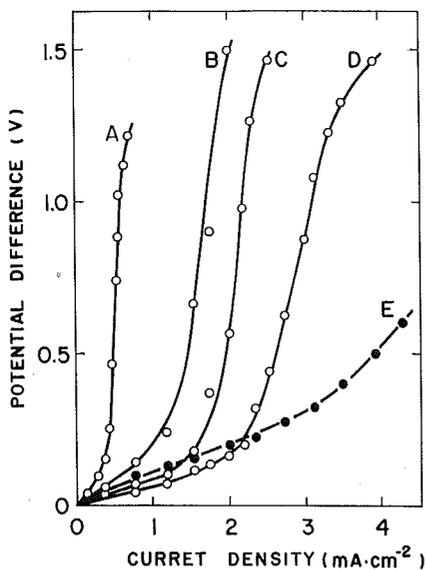


Fig. 3. Potentiostatic I-V curves of CMV in various concentrations of NaCl.
A: 0.01 M, B: 0.02 M, C: 0.04 M,
D: 0.04 M, E: 0.01 M and stirred.

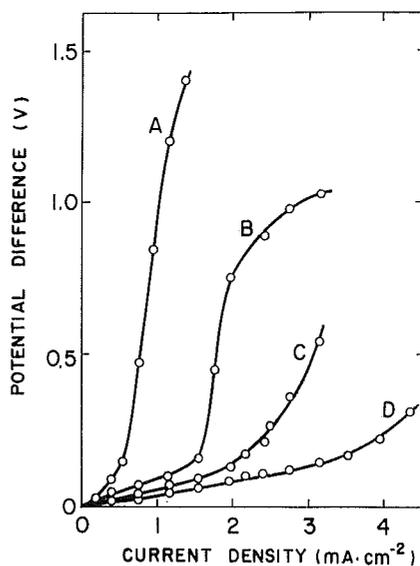


Fig. 4. Potentiostatic I-V curves of AMV in various concentrations of NaCl.
A: 0.01 M, B: 0.02 M,
C: 0.03 M, D: 0.04 M.

relatively low steady current densities can be attributed to the ohmic polarization of the solution; calculation using solution conductivity agrees with the ohmic relation. As the potential difference across the membrane is increased further, the linear relation between the potential difference and the current breaks at a

critical current density called the limiting current density. In the non-linear part of the curve, the concentration polarization is predominant, which results from an increase and decrease of the concentration of the moving ion at both sides of the membrane-solution interfaces. From the polarization curves, the limiting current density of membranes in various solutions can be estimated and the estimated values are listed in Table 2.

TABLE 2 Limiting current densities ($\text{mA}\cdot\text{cm}^{-2}$) of CMV and AMV in sodium chloride aqueous solution at $20\sim 21^\circ\text{C}$.

Concentration (M)	0.01	0.02	0.03	0.04
CMV	0.40	1.00	1.60	2.30
AMV	0.55	1.35	2.20	3.95

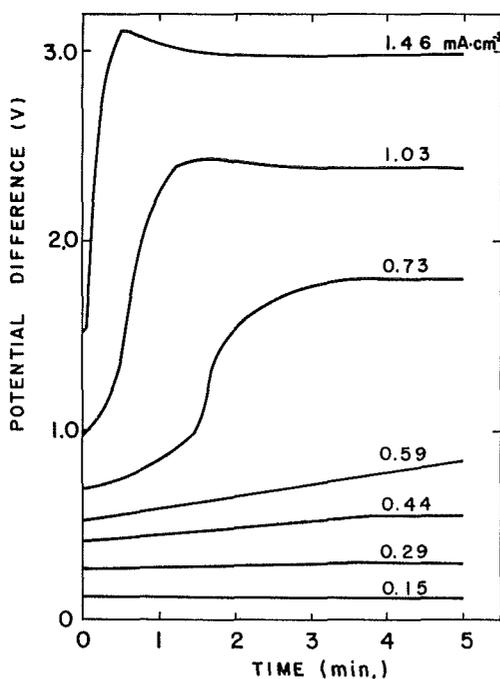


Fig. 5. Variation of potential difference with time in galvanostatic polarization of CMV in 0.01 M NaCl.

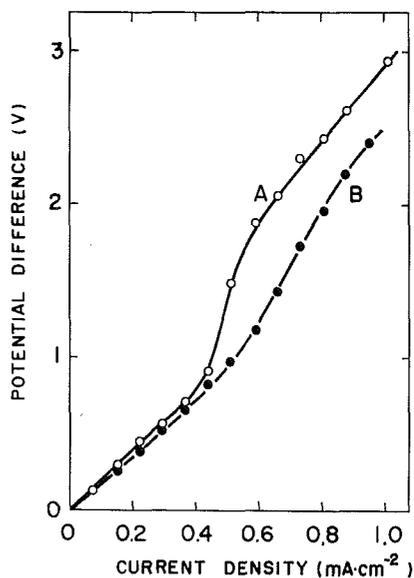


Fig. 6. Galvanostatic I-V curves of CMV and AMV in 0.01 M NaCl. A: CMV, B: AMV.

The variation of the potential difference across the membrane with time during galvanostatic polarization for CMV in 0.01 M NaCl are shown in Fig. 5. At current densities less than $0.29\text{ mA}\cdot\text{cm}^{-2}$, no appreciable change of the potential difference occurs for 5 minutes. At current densities larger than $0.44\text{ mA}\cdot\text{cm}^{-2}$, however, the potential difference increases before reaching a steady state value. The galvanostatic polarization curves (the relation between the current density and

the steady potential difference) for CMV and AMV in 0.01 M NaCl are shown in Fig. 6. The galvanostatic polarization curve is seen also to consist of the two parts, and the limiting current density is estimated which agrees fairly well with that estimated from the potentiostatic polarization curve.

As for the method of estimating the limiting current density, however, the potentiostatic method is superior to the galvanostatic method in that the measurement of polarization curve can be made stable, particularly, in the transition region from the linear to the non-linear part of the curve. The author, therefore, recommends the use of the potentiostatic method for polarization of membranes: No attempt has so far been reported to construct a potentiostat for membrane studies and to make use of it for polarization of membranes.

3-2. pH Change

The pH measurements of 0.01 M NaCl in compartment (C) were made after certain amounts of coulomb had passed across the membrane. The results are shown in Fig. 7. The solution pH changed at a current density larger than $0.4 \text{ mA}\cdot\text{cm}^{-2}$ for CMV and larger than $0.5 \text{ mA}\cdot\text{cm}^{-2}$ for AMV. These critical current densities for CMV and AMV are coincident with the limiting current densities given in Table 2, which have been estimated from the polarization curve

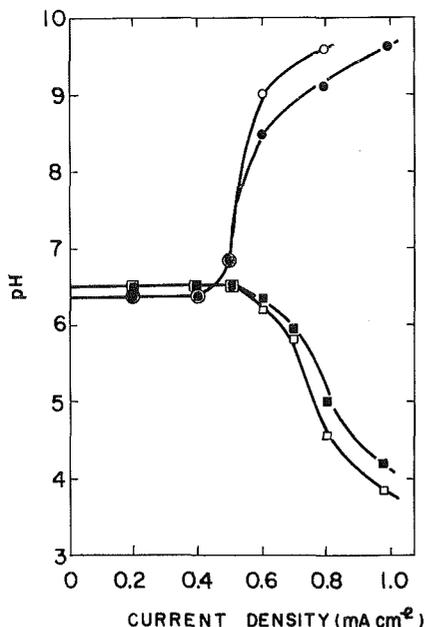


Fig. 7. Variation of pH in compartment C with current density in 0.01 M NaCl.

(○, ●): 3.6 and 1.8 coulomb for CMV, respectively.

(□, ■): 3.6 and 1.8 coulomb for AMV, respectively.

of the two membranes. In the CMV system, the concentration of 0.1 M NaCl in compartment (D) which supplies sodium ions to compartment (C) is so large that the current density shown in Fig. 7 is far less than the limiting current density for membrane (M_3) separating these two compartments. The increase of the pH value in the CMV system, therefore, can be attributed to the proton transport from compartment (C) to (B) through membrane (M_2); as a result, the concentration of hydroxyl ion in compartment (C) increased. Similarly, the decrease of the pH value in the AMV system can be attributed to the hydroxyl ion transport.

The pH change in membrane systems has already been reported²⁾ at current densities larger than the limiting current density, and explained to be due to the dissociation of the water molecule in the interfacial solution layer of the membrane. From the measurements of the pH change in this work, in which the solution in each compartment was separated by the same membrane, CMV or AMV, one

can estimate the transport number of proton or hydroxyl ion through the membranes.

3-3. Ion Transport

The amount of chloride ion transported through CMV at constant current densities and at a constant total charge of 1 coulomb was measured by using ^{36}Cl . The chloride ion transport thus measured consists of the co-ion transport, self diffusion, and the salt flow. The self-diffusion constant of chloride ion through CMV, \bar{D}_{Cl} = $5 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$, was obtained by measuring the ^{36}Cl flow at zero external current flowing. Because the diffusion constant of NaCl, $\bar{D}_{\text{NaCl}} < 1 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$, is smaller than the self-diffusion constant of chloride ion, the salt flow can be negligibly small except for the case where a large concentration difference of NaCl is induced. The co-ion transport, therefore, can be calculated by subtracting the amount of chloride ion transported by self diffusion during current flowing from the total amount of transported chloride ion. The relationship between the amount of chloride ion transported by the co-ion transport process and the current density is shown in Fig. 8.

The co-ion transport of chloride ions through the cation exchange membrane can be represented by the following Nernst-Planck^{3,4)} equation:

$$\phi_{\text{Cl}} = -\bar{D}_{\text{Cl}} \cdot \frac{d\bar{C}_{\text{Cl}}}{dx} + \bar{D}_{\text{Cl}} \cdot \bar{C}_{\text{Cl}} \cdot \frac{F}{RT} \cdot \frac{d\bar{\phi}}{dx} \quad (1)$$

where \bar{D}_{Cl} and \bar{C}_{Cl} are respectively the diffusion constant and the concentration of chloride ion in membrane, and $\bar{\phi}$ the electrical potential at distance x in the membrane. In equation (1), the first term is the flow due to the concentration gradient across the membrane, and the second term is the flow due to the potential gradient. In the membrane in which the concentration of fixed ion is large and the specific resistance of ion migration is small, as is the case in this work, the flow due to the potential gradient is negligibly small⁵⁾. Therefore, the flow of chloride ions can be represented by equation (2), assuming a linear concentration gradient in the membrane:

$$\phi_{\text{Cl}} = -\bar{D}_{\text{Cl}} \cdot \frac{(\bar{C}_{\text{Cl}}^{\text{H}} - \bar{C}_{\text{Cl}}^{\text{I}})}{\delta} \quad (2)$$

where $\bar{C}_{\text{Cl}}^{\text{I}}$ and $\bar{C}_{\text{Cl}}^{\text{H}}$ are the concentrations of chloride ions in the membrane at

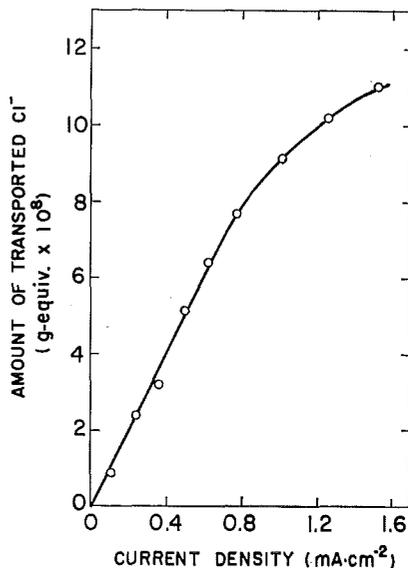


Fig. 8. Relationship between current density and amount of chloride ion transported through CMV for 1.0 coulomb in 0.01 M NaCl.

both sides of the membrane interfaces and δ the membrane thickness.

At each interface of the membrane, the Donnan equilibrium will be established with respect to chloride ion; $\bar{C}_{Cl}/C_{Cl}=l_{Cl}=\text{const}^{(6)}$. The ratio, l_{Cl} , can then be obtained from the ratio of the chloride ion concentration in the membrane and that in the solution. The flow of chloride ions at current flowing through CMV is thus finally represented by equation (3):

$$\phi_{Cl} = -\bar{D}_{Cl} \cdot l_{Cl} \cdot \frac{(C_{Cl}^H - C_{Cl}^I)}{\delta} \quad (3)$$

where C_{Cl}^I and C_{Cl}^H are the concentrations of chloride ion in the solution at both sides of membrane interfaces.

The concentration difference, induced by current flowing, between the interfacial solutions at both sides of the membrane can be calculated from the flow of chloride ions shown in Fig. 8 with the aid of equation (3), and the result of calculation is plotted in Fig. 9. It may be seen that the concentration difference is small when the flow of electric current is less than the limiting current density. However, the current density larger than the limiting current induces a large concentration difference of chloride ions; for example 1 g-equiv. l^{-1} was obtained at $0.7 \text{ mA} \cdot \text{cm}^{-2}$ in the interfacial solution layer of catholyte ($0.01 \text{ mol} \cdot \text{l}^{-1}$). Under this condition, the salt flow from the catholyte to the anolyte can not be neglected.

Furthermore, the amount of sodium ion, which is the major carrier of ion transport through CMV, can be calculated by subtracting the amount of trans-

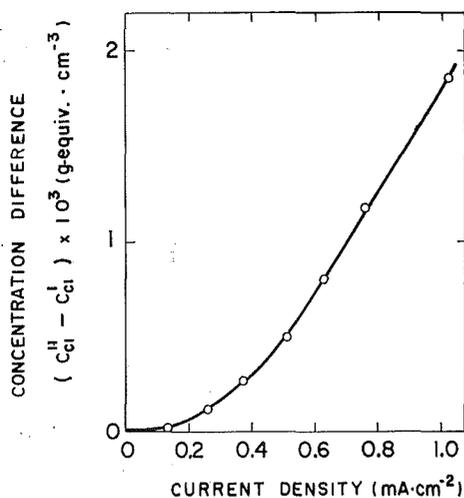


Fig. 9. Variation of calculated chloride ion concentration difference in the interfacial solution layer between both sides of membrane, CMV, with current density in 0.01 M NaCl.

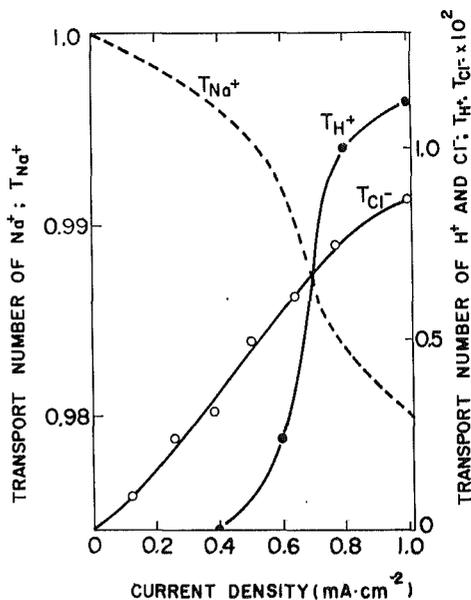


Fig. 10. Variation of transport numbers with current density for CMV in 0.01 M NaCl.

ported chloride ion and proton from the total charge transported, since the ions that can migrate through the membrane are sodium ion, chloride ion, and proton. The variation of transport number for each ion with the current density is shown in Fig. 10. It may be seen that the transport number of chloride ion increases with increasing current density, but its value is smaller than 0.01 in a current range less than $1.0 \text{ mA} \cdot \text{cm}^{-2}$. The transport number of proton which can migrate only above the limiting current density is also found to be relatively small.

As is shown in Fig. 9 and Fig. 10, it can be expected in the electro dialysis process below the limiting current density that the salt flow due to the concentration gradient can be ignored, and that the transport number of sodium ion is close to 1. In this investigation, the transport numbers of ionic species have been estimated for the cation exchange membrane (CMV) only. For the anion exchange membrane (AMV) containing concentrated fixed ion, it could also be expected the co-ion transport is small enough to be ignored.

4. Conclusion

The desalination by means of electro dialysis which uses ion exchange membranes should be operated below the limiting current density. The limiting current density for the membrane-solution systems can be determined by measuring the potentiostatic polarization curve. If the co-ion transport and the salt flow through the membrane are small, it is possible to produce fresh water from sea water or salt water with the current efficiency close to 100 per cent.

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