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Concentration Polarization Phenomena in Ion-exchange Membrane Electrodialysis. II. The Effect of the Condition of the Diffusion-boundary Layer on the Limiting-current Density and on the Relative Transport Numbers of Ions*[1]

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The effect of the condition of the diffusion-boundary layer in the ion-exchange membrane electrodialysis on the limiting-current density and on the relative transport numbers of ionic species with the same sign was studied. The limiting-current density in the laminar flow is approximately proportional to the first power of the concentration of the solution, the one-half power of the flow velocity of the solution, and, inversely, the one-half power of the membrane length in the direction of the flow. In the natural convection, it is proportional to the five-quarters power of the concentration of the solution. These experimental results agree with the relation of the equations of the limiting-current density for the electrode process. The change in the relative transport numbers of ionic species with the same sign, such as the magnesium and sodium ions or the sulfate and chloride ions, with the flow velocity, the concentration, and the temperature of the solution, the dimension of the membrane in the direction of the flow, and the current density were observed. The results were explained in terms of the change in the condition of the diffusion-boundary layer.

On the demineralization or concentration of sea water by ion-exchange membrane electrodialysis, one of the most serious problems is the concentration polarization phenomenon. In concentrating sea water especially, it is recognized that the concentration polarization on the desalting side of the membrane-solution interfaces causes a change in the relative transport numbers of ionic species with the same sign, an increase in the electric resistance of the electrodialysis cell, and often a change in the solution pH. Industrially, these changes are very important. The increase in the electric resistance makes necessary much more electric power, and the change in the relative transport numbers influences the current efficiency of the sodium ions and may cause the precipitation of calcium sulfate in the concentrating compartment of the cell. Also, when the pH-change of the solution occurs, carbonate and hydroxide of alkali earth metals are often precipitated on the membrane surfaces.

In this work, the effect of the condition of the diffusion-boundary layer on the limiting-current density and the relative transport numbers was studied.

The limiting-current density was obtained from the current-voltage curve in electrodialysis cells; we then investigated how the limiting-current density was affected by the flow velocity, the concentration and temperature of the solution, the dimensions of the membrane, and ionic species.

Moreover, the change in the relative transport numbers of the magnesium to sodium ions and of the sulfate to chloride ions was investigated in connection with the behavior of the diffusion-boundary layer when sea water was concentrated by electrodialysis.

Theoretical

The following equation shows the limiting-current density, i_{llm}, in the ion-exchange membrane electrodialysis:

$$i_{\mathrm{llm}} = \frac{\boldsymbol{F}DC_b}{\delta(t_m - t_s)} \tag{1}$$

where $\boldsymbol{F}$ is the Faraday constant; D, the diffusion coefficient of the electrolyte in the free solution; C_b, the concentration of the bulk solution; δ, the thickness of the diffusion-boundary layer, and t_m and t_s, the transport numbers of the counterion in the membrane and in a free solution respectively.

At current densities near the limiting-current density, the transport of ions consists mainly of diffusion and convection. Levich,[1] Wilke *et al.*,[2]

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*[1] Studies on ion-exchange membranes. XXVIII. Presented at the 17th Meeting CITCE (Comité International de Thermodynamique et de Cinetique Electrochemiques) held in Tokyo Japan, in September, 1966.

[1] B. Levich, *Discussions Faraday Soc.*, **1**, 37 (1947).

[2] C. R. Wilke, M. Eisenberg and C. W. Tobias, *J. Electrochem. Soc.*, **100**, 513 (1953).

and other investigators have given relations for the thickness of the diffusion-boundary layer in the electrode process at current densities near the limiting-current density. The membrane-solution system is similar to the electrode-solution system, as an ion-exchange membrane removes ions from the solution or adds ions to the solution. Accordingly, the relations in the electrode process can be used to explain the behavior of the diffusion-boundary layer in ion-exchange-membrane electrodialysis.

The equations for the thickness are as follows: for the laminar flow:

$$\delta = K_1\left(\frac{D}{\nu}\right)^{1/3}\left(\frac{\nu x}{V}\right)^{1/2} \tag{2}$$

for the natural convection:

$$\delta = K_2\left(\frac{\nu}{D}\right)^{-1/4}\left(\frac{g\alpha}{\nu^2}\right)^{-1/4} x^{1/4} C_b{}^{-1/4} \tag{3}$$

where ν is the kinematic viscosity; g, the acceleration of gravity; x, the distance from the bottom edge of a membrane; α, the specific density coefficient of the electrolyte solution $\left(=\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}c},\ \rho\text{: specific density}\right)$; V, the flow velocity of the solution in the laminar flow, and K_1 and K_2, constants.

The limiting-current density, i_{lim}, in the laminar flow is given from Eqs. (1) and (2) as the following equation:

$$i_{\mathrm{lim}} = \frac{1}{K_1}\frac{\boldsymbol{F}DC_b}{(t_m-t_s)}\left(\frac{\nu}{D}\right)^{1/3}\left(\frac{V}{x\nu}\right)^{1/2} \tag{4}$$

On the other hand from Eqs. (1) and (3) in the natural convection it is given as the following equation:

$$i_{\mathrm{lim}} = \frac{1}{K_2}\frac{\boldsymbol{F}DC_b{}^{5/4}}{(t_m-t_s)}\left(\frac{\nu}{D}\right)^{1/4}\left(\frac{g\alpha}{\nu^2}\right)^{1/4} x^{-1/4} \tag{5}$$

Equation (4) indicates that the limiting-current density is proportional to the first power of the concentration of the bulk solution, the one-half power of the flow velocity, and, inversely, the one-half power of the membrane length in the direction of the flow. Equation (5) indicates that the limiting-current density is proportional to the five-quarters power of the concentration of the bulk solution.

The temperature of the solution affects the limiting-current density, for the diffusion coefficient and the kinematic viscosity are functions of the temperature. If the transport numbers of the counter ion in the membrane and free solution are constant, the temperature coefficient, β, of the limiting-current density in the laminar flow can be obtained by the following method; Equation (4) is differentiated with respect to the absolute temperature, T:

$$\beta = \frac{1}{i_{\mathrm{lim}}}\frac{\mathrm{d}i_{\mathrm{lim}}}{\mathrm{d}T} = \frac{2}{3}\frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}T} - \frac{1}{6}\frac{1}{\nu}\frac{\mathrm{d}\nu}{\mathrm{d}T} \tag{6}$$

Using Nernst's equation of the diffusion coefficient (8), and also Walden's equation (9), the temperature coefficient of the diffusion coefficient is obtained as follows:

$$\frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}T} = -\frac{1}{\nu}\frac{\mathrm{d}\nu}{\mathrm{d}T} + \frac{1}{T} \tag{7}$$

$$D = \frac{\lambda \boldsymbol{R}T}{\boldsymbol{F}^2 Z} \tag{8}$$

$$\lambda\nu = \text{constant} \tag{9}$$

where λ is the equivalent conductance of the electrolyte at an infinite dilution and where Z is the valence of the ions. Accordingly, the temperature coefficient, β, is:

$$\beta = \frac{1}{i_{\mathrm{lim}}}\frac{\mathrm{d}i_{\mathrm{lim}}}{dT} = \frac{2}{3}\frac{1}{T} - \frac{5}{6}\frac{1}{\nu}\frac{\mathrm{d}\nu}{\mathrm{d}T} \tag{10}$$

The viscosity of water can be used for ν, as the concentration on the desalting side at the membrane surfaces is low at current densities near the limiting-current density.

Experimental

Membranes. Throughout this investigation commercial ion-exchange membranes prepared by the "Paste Method,"[3-5] *i. e.*, two anion-exchange membranes, NEOSEPTA AV-4T and NEOSEPTA AVS-4T, and are cation-exchange membrane, NEOSEPTA CL-2.5T, were used. The characteristics of these membranes are shown in Table 1.

Cells. Five different electrodialysis cells were used. The cells 1, 2, 3 and 4 were used for the laminar flow experiments, and the cell 5 for the natural convection experiments. In the cells 1, 2 and 3, the thickness of the compartment in which the solution flows was 1.0 cm in order to eliminate the effect of the desalting of the solution on the current-voltage curve. The characteristics of the cells are shown in Table 2.

Procedures. *The Determination of the Current-voltage Curve.* The current-voltage curve was measured with a high-impedance valve voltmeter (Tōadempa Co., Ltd., Model PM-20) connected to a pair of silver-silver chloride or calomel probe electrodes situated on the opposite sides of the membrane. Silver-silver chloride probe electrodes were put close to a membrane (about 2 mm apart in the cell 1). Calomel probe electrodes were connected to luggin capillaries (about 2mm apart from the membrane surfaces) and were used in the cells 2, 3, 4 and 5. The current-voltage curve was obtained as follows: the current was increased gradually and the voltage between the probe electrodes was measured with a valve voltmeter. The current density at which the voltage increased abruptly in the current-voltage relation was defined as the limiting-current density in the cell.

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[3] Y. Mizutani, R. Yamane, H. Ihara and H. Motomura, This Bulletin, **36**, 361 (1963).

[4] Y. Mizutani, R. Yamane and H. Motomura, *ibid.*, **38**, 689 (1965).

[5] R. Yamane, Y. Mizutani, H. Motomura and R. Izuo, *Denki Kagaku (J. Electrochem. Soc. Japan).*, **32**, 134 (1964).

TABLE 1. CHARACTERISTICS OF ION-EXCHANGE MEMBRANES

	Designation of membranes		
	NEOSEPTA*1 AV-4T	NEOSEPTA*2 AVS-4T	NEOSEPTA3* CL-2.5T
Backing	Polyvinyl chloride	Polyvinyl chloride	Polyvinyl chloride
Thickness (mm)	0.15—0.17	0.15—0.17	0.15—0.17
Burst strength (kg/cm^2)	5—7	4—6	3—4
Electric resistance ($\Omega-$cm^2)*4	3.5—4.5	3.7—4.7	2.7—3.2
Transport number5*	>0.98	>0.98	>0.98
Water content*6	0.20—0.25	0.25—0.35	0.30—0.40
Ion-exchange capacity*7	1.5—2.0	1.5—2.0	1.8—2.0

*1 Strongly basic anion-exchange membrane.
*2 Strongly basic anion-exchange membrane (univalent anion permselective).
*3 Strongly acidic cation-exchange membrane.
*4 Equilibrated with 0.5 N NaCl solution, at 25.0°C.
*5 Measured by electrodialysis in 0.5 N NaCl solution, current density: 10 mA/cm^2, at 25.0°C.
*6 Equilibrated with 0.5 N NaCl solution [g. H_2O/g dry membrane in Na-form (or Cl-form)].
*7 [meq./g dry membrane in Na-form (or Cl-form)].

TABLE 2. TYPES OF CELLS AND EXPERIMENTS PERFORMED

	Cells*1				
	1	2	3	4	5
Anode Cathode	Ag-AgCl	graphite iron	graphite iron	graphite iron	Ag-AgCl
Membrane (a)*1	10	40	20	20	10
Dimension (b)	20	250	variable*3	variable*4	10
Membrane*5	A or C	A and C (a pair)	A or C	A and C (a pair)	A or C
Measurement	E-I curve	1) E-I curve 2) P^A_B	E-I curve	1) E-I curve 2) P^A_B	E-I curve
B*6	10	10	10	2	30

*1 Cells except the cell 5 were used in laminar flow and the cell 5 was used in natural convection.
*2 Membrane dimension, (a) the width of the membrane, (b) the length of the membrane in the direction of the flow (mm).
*3 Lengths of the membrane are 20, 80, 250 and 400 mm.
*4 Lengths of the membrane are 250, 600 and 1200 mm.
*5 A means an anion-exchange membrane and C means a cation-exchange membrane.
*6 Thickness of the desalting compartment (mm).

The Determination of the Relative Transport Numbers of Ionic Species with the Same Sign. The relative transport numbers of ionic species with the same sign were determined by means of the concentration of sea water. The sample of the concentrated solution was taken after its composition attained an equilibrated condition (after the concentration had been carried out for about 12 hr). The chloride ions were analyzed by the Mohr method, and the magnesium and calcium ions, by the EDTA titration, while the potassium and sulfate ions were analyzed by the gravimetric method, using tetraphenyl borate and barium chloride respectively. The concentration of the sodium ions was calculated by subtracting the concentration of the magnesium, calcium and potassium ions from that of all the cations.

The relative transport numbers, P^A_B, were as follows:

$$P^A_B = \frac{(t^A_m/t^B_m)}{(C^A_b/C^B_b)}$$

where t^A_m and t^B_m are the transport numbers of the counterions, A and B, in the membrane, and C^A_b and C^B_b, the concentrations of A and B ions in the bulk solution.

Measurements. *The Effect of the Flow Velocity on the Limiting-current Density.* The measurements were made in the laminar flow at 30.0°C. The cells 1 and 2 were used for obtaining the current-voltage curve for a single membrane, NEOSEPTA AV-4T, AVS-4T or CL-2.5T, in a sodium chloride solution of 0.500 N and for a pair of membranes, NEOSEPTA AVS-4T and CL-2.5T, in diluted sea water (the concentration of chloride ions was 0.35 N) respectively.

The Effect of the Concentration of the Solution on the Limiting-current Density. Current-voltage curves in the laminar flow for NEOSEPTA AVS-4T at 30.0°C and in the natural convection for NEOSEPTA CL-2.5T at 25.0°C were measured in sodium chloride solutions of various concentrations by the use of the cells 2 and 5, respectively.

The Effect of the Temperature on the Limiting-current Density. In this measurement a sodium chloride solution of 0.104 N was used in the laminar flow by the use of the cell 1. The temperatures of the measurement were 15.7, 25.0 and 35.5°C for NEOSEPTA AVS-4T, and 15.0, 25.0 and 35.0°C for NEOSEPTA CL-2.5T.

The Effect of the Membrane's Dimensions on the Limiting-current Density. The current-voltage curve was obtained by the use of the cells 3 and 4. The former cell contained a single membrane, NEOSEPTA AVS-4T or CL-2.5T, while the latter cell contained a pair of anion- and cation-exchange membranes, NEOSEPTA AVS-4T and CL-2.5T. The lengths of the membranes in the direction of the flow were 2.0, 8.0, 25.0 and 40.0 cm in the cell 3, and 25.0, 60.0 and 120.0 cm in the cell 4. Each measurement was made in a laminar flow of sea water (the concentration of chloride ions was 0.52 N) at 28.0°C.

The Effect of Ionic Species on the Limiting-current Density. Current-voltage curves in aqueous solutions of several ionic species were measured with the cell 5, containing an anion- or cation-exchange membrane, in the natural convection at 25.0°C. The ionic species were hydrogen, lithium, potassium, sodium, calcium, barium, ammonium, aluminium, ferric and cupric ions as cations, and chloride and sulfate ions as anions. All these ions had a concentration of 0.50 N.

The Change in the Relative Transport Numbers with the Condition of the Diffusion-boundary Layer. The change in the relative transport numbers of the magnesium to sodium ions or of the sulfate to chloride ions with the flow velocity, the concentration, the temperature of sea water, the dimensions of the membrane, and the current density was examined when sea water was concentrated by electrodialysis. The change in the relative transport numbers by all factors except the dimensions of the membrane was examined by concentrating sea water by the use of the cell 2. The change in the relative transport numbers by the membrane length was examined by the use of the cell 4 in which long membranes were inserted. The experimental conditions are shown in Table 3.

Results and Discussion

A typical current-voltage curve for a cation-exchange membrane, NEOSEPTA CL-2.5T, in a sodium chloride solution at 25.0°C is shown in Fig. 1. This measurement was carried out by the use of the cell 5.

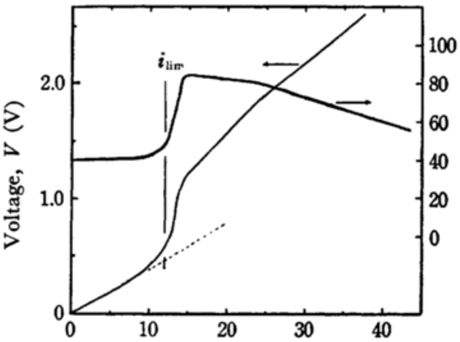

Fig. 1. An example of current-voltage curve and current $-V/i$ curve in natural convection at 25.0°C.
Membrane: CL-2.5T (with cell 5)
Solution: 0.104 N NaCl solution

The relationship between the limiting-current density and the flow velocity is shown in Fig. 2. The following relation can be found in Fig. 2.:

$$i_{\mathrm{lim}} = mV^n \tag{11}$$

According to Eq. (4) the constant, n, corresponds to 1/2, but the experimental values of Table 4 do not necessarily agree with 1/2. This disagreement is probably due to the difference in the structure of the cell.

If the transport numbers of counterions in the membrane and in the free solution, the diffusion coefficient, and the kinematic viscosity are nearly constant with respect to the concentration of the bulk solution, the limiting-current density is proportional to the concentration of the bulk solution. The results for an anion-exchange membrane, NEOSEPTA AVS-4T, show that the limiting-current density in the laminar flow is proportional

TABLE 3. EXPERIMENTAL CONDITIONS FOR CONCENTRATION OF SEA WATER

		Measurements				
		L (cm)	i (mA/cm²)	t (°C)	v (cm/sec)	c (N)
Effect of chloride concentration (C)	⊘	25.0	20.0	31	4	0.29—0.50
Effect of flow velocity (v)	●	25.0	20.0	20	1—16	0.52
Effect of temperature (t)	◒	25.0	>0.0	11—31	4	0.52
Effect of current density (i)	⊕	25.0	10.0—30.0	20	4	0.52
Effect of membrane length (L)	○	25.0—120.0	20.0	28	6	0.52

Marks in table are the same as those in Figs. 9 and 10.
c denotes the concentration of chloride ions of sea water.

TABLE 4. EMPIRICAL CONSTANTS OF Eq. (11)

	Membranes			
	AV-4T	AVS-4T	CL-2.5T	AVS-4T and CL-2.5T
Cell No.	1	1	1	2
m^{*1}	100	100	66	31
n	0.3	0.5	0.4	0.5

*1 The units of the limiting-current density and the flow velocity are mA/cm² and cm/sec, respectively.

to the concentration of the bulk solution, as is shown in Fig. 3. Equation (5) shows that the limiting-current density is proportional to the five-quarters power of the concentration in the natural convection. The experimental results in the natural convection agree with the theoretical value, as is shown in Fig. 4.

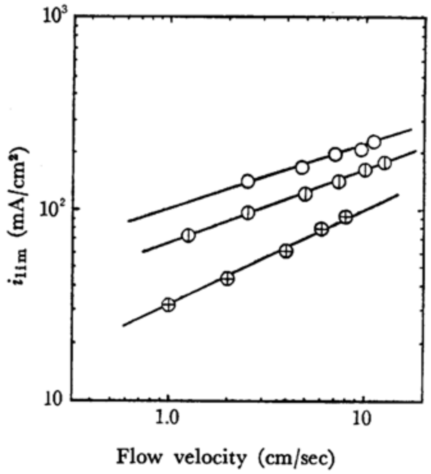

Fig. 2. The effect of the flow velocity on the limiting-current density.
cell 1: 0.500 N NaCl solution in laminar flow at 30.0°C
cell 2: diluted sea water (Cl: 0.35 N) in laminar flow at 30.0°C
○ AV-4T (with cell 1)
⦶ CL-2.5T (with cell 1)
⊕ AVS-4T and CL-2.5T

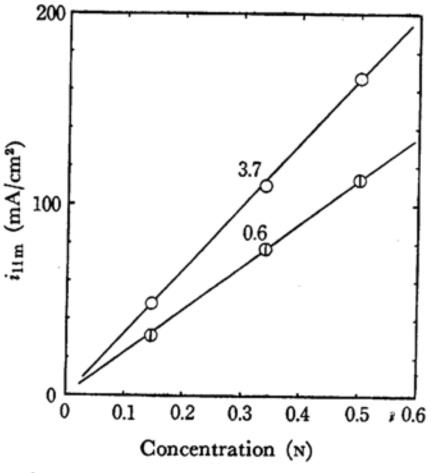

Fig. 3. The effect of the concentration on the limiting-current density in laminar flow.
Membrane: AVS-4T (with cell 1)
Solution: NaCl solution at 30.0°C
Numbers in the figure are the flow velocity of the solution (cm/sec).

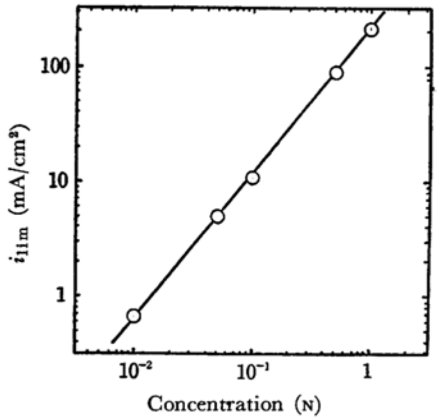

Fig. 4. The effect of the concentration on the limiting current-density in natural convection.
Membrane: CL-2.5T (with cell 5)
Solution: NaCl solution at 25.0°C

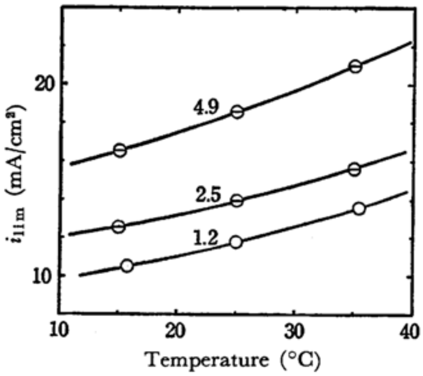

Fig. 5. The effect of the temperature on the limiting-current density.
Membrane: AVS-4T, CL-2.5T (with cell 1)
Solution: 0.104 N NaCl solution in laminar flow
Numbers in the figure are the flow velocity of the solution (cm/sec).
○ AVS-4T, ⊖ CL-2.5T

Figure 5 shows the effect of the temperature of the solution on the limiting-current density. The temperature coefficient of the limiting-current density at 25.0°C was calculated to be 2.1% from Eq. (10). However, the experimental values which were evaluated from Fig. 5 were 1.4% for the anion-exchange membrane, NEOSEPTA AVS-4T, and 1.2% for the cation-exchange membrane, NEOSEPTA CL-2.5T, at 25.0°C.

The effect on the limiting-current density of the length of a membrane in the direction of the flow is shown in Fig. 6. The concentration of the effluent decreases in comparison with that of the feed solution in the cell which contains long membranes. However, when sea water was concentrated using the cell 4 (the flow velocity of the solution was 6.0 cm/sec, the membrane length was 120 cm, and the current density was 35 mA/cm²), the concentration of the effluent decreased only about 2% in comparison with that of the feed solution. Accordingly, the effect of the desalting of the solution on the limiting-current density is negligible. Figure 7 shows current voltage curves measured at three different points from the bottom edge of a membrane 40 cm long. This figure demonstrates that the diffusion-boundary layer grows as the feed solution nears the upper edge of the membrane.

In the cell 3 the empirical equations of the limiting-current density to the length of the membrane show as follows:

for NEOSEPTA AVS-4T:

$$i_{\mathrm{lim}} = 50L^{-0.45} \tag{12}$$

for NEOSEPTA CL-2.5T:

$$i_{\mathrm{lim}} = 30L^{-0.45} \tag{13}$$

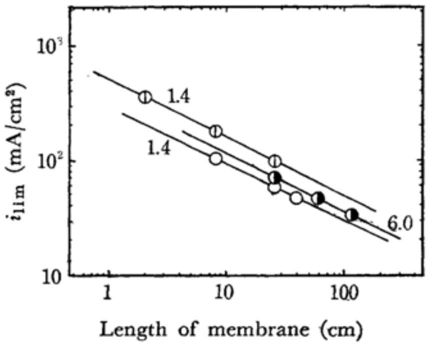

Fig. 6. The effect of a length of the membrane in the direction of flow on the limiting-current density.
Cell: cell 3 for AVS-4T or CL-2.5T
cell 4 for a pair of AVS-4T and CL-2.5T
Solution: sea water (Cl: 0.52 N) in laminar flow at 28.0°C
Numbers in the figure are the flow velocity of the solution (cm/sec).
⦶ AVS-4T, ○ CL-2.5T,
◑ AVS-4T and CL-2.5T

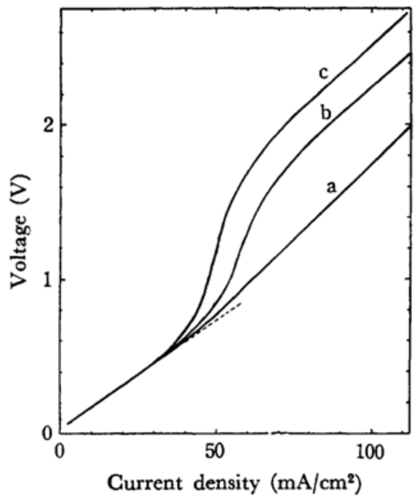

Fig. 7. Current-voltage curves measured at three different points in a membrane having a length of 40 cm in the direction of flow.
a : Measured at a distance of 2.0 cm from bottom edge of a membrane,
b : Measured at a distance of 20.0 cm from the bottom edge of a membrane,
c : Measured at a distance of 38.0 cm from the bottom edge of a membrane.
Membrane: CL-2.5T (with cell 3)
Solution: sea water (Cl: 0.52 N) in laminar flow at 28.0°C.

where L is the total length of the membrane in the direction of the flow (cm). For the cell 4 containing a pair of membranes, NEOSEPTA AVS-4T and CL-2.5T, the following equation is obtained:

$$i_{\mathrm{lim}} = 35L^{-0.48} \tag{14}$$

These results show that the limiting-current density is approximately proportional, inversely, the one-half power of the membrane length in the laminar flow.

The concentration of the solution on both sides of the membrane was the same when the current-voltage curves were measured in the cells 1, 3 and 5. However, in practical electrodialyzers one side of the membrane is in contact with the concentrated solution, and the other, with the desalted. An electrolyte diffuses through the membrane from the concentrating compartment to the desalting. Accordingly, the effect on the limiting-current density of the diffusion of the electrolyte through the membrane must be considered in a practical electrodialyzer. If the amount of the electrolyte which diffuses through the membrane is introduced into Eq. (1), Eq. (1) is modified as follows:

$$i_{\mathrm{lim}} = \frac{\boldsymbol{F}C_b}{(t_m - t_s)\delta}\left\{D + \left(\frac{C_c}{C_b}\right)\left(\frac{D_m}{\delta_m}\right)\delta\right\} \tag{15}$$

where δ_m is the thickness of the membrane; D_m, the diffusion coefficient of the electrolyte through the membrane, and C_c, the concentration of the concentrated solution. It was estimated from Eq. (15) that the limiting-current density increased about 4.7% in the cell 4 (the membrane length was 120 cm, the limiting-current density was 35 mA/cm^2, the concentration of the concentrated solution was 4.0 N, and D_m/δ_m was 2.7×10^{-6} cm/sec).

All the experiments mentioned above were performed in solutions of sodium chloride or sea water. It is apparent in Eqs. (4) and (5) that the limiting-current density changes with the ionic species as a result of the differences in the transport number and the diffusion coeffcient in the free solution, and in the viscosity of the solution. The relation of the limiting-current density in the natural convection to the diffusion coefficient and the transport numbers in various electrolytes (*e.g.*, sodium chloride, lithium chloride, potassium chloride, calcium chloride, hydrogen chloride, cupric chloride and ammonium chloride) is shown in Fig. 8; it agrees with the relation of Eq. (5).

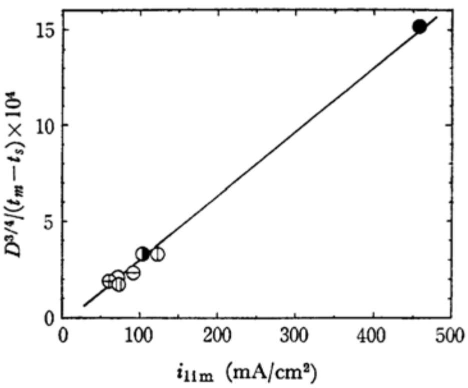

Fig. 8. The relation of the diffusion coefficient and transport numbers of the counterion in the membrane and solution to the limiting current density.
Membrane: CL-2.5T (with cell 5)
Solution: 0.5 N aqueous solution in natural convection at 25.0°C
● HCl, ⊕ LiCl, ⊖ NaCl, ⦶ KCl, ⦷ CaCl$_2$, ◐ NH$_4$Cl, ○ CuCl$_2$

With barium chloride, ferric chloride and aluminium chloride, the limiting-current density was not obtained because the current-voltage curve did not show any inflexion point or because their hydroxide precipitated on the surface of the membrane at a current density lower than the inflexion point.

If the current-voltage curve was measured in a solution containing two ionic species of the counterion, and if their limiting-current density differed from one another, the current-voltage curve might show two different limiting-current densities. An experiment was carried out with the anion-exchange membrane, NEOSEPTA AVS-4T, inserted in a mixed solution of sodium chloride and sodium sulfate. However, two different limiting-current densities were not observed; rather a limiting-current density was observed between the limiting-current densities observed in chloride and sulfate solutions.

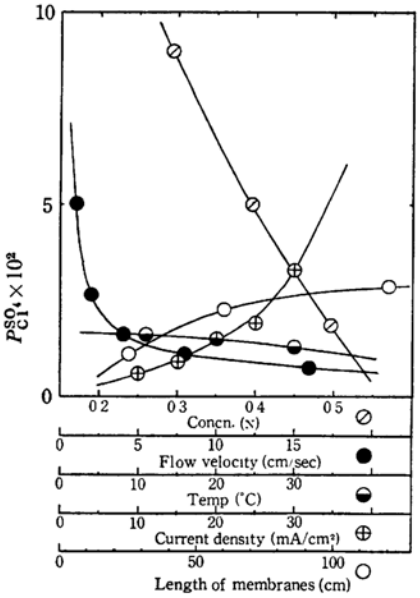

Fig. 9. The effect of conditions of the electrodialytic concentration of sea water on the relative transport numbers of SO$_4^{2-}$ to Cl$^-$. The conditions are shown in Table 3.

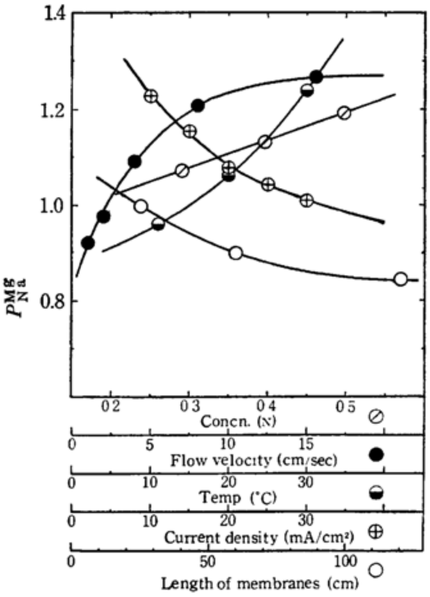

Fig. 10. The effect of conditions of the electrodialytic concentration of sea water on the relative transport numbers of Mg^{2+} to Na$^+$. The conditions are shown in Table 3.

In a multiple-ionic-species system, the change in the diffusion-boundary layer causes a difference of the composition of ions at the membrane-solution interfaces from that in the bulk solution, so that the relative transport numbers between ions change. The concentration ratio at the desalting membrane-solution interface of sulfate to chloride ions, which pass through the anion-exchange membrane more easily than do sulfate ions, increases in comparison with that of the bulk solution when the electrodialysis is carried out at a low concentration, a low flow velocity, a low temperature, and a high current density and with a long membrane. Consequently, the transport number of sulfate ions increases, as is shown in Fig. 9. Inversely, the concentration ratio at the desalting membrane-solution interface of magnesium to sodium ions, which pass through the cation-exchange membrane with more difficulty than do magnesium ions, decreases in comparison with that of the bulk solution when the electrodialysis is carried out at a low concentration, a low flow velocity, a low temperature, and a high current density and with a long membrane. Consequently, the transport number of magnesium ions decreases, as is shown in Fig. 10. The condition of the diffusion-boundary layer has a remarkable influence on the relative transport numbers.

After all, the limiting-current density and the relative transport number are relative values; they vary with the condition of the diffusion-boundary layer.

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