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Donnan Dialysis with Ion-Exchange Membranes. II. Diffusion Coefficients Using Same Valence Ions

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ABSTRACT

Donnan dialysis with ion-exchange membranes was investigated experimentally. The equation derived theoretically in the previous paper was fitted to the results of a Donnan dialytic experiment, and the diffusion coefficients of various kinds of ions and in various kinds of ion-exchange membranes were obtained. The flux of monovalent ions in Donnan dialysis was much larger than that of bivalent ions. Thus, monovalent drive ions are the best kind of drive ions to employ. It was found that the ratio of the diffusion coefficient in the ion-exchange membrane to that in the solution remained constant at 70 for monovalent feed and drive ions except for H^+ ions, and at 175 for bivalent feed and drive ions. It became apparent that the fundamental equation derived from Fick's equation and no electric current might be used for Donnan dialysis instead of the Nernst–Planck equation.

INTRODUCTION

Ion-exchange membranes have been used in the industrial separation field because ion-exchange membranes have the good characteristic to being able to separate an object continuously without changing the phase. Donnan dialysis is important for separations using ion-exchange membranes because it does not need an electric current, such as does electrodialysis, and it can also be applied to drug delivery systems.

There are many studies on Donnan dialysis with ion-exchange membranes (1–11). Kojima et al. (2) obtained the diffusion coefficients in the

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membrane by separating the mass transfer resistance of ions in the boundary film from the overall resistance. Sudoh et al. (3) obtained the diffusion coefficient in the membrane by using a simple diffusion system. Ho et al. (7) assumed that the ratio of the diffusion coefficients of two counterions in the membrane was equal to that in the aqueous solution, and they obtained the values of the diffusion coefficients by fitting the Nernst–Planck equation to the experimental data, but their assumption has not been confirmed and is doubtful.

In this study the transfer of ions through ion-exchange membranes for Donnan dialysis was measured. The diffusion coefficients of ions in the membrane were determined by curve fitting of the equation derived in the previous paper (12) to the results of Donnan dialytic experiments. The kinds of ions and ion-exchange membranes are discussed as they relate to the flux of Donnan dialysis.

THEORETICAL METHOD

Theoretical Equation

Equation, (1), a fundamental equation for Donnan dialysis, was derived in the previous paper (12) by using Fick's equation and no electric current.

$$\begin{aligned} z_A J_A &= -\frac{z_A D_A}{2}\frac{dq_A}{dx} + \frac{z_B D_B}{2}\frac{dq_B}{dx} \\ z_B J_B &= \frac{z_A D_A}{2}\frac{dq_A}{dx} - \frac{z_B D_B}{2}\frac{dq_B}{dx} \end{aligned} \qquad (1)$$

where D, J, q, and z are a diffusion coefficient, a flux, a concentration, and a valence of ions in the membrane, respectively. x is a distance. The subscripts A and B denote feed ions and drive ions, respectively.

When it is assumed that the valence of feed ions is equal to that of drive ions, i.e., $z_A = z_B$, the relationship between the time and the concentration of ions in the membrane on Donnan dialysis from Eq. (1) was represented by Eq. (2), which was derived in the previous paper (12) and includes various kinds of characteristic coefficients of the membrane.

$$\frac{dC_{AI}}{dt} = \frac{(D_A + D_B)QS(V_I + V_{II})}{4LV_I V_{II}} \qquad (2)$$

$$\times\left[\left\{\frac{C_{AT} - C_{AI}}{z(1 - K^{1/z})(C_{AT} - C_{AI}) + K^{1/z}C_{TII}}\right\} - \left\{\frac{C_{AI}}{z(1 - K^{1/z})C_{AI} + K^{1/z}C_{TI}}\right\}\right]$$

where C is the concentration of ions in the solution. K and Q are the selectively coefficient and the exchange capacity of ions in the membrane, respectively. L and S are the thickness and the area of the membrane, respectively. V is the volume of the cell. t is the time. The subscripts T, I, and II denote the total ions, cell I, and cell II, respectively.

Determination of the Diffusion Coefficients

When four or six kinds of the Donnan dialytic experiments for the diffusion coefficients of α, β, and γ ions (i.e., combinations of α–β, β–α, α–γ, γ–α, β–γ, and γ–β for feed ions and drive ions, respectively) were carried out, the diffusion coefficients (D_α, D_β, and D_γ) of α, β, and γ ions are determined as follows.

1. Eq. (2) is fitted to the experimental result of α feed ions and β drive ions. The diffusion coefficients (D_α and D_β) of α and β ions were determined.
2. Eq. (2) is again fitted to the experimental result of β feed ions and α drive ions. D_α and D_β obtained at step 1 are corrected until Eq. (2) substituted by D_α and D_β is fitted to the experimental results for α feed and β drive ions or for β feed and α drive ions, respectively.
3. Eq. (2) substituted by D_α obtained at step 2 is fitted to the experimental results of α feed ions and γ drive ions. D_α is corrected, and the diffusion coefficient (D_γ) of γ ions is determined.
4. Eq. (2) is again fitted to the experimental result of γ feed ions and α drive ions. D_α and D_γ obtained at step 3 are corrected.
5. Eq. (2) substituted by D_β obtained at step 2 and D_γ obtained at step 4 is fitted to the experimental results of β feed ions and γ drive ions. D_β and D_α are corrected.
6. Eq. (2) substituted by D_β and D_γ obtained at step 5 is fitted to the experimental results of γ feed ions and β drive ions. D_β and D_γ are corrected.
7. The operations from step 1 to step 6 are repeated until Eq. (2) substituted by D_α, D_β, and D_γ satisfies all experimental results of combinations α–β, β–α, α–γ, γ–α, β–γ, and γ–β for feed and drive ions.

EXPERIMENTAL PROCEDURE

A schematic diagram of the Donnan dialytic equipment used in this study is shown in Fig. 1. The volume of cell I is equal to that of cell II ($V_I = V_{II}$) and is 2.48×10^{-4} m^3. The area of the membrane (S) is 2.83×10^{-3} m^2. The kinds of ion-exchange membranes used are Neosepta C66-5T (Tokuyama Co.), Selemion CMV (Asahi Glass Co.), Aciplex K101 (Asahi Chemical Industry Co.), and Nafion 417 cation-exchange mem-

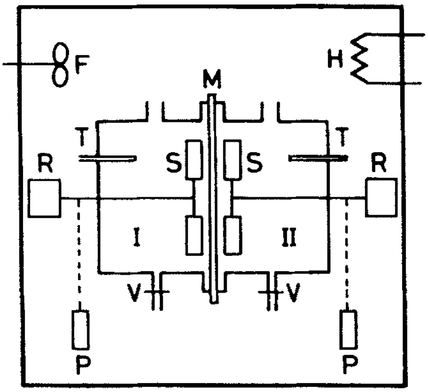

FIG. 1 Schematic diagram of the experimental equipment of Donnan dialysis. F, fan; H, thermostat; I and II, cells; M, ion-exchange membrane; P, photo tachometer; R, motor; S, stirrer; T, thermometer; V, valve.

branes (DuPont Co.). The characteristics of these membranes (13–15) are shown in Table 1.

Only feed ions (A^{z_A+}-ions) exist in cell I. Both feed ions and drive ions (B^{z_B+}-ions) are entered into cell II. Thus, initially there are no B^{z_B+}-ions in cell I. The initial concentration of feed ions in cell I is equal to that in cell II. Unit volumes (1.0×10^{-6} m^3) of the solutions from both cell I and cell II were sampled at each time (t). The monovalent cations used were H^+, K^+, and Na^+ ions, and the bivalent cations were Ca^{2+}, Cu^{2+},

TABLE 1
Characteristic Coefficients of Various Kinds of Ion-Exchange Membranes[a]

	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417
Q (kmol·m^{-3})	2.84	2.25	1.62	0.938
$L \times 10^4$ (m)	1.33	1.30	1.88	4.18
K_K^{Na}	0.674	0.708	0.533	0.305
K_K^H	0.397	0.606	0.753	0.381
K_{Na}^H	0.564	0.705	0.975	0.553
K_{Ca}^{Cu}	0.310	0.305	0.341	0.253
K_{Ca}^{Mg}	0.108	0.0986	0.114	0.101
K_{Cu}^{Mg}	0.725	0.782	0.614	0.929

[a] Values measured in previous papers (13–15).

TABLE 2
Experimental Conditions

Run	Stirrer speed (rpm)	Cell I: Feed ions	Cell I: C_{AI0} (kmol·m^{-3})	Cell II: Feed ions	Cell II: C_{AII0} (kmol·m^{-3})	Cell II: Strip ions	Cell II: C_{BII0} (kmol·m^{-3})
1[a]	300	Na^+	0.01	Na^+	0.01	H^+	1.0
2[a]	500	Na^+	0.01	Na^+	0.01	H^+	1.0
3[a]	600	Na^+	0.01	Na^+	0.01	H^+	1.0
4[a]	700	Na^+	0.01	Na^+	0.01	H^+	1.0
5[a]	600	K^+	0.01	K^+	0.01	Na^+	1.0
6[a]	600	K^+	0.01	K^+	0.01	H^+	1.0
7[a]	600	Na^+	0.01	Na^+	0.01	K^+	1.0
8[a]	600	Ca^{2+}	0.01	Ca^{2+}	0.01	Cu^{2+}	1.0
9[a]	600	Ca^{2+}	0.01	Ca^{2+}	0.01	Mg^{2+}	1.0
10[a]	600	Cu^{2+}	0.01	Cu^{2+}	0.01	Ca^{2+}	1.0
11[a]	600	Cu^{2+}	0.01	Cu^{2+}	0.01	Mg^{2+}	1.0
12[a]	600	Mg^{2+}	0.01	Mg^{2+}	0.01	Ca^{2+}	1.0
13[a]	600	Mg^{2+}	0.01	Mg^{2+}	0.01	Cu^{2+}	1.0
14[b]	600	K^+	0.01	K^+	0.01	Na^+	1.0
15[c]	600	K^+	0.01	K^+	0.01	Na^+	1.0
16[d]	600	K^+	0.01	K^+	0.01	Na^+	1.0

[a] Neosepta C66-5T membrane.
[b] Selemion CMV membrane.
[c] Aciplex K101 membrane.
[d] Nafion 417 membrane.

and Mg^{2+} ions. The concentrations of cations in the solution were measured with a Perkin-Elmer 403 atomic absorption spectrophotometer or by a titration method. These experimental conditions are shown in Table 2.

The resistance of the boundary layer of the solution was investigated by changing the stirrer speed at Runs 1–4 in Table 2. The effect of kinds of ions on the flux was studied at Runs 3 and 5–13. The influence of kinds of cation-exchange membranes on the flux was investigated at Runs 5 and 14–16. The temperature of the solution in each cell was kept at 298 ± 0.5 K.

RESULTS AND DISCUSSION

Stirrer Speed

In order to investigate the influence of stirrer speed on the flux of Donnan dialysis, the concentration of feed ions in cell I was measured for various kinds of stirrer speeds as shown at Runs 1–4 in Table 2. The relation between the time (t) and the concentration (C_{AI}/C_{AI0}) is shown in Fig. 2, where C_{AI} and C_{AI0} are the concentrations of feed ions at t second and at the initial time, respectively.

Figure 2 shows that C_{AI}/C_{AI0} decreases with an increase of stirrer speed from 300, 500, to 600 rpm. The resistance in the boundary layer of the solution on the surface of the membrane decreases and the flux in the boundary layer increases with an increase of stirrer speed from 300, 500, to 600 rpm. However, C_{AI}/C_{AI0} at 600 rpm was equal to that at 700 rpm. It was found that the resistance in the boundary layer above 600 rpm was negligibly smaller than that in the membrane. Therefore, the stirrer speed in the following experiments was 600 rpm.

Diffusion Coefficients of Ions in the Membrane

Figures 3 and 4 show the relationship between t and C_{AI}/C_{AI0} using H^+, K^+, and Na^+ ions as monovalent ions and using Ca^{2+}, Cu^{2+}, and Mg^{2+} ions as bivalent ions. A Neosepta C66-5T cation-exchange membrane was used in Figs. 3 and 4. It was found from Figs. 3 and 4 that the flux of monovalent ions is larger than that of bivalent ions because C_{AI}/C_{AI0} in Fig. 3 is smaller than that in Fig. 4.

Equation (2) substituted by the characteristic coefficients of the membrane shown in Table 1 was calculated and fitted to the Donnan dialytic experiments as described in the previous section, i.e., determination of the diffusion coefficient. The values of the diffusion coefficients (D) ob-

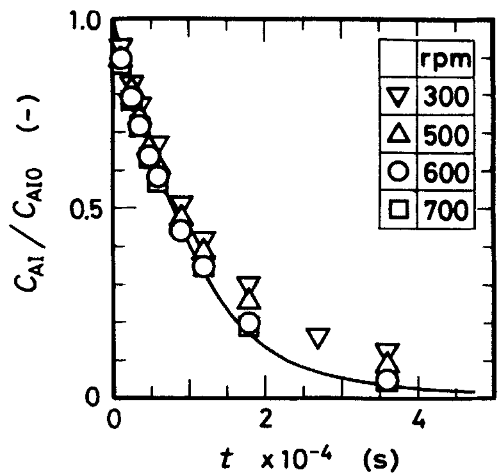

FIG. 2 Influence of the speed of the stirrer on the relationship between t and C_{AI}/C_{AI0}. The solid line represents the values calculated from Eq. (2).

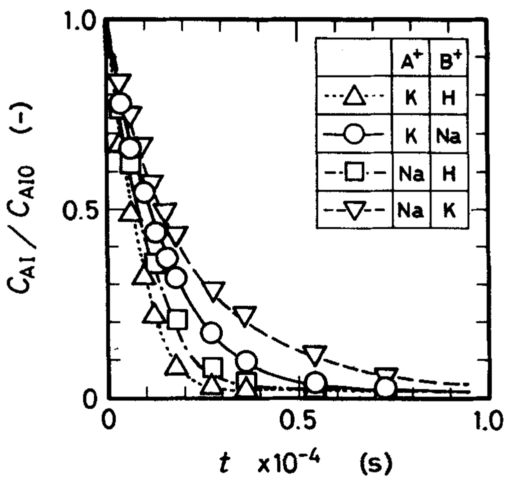

FIG. 3 Relationship between t and C_{AI}/C_{AI0} when both feed ions (A^+) and drive ions (B^+) are monovalent ions. Each line expresses values calculated from Eq. (2).

tained are shown in Table 3. The diffusion coefficient in the solution (D_s) was calculated from Ref. 16. The values of D_s/D are also shown in Table 3. It is found from Table 3 that the order of ions for the diffusion coefficients in the membrane (D) is equal to that in the solution (D_s). The values

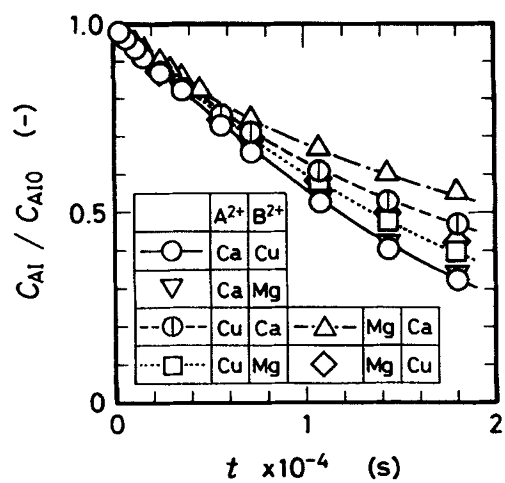

FIG. 4 Dependence of t on C_{AI}/C_{AI0} when both feed ions (A^{2+}) and drive ions (B^{2+}) are bivalent ions. Each line denotes values calculated from Eq. (2).

TABLE 3
Diffusion Coefficients in the Ion-Exchange Membrane (D) and in the Solution[a] (D_s)

	$D \times 10^{11}$ ($m^2 \cdot s^{-1}$)	$D_s \times 10^9$ ($m^2 \cdot s^{-1}$)	D_s/D
H^+	4.66	9.31	200
K^+	2.80	1.96	70
Na^+	1.90	1.33	70
Ca^{2+}	0.453	0.792	175
Cu^{2+}	0.418	0.732	175
Mg^{2+}	0.403	0.706	175
H^+ [b]	11.2	9.31	83.1
H^+ [c]	18.6	9.31	50.1
H^+ [d]	2.10–4.22	9.31	443–221
Na^+ [d]	3.01–6.05	1.33	44–22
Cu^{2+} [b]	0.89	0.732	82.2
Cu^{2+} [c]	2.07	0.732	35.4

[a] Values calculated by using the limit conductivities of cations in *Kagaku Binran II* (16).
[b] Data measured by Kojima et al. (2).
[c] Data measured by Sudoh et al. (3).
[d] Data measured by Ho et al. (7).

of the diffusion coefficients as measured by Kojima et al. (2), Sudoh et al. (3), and Ho et al. (7) are also shown in Table 3. The values of the diffusion coefficient of H^+ ions measured by the workers of Refs. 2 and 3 are larger than that obtained in this study, but that measured by the workers of Ref. 7 is approximately equal to our value. It was found from Table 3 that the values of D_s/D for K^+ and Na^+ ions are constant at 70, and those of all kinds of bivalent ions are constant at 175.

Each line shown in Figs. 3 and 4 represents values calculated from Eq. (2) substituted by the values of the diffusion coefficient shown in Table 3. Equation (2) was calculated for all experimental results using bivalent feed and drive ions, but two lines for Ca^{2+}–Mg^{2+} and Mg^{2+}–Cu^{2+} systems for bivalent feed and drive ions, respectively, are omitted because these lines are complicated. It is evident from Figs. 3 and 4 that all lines calculated from Eq. (2) are in good agreement with the experimental values measured by using monovalent or bivalent ions.

When H^+ ions are adopted as drive ions in Fig. 3, the flux of H^+ is the largest of those ions used whatever the kind of feed ions because the diffusion coefficient of H^+ has the largest value of all ions in Table 3. The flux of monovalent feed and drive ions in Fig. 3 is larger than that of bivalent ions in Fig. 4. It is important to use drive ions with a large diffusion coefficient value for Donnan dialysis. Therefore, it is evident that H^+ ions are the best ions to use as the drive ions of Donnan dialysis.

Kinds of Ion-Exchange Membranes

The influence of the kinds of ion-exchange membranes, i.e., Neosepta C66-5T, Selemion CMV, Aciplex K101, and Nafion 417 cation-exchange membranes, on the flux of Donnan dialysis is shown in Fig. 5 when the feed ions in cells I and II are Na^+ ions of 0.01 kmol·m^{-3} and the drive ions in cell II are K^+ ions of 1.0 kmol·m^{-3}.

It is found from Table 3 that the ratio of the diffusion coefficient in the Neosepta C66-5T membrane to that in the solution (D_s/D) was constant. Thus, it is assumed that the same conclusion can be applied to each membrane. The diffusion coefficients (D_K and D_{Na}) of Na^+ and K^+ ions obtained for each cation-exchange membrane, the diffusion coefficient in the solution (D_s), and the ratio (D_s/D) of the diffusion coefficient in each ion-exchange membrane to that in the solution are shown in Table 4. All lines in Fig. 5 represent values calculated from Eq. (2) substituted by the diffusion coefficients in Table 4. All lines are good agreement with the experimental values in Fig. 5.

The values of C_{AI}/C_{AI0} in Fig. 5 increase in the order Neosepta C66-5T, Selemion CMV, Aciplex K101, Nafion 417 cation-exchange membranes. It was found that the value of the diffusion coefficient of the Nafion 417 membrane is largest of those membranes listed in Table 4, although the flux of the Nafion 417 membrane is the smallest of the membranes shown in Fig. 5. This result means that the flux of Donnan dialysis

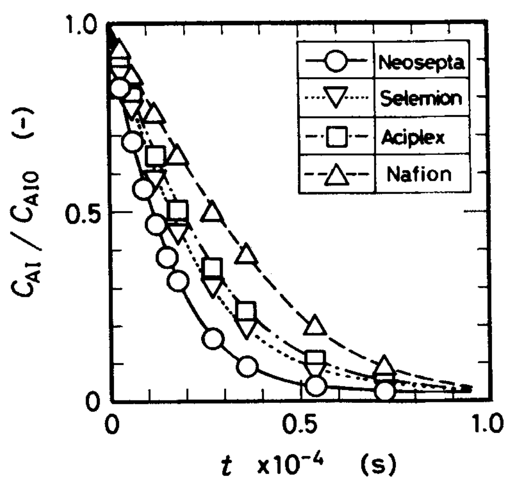

FIG. 5 Influence of kinds of ion-exchange membranes on relation between t and C_{AI}/C_{AI0}. Each line shows values calculated from Eq. (2).

TABLE 4
Diffusion Coefficients D ($m^2 \cdot s^{-1}$) in Various Kinds of Ion-Exchange Membranes

Ion[a]	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417
K, $D_K \times 10^{11}$ $m^2 \cdot s^{-1}$	2.80	2.45	3.92	9.80
K, $D_{SK} \times 10^9$ $m^2 \cdot s^{-1}$	1.96	1.96	1.96	1.96
K, D_{SK}/D_K	70	80	50	20
Na, $D_{Na} \times 10^{11}$ $m^2 \cdot s^{-1}$	1.90	1.66	2.66	6.65
Na, $D_{SNa} \times 10^9$ $m^2 \cdot s^{-1}$	1.33	1.33	1.33	1.33
Na, D_{SNa}/D_{Na}	70	80	50	20

[a] D: Diffusion coefficient in the ion-exchange membrane. D_s: Diffusion coefficient in the solution.

is strongly influenced by the characteristics of the membrane, i.e., the diffusion coefficient, the exchange capacity, the selectivity coefficient, and the thickness of the membrane.

The Nernst–Planck equation is usually used for the transfer of ions in an ion-exchange membrane. However, this equation is very complicated. As we mentioned in the previous paper (12), Eq. (1) was derived from Fick's equation and no electric current. The diffusion coefficients in Tables 3 and 4 can be obtained by using Eq. (2) derived from Eq. (1) and the experimental results. Therefore, Eq. (1), which is simpler than the Nernst–Planck equation, can be used as a fundamental equation of Donnan dialysis.

CONCLUSIONS

1. The diffusion coefficients of various kinds of ions in ion-exchange membranes were obtained by fitting Eq. (2) to the experimental values of Donnan dialysis.
2. The ratio D_s/D of the diffusion coefficient in the ion-exchange membranes to that in the solution remained constant at 70 for monovalent feed and drive ions except for H^+ ions, and at 175 for bivalent feed and drive ions.
3. The diffusion coefficients of ions in various kinds of ion-exchange membranes were obtained.
4. The flux of monovalent feed and drive ions on Donnan dialysis was much larger than that of bivalent feed and drive ions. Thus, monovalent drive ions are the best kind of drive ions to employ.
5. A fundamental equation describing the transfer of ions in the ion-

exchange membrane is Eq. (1), which is much simpler than the Nernst–Planck equation.

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SYMBOLS

C	concentration in the solution (kmol·m^{-3})
D	diffusion coefficient (m^2·s^{-1})
K	selectivity coefficient (—)
L	thickness of the membrane (m)
Q	exchange capacity of the membrane (kmol·m^{-3})
S	area of the membrane (m^2)
t	time (s)
V	volume of cell (m^3)
z	valence (—)

Greek Letters

α	ions
β	ions
γ	ions

Subscripts

A	feed ions
B	drive ions
I	value in cell I
II	value in cell II
s	value in solution
T	total value
0	initial value

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