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Donnan Dialysis with Ion-Exchange Membranes. III. Diffusion Coefficients Using Ions of Different Valence

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ABSTRACT

Donnan dialysis with ion-exchange membranes was studied under various kinds of experimental conditions using ions of different valences. The diffusion coefficients (D_d) of various kinds of ions in the ion-exchange membrane were obtained by curve fitting an equation derived from the mass balance to three kinds of Donnan dialytic experiments. It was found that the value of D_d/D_s using D_d of monovalent ions in Donnan dialysis with a set of monovalent feed ions and bivalent driving ions was 1/175, where D_s represents a diffusion coefficient in solution. D_s was calculated from the Nernst–Einstein equation substituted by the ionic conductance of ions at infinite dilution in water. Using D_d of bivalent ions in Donnan dialysis with the same set led to a D_d/D_s value of 1/438. Moreover, using D_d in Donnan dialysis with the same set, the value of D_d/D_e was kept constant at 0.4 (D_e expresses the diffusion coefficient in the membrane when the valences of the feed and driving ions are equal). On the other hand, both D_d/D_s and D_d/D_e using D_d in Donnan dialysis with a set of bivalent feed ions and monovalent driving ions were not constant.

INTRODUCTION

Ion-exchange membranes are generally used for electrodialysis around the world. These membranes are good for the continuous separation of an object without changing its phase. Donnan dialysis is an example of such a separation set that uses an ion-exchange membrane. The Donnan dialytic method is based on the Donnan equilibrium. Kojima et al. (1), Sudoh et al. (2), Ho et al. (3), Sionkowski and Wodzki (4), Guirao et al. (5), and Dammak et al. (6) studied Donnan dialysis and obtained values for the diffusion coefficients by using a pair of feed and driving ions. But it is difficult to determine the diffusion coefficient of each ion in the membrane by fitting the Nernst–Planck equation to experimental data of a single set of feed and driving ions. Thus, the values of the diffusion coefficients obtained so far should be reinvestigated.

In previous papers (7–9) the mass balance equation was discussed instead of the Nernst–Planck equation. The mass balance equation was applied to the transfer of ions in the ion-exchange membrane in Donnan dialysis and then a new equation was derived. In this study a Donnan dialytic experiment is carried out under conditions in which the valence of the feed ions is different from that of the driving ions. The equations derived in a previous paper (7) are fitted to the experimental values that are measured for three sets of feed and driving ions in the present study. The diffusion coefficients included in these equations are determined for various kinds of ions. Moreover, the mass balance equation derived in a previous paper (7) is discussed.

THEORETICAL METHOD

The Donnan dialysis set chosen for this study sandwiches the ion-exchange membrane between cells I and II. It is the same set used in previous papers (7–9). The concentration of feed ions (A^{zA} ions with z_A valences) in cell I is equal to that in cell II, but the concentration of driving ions (B^{zB} ions with z_B valences) in cell I is very much smaller than that in cell II. In this case, driving ions diffuse from cell II to I through the ion-exchange membrane. The driving force of the driving ions pumps feed ions from cell I to II. Feed ions are then concentrated in cell II.

In a previous paper (7) the mass balance equation was chosen instead of the Nernst–Planck equation. The mass balance equation was applied to the transfer of ions in the ion-exchange membrane in Donnan dialysis. Two new equations were derived when the valence of feed ions became different from that of driving ions. The relation between a time (t) and a concentration (C_{AI}) of feed ions in cell I is represented by Eq. (1), rewritten from D to D_d in the corresponding equation in a previous paper (7). This equation is relevant when feed ions are monovalent ($z_A = 1$) and driving ions are bivalent ($z_B = 2$), where z is a valence of ions (i.e., A^+–B^{2+} ions set):

$$\frac{dC_{AI}}{dt} = \frac{(D_{dA} + D_{dB})S(V_I + V_{II})}{8LV_IV_{II}} [\{(X_{II}^2 + 4QX_{II})^{0.5} - X_{II}\} - \{(X_I^2 + 4QX_I)^{0.5} - X_I\}] \quad (1)$$

D_d and Q are the diffusion coefficient of counterions and the concentration of fixed 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. The subscripts of A, B, I, and II denote feed ions, driving ions, and cells I and II, respectively. X_I and X_{II} have a dimension of concentration and are defined in Eq. (2):

$$\begin{aligned} X_{\mathrm{I}} &= \frac{(z_{\mathrm{A}} q_{\mathrm{AI}})^{\mathrm{zB}}}{(z_{\mathrm{B}} q_{\mathrm{BI}})^{\mathrm{zA}}} = \frac{q_{\mathrm{AI}}^2}{2q_{\mathrm{BI}}} = \frac{C_{\mathrm{AI}}^2}{2K_{\mathrm{AI}}^{\mathrm{B}} C_{\mathrm{BI}}} = \frac{C_{\mathrm{AI}}^2}{K_{\mathrm{AI}}^{\mathrm{B}}(C_{\mathrm{TI}} - C_{\mathrm{AI}})} \\ X_{\mathrm{II}} &= \frac{(z_{\mathrm{A}} q_{\mathrm{AII}})^{\mathrm{zB}}}{(z_{\mathrm{B}} q_{\mathrm{BII}})^{\mathrm{zA}}} = \frac{q_{\mathrm{AII}}^2}{2q_{\mathrm{BII}}} = \frac{C_{\mathrm{AII}}^2}{2K_{\mathrm{AII}}^{\mathrm{B}} C_{\mathrm{BII}}} = \frac{(C_{\mathrm{AT}} - C_{\mathrm{AI}})^2}{K_{\mathrm{AII}}^{\mathrm{B}}(C_{\mathrm{TII}} - C_{\mathrm{AT}} + C_{\mathrm{AI}})} \end{aligned} \tag{2}$$

where K is a selectivity coefficient of ions in the membrane. C_{AT}, C_{TI}, and C_{TII} are defined by Eq. (3):

$$\begin{aligned} C_{\mathrm{AT}} &= C_{\mathrm{AI}} + C_{\mathrm{AII}} \\ C_{\mathrm{TI}} &= z_{\mathrm{A}} C_{\mathrm{AI}} + z_{\mathrm{B}} C_{\mathrm{BI}} \\ C_{\mathrm{TII}} &= z_{\mathrm{A}} C_{\mathrm{AII}} + z_{\mathrm{B}} C_{\mathrm{BII}} \end{aligned} \tag{3}$$

where the subscript T denotes the total value.

The influence of t on C_{AI} of feed ions in cell I is also represented by Eq. (4), rewritten from D to D_{d} in the corresponding equation in a previous paper (7). Equation (4) is used when feed ions are bivalent ($z_{\mathrm{A}} = 2$) and driving ions are monovalent ($z_{\mathrm{B}} = 1$) (i.e., A^{2+}–B^{+} ions set):

$$\begin{aligned} \frac{dC_{\mathrm{AI}}}{dt} = & \frac{(D_{\mathrm{dA}} + D_{\mathrm{dB}}) S (V_{\mathrm{I}} + V_{\mathrm{II}})}{16 L V_{\mathrm{I}} V_{\mathrm{II}}} \\ & [\{Y_{\mathrm{II}} - (Y_{\mathrm{II}}^2 + 4QY_{\mathrm{II}})^{0.5}\} - \{Y_{\mathrm{I}} - (Y_{\mathrm{I}}^2 + 4QY_{\mathrm{I}})^{0.5}\}] \end{aligned} \tag{4}$$

where Y_{I} and Y_{II} have a dimension of concentration and are defined by Eq. (5):

$$\begin{aligned} Y_{\mathrm{I}} &= \frac{(z_{\mathrm{B}} q_{\mathrm{BI}})^{\mathrm{zA}}}{(z_{\mathrm{A}} q_{\mathrm{AI}})^{\mathrm{zB}}} = \frac{q_{\mathrm{BI}}^2}{2q_{\mathrm{AI}}} = \frac{K_{\mathrm{AI}}^{\mathrm{B}} C_{\mathrm{BI}}^2}{2C_{\mathrm{AI}}} = \frac{K_{\mathrm{AI}}^{\mathrm{B}}(C_{\mathrm{TI}} - 2C_{\mathrm{AI}})^2}{2C_{\mathrm{AI}}} \\ Y_{\mathrm{II}} &= \frac{(z_{\mathrm{B}} q_{\mathrm{BII}})^{\mathrm{zA}}}{(z_{\mathrm{A}} q_{\mathrm{AII}})^{\mathrm{zB}}} = \frac{q_{\mathrm{BII}}^2}{2q_{\mathrm{AII}}} = \frac{K_{\mathrm{AII}}^{\mathrm{B}} C_{\mathrm{BII}}^2}{2C_{\mathrm{AII}}} = \frac{K_{\mathrm{AII}}^{\mathrm{B}}(C_{\mathrm{TII}} - 2C_{\mathrm{AT}} + 2C_{\mathrm{AI}})^2}{2(C_{\mathrm{AT}} - C_{\mathrm{AI}})} \end{aligned} \tag{5}$$

Equations (4) and (5) are slightly modified from equations derived in a previous paper (7) because the definition of Y in Eq. (5) becomes the same as that of X in Eq. (2).

EXPERIMENTAL PROCEDURE

The Donnan dialytic equipment used in this study is the same as mentioned in previous papers (8, 9). The volume of each cell is the same ($V_{\mathrm{I}} = V_{\mathrm{II}}$) and is 2.48×10^{-4} m^3. Each cell was stirred at 600 rpm, at which the resistance of the flux of ions in the boundary layer became negligibly smaller than that in the membrane (8, 9). The area of the membrane (S) is 2.83×10^{-3} m^2. The ion-exchange membrane used is the Neosepta C66-5T cation-

TABLE 1
Thickness (L), Water Content (W), Density (ρ), Exchange Capacity (E), and Concentration (Q) of Fixed Ions in the Neosepta C66-5T Membrane (10)

L (m)	W	ρ (kg m^{-3})	E (mol·kg^{-1})	Q (kmol·m^{-3})
1.33×10^{-4}	0.413	1.14×10^{-3}	2.48	2.84

exchange membrane (Tokuyama Co., Ltd.) which is a sulfonated copolymer of styrene and divinylbenzene. The characteristic coefficients of the membrane are shown in Table 1 (10).

Initially, only feed ions (A^{zA} ions) exist in cell I and there are no driving ions (B^{zB} ions) in cell I. Both feed ions and driving ions are introduced into cell II. The initial concentration of feed ions in cell I is equal to that in cell II. The monovalent cations used are K^+, Na^+, and H^+ ions, and the bivalent cations are Ca^{2+}, Mg^{2+}, and Cu^{2+} ions. The concentration of cations in the solution was measured with an atomic absorption spectrophotometer or by titration. These experimental conditions are shown in Table 2. The temperature of the solution in each cell was kept at 298 ± 0.5 K.

TABLE 2
Experimental Conditions[a]

	Cell I	Cell II	
Run	Feed ions	Feed ions	Driving ions
1	K^+	K^+	Ca^{2+}
2	K^+	K^+	Cu^{2+}
3	K^+	K^+	Mg^{2+}
4	Na^+	Na^+	Ca^{2+}
5	Na^+	Na^+	Cu^{2+}
6	Na^+	Na^+	Mg^{2+}
7	Ca^{2+}	Ca^{2+}	H^+
8	Ca^{2+}	Ca^{2+}	K^+
9	Ca^{2+}	Ca^{2+}	Na^+
10	Cu^{2+}	Cu^{2+}	H^+
11	Cu^{2+}	Cu^{2+}	K^+
12	Cu^{2+}	Cu^{2+}	Na^+
13	Mg^{2+}	Mg^{2+}	H^+
14	Mg^{2+}	Mg^{2+}	K^+
15	Mg^{2+}	Mg^{2+}	Na^+

[a] $C_{AI0} = 0.01$ kmol·m^{-3}. $C_{AII0} = 0.01$ kmol·m^{-3}. $C_{BI0} = 0$. $C_{BII0} = 1.0$ kmol·m^{-3}.

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RESULTS AND DISCUSSION

A^+–B^{2+} Ions Set

A Donnan dialytic experiment with a set of monovalent feed ions and bivalent driving ions (i.e., A^+–B^{2+} ions set) was carried out in Runs 1–6 in Table 2. The concentration (C_{AI}) of feed ions in cell I was measured at each interval. The relation between a time (t) and a dimensionless concentration (C_{AI}/C_{AI0}) of feed ions in cell I is shown in Fig. 1, where C_{AI0} is a concentration of feed ions in cell I at the initial time. Figure 1 shows that the value of vertical axis, i.e., C_{AI}/C_{AI0}, decreases with an increase of t.

C_{AI}/C_{AI0} measured with a set of K^+ as feed ions and Cu^{2+} as driving ions (K^+–Cu^{2+} ions set) represents the fastest decrease in value among those of all ions employed. The flux of the K^+–Cu^{2+} ions set is therefore the largest in flux of all ions sets because the more quickly decreasing value of C_{AI}/C_{AI0} represents a larger flux of ions in the membrane. On the other hand, C_{AI}/C_{AI0} measured with an Na^+–Ca^{2+} ions set has the slowest decreasing value among all ions sets used.

A^{2+}–B^+ Ions Set

The result of this Donnan dialytic experiment with a set of bivalent feed ions and monovalent driving ions (i.e., A^{2+}–B^+ ions set) is shown in Fig. 2.

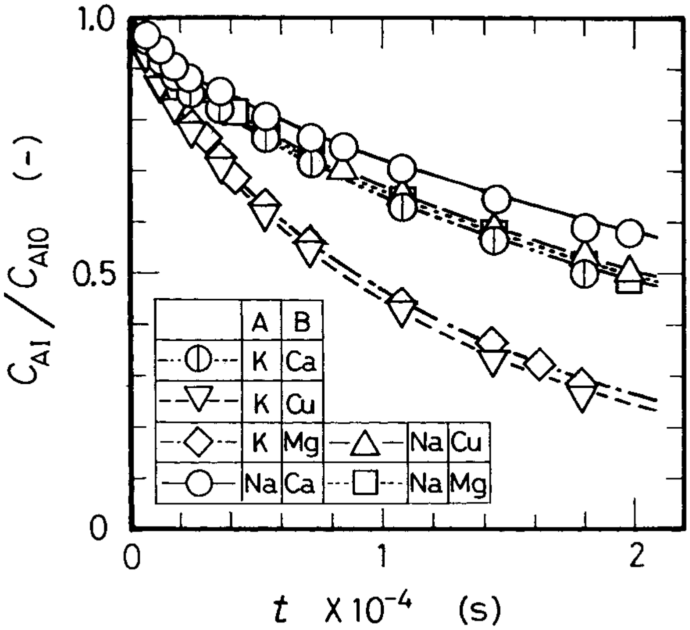

FIG. 1 Relation between the time (t) and the dimensionless concentration (C_{AI}/C_{AI0}) of feed ions in cell I when the feed ions are monovalent and the driving ions are bivalent, i.e., A^+–B^{2+} ions set. All lines represent values calculated from Eq. (1) substituted by D_d in Table 4.

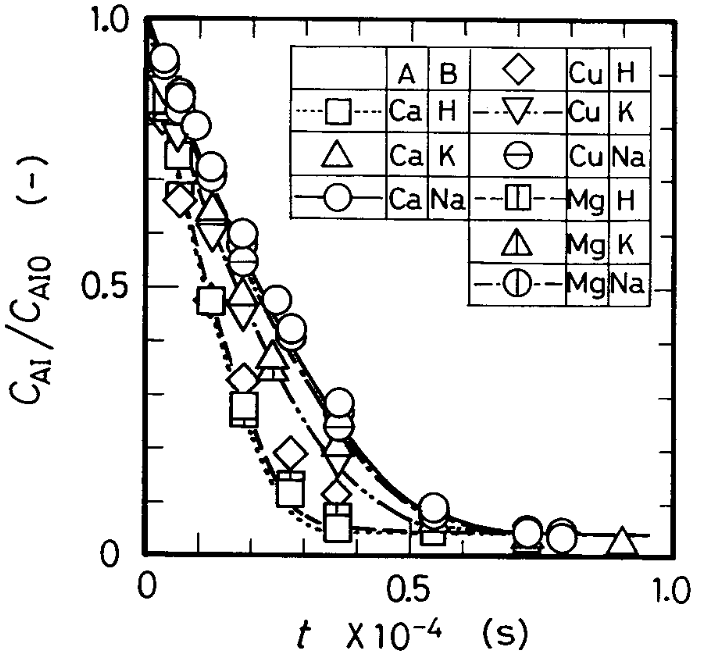

FIG. 2 Influence of t on C_{AI}/C_{AI0} in the which the feed ions are bivalent and the driving ions are monovalent, i.e., A^{2+}–B^{+} ions set. Each line expresses values calculated from Eq. (4) substituted by D_d in Table 4.

It can be seen in Figs. 1 and 2 that the flux in Donnan dialysis with an A^{2+}–B^{+} ions set was larger than that with an A^{+}–B^{2+} ions set because the vertical axis in Fig. 2 (e.g., $C_{AI}/C_{AI0} \cong 0.065$ for a Cu^{2+}–K^{+} ions set) was much smaller than that in Fig. 1 (e.g., $C_{AI}/C_{AI0} \cong 0.63$ for a K^{+}–Cu^{2+} ions set) with the same time (e.g., $t = 0.5 \times 10^4$ s). Therefore, it is evident that it is better to use monovalent ions as driving ions to obtain a larger flux by Donnan dialysis. This would be useful, for example, for the process by which metal ions are recovered from wastewater. On the other hand, it is better to employ ions with a higher valence than bivalent ions as driving ions in order to obtain a lower flux. This is useful, for example, in the delivery process by which drugs are released into the human body.

Diffusion Coefficient

Using the separation factor (α) shown in Table 3 (10, 11), the selectivity coefficient (K) included in Eqs. (2) and (5) is defined by Eq. (6):

$$K_{B}^{A} = \frac{(z_B q_B)^{ZA}(z_A C_A)^{zB}}{(z_A q_A)^{zB}(z_B C_B)^{zA}} = \alpha_{A}^{B}\left(\frac{C_T}{Q}\right)^{zB \cdot zA} \qquad (6)$$

TABLE 3
Separation Factors of Ions in the Neosepta C66-5T Membrane (10, 11)

α_{H}^{Ca}	α_{H}^{Cu}	α_{H}^{Mg}	α_{K}^{Ca}	α_{K}^{Cu}	α_{K}^{Mg}	α_{Na}^{Ca}	α_{Na}^{Cu}	α_{Na}^{Mg}
296	7.50	14.3	61.5	8.05	9.37	69.4	32.4	29.6

Equation (1) substituted by the values of L and Q shown in Table 1 and by K calculated from α shown in Table 3 was fitted to each experimental value shown in Fig. 1. The values of the diffusion coefficient (D_d) in Donnan dialysis with an A^+–B^{2+} ions set were obtained by trial and error, as described in a previous paper (8). For example, D_d of K^+ ions was determined by fitting Eq. (1) to three kinds of experimental data (i.e., K^+–Ca^{2+}, K^+–Cu^{2+}, and K^+–Mg^{2+} ions sets) as shown in Table 2. The values of D_d obtained for all ions are shown in Table 4. The values of D_d in Donnan dialysis with an A^{2+}–B^+ ions set were also obtained by curve fitting Eq. (4) to experimental values in Fig. 2, and the values of D_d are also shown in Table 4. However,

TABLE 4
Diffusion Coefficients D_d and D_e[a] in the Membrane and Diffusion Coefficient D_s[b] in Solution

			$z_A = 1$ (A^+), $z_B = 2$ (B^{2+})			$z_A = 2$ (A^{2+}), $z_B = 1$ (B^+)		
	$D_s \times 10^{11}$ [b] ($m^2 \cdot s^{-1}$)	$z_A = z_B$, $D_e \times 10^{11}$ [a] ($m^2 \cdot s^{-1}$)	$D_d \times 10^{11}$ ($m^2 \cdot s^{-1}$)	D_d/D_s	D_d/D_e	$D_d \times 10^{11}$ ($m^2 \cdot s^{-1}$)	D_d/D_s	D_d/D_e
H^+	931	4.66	—	—	—	23.3[c]	1/40.0	5.0
H^+	931	4.66	—	—	—	9.31[d]	1/100	2.0
K^+	196	2.80	1.12	1/175	0.4	5.60	1/35.0	2.0
Na^+	133	1.90	0.760	1/175	0.4	5.70	1/23.3	3.0
Ca^{2+}	79.2	0.453	0.181	1/438	0.4	2.26	1/35.0	5.0
Cu^{2+}	73.2	0.418	0.167	1/438	0.4	0.837	1/87.5	2.0
Mg^{2+}	70.6	0.403	0.161	1/439	0.4	0.807	1/87.5	2.0
H^+ [e]	931	—	—	—	—	11.2	1/83	—
H^+ [f]	931	—	—	—	—	18.6	1/50	—
Cu^{2+} [e]	73.2	—	—	—	—	0.89	1/82	—
Cu^{2+} [f]	73.2	—	—	—	—	2.07	1/35	—

[a] Values measured by Miyoshi and Yamagami (8).

[b] Values calculated from the Nernst–Einstein equation substituted by the ionic conductance of ions at infinite dilution in water, in *Kagaku Binran* (12).

[c] Value of Ca^{2+}–H^+ ions set.

[d] Value of Cu^{2+}–H^+ and Mg^{2+}–H^+ ions sets.

[e] Values measured by Kojima et al. (1).

[f] Values measured by Sudoh et al. (2).

it was impossible to fit Eq. (4) to the experimental data of Ca^{2+}–H^+ (Ca^{2+} feed and H^+ driving ions set), Cu^{2+}–H^+, and Mg^{2+}–H^+ ions sets by using one constant diffusion coefficient of H^+ ions. One value of the diffusion coefficients of H^+ ions was 23.3×10^{-11} $m^2 \cdot s^{-1}$ for the Ca^{2+}–H^+ ions set and another was 9.31×10^{-11} $m^2 \cdot s^{-1}$ for the Cu^{2+}–H^+ and Mg^{2+}–H^+ ions sets, as shown in Table 4. This is considered to be one explanation of why the separation factor (α_{Ca}^{H}) of the Ca^{2+}–H^+ ions set is very different from other separation factors (α_{Cu}^{H} and α_{Mg}^{H}), as shown in Table 3.

All lines in Fig. 1 or 2 were calculated from Eq. (1) or (4) which was substituted by the values of L, Q, α, and D_d shown in Tables 1, 3, and 4, respectively. All influences of t on C_{AI}/C_{AI0} in Fig. 2 were calculated from Eq. (4). However for the sake of simplicity, only the lines for Ca^{2+}–H^+, Ca^{2+}–Na^+, Cu^{2+}–K^+, Mg^{2+}–H^+, and Mg^{2+}–Na^+ ions sets are shown in Fig. 2. It was found that the lines in Figs. 1 and 2 were in agreement with the experimental data. The constant diffusion coefficient of H^+ ions could not be only obtained for an A^{2+}–B^+ ions set. In spite of this, it became apparent that Eqs. (1) and (4), derived from the mass balance with no electric potential factor different from the Nernst–Planck equation, could be applied to the transfer of ions in the membrane on Donnan dialysis.

It is evident from Table 4 that the values of D_d of H^+ and Cu^{2+} ions as measured by Kojima et al. (1) are approximately equal to those measured in this study. But the values of D_d of H^+ and Cu^{2+} ions measured by Sudoh et al. (2) are larger than those in this study. One of the reasons for this may be that the data measured by Sudoh et al. (2) were calculated from the Nernst–Planck equation.

The values of the diffusion coefficient (D_s) of ions in solution are also shown in Table 4, where D_s denotes a diffusion coefficient calculated from the Nernst–Einstein equation substituted by the ionic conductance of ions at infinite dilution in water (12). The values of D_d/D_s were calculated and are also shown in Table 4. Table 4 shows that the value of D_d of monovalent ions in Donnan dialysis with an A^+–B^{2+} ions set is 1/175 times D_s, and D_d of bivalent ions in Donnan dialysis with the same ions set was 1/438 times D_s. On the other hand, the value of D_d/D_s using the D_d of ions in Donnan dialysis with an A^{2+}–B^+ ions set was not constant.

Moreover, the relationship between D_e and D_d was calculated and is shown in Table 4 as well, where D_e represents a diffusion coefficient in Donnan dialysis when the valence of feed ions is equal to that of driving ions (e.g., A^+–B^+ or A^{2+}–B^{2+} ions set). The values of D_e have been measured in previous papers (8, 9). It is evident from Table 4 that all values of D_d/D_e using D_d in Donnan dialysis with an A^+–B^{2+} ions set are rendered constant at 0.4. However, it is apparent from this study that the values of D_d/D_e using D_d in Donnan dialysis with an A^{2+}–B^+ ions set changed from 2.0 to 3.0 and 5.0.

Therefore, it is evident from Table 4 that the relationship between D_d and D_e can be represented by

$$\begin{aligned} D_d\ (\text{at } z_A = 1, z_B = 2) &< D_e\ (\text{at } z_A = z_B) \\ &< D_d(\text{at } z_A = 2, z_B = 1) \end{aligned} \tag{7}$$

Motion of Monovalent Ions and Bivalent Ions

A monovalent ion in the ion-exchange membrane makes an ion pair with a fixed ion and transfers from one fixed ion to another neighboring fixed ion. A bivalent ion makes an ion pair with two fixed ions and transfers from two fixed ions to two other neighboring fixed ions, that is, a set of two fixed ions is necessary for the motion of one bivalent ion in the membrane. However, one monovalent ion needs only one fixed ion, that is, a half set of a bivalent ion. When both monovalent and bivalent ions exist in the ion-exchange membrane, a monovalent ion can transfer along with a usual fixed ion. Moreover, a monovalent ion in this situation can move by using a remaining fixed ion that did not combine with a bivalent ion. Thus, when both monovalent and bivalent ions exist in the membrane, the monovalent ion can move more easily from one fixed ion to the next than it can when only monovalent ions exist in the membrane. On the other hand, when both monovalent and bivalent ions exist in the membrane, bivalent ions do not move more easily. This is because bivalent ions need two fixed ions in the membrane, hence their motion is interfered with by the coexistence of monovalent ions.

When feed ions are bivalent and driving ions are monovalent, (i.e., A^{2+}–B^{+} ions set), the motion of monovalent driving ions (B^{+} ions) in the membrane is interfered with to a lesser extent by the presence of bivalent feed ions (A^{2+} ions), as has been described above. Under these circumstances, many B^{+} ions can move from cell II to I. Furthermore, the quantity of A^{2+} ions moving through the membrane increases simultaneously with an increase of the driving force of B^{+} ions by electroneutrality. Therefore, the driving force of driving ions with an A^{2+}–B^{+} ions set is larger than that with a set of monovalent feed ions and monovalent driving ions (A^{+}–B^{+} ions set), or with a set of bivalent feed ions and bivalent driving ions (A^{2+}–B^{2+} ions set). Of course, the driving force of driving ions with an A^{2+}–B^{+} ions set is larger than that with an A^{+}–B^{2+} ions set. On the other hand, the driving force of bivalent driving ions (B^{2+} ions) in an A^{+}–B^{2+} ions set becomes smaller than that of B^{+} ions in an A^{+}–B^{+} ions set and that of B^{2+} ions in an A^{2+}–B^{2+} ions set. For this reason, the relationship between D_d and D_e can be represented by Eq. (7), i.e., D_d in the A^{2+}–B^{+} ions set is the largest, D_e in the A^{+}–B^{+} or A^{2+}–B^{2+} ions set is in the middle, and D_d in the A^{+}–B^{2+} ions set is the smallest in Table 4. D_d/D_e using D_d in an A^{+}–B^{2+} ions set becomes 0.4, and D_d/D_e

using D_d in an A^{2+}–B^{+} ions set results in values of 2.0 to 5.0. Future studies will be necessary to investigate why the value of D_d/D_e becomes exactly 0.4.

The set of the diffusion coefficient of K^{+} ions as feed ions and that of Ca^{2+} ions as driving ions is the largest in those of each ion in Table 4, but the flux of a K^{+}–Cu^{2+} ions set is the largest of those in Fig. 1. This is because the flux in the membrane is not only influenced by the diffusion coefficient but also by the selectivity coefficient and the valence of the ions.

CONCLUSIONS

1. It is evident that Eq. (1), derived from the mass balance, can be applied to the transfer of all kinds of ions in the membrane in Donnan dialysis with an A^{+}–B^{2+} ions set. Equation (4) can also be used for determining the motion of ions in the membrane in Donnan dialysis with an A^{2+}–B^{+} ions set with the exception of H^{+} ions.
2. The value of D_d/D_s using D_d of monovalent ions in Donnan dialysis with an A^{+}–B^{2+} ions set became 1/175. D_d/D_s using D_d of bivalent ions in Donnan dialysis with the same ions set led to 1/438. On the other hand, D_d/D_s in Donnan dialysis with an A^{2+}–B^{+} ions set was not constant.
3. A constant value of 0.4 was obtained for the relation between D_e in Donnan dialysis, when the valences of feed ions and monovalent ions were equal, and D_d in Donnan dialysis with an A^{+}–B^{2+} ions set. The ratio of D_e to D_d in Donnan dialysis with an A^{2+}–B^{+} ions set changed from 2.0 to 3.0 and 5.0.

SYMBOLS

C	concentration of counterions in solution ($\text{kmol}\cdot\text{m}^{-3}$)
D	diffusion coefficient of counterions in the membrane ($\text{m}^2\cdot\text{s}^{-1}$)
E	exchange capacity of fixed ions in the membrane ($\text{mol}\cdot\text{kg}^{-1}$)
K	selectivity coefficient defined by Eq. (6) (—)
L	thickness of the membrane (m)
Q	concentration of fixed ions in the membrane ($\text{kmol}\cdot\text{m}^{-3}$)
q	concentration of counterions in the membrane ($\text{kmol}\cdot\text{m}^{-3}$)
S	area of the membrane (m^2)
t	time (s)
V	volume of cell (m^3)
W	water content (—)
X	defined by Eq. (2) ($\text{kmol}\cdot\text{m}^{-3}$)
Y	defined by Eq. (5) ($\text{kmol}\cdot\text{m}^{-3}$)
z	valence (—)

Greek Letters

α	separation factor (—)
ρ	density (kg·m^{-3})

Subscripts

A	feed ions
B	driving ions
d	value when the valence of feed ions is different from that of driving ions
e	value when the valence of feed ions is equal to that of driving 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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