This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Donnan Dialysis with Ion-Exchange Membranes. I. Theoretical Equation

Hirofumi Miyoshi[a]
[a] RESEARCH INSTITUTE FOR ADVANCED SCIENCE AND TECHNOLOGY, OSAKA PREFECTURE UNIVERSITY, OSAKA, JAPAN

To cite this Article Miyoshi, Hirofumi(1996) 'Donnan Dialysis with Ion-Exchange Membranes. I. Theoretical Equation', Separation Science and Technology, 31: 15, 2117 — 2129

To link to this Article: DOI: 10.1080/01496399608001034

URL: http://dx.doi.org/10.1080/01496399608001034

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **31**(15), pp. 2117–2129, 1996

Donnan Dialysis with Ion-Exchange Membranes. I. Theoretical Equation

HIROFUMI MIYOSHI
RESEARCH INSTITUTE FOR ADVANCED SCIENCE AND TECHNOLOGY
OSAKA PREFECTURE UNIVERSITY
1-2, GAKUEN-CHO, SAKAI, OSAKA 593, JAPAN

ABSTRACT

The transfer of ions through ion-exchange membranes was investigated theoretically for Donnan dialysis. By applying Fick's equation and no electric current to the flux through the ion-exchange membrane on Donnan dialysis, and by changing the valences of feed and drive ions, three kinds of equations were derived: 1) feed ions and drive ions are of equal valence, 2) feed ions are monovalent and drive ions are bivalent, and 3) feed ions are bivalent and drive ions are monovalent. The equations were evaluated by use of a computer by the Runge–Kutta method. The relation between the valence of ions and the characteristic coefficients of the membrane became apparent from the calculated results.

INTRODUCTION

Ion-exchange membranes have been used industrially for separation by electrodialysis (1–3), diffusion dialysis (4, 5), and Donnan dialysis (6, 7), offering the advantage of allowing continuous separation without a change of phase. Donnan dialysis is an important form of separation with ion-exchange membranes because it does not require the application of an electric current, as does electrodialysis, and it can be applied to drug delivery, which has recently attracted worldwide attention. The transfer mechanism of Donnan dialysis is very complicated, involving an electric potential during the diffusion of ions, and has not been fully clarified.

The transfer of ions in the ion-exchange membrane on Donnan dialysis is usually represented by the Nernst–Planck equation, which takes into consideration both Fick's equation and the electric potential. But the Nernst–Planck equation is very complex because it contains the electric potential. Thus, a simple equation which considers Fick's equation and no electric current is derived in this study. The equation includes the characteristic coefficients of the ions and the membrane, and it represents the relationship between the concentration in the solution and time.

THEORETICAL EQUATION

General Formula

The simulation of Donnan dialysis with an ion-exchange membrane is shown as Fig. 1, in which the membrane separates cells I and II. It is assumed that ions move only in the direction of the thickness of the membrane (x-axis), and the mass transfer coefficients in both boundary layers throughout the solution on the surface of the ion-exchange membrane are much larger than that in the membrane M, because the solution in both cells is stirred very well, making the thickness of the boundary layer of the solution negligibly small.

When the concentration of the solution in cell I is different from that in cell II, in general, the flux (J_A) of A^{z_A}-ions with valence z_A and that (J_B) of B^{z_B}-ions with valence z_B in the membrane are represented by Eq. (1) from Fick's equation.

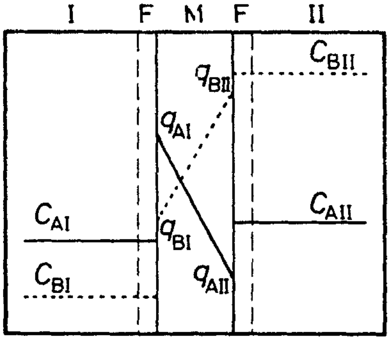

FIG. 1 Simulation of Donnan dialysis with ion-exchange membrane. C_{AI}, C_{AII}, concentrations of feed ions in cell I and cell II, respectively; C_{BI}, C_{BII}, concentrations of drive ions in cell I and cell II, respectively; F, boundary layer; I and II, cells; M, ion-exchange membrane; q_{AI}, q_{AII}, concentrations of feed ions at the surface of the membrane in cell I and cell II, respectively; q_{BI}, q_{BII}, concentrations of drive ions at the surface of the membrane in cell I and cell II, respectively.

$$J_A = -D_A \frac{dq_A}{dx}$$
$$J_B = -D_B \frac{dq_B}{dx} \tag{1}$$

where J, D, and q are flux, diffusion coefficient, and concentration in the membrane, respectively.

It is assumed that the concentration of the drive ions (B^{zB}-ions) in cell II is much higher than that in cell I as shown in Fig. 1, but the concentration of feed ions (A^{zA}-ions) in cell I is approximately equal to that in cell II. In this case, B^{zB}-ions diffuse from cell II to cell I through the ion-exchange membrane, many B^{zB}-ions exist on the surface in cell I, and B^{zB}-ions can no longer diffuse from cell II to cell I by Donnan equilibrium. However, in this time, when the same quantity of A^{zA}-ions as that of B^{zB}-ions transferred has moved from cell I to cell II, B^{zB}-ions again become able to diffuse from cell II to cell I. The diffusion of B^{zB}-ions depends on that of A^{zA}-ions, and vice versa. Therefore, by the diving force of B^{zB}-ions, A^{zA}-ions are pumped from cell I to cell II.

Moreover, with no electric current, the relation between J_A and J_B is represented by

$$z_A J_A + z_B J_B = 0 \tag{2}$$

From Eqs. (1) and (2), the fluxes of A^{zA}-ions and B^{zB}-ions in the membrane on Donnan dialysis can be represented by

$$z_A J_A = -\frac{z_A D_A}{2} \frac{dq_A}{dx} + \frac{z_B D_B}{2} \frac{dq_B}{dx}$$
$$z_B J_B = \frac{z_A D_A}{2} \frac{dq_A}{dx} - \frac{z_B D_B}{2} \frac{dq_B}{dx} \tag{3}$$

This equation, a fundamental equation for Donnan dialysis, is derived by using the Fick's equation and no electric current.

Boundary conditions are expressed by Eq. (4).

$$\begin{aligned} q_A &= q_{AI} && \text{at} \quad x = 0 \\ q_B &= q_{BI} && \text{at} \quad x = 0 \\ q_A &= q_{AII} && \text{at} \quad x = L \\ q_B &= q_{BII} && \text{at} \quad x = L \end{aligned} \tag{4}$$

where L is the thickness of the membrane.

Equation (3) integrated by using Eq. (4) is described by

$$\begin{aligned} z_A J_A &= -\frac{z_A D_A}{2L}(q_{AII} - q_{AI}) + \frac{z_B D_B}{2L}(q_{BII} - q_{BI}) \\ z_B J_B &= \frac{z_A D_A}{2L}(q_{AII} - q_{AI}) - \frac{z_B D_B}{2L}(q_{BII} - q_{BI}) \end{aligned} \tag{5}$$

In an electric neutral condition, the concentration of all counterions in the membrane ($z_A q_A$ and $z_B q_B$) is equal to that of the fixed ions, that is, the exchange capacity (Q). Thus, the relationships of the concentrations at the surfaces of the membrane in cell I or cell II are represented by

$$\begin{aligned} z_A q_{AI} + z_B q_{BI} &= Q \quad \text{at} \quad x = 0 \\ z_A q_{AII} + z_B q_{BII} &= Q \quad \text{at} \quad x = L \end{aligned} \tag{6}$$

Substitution of Eq. (6) into Eq. (5) gives

$$\begin{aligned} J_A &= -\frac{D_A + D_B}{2L}(q_{AII} - q_{AI}) \\ J_B &= -\frac{D_A + D_B}{2L}(q_{BII} - q_{BI}) \end{aligned} \tag{7}$$

This equation shows that for Donnan dialysis the flux of ions in the membrane is represented by the reciprocal of the thickness of the membrane and by the product of the mean values of the diffusion coefficients of A^{z_A}-ions and B^{z_B}-ions and the difference between the concentrations at both surfaces in the membrane of cells I and II.

On the other hand, the flux of A^{z_A}-ions through the ion-exchange membrane (J) is equal to that in the solution, by the law of conservation of mass. The relation between the flux in the membrane and the concentration in the solution is expressed by

$$\begin{aligned} -\frac{V_I}{S}\frac{dC_{AI}}{dt} &= J_A \\ \frac{V_{II}}{S}\frac{dC_{AII}}{dt} &= J_A \end{aligned} \tag{8}$$

where C is the concentration of the solution, and S and V are the area of the membrane and the volume of the cell, respectively. Thus, the dependence of the concentrations of A^{z_A}-ions in cell I and cell II on time is represented by

$$
\begin{aligned}
-\frac{V_I}{S}\frac{dC_{AI}}{dt} &= -\frac{D_A + D_B}{2L}(q_{AII} - q_{AI}) \\
\frac{V_{II}}{S}\frac{dC_{AII}}{dt} &= -\frac{D_A + D_B}{2L}(q_{AII} - q_{AI})
\end{aligned}
\tag{9}
$$

The concentration of all ions in the solution in cell I or cell II is expressed by Eq. (10). Because the quantity of A^{zA}-ions transferred from cell I to cell II is equal to that of B^{zB}-ions transferred from cell II to cell I, the total equivalent of ions in the solution in cell I or cell II is kept constant:

$$
\begin{aligned}
z_A C_{AI} + z_B C_{BI} &= C_{TI} \quad \text{at} \quad \text{cell I} \\
z_A C_{AII} + z_B C_{BII} &= C_{TII} \quad \text{at} \quad \text{cell II}
\end{aligned}
\tag{10}
$$

Moreover, the total concentration of A^{zA}-ions or B^{zB}-ions in cell I and cell II is constant:

$$
\begin{aligned}
C_{AI} + C_{AII} &= C_{AT} \quad \text{at} \quad A^{zA}\text{-ions} \\
C_{BI} + C_{BII} &= C_{BT} \quad \text{at} \quad B^{zB}\text{-ions}
\end{aligned}
\tag{11}
$$

From Eqs. (9) and (11), the relationship between the concentration of A^{zA}-ions in cell I and time is represented by

$$
\frac{dC_{AI}}{dt} = \frac{(D_A + D_B)\,S\,(V_I + V_{II})}{4LV_IV_{II}}(q_{AII} - q_{AI}) \tag{12}
$$

The selectivity coefficients (K^B_{AI} and K^B_{AII}) on the two surfaces of the ion-exchange membrane in cell I and cell II are represented by

$$
\begin{aligned}
K^B_{AI} &= \frac{q^{zA}_{BI}\,C^{zB}_{AI}}{q^{zB}_{AI}\,C^{zA}_{BI}} \quad \text{at} \quad x = 0 \\
K^B_{AII} &= \frac{q^{zA}_{BII}\,C^{zB}_{AII}}{q^{zB}_{AII}\,C^{zA}_{BII}} \quad \text{at} \quad x = L
\end{aligned}
\tag{13}
$$

Case 1: $z_A = z_B = z$

It is assumed that a valence (z_A) of A^{zA}-ions is equal to that (z_B) of B^{zB}-ions:

$$
z_A = z_B = z \tag{14}
$$

In this case, it is known that Eq. (15) is valid at $z_A = z_B$ (8–10).

$$
K^B_{AI} = K^B_{AII} = K \tag{15}
$$

From Eqs. (6), (10), (11), (13), (14), and (15), the concentrations at both surfaces of the membrane in cell I and cell II are represented by

$$\begin{aligned} q_{\mathrm{AI}} &= \frac{QC_{\mathrm{AI}}}{z(1 - K^{1/z})C_{\mathrm{AI}} + K^{1/z}C_{\mathrm{TI}}} && \text{at} \quad x = 0 \\ q_{\mathrm{AII}} &= \frac{Q(C_{\mathrm{AT}} - C_{\mathrm{AI}})}{z(1 - K^{1/z})(C_{\mathrm{AT}} - C_{\mathrm{AI}}) + K^{1/z}C_{\mathrm{TII}}} && \text{at} \quad x = L \end{aligned} \tag{16}$$

Substitution of Eq. (16) into Eq. (7) and rearrangement gives

$$\begin{aligned} J_{\mathrm{A}} = \frac{(D_{\mathrm{A}} + D_{\mathrm{B}})Q}{2L} & \left[\left\{ \frac{C_{\mathrm{AI}}}{z(1 - K^{1/z})C_{\mathrm{AI}} + K^{1/z}C_{\mathrm{TI}}} \right\} \right. \\ & \left. - \left\{ \frac{C_{\mathrm{AT}} - C_{\mathrm{AI}}}{z(1 - K^{1/z})(C_{\mathrm{AT}} - C_{\mathrm{AI}}) + K^{1/z}C_{\mathrm{TII}}} \right\} \right] \end{aligned} \tag{17}$$

Moreover, substitution of Eq. (16) into Eq. (12) gives

$$\begin{aligned} \frac{dC_{\mathrm{AI}}}{dt} = \frac{(D_{\mathrm{A}} + D_{\mathrm{B}})QS(V_{\mathrm{I}} + V_{\mathrm{II}})}{4LV_{\mathrm{I}}V_{\mathrm{II}}} & \left[\left\{ \frac{C_{\mathrm{AT}} - C_{\mathrm{AI}}}{z(1 - K^{1/z})(C_{\mathrm{AT}} - C_{\mathrm{AI}}) + K^{1/z}C_{\mathrm{TII}}} \right\} \right. \\ & \left. - \left\{ \frac{C_{\mathrm{AI}}}{z(1 - K^{1/z})C_{\mathrm{AI}} + K^{1/z}C_{\mathrm{TI}}} \right\} \right] \end{aligned} \tag{18}$$

The integral condition of Eq. (18) is denoted by

$$\begin{aligned} C_{\mathrm{AI}} &= C_{\mathrm{AI0}} && \text{at} \quad t = 0 \\ C_{\mathrm{AI}} &= C_{\mathrm{AI}} && \text{at} \quad t = t \end{aligned} \tag{19}$$

The solution of Eq. (18) by using Eq. (19) is represented by

$$\begin{aligned} & \frac{z^2(1 - K^{1/z})^2}{2K^{1/z}(C_{\mathrm{TI}} + C_{\mathrm{TII}})}(C_{\mathrm{AI}} - C_{\mathrm{AI0}})^2 \\ & + \frac{z(1 - K^{1/z})}{K^{1/z}(C_{\mathrm{TI}} + C_{\mathrm{TII}})^2}\{K^{1/z}C_{\mathrm{TI}}^2 - K^{1/z}C_{\mathrm{TII}}^2 - z(1 - K^{1/z})C_{\mathrm{TII}}C_{\mathrm{AT}}\} \\ & \times (C_{\mathrm{AI}} - C_{\mathrm{AI0}}) - \frac{C_{\mathrm{TI}}C_{\mathrm{TII}}}{K^{1/z}(C_{\mathrm{TI}} + C_{\mathrm{TII}})^3}[z(1 - K^{1/z})C_{\mathrm{AT}}\{2K^{1/z}C_{\mathrm{TI}} + 2K^{1/z}C_{\mathrm{TII}} \\ & + z(1 - K^{1/z})C_{\mathrm{AT}}\} + K^{2/z}(C_{\mathrm{TI}} + C_{\mathrm{TII}})^2] \\ & \times \ln\frac{(C_{\mathrm{TI}} + C_{\mathrm{TII}})C_{\mathrm{AI}} - C_{\mathrm{TI}}C_{\mathrm{TII}}}{(C_{\mathrm{TI}} + C_{\mathrm{TII}})C_{\mathrm{AI0}} - C_{\mathrm{TI}}C_{\mathrm{TII}}} = \frac{(D_{\mathrm{A}} + D_{\mathrm{B}})QS}{4L}\left(\frac{V_{\mathrm{I}} + V_{\mathrm{II}}}{V_{\mathrm{I}}V_{\mathrm{II}}}\right)t \end{aligned} \tag{20}$$

Case 2: $z_A = 1$ and $z_B = 2$

It is assumed that the valence (z_A) of A^{z_A}-ions is 1 and that (z_B) of B^{z_B}-ions is 2, as represented by

$$\begin{aligned} z_A &= 1 \\ z_B &= 2 \end{aligned} \tag{21}$$

Substitution of Eqs. (6), (10), (11), and (21) into Eq. (13) and rewriting gives

$$\begin{aligned} K_{AI}^{B} &= \frac{Q - q_{AI}}{q_{AI}^2}\frac{C_{AI}^2}{C_{TI} - C_{AI}} \quad \text{at} \quad x = 0 \\ K_{AII}^{B} &= \frac{Q - q_{AII}}{q_{AII}^2}\frac{C_{AII}^2}{C_{TII} - C_{AII}} \quad \text{at} \quad x = L \end{aligned} \tag{22}$$

From Eqs. (22), the concentrations at both surfaces of the membrane at cell I or cell II are expressed by

$$\begin{aligned} q_{AI} &= \frac{(X_I^2 + 4QX_I)^{0.5} - X_I}{2} \quad \text{at} \quad x = 0 \\ q_{AII} &= \frac{(X_{II}^2 + 4QX_{II})^{0.5} - X_{II}}{2} \quad \text{at} \quad x = L \end{aligned} \tag{23}$$

where X_I and X_{II} are defined by

$$\begin{aligned} X_I &= \frac{C_{AI}^2}{K_{AI}^{B}(C_{TI} - C_{AI})} \\ X_{II} &= \frac{(C_{AT} - C_{AI})^2}{K_{AII}^{B}(C_{TII} - C_{AT} + C_{AI})} \end{aligned} \tag{24}$$

Thus, Eq. (7) substituted by Eq. (23) is expressed by

$$J_A = \frac{(D_A + D_B)}{4L}[\{(X_I^2 + 4QX_I)^{0.5} - X_I\} - \{(X_{II}^2 + 4QX_{II})^{0.5} - X_{II}\}] \tag{25}$$

Equation (12) substituted by Eq. (22) is represented by

$$\frac{dC_{AI}}{dt} = \frac{(D_A + D_B)S(V_I + V_{II})}{8LV_IV_{II}} \times [\{(X_{II}^2 + 4QX_{II})^{0.5} - X_{II}\} - \{(X_I^2 + 4QX_I)^{0.5} - X_I\}] \tag{26}$$

Case 3: $z_A = 2$ and $z_B = 1$

It is assumed that the valence (z_A) of A^{z_A}-ions is 2 and that (z_B) of B^{z_B}-ions is 1, as denoted by

$$\begin{aligned} z_A &= 2 \\ z_B &= 1 \end{aligned} \tag{27}$$

By substitution of Eqs. (6), (10), (11), and (27), Eq. (13) can be represented by

$$\begin{aligned} K^{B}_{AI} &= \frac{(Q - 2q_{AI})^2}{q_{AI}} \frac{C_{AI}}{(C_{TI} - 2C_{AI})^2} \qquad \text{at} \quad x = 0 \\ K^{B}_{AII} &= \frac{(Q - 2q_{AII})^2}{q_{AII}} \frac{C_{AII}}{(C_{TII} - 2C_{AII})^2} \qquad \text{at} \quad x = L \end{aligned} \tag{28}$$

From Eqs. (28), the concentrations at both surfaces of the membrane at cell I or cell II are expressed by

$$\begin{aligned} q_{AI} &= \frac{Y_I - (Y_I^2 - 16Q^2)^{0.5}}{8} \qquad \text{at} \quad x = 0 \\ q_{AII} &= \frac{Y_{II} - (Y_{II}^2 - 16Q^2)^{0.5}}{8} \qquad \text{at} \quad x = L \end{aligned} \tag{29}$$

where Y_I and Y_{II} are defined by

$$\begin{aligned} Y_I &= 4Q + K^{B}_{AI} \frac{(C_{TI} - 2C_{AI})^2}{C_{AI}} \\ Y_{II} &= 4Q + K^{B}_{AII} \frac{(C_{TII} - 2C_{AT} + 2C_{AI})^2}{(C_{AT} - C_{AI})} \end{aligned} \tag{30}$$

Therefore, Eq. (7) substituted by Eq. (29) is expressed by

$$J_A = \frac{(D_A + D_B)}{16L} [\{Y_I - (Y_I^2 - 16Q^2)^{0.5}\} - \{Y_{II} - (Y_{II}^2 - 16Q^2)^{0.5}\}] \tag{31}$$

Moreover, Eq. (12) substituted by Eq. (30) is represented by

$$\begin{aligned} \frac{dC_{AI}}{dt} &= \frac{(D_A + D_B)S(V_I + V_{II})}{32LV_I V_{II}} \\ &\quad \times [\{Y_{II} - (Y_{II}^2 - 16Q^2)^{0.5}\} - \{Y_I - (Y_I^2 - 16Q^2)^{0.5}\}] \end{aligned} \tag{32}$$

Equations (18), (26), and (32) represent the relationship between the concentration (C_{AI}) of A^{z_A}-ions in cell I and time (t). They are derived by using Fick's equation and no electric current, and will be readily analyzable by use of a computer.

THEORETICAL VALUES

Conditions for Calculation

To evaluate Eqs. (18), (26) and (32), the exchange capacity of the ion-exchange membrane (Q), the dimensions of the equipment for Donnan dialysis (L, S, and V), and the initial concentration of ions in the solution in each cell (C_{AIO}, C_{AIIO}, C_{BIO}, and C_{BIIO}) are assumed to have the values shown in Table 1. The valence of ions, diffusion coefficients of $\mathrm{A}^{z\mathrm{A}}$-ions (D_{A}) and $\mathrm{B}^{z\mathrm{B}}$-ions (D_{B}) in the ion-exchange membrane, and the separation factor ($\alpha_{\mathrm{A}}^{\mathrm{B}}$) employed for calculation are shown in Table 2. The values of the separation factor are adopted by reference to values measured previously (8–10). The relationship between the separation factor and the selectivity coefficient ($K_{\mathrm{A}}^{\mathrm{B}}$) is represented by Eq. (33) (10):

$$\begin{aligned} K_{\mathrm{A}}^{\mathrm{B}} &= \frac{(z_{\mathrm{B}}q_{\mathrm{B}})^{z\mathrm{A}}}{(z_{\mathrm{A}}q_{\mathrm{A}})^{z\mathrm{B}}} \frac{(z_{\mathrm{A}}C_{\mathrm{A}})^{z\mathrm{B}}}{(z_{\mathrm{B}}C_{\mathrm{B}})^{z\mathrm{A}}} \\ &= \alpha_{\mathrm{A}}^{\mathrm{B}} \left(\frac{C_{\mathrm{T}}}{Q}\right)^{z\mathrm{B}-z\mathrm{A}} \end{aligned} \tag{33}$$

where C_{T} is the total concentration of ions in the solution in each cell; that is, C_{TI} or C_{TII} as defined by Eq. (10).

Results

Figure 2 shows the relationships between t and $C_{\mathrm{AI}}/C_{\mathrm{AIO}}$ which were calculated from Eq. (18) or (20) by the Runge–Kutta method by use of a

TABLE 1
Exchange Capacity of the Ion-Exchange Membrane, Values of Equipment, and Initial Concentration

$Q = 2.0\ \mathrm{kmol{\cdot}m^{-3}}$
$L = 1.5 \times 10^{-4}\ \mathrm{m}$
$V_{\mathrm{I}} = V_{\mathrm{II}} = 2.0 \times 10^{-4}\ \mathrm{m^3}$
$S = 3.0 \times 10^{-3}\ \mathrm{m^2}$
$C_{\mathrm{AI}} = 0.01\ \mathrm{kmol{\cdot}m^{-3}}$
$C_{\mathrm{AII}} = 0.01\ \mathrm{kmol{\cdot}m^{-3}}$
$C_{\mathrm{BI}} = 0\ \mathrm{kmol{\cdot}m^{-3}}$
$C_{\mathrm{BII}} = 1.0\ \mathrm{kmol{\cdot}m^{-3}}$

TABLE 2
Values of Valence, Diffusion Coefficient, and Separation Factor of Ions for Evaluating Eqs. (18), (27), and (30)

Run	z_A	z_B	$D_A \times 10^{11}$ ($m^2 \cdot s^{-1}$)	$D_B \times 10^{11}$ ($m^2 \cdot s^{-1}$)	α_A^B
1	1	1	1	0.1	1
2	1	1	1	1	1
3	1	1	1	10	1
4	1	1	0.1	1	1
5	1	1	10	1	1
6	2	2	1	1	1
7	1	2	1	1	10
8	2	1	1	1	0.1
9	1	1	1	1	0.1
10	1	1	1	1	10

computer for the cases of Runs 1–5 in Table 2 for $z_A = z_B = 1$. It was found from Fig. 2 that C_{AI}/C_{AIO} decreased with an increase of t. The flux increased with an increase of the diffusion coefficients from 0.1 to 1 to 10×10^{-11} $m^2 \cdot s^{-1}$ because the value of C_{AI}/C_{AIO} at each time decreased with an increase of the diffusion coefficient.

When D_A is equal to D_B and is 1×10^{-11} $m^2 \cdot s^{-1}$, the calculated relationships between t and C_{AI}/C_{AIO} are as shown in Fig. 3, in which only the

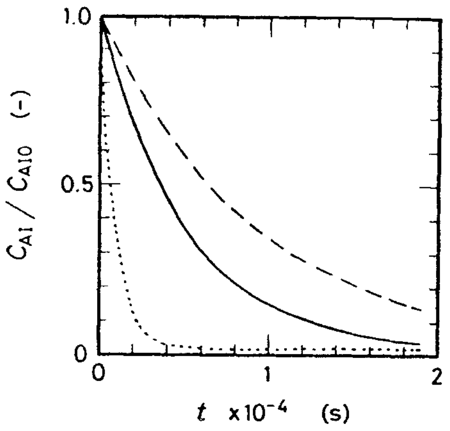

FIG. 2 The relation between time (t) and the dimensionless concentration (C_{AI}/C_{AIO}) calculated from Eq. (18) or (20) at $z_A = z_B = 1$. (– –), Runs 1 and 4; (——), Run 2; (···), Runs 3 and 5.

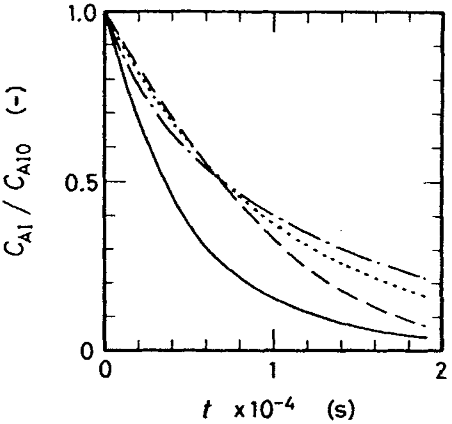

FIG. 3 The dependence of t on C_{AI}/C_{AIO} calculated from Eqs. (18), (26), and (32) at $D_A = 1$ and $D_B = 1 \times 10^{-11}$ $m^2 \cdot s^{-1}$. (——), Run 2 of $z_A = 1$ and $z_B = 1$; (···), Run 6 of $z_A = 2$ and $z_B = 2$; (-·-), Run 7 of $z_A = 1$ and $z_B = 2$; (– –), Run 8 of $z_A = 2$ and $z_B = 1$.

valences of A^{z_A}-ions and B^{z_B}-ions are changed from 1 to 2, respectively. It is evident from Fig. 3 that the flux decreases with an increase of the valence of ions from 1 to 2. Moreover, the flux in the case of $z_A = z_B = 1$ is the largest of those calculated in this study.

In Fig. 2 the relationship between t and C_{AI}/C_{AIO} in Run 1 ($D_A = 1$ and $D_B = 0.1 \times 10^{-11}$ $m^2 \cdot s^{-1}$) is equal to that in Run 4 (D_A and D_B

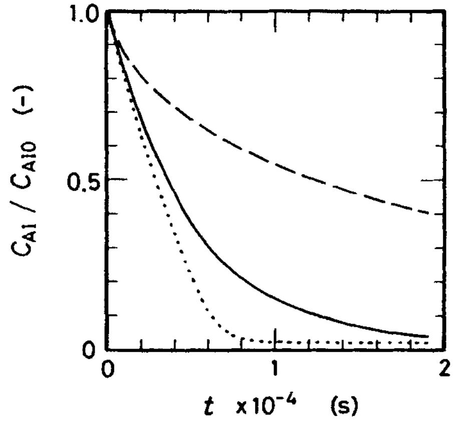

FIG. 4 The influence of t on C_{AI}/C_{AIO} calculated from Eq. (18) or (20) at $z_A = z_B = 1$. (···), Run 9 of $\alpha_A^B = 0.1$; (——), Run 2 of $\alpha_A^B = 1$; (– –), Run 10 of $\alpha_A^B = 10$.

values inverted) where the sum of D_A and D_B is kept constant at 1.1×10^{-11} $m^2 \cdot s^{-1}$. The same result is obtained in Runs 3 and 5 where (D_A + D_B) is kept constant at 11×10^{-11} $m^2 \cdot s^{-1}$. If D_A is equal to D_B, the separation factor (K_A^B) of A^{z_A}-ions to B^{z_B}-ions is mostly unequal to K_B^A. The influence of K_A^B on the relationship between t and C_{AI}/C_{AIO} is shown in Fig. 4. Figure 4 shows that the flux at $K_A^B = 0.1$ (i.e., $\alpha_A^B = 0.1$) is larger than those at $K_A^B = 1$ ($\alpha_A^B = 1$) and $K_A^B = 10$ ($\alpha_A^B = 10$). Therefore, it was found that the flux increased with a decrease of K_A^B, that is, an increase of the affinity of the feed ions (A^{z_A}-ions) in the membrane compared with the drive ions (B^{z_B}-ions).

CONCLUSIONS

By applying Fick's equation and no electric current to Donnan dialysis, three equations which included the characteristic coefficients of the membrane were derived for different valences of feed ions and drive ions: Eq. (18) or (20) in the case of $z_A = z_B$, Eq. (26) in the case of $z_A = 1$ and $z_B = 2$, and Eq. (32) in the case of $z_A = 2$ and $z_B = 1$. The relationship between the valence of ions and the characteristic coefficients of the membrane became apparent by the results calculated from Eqs. (18), (26), and (32).

SYMBOLS

C	concentration in the solution ($kmol \cdot m^{-3}$)
D	diffusion coefficient ($m^2 \cdot s^{-1}$)
J	flux ($kmol \cdot m^{-2} \cdot s^{-1}$)
K	selectivity coefficient (—)
L	thickness of the membrane (m)
Q	exchange capacity of the membrane ($kmol \cdot m^{-3}$)
q	concentration in the membrane ($kmol \cdot m^{-3}$)
S	area of the membrane (m^2)
t	time (s)
V	volume of cell (m^3)
x	distance from the surface of the membrane (m)
X	defined by Eq. (24) (—)
Y	defined by Eq. (30) (—)
z	valence (—)

Greek Letters

α	separation factor (—)

Subscripts

A	feed ions
B	drive ions
I	value in cell I
II	value in cell II
T	total value

REFERENCES

1. H. Miyoshi, T. Fukumoto, and T. Kataoka, *Sep. Sci. Technol.*, *23*, 585 (1988).
2. H. Miyoshi and T. Kataoka, *Ibid.*, *24*, 507 (1989).
3. A. T. Cherif, A. Elidaoui, and C. Gavach, *J. Membr. Sci.*, *76*, 39 (1993).
4. H. Miyoshi, T. Fukumoto, and T. Kataoka, *Desalination*, *48*, 43 (1983).
5. C. H. Hamann, V. Theile, and S. Koter, *J. Membr. Sci.*, *78*, 147 (1993).
6. R. W. Wallace, *J. Phys. Chem.*, *68*, 2418 (1964).
7. C.-C. Ho, D.-S. Jan, and F.-N. Tsai, *J. Membr. Sci.*, *81*, 287 (1993).
8. H. Miyoshi, M. Yamagami, and T. Kataoka, *Chem. Express*, *5*, 717 (1990).
9. H. Miyoshi, M. Chubachi, M. Yamagami, and T. Kataoka, *J. Chem. Eng. Data*, *37*, 120 (1992).
10. H. Miyoshi, M. Yamagami, M. Chubachi, and T. Kataoka, *Ibid.*, *39*, 595 (1994).

Received by editor October 31, 1995