MASS TRANSFER ACROSS CATION EXCHANGE MEMBRANE

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The transfer rates of Na^+ , K^+ , Mg^{2+} and Ca^{2+} across a cation exchange membrane were investigated. Two models were examined to explain the experimental results. The first model is based on the ion exchange equilibrium at the membrane surface, the second on the nonequilibrium exchange kinetics at the membrane surface and within the membrane. The transfer rates calculated by the second model were in good agreement with the experimental results for both monovalent and divalent ions.

Introduction

Separation processes using ion exchange membranes are widely used in industry, e.g. the desalination of sea water, waste water treatment and the recovery of acid and metals.⁸⁾ Many investigations of ion transfer across the ion exchange membrane^{4,6,12-14,16)} have been reported. The transfer rate without electric field has been expressed on the basis of the ion exchange equilibrium at the membrane surfaces and the diffusion across the aqueous boundary films and the membrane. Helfferich²⁾ reported that the diffusion coefficient based on the Nernst-Planck equation could be applied to diffusion within membrane. However, the diffusion coefficient for divalent ion within the membrane was reported to increase with increases in aqueous concentration,^{1,7,11,17)} and it was suggested that there might be specific interactions between the counterion and the fixed exchange site.^{11,17)} The mechanism of ion transfer within the membrane is not clear.

In the present work, the transfer rates of Na^+ , K^+ , Mg^{2+} or Ca^{2+} across a cation exchange membrane were measured and were compared with values calculated by two different models. The first model was based on the ion exchange equilibrium at the membrane surface and the diffusion within the membrane. The second was newly developed on the assumption that the ion exchange reaction proceeded in nonequilibrium at the membrane surface and within the membrane.

1. Experimental

The experimental apparatus used for metal ion transfer across a cation exchange membrane is shown

in Fig. 1. The cation exchange membrane is Neoceptor CM-1 of 145 μm thickness, produced by Tokuyama Soda Co., Ltd., Japan. A channel of 2 mm depth, 10 mm width and 40 cm length was prepared on each sides of the membrane. A feed solution, HCl aqueous solution of NaCl, KCl, MgCl_2 or CaCl_2 , was circulated through one channel and an aqueous recovery solution of HCl was pumped through the other. Metal concentration of the effluent of recovery solution was measured by flame spectrochemical analysis. Since the metal concentration became constant in a few minutes, the transfer rate of metal ion across the membrane at steady state was determined from the concentration at ten minutes after the experimental start.

In the measurement of ion exchange equilibrium, a piece of membrane in H-form prepared by soaking in a 1.2 kmol/ m^3 HCl solution was shaken with a metal ion solution for over five hours. After washing of the membrane by deionized water, the metal ion in the membrane was stripped by the 1.2 kmol/ m^3 HCl solution several times. The amount of metal ion adsorbed in the membrane due to ion exchange was

Fig. 1. Experimental apparatus for metal ion transfer across cation exchange membrane

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determined from the metal concentration in the stripping solution used. The membrane in equilibrium with the metal solution was quickly wiped with a filter paper, and the metal ion adsorbed as salt within the membrane was desorbed by deionized water. The concentration of salt was measured by an electric conductivity meter. All chemical reagents used in this work were of reagent grade from Wako Pure Chem. Ind., Ltd., and the experiments were carried out at a room temperature of 298 ± 1 K.

2. Results and Discussion

2-1. Ion exchange equilibrium

Cation exchange reaction between the metal ion in the aqueous phase and the cation exchange site in H-form, HR, in the membrane is expressed by

where the superscript bar refers to the membrane phase. Distribution ratios $K_d (= [\overline{MR}_n]/[M^{n+}])$ for Na^+ and Mg^{2+} are shown in Figs. 2 and 3, respectively. For the large $[M^{n+}]$ at pH=3, K_d is in inverse proportion to $[M^{n+}]$; i.e., the metal concentration in the membrane $[\overline{MR}_n]$ does not vary with $[M^{n+}]$ because all of the exchange site changes into M-form. From these data the ion exchange capacity, Q , was found to be 2.0 for Na^+ and K^+ and 2.3 for Mg^{2+} and Ca^{2+} .

According to Eq. (1), the equilibrium constant, K_{ex} , of ion exchange is given by

$$K_{ex} = [\overline{MR}_n][H^+]^n / ([M^{n+}][\overline{HR}]^n) \quad (2)$$

Kojima *et al.*⁹⁾ reported that K_{ex} for Cu^{2+} varied with the ion strength, I . The value of K_{ex} for Mg^{2+} increased with I as shown in Fig. 4, while K_{ex} for Na^+ did not vary. If a modified equilibrium constant, K'_{ex} , for divalent ion is defined as

$$K'_{ex} = [\overline{MR}_2][H^+] / ([M^{2+}][\overline{HR}]) \quad (3)$$

then the value of K'_{ex} did not vary with I , as shown in Fig. 4. The ion exchange reaction for divalent ion involves two steps:

If it is assumed that $\overline{MR}_i^+$ is unstable and $[\overline{MR}_i^+]$ is very small, $\overline{MR}_i^+$ might turn into M^{2+} or $\overline{MR}_2$ independently of $[H^+]$ or $[\overline{HR}]$. Then the reaction apparently might be expressed by

The equilibrium constant for Eq. (6) is given by Eq. (3). The values of K_{ex} or K'_{ex} are shown in Table 1. The distribution ratio K_d is given in terms of K_{ex} (or K'_{ex} for divalent ion) as follows:

Fig. 2. Distribution ratio of Na between cation exchange membrane and aqueous solution against aqueous concentration of Na.

Fig. 3. Distribution ratio of Mg between cation exchange membrane and aqueous solution against aqueous concentration of Mg.

Fig. 4. Equilibrium constant of ion exchange reaction and modified equilibrium constant defined by Eq. (3) for divalent ion against $\sqrt{I}$.

Table 1. Ion exchange constant and reaction rate constants

Ion species	K_{ex} or K'_{ex}	k_f $m^4/kmol \cdot s$	K_{ex} $m^5/(kmol \cdot s)$
Na^+	1.18	4.0×10^{-5}	3.5×10^{-11}
K^+	2.80	8.0×10^{-5}	3.5×10^{-11}
Mg^{2+}	9.0	3.0×10^{-5}	3.5×10^{-11}
Ca^{2+}	17	5.5×10^{-5}	3.5×10^{-11}

$$K_d = [\overline{MR}_n]/[M^{n+}] = K_{ex}Q/([H^+] + nK_{ex}[M^{n+}]) \quad (7)$$

Lines in Figs. 2 and 3 represent the values calculated by Eq. (7).

Fig. 5. Concentration of salt in membrane phase against aqueous concentration

Fig. 6. Effect of flow velocity in the channel on transfer rate of Na across the membrane.

Figure 5 shows the concentration of salt in the membrane against the aqueous concentration. Since the ratio $[MCl_n]/[M^{n+}]$ is below 0.1, which is much smaller than K_d in Figs. 2 and 3, the transfer of anion across the membrane might be negligible.

2-2. Transfer rate of metal ion

Transfer rate, N_{Na} , of Na^+ across the membrane is plotted against the flow velocity, U , in Fig. 6, where the velocity of the recovery solution is equal to that of the feed solution. The following correlation can be applied to mass transfer within aqueous phase in the channel.^{15,18)}

$$Sh = C \cdot Re^{1/2} Sc^{1/3} \quad (8)$$

The results in Fig. 6, corresponding to Eq. (8), indicates that the mass transfer resistance in the aqueous phase is significant at any velocity in the range measured. Hereafter, all experiments were carried out at $U = 0.12$ m/s.

For the various conditions of feed and recovery solutions, N_{Na} and N_{Mg} are shown in Figs. 7 and 8, respectively. At small $[M^{n+}]_F$ and large pH_F in the feed solution where N_M is proportional to $[M^{n+}]_F$, the boundary film in the feed solution may be rate-controlling. The resistance of the ion exchange membrane becomes appreciable with increasing $[M^{n+}]_F$ and decreasing pH_F or $[H^+]_R$ in the recovery solution.

2-3. Model of metal ion transfer

The transfer rates, N_M and N_H , of metal and

Fig. 7. Transfer rate of Na across cation exchange membrane against Na concentration in feed solution. Lines are calculated by Model I with $\bar{D} = 4.8 \times 10^{-11}$ m²/s.

Fig. 8. Transfer rate of Mg across cation exchange membrane against feed concentration. Solid lines are calculated by Model I with $\bar{D} = 4.1 \times 10^{-11}$ m²/s, and dashed lines by Model II.

hydrogen ions across the aqueous boundary film on the feed and the recovery sides are expressed as follows for the steady state.

$$N_M = k_{w,M}([M^{n+}]_F - [M^{n+}]_{F,i}) = k_{w,M}([M^{n+}]_{R,i} - [M^{n+}]_R) \quad (9)$$

$$N_H = -nN_M = k_{w,H}([H^+]_{F,i} - [H^+]_F) = k_{w,H}([H^+]_R - [H^+]_{R,i}) \quad (10)$$

At a constant flow velocity the mass transfer coefficient, k_w , can be estimated from Eq. (8) in proportion to $D^{2/3}$ where the aqueous diffusion coefficient D can be evaluated from the Vinograd-McBain equation¹⁹⁾ based on the Nernst-Planck equation. The value of D depends not only on the ion species but also on the concentration of ions. A value

of $k_w/D^{2/3} = 17$ was determined from the experimental N_M at small $[M^{n+}]_F$ and large pH_F and was used to estimate k_w under other conditions. For a given N_M the respective concentrations of $[M^{n+}]_{F,i}$, $[M^{n+}]_{R,i}$, $[H^+]_{F,i}$ and $[H^+]_{R,i}$ at the membrane surface were determined by Eqs. (9) and (10).

Model I: It was assumed that ion exchange equilibrium held at the membrane surface, and that ions transferred due to diffusion within the membrane. The surface concentrations, $[\overline{MR}_n]_F$ and $[\overline{MR}_n]_R$, in the membrane are calculated by Eq. (7). When the transfers of anion and water across the membrane are negligible, the following expression for the metal diffusion within the membrane is obtained on the basis of the Nernst-Planck equation.^{3,5)}

$$N_M = -\bar{D}(d[\overline{MR}_n]/dx) \quad (11)$$

$$\bar{D} = \bar{D}_M \bar{D}_H (n^2 [\overline{MR}_n] + [\overline{HR}]/(n^2 \bar{D}_M [\overline{MR}_n] + \bar{D}_H [\overline{HR}])) \quad (12)$$

where $\bar{D}_M$ and $\bar{D}_H$ are the self-diffusion coefficients of metal and hydrogen ions, respectively. Helfferich²⁾ reported $\bar{D}_{Na}$ and $\bar{D}_H$ with which $\bar{D}_H/\bar{D}_{Na} = D_{Na}/\bar{D}_{Na} = 3.9$, and Kojima *et al.*¹⁰⁾ found that

$$\bar{D}_H/\bar{D}_{Na} \approx D_{Cu}/\bar{D}_{Cu}.$$

Under the assumption of $D_{Na}/\bar{D}_{Na} = D_H/\bar{D}_H$, the ratio $\beta = D_{Na}/\bar{D}_{Na}$ was determined by solving Eq. (11) with the Runge-Kutta method for the results shown in Fig. 7 ($[Na^+]_F > 0.01 \text{ kmol/m}^3$), and is plotted against $[\overline{NaR}]_{av}/Q$ in Fig. 9. The change in β with $[\overline{NaR}]_{av}/Q$ is similar to that in $\bar{D}_{\beta=1}$ shown by a solid line in Fig. 9; i.e., $\bar{D}$ given approximately by $\bar{D}_{\beta=1}/\beta$ does not vary with $[\overline{NaR}]$. Therefore, $\bar{D}$ was calculated by

$$\bar{D} = N_M \delta / ([\overline{NaR}]_F - [\overline{NaR}]_R) \quad (13)$$

and $\bar{D} = 4.8 \times 10^{-11} \text{ m}^2/\text{s}$ was obtained as an average.

With the value of $\bar{D}$, N_{Na} was calculated by a trial-and-error method with Eqs. (7), (9), (10) and (13), and these values are shown in Fig. 7 with solid and dashed lines. They are in good agreement with the experimental results. In Fig. 8, however, the calculated N_{Mg} values shown with solid lines do not agree with the experimental results. Under the assumption of equilibrium at the membrane surface, it is considered that $[\overline{MgR}_2]_F$ closes on $Q/2$ with increasing $[Mg^{2+}]_F$ because K_{ex} of divalent ion is large, and that $[\overline{MgR}_2]_F$ does not increase with further increase in $[Mg^{2+}]_F$. Then the calculated N_{Mg} does not change with $[Mg^{2+}]_F$ for large $[Mg^{2+}]_F$, while the experimental N_{Mg} increases with $[Mg^{2+}]_F$ as shown in Fig. 8. Therefore, we can conclude that the assumption of equilibrium at the membrane surface is unreasonable.

Fig. 9. Ratio of diffusion coefficient in aqueous phase to that in membrane. Line is the membrane diffusion coefficient calculated by Eq. (12) for $\beta = 1$.

Fig. 10. Mechanism of ion transfer within cation exchange membrane, (a) for monovalent ion and (b) for divalent ion

Model II: It was assumed that the ion exchange reaction proceeded in nonequilibrium at the membrane surface and also within the membrane. Thus the transfer rate of M^{n+} is equal to the reaction rate at the membrane surface. By assuming that Eq. (6) can be adopted as the apparent reaction for divalent ion, one can obtain $[\overline{MR}_n]_F$ as follows.

$$N_M = k_f \{ [M^{n+}]_{F,i} (Q - n[\overline{MR}_n]_F) - (1/K_{ex}) [\overline{MR}_n]_F [H^+]_{F,i} \} \quad (14)$$

$$[\overline{MR}_n]_F = \frac{K_{ex} (k_f Q [M^{n+}]_{F,i} - N_M)}{k_f ([H^+]_{F,i} + n K_{ex} [M^{n+}]_{F,i})} \quad (15)$$

In a similar way $[\overline{MR}_n]_R$ is given by

$$[\overline{MR}_n]_R = \frac{K_{ex} (k_f Q [M^{n+}]_{R,i} + N_M)}{k_f ([H^+]_{R,i} + n K_{ex} [M^{n+}]_{R,i})} \quad (16)$$

For divalent ion K'_{ex} is used instead of K_{ex} .

Here, we assume that the ion exchange reaction among monovalent M^+ , H^+ and the fixed exchange sites R^a and R^b in the membrane proceeds as shown in Fig. 10(a). N_M is given by the difference between the reaction rates for $I \rightarrow II$ and $II \rightarrow I$.

$$\begin{aligned} N_M &= (r_{I \rightarrow II} - r_{II \rightarrow I})(x^b - x^a) \\ &= K_{ex} ([\overline{MR}^a][\overline{HR}^b] - [\overline{MR}^b][\overline{HR}^a])(x^b - x^a) \\ &= K_{ex} \{ [\overline{MR}^a](Q - [\overline{MR}^b]) - [\overline{MR}^b](Q - [\overline{MR}^a]) \} (x^b - x^a) \\ &= K_{ex} Q ([\overline{MR}^a] - [\overline{MR}^b])(x^b - x^a) \end{aligned} \quad (17)$$

where $\bar{K}_{ex}$ is the reaction rate constant in the membrane phase. By using $[\overline{MR}^a] - [\overline{MR}^b]/(x^b - x^a) = -d[\overline{MR}]/dx$, Eq. (17) can be rewritten in terms of the modified reaction rate constant, $\bar{K}_{ex}$, as follows.

$$N_M = -\bar{K}_{ex}Q(d[\overline{MR}]/dx) \quad (18)$$

In the equation, $\bar{K}_{ex}Q$ expresses the apparent diffusion coefficient independently of $[\overline{MR}]$; this may correspond to the constant $\bar{D}$ of Na^+ in Model I as described above.

On the other hand, from the assumption of the successive reaction for divalent M^{2+} as shown in Fig. 10(b), N_M is expressed by

$$\begin{aligned} N_M &= \{r_{I \rightarrow II} + r_{II \rightarrow III} - (r_{III \rightarrow II} + r_{II \rightarrow I})\}(x^b - x^a) \\ &= \bar{K}_{ex}(Q + 2[\overline{MR}^a\overline{R}^b])([\overline{MR}_2^a] - [\overline{MR}_2^b])(x^b - x^a) \\ &= -\bar{K}_{ex}(Q + 2[\overline{MR}_2])(d[\overline{MR}_2]/dx) \end{aligned} \quad (19)$$

The values of k_f in Eqs. (15) and (16) and $\bar{K}_{ex}$ in Eqs. (18) and (19) were determined from the experimental results and are shown in Table 1. In this calculation the value of $k_w/D^{2/3} = 23$ was used instead of 17 because the reaction resistance with Model II cannot be neglected for any condition, as will be discussed below. The value of k_f shown in Table 1 increases with increasing K_{ex} for monovalent ion or K'_{ex} for divalent ion. The difference in k_f between monovalent and divalent ions is small, though there are large differences in K_{ex} and K'_{ex} ; i.e., the backward rate constant of divalent ion is smaller than that of monovalent ion. The value of $\bar{K}_{ex}$ was independent of ion species.

The transfer rate of metal ion can be calculated by Model II as follows. For an assumed value of N_M , $[\overline{MR}_n]_F$ and $[\overline{MR}_n]_R$ are determined from Eqs. (9), (10), (15) and (16); then Eqs. (18) or (19) is integrated from $x=0$ and $[\overline{MR}_n] = [\overline{MR}_n]_F$ to $x=\delta$ by the Runge-Kutta method. The value of N_M is determined so that the integrated value of $[\overline{MR}_n]$ agrees with that of $[\overline{MR}_n]_R$ at $x=\delta$.

The calculated results for Mg^{2+} , shown in Fig. 8 with dashed lines, agree well with the experimental results for any condition. The N_{Ca} values calculated by Model II are also in good agreement with the experimental results, as shown in Fig. 11. In the figure the solid lines were calculated by Model I with $k_w/D^{2/3} = 23$, which is the same value as used in Model II. The difference between lines 1 and 4 indicates that the reaction resistance cannot be neglected in Model II even at small $[\text{M}^{n+}]_F$. The transfer rates of Na^+ and K^+ calculated by Model II are compared with the experimental values in Figs. 12 and 13, respectively. It was found that Model II is useful for evaluating the transfer rate of either divalent ion or monovalent ion across the cation exchange membrane.

Fig. 11. Transfer rate of Ca across membrane against feed concentration. Solid lines are calculated by Model I with $\bar{D} = 6.1 \times 10^{-11} \text{ m}^2/\text{s}$ and $k_w/D^{2/3} = 23$, and dashed lines by Model II.

Fig. 12. Comparison of experimental transfer rates of Na with those calculated by Model II

Fig. 13. Comparison of experimental transfer rates of K with those calculated by Model II

Conclusion

Two models, I and II, were used to explain the transfer rate of metal ion across a cation exchange

membrane. Model I is based on the ion exchange equilibrium at the membrane surface, Model II on nonequilibrium kinetics at the membrane surface and within the membrane. Both models have three parameters to be determined to calculate the transfer rate within the membrane: for Model I the equilibrium constant K_{ex} and the self-diffusion coefficients $\bar{D}_M$ and $\bar{D}_H$, and for Model II K_{ex} , the reaction rate constant k_f at the membrane surface and the modified reaction rate constant $\bar{K}_{ex}$ in the membrane. Model I could be applied to monovalent ion transfer with a constant diffusion coefficient in the membrane, but not to the divalent case. Model II could be applied for both monovalent and divalent ion transfers. It is better to assume that the aqueous phase and the membrane phase are not in equilibrium at the membrane surface for metal ion transfer across the cation exchange membrane.

Nomenclature

D	= diffusion coefficient in aqueous phase	[m ² /s]
$\bar{D}$	= diffusion coefficient in membrane	[m ² /s]
I	= ion strength	[kmol/m ³]
K_d	= distribution ratio of metal ion between aqueous and membrane phase	[—]
K_{ex}	= equilibrium constant defined by Eq. (2)	[—]
$\bar{K}_{ex}$	= modified equilibrium constant defined by Eq. (3)	[—]
K_{ex}	= rate constant of ion exchange reaction within the membrane	[m ³ /(kmol·s)]
$\bar{K}_{ex}$	= modified rate constant of ion exchange reaction within the membrane, $\bar{K}_{ex}(x^b - x^a)^2$	[m ⁵ /(kmol·s)]
k_f	= forward rate constant of ion exchange reaction at membrane surface	[m ⁴ /(kmol·s)]
k_w	= aqueous-phase mass transfer coefficient	[m/s]
L	= length of channel	[m]
M	= metal	
N	= mass transfer rate	[kmol/(m ² s)]
n	= valency of ion	[—]
Q	= ion exchange capacity	[kmol/m ³]
R	= ion exchange site within the membrane	
Re	= Reynolds number, $UL\rho/\mu$	[—]
r	= reaction rate within the membrane	[kmol/(m ³ s)]
Sc	= Schmidt number, $\mu/\rho D$	[—]
Sh	= Sherwood number, $k_w L/D$	[—]
U	= velocity of aqueous solution	[m/s]
x	= distance within the membrane	[m]
β	= ratio of diffusion coefficient in aqueous	

	phase to that in membrane	[—]
δ	= thickness of membrane	[m]
μ	= viscosity	[Pa·s]
ρ	= density	[kg/m ³]

<Superscripts>

—	= membrane phase
a, b	= position of exchange site in membrane

<Subscripts>

av	= average
F	= feed solution or feed side
i	= membrane surface
R	= Recovery solution or recovery side

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