

ESTIMATION OF DIFFUSIVITY FOR CORRELATION OF MASS TRANSFER COEFFICIENT BETWEEN PARTICLES AND LIQUID IN ION EXCHANGE IN A STIRRED TANK

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The ionic diffusion in ion exchange is generally influenced by the electric field. Therefore, we often encounter difficulty in evaluating an appropriate diffusivity when correlating the liquid-side mass transfer coefficient in ion exchange. It has been under discussion which one should be used as a suitable value of diffusivity in ion exchange, especially in a fully developed turbulence field as observed in stirred tanks.^{2,6,14,16,18} Various diffusivities have been adopted in previous studies of mass transfer in various systems of ion exchange: the self-diffusivity of ion transferred from the liquid phase to the resin phase;^{9,10,15} the diffusivity directly derived from the Nernst-Planck equation;^{2,4,12,13} the effective diffusivity introduced on the basis of film diffusion theory with the Nernst-Planck equation.^{5,6,17,18} But little research has appeared which compares the applicability of the above-mentioned diffusivities to the correlation of mass transfer coefficient.

In this paper, we obtained the mass transfer coefficient between particles and liquid in a stirred tank by measuring the ion-exchange rate for systems that ranged widely in magnitude of diffusivities, and evaluated the appropriate diffusivity for the correlation of liquid-side mass transfer coefficient.

1. Experimental Apparatus and Procedure

Experiments were conducted with the same apparatus and procedure as those described in a previous paper⁷) although only the C type of stirred tank was used. The resin beads used were of styrene-type sulfonic acid cation-exchange resin (DIAION SK1B), 805 μm in diameter, 1.28 Mg/m^3 in density for the Na^+ form, and 2.32 mol/kg -resin in ion-exchange capacity.

The condition for liquid-side mass transfer control

was satisfied by adopting a dilute electrolyte concentration of 0.50–0.72 mol/m^3 and a short run time of 2 min, which caused the lower extent of ion exchange less than 2%. Under such conditions, the mass transfer coefficient was calculated by Eq. (2) from the mass balance for ion species B transferred from liquid phase to resin phase in the ion exchange expressed by Eq. (1).

$$Z_B R - A^{Z_A} + Z_A B^{Z_B} = Z_A R - B^{Z_B} + Z_B A^{Z_A} \quad (1)$$

$$k_L = -(D_p/6m_c\theta) \ln(c_B/c_{B0}) \quad (2)$$

2. Diffusivity

The typical diffusivities proposed for ion exchange are as follows:

First is one introduced by Helfferich⁴) and several investigators^{2,12,13}) with the Nernst-Planck equation. It was extended to the exchange between multivalent ions by Kataoka *et al.*,⁵) being expressed by Eq. (3).

$$\mathcal{D}_{BA} = \frac{\alpha \mathcal{D}_B \{c_B M(M+1) + c_A N(1+N)\}}{c_B M(M+\alpha) + c_A \alpha N(1+N)} \quad (3)$$

where

$$M = Z_B/Z_Y, N = Z_A/Z_Y \text{ and } \alpha = \mathcal{D}_A/\mathcal{D}_B.$$

$\mathcal{D}_A$ and $\mathcal{D}_B$ are the self-diffusivities of ion species A and B, respectively, at infinite dilution, calculated by the Nernst equation.¹¹) Equation (3) reduces at the earlier stage of ion exchange during $c_A \approx 0$ to the following form:

$$\mathcal{D}_{BA} = \alpha \mathcal{D}_B (M+1)/(M+\alpha) \quad (4)$$

Another one, based on the film diffusion model with the Nernst-Planck equation, was derived for the exchange between monovalent ions by Turner *et al.*¹⁸) and for multivalent ions by Kataoka *et al.*^{5,6}) The latter, Kataoka's effective diffusivity, is formulated at the start of ion exchange by the following equation:^{5,6})

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$$\mathcal{D}_e = \frac{\alpha \mathcal{D}_B}{1 - \alpha \left(\frac{N+1}{M+1} \right)} \left[(N+1) \left\{ \left(\frac{M+1}{\alpha(N+1)} \right)^{S/(S+1)} - 1 \right\} + \left(\frac{M-N}{\alpha N - M} \right) \left\{ \left(\frac{\alpha(N+1)}{M+1} \right)^{1/(S+1)} - 1 \right\} \right] \quad (5)$$

where $S = (\alpha - 1)/(\alpha N - M)$.

Table 1 shows the values of diffusivities for ion-exchange systems studied, calculated by the Nernst equation, Eqs. (4), and (5).

3. Experimental Results and Discussion

Experimental conditions are listed in **Table 2**. Impeller speed was chosen so that most of the resin beads were well suspended. In those conditions, Eq. (2) gave a constant value of mass transfer coefficient during the run time of ion exchange.

Figure 1 shows the experimental results for various impeller speeds and ion-exchange systems at 30°C. The observed value of mass transfer coefficient strongly depends on the kinds of ion species A even if ion species B is identical, which suggests the effect of the electric field on the diffusion of ions.

We will correlate the experimental results by a widely employed method with the following equation including specific power group ($\varepsilon^{1/3} D_p^{4/3}/\nu$):

$$Sh = 2 + K(\varepsilon^{1/3} D_p^{4/3}/\nu)^\beta Sc^\gamma \quad (6)$$

where energy dissipation rate ε is calculated by Eq. (7).

$$\varepsilon = P/\rho V \quad (7)$$

The power of Schmidt number is determined by the observed values, varying the temperature levels and impeller speeds so as to keep a certain value of specific power group. **Figures 2(a), (b), and (c)** show $(Sh - 2)$ vs. Sc with the diffusivities, $\mathcal{D}'_e$, $\mathcal{D}_{BA}$, and $\mathcal{D}_B$, calculated by Eq. (5), Eq. (4), and the Nernst equation, respectively. The figure shows that the plots with $\mathcal{D}_e$ almost coincide for three kinds of ion-exchange systems with each other in contrast with the plots with $\mathcal{D}_{BA}$ and $\mathcal{D}_B$. **Figure 2(a)** indicates that the power of Schmidt number can be set at 1/3 based on the steady-state theory. **Figure 3** shows the correlation results for all the data in Figs. 1 and 2, plotting $(Sh - 2)Sc^{-1/3}$ against $(\varepsilon^{1/3} D_p^{4/3}/\nu)$. The adoption of $\mathcal{D}_e$ gives good correlation, as shown in Fig. 3(a). The observed values lie between the equations of Levins-Glastonbury⁸⁾ and Harriott.³⁾ Meanwhile, as shown in Fig. 3(b), the adoption of $\mathcal{D}_{BA}$ does not always give good correlation, especially for the ion-exchange systems including hydrogen ions. As for the adoption of $\mathcal{D}_B$, the same tendency as for $\mathcal{D}_{BA}$ is observed though it is not shown here.

According to Van Brocklin and David,^{19,20)} the

Table 1. Ion-exchange systems and diffusivities at 30°C

B	Diffusivity $\times 10^9$ [m ² /s]				
	$\mathcal{D}_B$	$\mathcal{D}_{BA}$		$\mathcal{D}_e$	
		A Na	A K	A Na	A K
H ⁺	10.1	2.62	3.60	5.63	6.42
K ⁺	2.19	1.78	—	1.98	—
Na ⁺	1.51	—	1.78	—	1.65
Ba ²⁺	0.95	1.26	1.53	1.11	1.27
Mg ²⁺	0.80	1.17	1.39	1.02	1.13

The stoichiometry for ion exchange is expressed by Eq. (1). $\mathcal{D}_B$, $\mathcal{D}_{BA}$, and $\mathcal{D}_e$ are calculated from the Nernst equation, Eq. (4), and Eq. (5), respectively.

Table 2. Experimental conditions

c_{B0} [mol/m ³]	0.50–0.72
V [dm ³]	5.4
Temp. [°C]	5–40
$m_c \times 10^4$ [—]	4.2–5.2
n_i [min ⁻¹]	200–1050
D_i [cm]	5.45
Sc [—] for $\mathcal{D}_B$	56–3100
$\mathcal{D}_{BA}$	200–2400
$\mathcal{D}_e$	98–2700

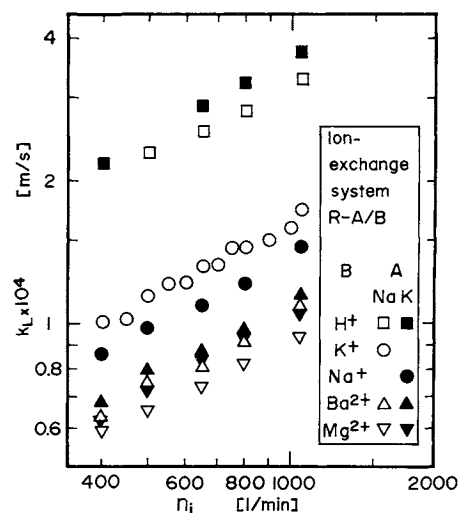


Fig. 1. Effect of impeller speed on liquid-side mass transfer coefficients for various kinds of ion-exchange systems in a stirred tank at 30°C.

effect of the electric field on ionic diffusion is estimated to be larger by the steady-state theory than by the unsteady-state theory. It is interesting that the present experimental results for the stirred tank were successfully correlated with the diffusivity based on steady-state theory though the electric field must generally be less effective for the unsteady-state diffusion of ions in a fully developed turbulence field. More experimental data should be accumulated for understanding the ionic transport phenomena in vari-

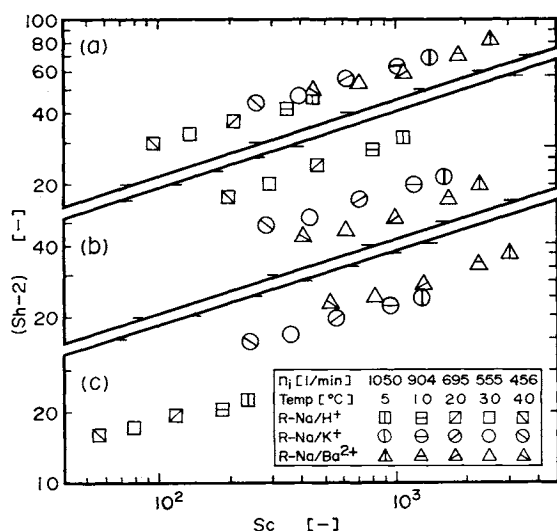


Fig. 2. Correlation of Sherwood number with Schmidt number at a specified specific power group (=69) for a stirred tank by using $\mathcal{D}_e$ (a), $\mathcal{D}_{BA}$ (b), and $\mathcal{D}_B$ (c).

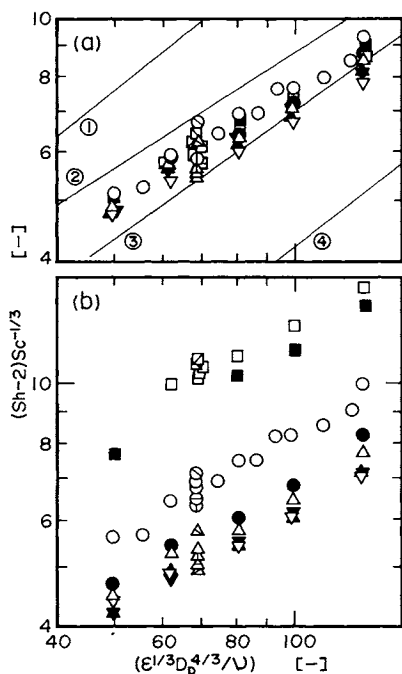


Fig. 3. Correlation of liquid-side mass transfer coefficient in ion exchange in a stirred tank using $\mathcal{D}_e$ (a) and $\mathcal{D}_{BA}$ (b). Keys are the same as those in Figs. 1 and 2. Lines are empirical equations: (1), Sano *et al.*¹⁴; (2), Levins-Glastonbury⁸; (3), Harriott³; (4), Calderbank-Moo Young¹.

ous turbulence fields.

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Nomenclature

c	= concentration of ion	[k mol/m ³]
$\mathcal{D}$	= ionic self-diffusivity	[m ² /s]
$\mathcal{D}_{BA}$	= diffusivity for ion B replacing ion A, defined by Eq. (4)	[m ² /s]

$\mathcal{D}_e$	= effective diffusivity, defined by Eq. (5)	[m ² /s]
D_i	= impeller diameter	[m]
D_p	= particle diameter	[m]
K	= constant	[—]
k_L	= liquid-side mass transfer coefficient	[m/s]
M	= ionic valence ratio (= Z_B/Z_V)	[—]
m_c	= particle concentration: volume fraction	[—]
N	= ionic valence ratio (= Z_A/Z_V)	[—]
n_i	= impeller speed	[1/s]
P	= power input to impeller	[W]
S	= $(\alpha - 1)/(\alpha N - M)$	[—]
Sc	= Schmidt number (= $v/\mathcal{D}_e$)	[—]
Sh	= Sherwood number (= $k_L D_p/\mathcal{D}_e$)	[—]
V	= liquid volume	[m ³]
Z	= ionic valence	[—]
α	= ionic self-diffusivity ratio (= $\mathcal{D}_A/\mathcal{D}_B$)	[—]
β	= power of specific power group	[—]
γ	= power of Schmidt number	[—]
ε	= energy dissipation rate per unit mass of liquid	[m ² /s ³]
θ	= time	[s]
ν	= kinematic viscosity of liquid	[m ² /s]
ρ	= liquid density	[kg/m ³]

<Subscripts>

A, B	= counter ion species
R	= resin phase
Y	= non-counter ion species (chlorine ion)
0	= initial

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