# Kinetics of Ion Exchange Accompanied by Neutralization Reaction

Ion exchange accompanied by a neutralization reaction has been analyzed for the general cases where the bulk solution contains a neutral salt and an acid or a base, e.g., [R · H] + (NaCl + NaOH). Both intraparticle and liquid film diffusion are considered. The Nernst-Planck equation was applied for the fluxes of the ionic species in the liquid film and the resin phase with a mobile reaction plane in the liquid film. When the solution contains acid or base more than 50%, the exchange rate is approximated by the case for pure acid or base solution: the reaction plane is located at the solid/liquid interface. When the solution contains acid or base less than 50% (this situation is generally encountered in the case where a neutral salt flows through a mixed bed of OH-form and H-form resins), the mobile reaction plane should be considered. When the ratio of intraparticle diffusion resistance to liquid diffusion resistance defined in the text is larger than 2, the exchange rate can be approximated by intraparticle diffusion control. The larger the ratio, the faster the reaction plane moves to the resin particle surface. Experimental uptake curves for the ion exchange systems [R · H] + (NaCl + NaOH) and [R · OH] + (NaCl + HCl) confirm the above conclusions.

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## Introduction

Helfferich (1965) developed a detailed analysis of ion exchange accompanied by chemical reaction, such as neutralization reaction, complex formation reaction, regeneration of metallic-form weak acid ion exchanger by HCl, etc. The neutralization reaction is expressed as follows:

$$R \cdot H + BOH \rightarrow R \cdot B + H_2O \text{ (for bases)} \tag{1}$$

$$R \cdot OH + HB \rightarrow R \cdot B + H_2O \text{ (for acids)} \tag{2}$$

These reactions are encountered not only in the treatment of base or acid solutions by H-form or OH-form resins, respectively, but also in the treatment of salts by a mixed bed of H-form and OH-form resins (Haub and Foutch, 1986). Helfferich assumed that the reaction plane is at the surface of the resin particle. He presented theoretical equations of fractional approach to equilibrium for both liquid-phase diffusion control and intraparticle diffusion control. For an individual ion flux, the Nernst-Planck (N-P) equation was applied. This model has been tested with good success for both cation exchange, Eq. 1, (Blickenstaff et al., 1967a, b; Wagner and Dranoff, 1967) and anion exchange, Eq. 2, (Graham and Dranoff, 1972). In a previous paper (Kataoka et al., 1977), we confirmed that when the solution concentration is lower than 0.5 mol/dm$^3$, the assumption that the reaction plane is at the solid/liquid interface is reasonable.

Industrial wastewater usually contains many kinds of salts and acids or bases. Further, even when a neutral salt flows through a mixed bed of OH-form and H-form resins, salt + base or salt + acid solutions are usually produced within an adsorption band in the column (Haub and Foutch, 1986). It is therefore important to develop a kinetic model of ion exchange accompanied by neutralization for reactions such as [R · OH] + (HCl + NaCl) or [R · H] + (NaOH + NaCl). We therefore proposed a kinetic model for liquid-phase diffusion control in the case when a mixed solution of a neutral salt and an acid or a neutral salt and a base is contacted with OH-form or H-form ion exchangers, respectively (Kataoka et al., 1976). An analytic solution for the fractional approach to equilibrium based on the N-P equation was presented. The experimental data however deviated from the analytic solution when the fractional attainment of equilibrium is larger than 0.7–0.8,

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even in the case when the bulk solution concentration is relatively low (e.g., 0.005 mol/dm$^3$). This may be caused by the effect of intraparticle diffusion resistance. Since the higher the solution concentration, the greater is the effect of the intraparticle diffusion resistance, it is important to clarify the way in which the intraparticle diffusion affects the ion exchange mechanism and the ion exchange rate.

It is the purpose of this work to develop a theory for the more general case when both intraparticle and liquid-phase diffusion resistances exist and to show the way in which the neutralization reaction affects the exchange rate when the bulk solution contains a neutral salt and an acid or a base. The N-P equation is applied for the fluxes of ionic species in the liquid film and the resin particle. We also report the results of an experimental study that was carried out for the two typical systems, $[R \cdot H] + (NaCl + NaOH)$ and $[R \cdot OH] + (NaCl + HCl)$, in order to test the theory.

## Theory

We consider the case where $R \cdot A^+$ resin makes contact with a neutral salt ($B^+ - E^-$) coexisting with an acid or base ($B^+ - D^-$), such as the following (and others):

| where | A | B | D | E |
|---|---|---|---|---|
| $R \cdot H + (NaCl + NaOH)$ | $H^+$ | $Na^+$ | $OH^-$ | $Cl^-$ |
| $R \cdot OH^- + (NaCl + HCl)$ | $OH^-$ | $Cl^-$ | $H^+$ | $Na^+$ |
| $R \cdot OH^- + (CH_3COONa + CH_3COOH)$ | $OH^-$ | $CH_3COO^-$ | $H^+$ | $Na^+$ |

To avoid a confusion in the notation for ion species, we use the notation for the $[R \cdot H^+] + (NaCl + NaOH)$ system in the derivation of the theoretical equations. However, the derived equations can be used not only for the $[R \cdot H] + (NaCl + NaOH)$ system but also for any ion exchange accompanied by instantaneous irreversible reaction, by changing the notation of ion species according to the definitions of the A, B, D, and E ion species.

The ion exchange reactions are expressed as follows:

$$R \cdot A^+ + B^+ \rightleftharpoons R \cdot B^+ + A^+ \tag{3}$$

$$A^+ + D^- \longrightarrow (AD)_{\text{product}} \tag{4}$$

$[R \cdot H^+] + (NaCl + NaOH)$ system

$$R \cdot H^+ + Na^+ \rightleftharpoons R \cdot Na^+ + H^+ \tag{3a}$$

$$H^+ + OH^- \longrightarrow H_2O \tag{4a}$$

Figure 1 shows a conceptual diagram of the concentration profiles.

The following assumptions are made to develop a theory:

*Intraparticle*

1. The self-diffusivities of counterions ($D_{Na}$ and $D_H$), the volume of a resin particle, and the activity coefficients are constant as the ion-exchange reaction progresses.
2. The electrolyte (NaCl) does not penetrate from the liquid phase into the resin phase because of the Donnan exclusion.
3. There is no coupling between the fluxes of ions except the one by the electric field caused by the difference of the diffusivities.

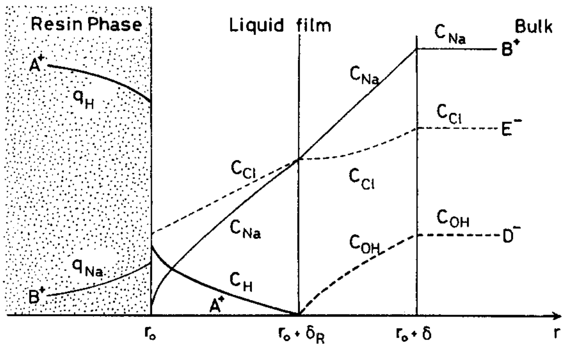

**Figure 1. Conceptual diagram of concentration profiles.**

*Solid/Liquid Interface*

4. The ion exchange equilibrium is reached between counterions ($H^+$ and $Na^+$).

*Liquid Film*

5. Equation 4 (or 4a) is an instantaneous irreversible reaction.
6. $H^+$, which is exchanged for $Na^+$, diffuses in the radial direction and disappears by instantaneous irreversible reaction with $OH^-$ at the reaction plane $r_o + \delta_R$.
7. Same as assumption 3.

Applying the N-P equation, the flux of $i$ ion in the liquid phase and resin phase is given by Eqs. 5 and 6, respectively.

$$j_i = -D_i \left[ \frac{\partial C_i}{\partial r} + \frac{Z_i C_i \mathcal{F}}{RT} \frac{\partial \phi}{\partial r} \right] \tag{5}$$

$$J_i = -\bar{D}_i \left[ \frac{\partial q_i}{\partial r} + \frac{Z_i q_i \mathcal{F}}{RT} \frac{\partial \phi}{\partial r} \right] \tag{6}$$

where $Z_i$ is $Z_H = Z_{Na} = 1$ and $Z_{OH} = Z_{Cl} = -1$. The conditions of electroneutrality and no net electric current are described as follows:

$$X_H + X_{Na} = X_{Cl}; \quad 1 \leqq \sigma \leqq 1 + \sigma_R \tag{7}$$

$$X_{Na} = X_{OH} + X_{Cl}; \quad 1 + \sigma_R \leqq \sigma \leqq 1 + \sigma_\delta \tag{8}$$

$$X_H = X_{OH} = 0 \quad \text{and} \quad X_{Na} = X_{Cl}; \quad \sigma = 1 + \sigma_R \tag{9}$$

$$Y_H + Y_{Na} = 1; \quad 0 \leqq \sigma \leqq 1 \tag{10}$$

$$j_H + j_{Na} = j_{Cl}; \quad 1 \leqq \sigma \leqq 1 + \sigma_R \tag{11}$$

$$j_{Na} = j_{OH} + j_{Cl}; \quad 1 + \sigma_R \leqq \sigma \leqq 1 + \sigma_\delta \tag{12}$$

$$J_H + J_{Na} = 0; \quad 0 \leqq \sigma \leqq 1 \tag{13}$$

where $X = C/C_o$, $Y = q/Q$, $\sigma = r/r_o$, $\sigma_R = \delta_R/r_o$, and $\sigma_\delta = \delta/r_o$. Since, when the solution concentration is less than about 0.5 mol/dm$^3$, net flux of noncounterion $Cl^-$ is neglible (Kataoka et al., 1977; present assumption 2):

$$j_{Cl} = 0; \quad 1 \leqq \sigma \leqq 1 + \sigma_\delta \tag{14}$$

At the reaction plane, the relation between the fluxes of $H^+$ and $OH^-$ ions are given by Eq. 15 (assumption 6).

$$j_H = -j_{OH} \tag{15}$$

For intraparticle diffusion, Helfferich and Plesset (1958) and Plesset et al. (1958) presented the following N-P model which is derived from Eqs. 6, 10, and 13 (assumptions 1–3):

$$\frac{\partial Y_{Na}}{\partial \tau} = \frac{1}{\sigma^2}\frac{\partial}{\partial \sigma}\left[\frac{\sigma^2}{1 + a(1 - Y_{Na})}\frac{\partial Y_{Na}}{\partial \sigma}\right] \tag{16}$$

Initial and boundary conditions are as follows:

$$Y_{Na} = 0; \quad \tau = 0 \tag{17}$$

$$Y_{Na} = \bar{Y}_{Na}; \quad \sigma = 1 \tag{18}$$

$$\left.\frac{-1}{1 + a(1 - \bar{Y}_{Na})}\frac{\partial Y_{Na}}{\partial \sigma}\right|_{\sigma=1} = \frac{r_o k_{Na} C_o}{\bar{D}_H Q}(1 - \bar{X}_{Na}) = \theta\xi(1 - \bar{X}_{Na}); \quad \sigma = 1 \tag{19}$$

$$\frac{\partial Y_{Na}}{\partial \sigma} = 0; \quad \sigma = 0 \tag{20}$$

where $\theta = r_o k_{Na,o} C_o / D_H Q$ and $\xi = k_{Na}/k_{Na,o}$ · $k_{Na}$ and $k_{Na,o}$ are the liquid-phase mass transfer coefficients respectively with and without the effect of the electric field caused by the difference in the diffusivities of the ions. The equilibrium relation between $\bar{Y}_{Na}$ and $\bar{X}_{Na}$ at the particle/liquid film interface is given by Eq. 21 according to the mass action law (assumption 4):

$$K = \frac{\bar{Y}_{Na}\bar{X}_H}{(1 - \bar{Y}_{Na})\bar{X}_{Na}} \tag{21}$$

Using Eqs. 5, 7-9, 11, 12, 14, 15, and 21, $j_{Na}$, $\bar{X}_H$, and $\bar{X}_{Na}$ are given as follows:

$$j_{Na} = -\frac{2\beta}{\beta + 1}\frac{D_{Na}C_o}{\delta - \delta_R}(1 - \phi) = \frac{2\alpha}{1 - \alpha}\frac{D_{Na}C_o}{\delta_R}[\Phi - (\bar{X}_H + \bar{X}_{Na})] \tag{22}$$

$$\bar{X}_H = \frac{(1 - \bar{Y}_{Na})K\Phi}{\zeta} \tag{23}$$

$$\bar{X}_{Na} = \frac{\bar{Y}_{Na}\Phi}{\zeta} \tag{24}$$

where

$$\Phi = (1 - \gamma_o)^{(\beta+1)/2} \tag{25}$$

$$\zeta = \{[(1 - K)\bar{Y}_{Na} + K][(1 - \alpha K)\bar{Y}_{Na} + \alpha K]\}^{1/2} \tag{26}$$

and $\gamma_o = C_{OH,o}/C_o$. Figure 2 shows a composition trajectory in the $\bar{X} - \bar{Y}$ plane calculated according to Eqs. 24–26. When the solution contains only an acid or base ($\gamma_o = 1$), the equilibrium isotherm becomes rectangular. When the solution contains only a neutral salt ($\gamma_o = 0$), it shows the usual pattern for a binary system without reaction. When $0 < \gamma_o < 1$, the $\bar{X} - \bar{Y}$ curve is not observed as an equilibrium steady state composition: at the end of any saturation experiment all the $H^+$ ions have reacted with $OH^-$ and $\bar{Y}_{Na} = 1$. From Eq. 22, the ratio of $\delta_R$ to $\delta$ is expressed by:

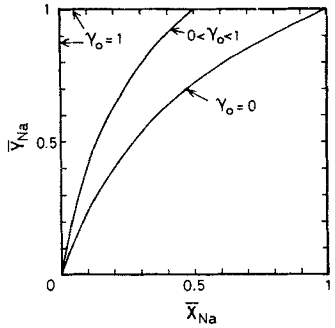

**Figure 2. Equilibrium relation calculated according to Eqs. 24–26.**

$$h = \frac{\delta_R}{\delta} = \frac{(1 - \zeta)\Phi}{(1 - \zeta)\Phi + \dfrac{\beta(\alpha - 1)}{\alpha(\beta + 1)}(1 - \Phi)} \tag{27}$$

The liquid-phase effective diffusivity $D_e$ is expressed by Eq. 29 according to Eq. 22 and the definition of $D_e$ shown by Eq. 28.

$$j_{Na} = -\frac{D_e}{\delta}C_o(1 - \bar{X}_{Na}) \tag{28}$$

$$\frac{D_e}{D_{Na}} = \frac{2\beta}{1 + \beta}\frac{1 - \Phi}{(1 - \bar{X}_{Na})(1 - h)} \tag{29}$$

The details for the above theoretical equations are given elsewhere (Kataoka et al., 1976). The liquid-phase mass transfer coefficients with and without the effect of the electric field are evaluated according to Eq. 30 (Kataoka et al., 1972, 1973).

$$\left.\begin{aligned} k_{Na} &= 1.85\left(\frac{u_f}{\epsilon}\right)\left(\frac{\epsilon}{1 - \epsilon}\right)^{1/3}(Re'Sc_e)^{-2/3} \\ k_{Na,o} &= 1.85\left(\frac{u_f}{\epsilon}\right)\left(\frac{\epsilon}{1 - \epsilon}\right)^{1/3}(Re'Sc_{Na})^{-2/3} \end{aligned}\right\} \tag{30}$$

where $Sc_e = \mu/D_e\rho$ and $Sc_{Na} = \mu/D_{Na}\rho$. The value of $\xi$ in Eq. 19, which shows the effect of the electric field in the liquid film, is given by:

$$\xi = \left(\frac{D_e}{D_{Na}}\right)^{2/3} \tag{31}$$

Equation 16 was transformed to the finite-difference equation and solved by using the conditions of Eqs. 17–20, 21, and 31.

The above theoretical equations were derived for the system [R · H] + (NaCl + NaOH). However, by changing the notation for the chemical species, the theoretical equations may be applied to any system accompanied by instantaneous irreversible reaction.

## Results of Numerical Computation

Numerical solutions were obtained for $\alpha(=D_A/D_B) = 10$, $\beta(=D_D/D_B) = 5$, $\bar{\alpha}(=\bar{D}_A/\bar{D}_B) = 10$, and the effects of $\gamma_o(=$

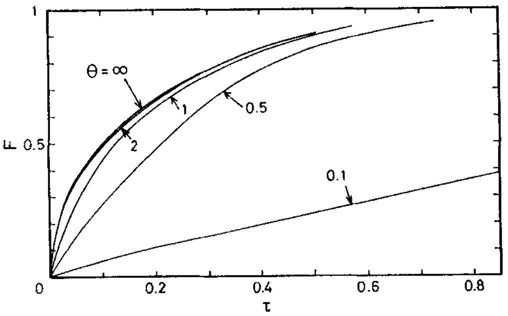

**Figure 3. Effect of $\theta$ on uptake curve.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; K = 2; \gamma_o = 0.5$

$C_{Do}/C_{Bo}$), $\theta(=r_o k_{Bo} C_o/\bar{D}_A Q)$, and equilibrium constant $K$ on the uptake curve are tested. Although those values of $\alpha$, $\beta$, and $\bar{\alpha}$ are not based on the experimental values for the $[R \cdot H] + (NaCl + NaOH)$ system ($\alpha = D_H/D_{Na}$, $\beta = D_{OH}/D_{Na}$, $\bar{\alpha} = \bar{D}_H/\bar{D}_{Na}$) presented later and in Table 2, they are close to those values. Figure 3 shows the effect of $\theta$ on the uptake curve. The larger $\theta$ is, the smaller the effect of the liquid-phase diffusion resistance. When $\theta > 2$, the uptake curve almost coincides with the line for intraparticle diffusion control ($\theta = \infty$). Figure 4 represents the effect of $K$ and $\gamma_o$ on the uptake curve. The larger $K$ is, the faster the exchange rate. The smaller $K$ is, the larger the effect of $\gamma_o$. When $\gamma_o > 0.5$, the effect of $K$ on the exchange rate is negligible.

To investigate the above phenomena more closely, the position of the reaction plane and the ratio of the exchange rates with and without the reaction were calculated. Figure 5 shows the effect of $\theta$ and $\gamma_o$ on the position of the reaction plane in the liquid film. The higher the concentration of ion $D^-(OH^-)$, which reacts with counterion $A^+(H^+)$ (that is, the larger $\gamma_o$ is), the nearer the reaction plane is to the surface of the particle. When liquid-phase diffusion is the rate-controlling step ($\theta = 0$), the reaction plane reaches to the surface when the exchange reaction is completed ($F = 1$). The larger the intraparticle diffusion resistance (the larger $\theta$ is), the faster the reaction plane reaches to the surface, because the larger $\theta$ is, the smaller is the value of $F$ at which $Y_B(Y_{Na})$ becomes unity. Figure 6 shows the effect of $K$ and $\gamma_o$ on the position of the reaction plane. When $K$ is small, $h$ changes a great deal in the initial stage of the ion exchange.

To make clear the effect of the reaction on the exchange rate, the ratio of the ion exchange rate with the reaction to that with-

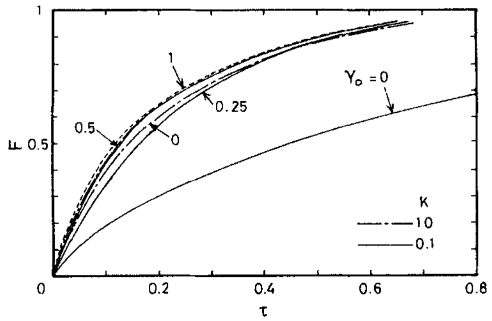

**Figure 4. Effect of $K$ and $\gamma_o$ on uptake curve.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; \theta = 1$

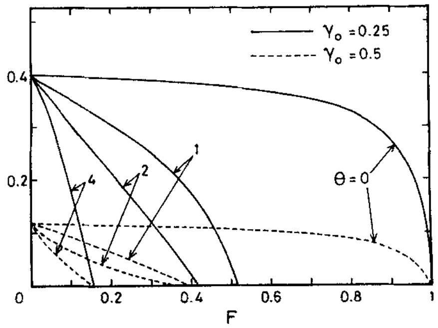

**Figure 5. Change of position of reaction plane with fractional attainment of equilibrium.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; K = 2$

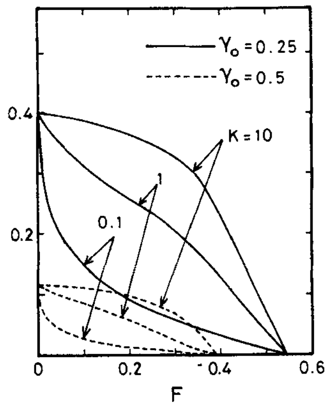

**Figure 6. Change of position of reaction plane with fractional attainment of equilibrium.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; \theta = 1$

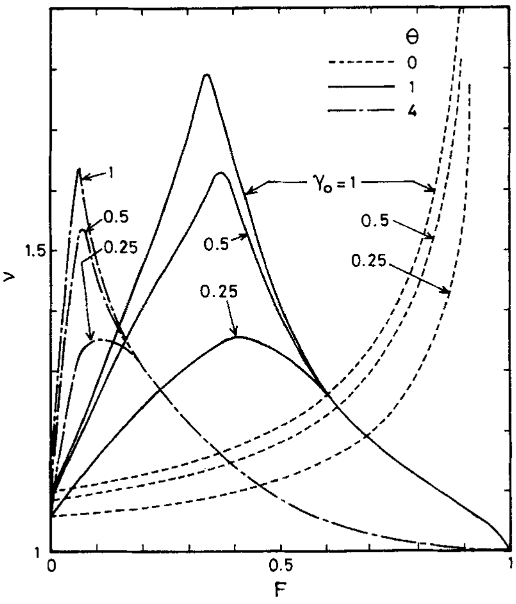

**Figure 7. Change of ratio of ion exchange rate accompanied by chemical reaction to exchange rate without reaction.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; K = 1$

**Table 1. Experimental Systems and Conditions**

| System | Resin | Particle Dia (m) | $\gamma_o$ | $C_{Bo}$ mol/dm$^3$ | $\theta$ | Temp. K |
|---|---|---|---|---|---|---|
| [R · OH] + (NaCl + HCl) | DIALION SA10A<br>$\lambda = 8\%$ | $6.11 \times 10^{-4}$ | $C_{\mathrm{HCl},o}/C_{Bo}$<br>1.0<br>0.75<br>0.5<br>0.25<br>0 | 0.005 | 0.20 | 298 |
| [R · H] + (NaCl + NaOH) | DIAION SK1B |  | $C_{\mathrm{NaOH},o}/C_{Bo}$ |  |  |  |
|  | $\lambda = 8\%$ | $6.1 \times 10^{-4}$ | 1, 0.5, 0 | 0.005 | 0.0312 |  |
|  |  | $8.22 \times 10^{-4}$ | 1, 0.5, 0 | 0.05 | 0.35 |  |
|  |  |  |  | 0.1 | 0.7 |  |

out the reaction is defined as in Eq. 32:

$$\nu = \frac{j_B(F)}{j_{Bo}(F)} = \frac{j_{\mathrm{Na}}(F)}{j_{\mathrm{Na},o}(F)} \tag{32}$$

When the liquid-phase diffusion is the rate-controlling step, $\nu$ is given by Eq. 33 (Kataoka et al., 1976).

$$\nu = \Phi + \frac{\beta(1-\alpha)(1-\Phi)}{\alpha(1+\beta)(\zeta-1)} \tag{33}$$

Figures 7 and 8 shows $\nu$ vs. $F$ curves. The larger $\gamma_o$ is, the larger the effect of the reaction on the exchange rate. The dotted lines in Figure 7 represent the case of liquid-phase diffusion control ($\theta = 0$). They increase exponentially with an increase of $F$. However, when intraparticle diffusion resistance exists ($\theta > 0$), a peak occurs in a $\nu - F$ curve, because the intraparticle diffusion resistance increases when $F$ becomes larger and therefore $\nu$ approaches unity. The smaller the intraparticle diffusion resistance (the smaller $\theta$ is), the larger the peak. Figure 8 shows that when $K < 1$, the effect of the reaction is great.

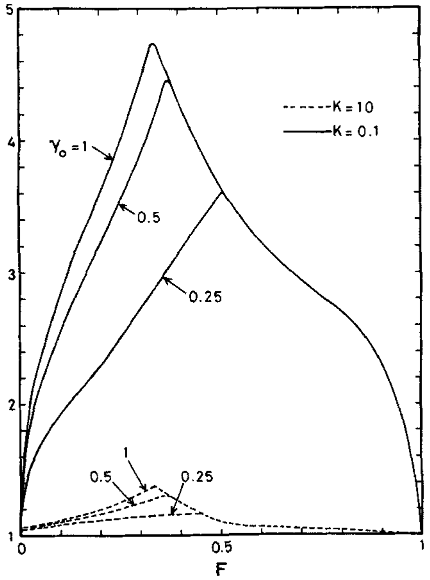

**Figure 8. Change of ratio of ion exchange rate accompanied by chemical reaction to exchange rate without reaction.**

$\alpha = 10; \beta = 5; \bar{\alpha} = 10; \theta = 1$

## Experimental Procedure

The systems and conditions used in the experimental study are given in Table 1. The kinetic data were measured by the shallow bed method. The column has a jacket to keep the inside temperature constant. Soaked resin particles of 0.125 and 0.25 g were placed between the glass beads in columns of 1.55 and 2.22 cm ID, respectively. The concentration history at the bottom of the column was recorded by measuring the electroconductivity when $C_o = 0.005$ mol/dm$^3$. When $C_o = 0.05$ and 0.1 mol/dm$^3$, the solution at the bottom was collected by a fractionater. $\mathrm{Na}^+$ and $\mathrm{Cl}^-$ were analyzed by flame analysis and by Fajan's method, respectively. Equilibrium relations were measured by the batch method. All experiments were conducted at 298 K.

## Experimental Results and Discussion

Figures 9–12 show the experimental uptake curves. The solid lines represent the theoretical lines calculated according to this model, using the parameter values shown in Table 2. The intraparticle self-diffusivities in Table 2 were estimated according to our equation presented elsewhere (Kataoka et al., 1974).

$$D = 0.55 \exp(-0.174 Z \lambda') D$$

$$\lambda' = (V^{W}_{\mathrm{H}}/V)\lambda$$

$$V^{W}_{\mathrm{H}}/V = \exp(-0.023 G e^{-0.192\lambda});$$

$$G \geqq 15, \quad \lambda \leqq 6 \quad \text{or} \quad G \geqq 10, \lambda \geqq 8$$

$$V^{W}_{\mathrm{H}}/V = 1.63 - 0.148\lambda + 0.0121\lambda^2 - 0.000324\lambda^3;$$

$$G \leqq 15, \lambda \leqq 6 \quad \text{or} \quad G \leqq 10, \lambda \geqq 8$$

**Table 2. Parameter Values**

| Liquid Phase Diffusivity (m$^2$/s) | Intraparticle Diffusivity (m$^2$/s) | Diffusivity Ratio and Equilib. Const. |
|---|---|---|
| $D_{\mathrm{OH}} = 5.32 \times 10^{-9}$ | SA10A* | [R · OH] + (NaCl + HCl) |
| $D_{\mathrm{Cl}} = 2.03 \times 10^{-9}$<br>$D_{\mathrm{H}} = 9.31 \times 10^{-9}$<br>$D_{\mathrm{Na}} = 1.33 \times 10^{-9}$ | $\bar{D}_{\mathrm{OH}} = 6.44 \times 10^{-10}$<br>$\bar{D}_{\mathrm{Cl}} = 2.12 \times 10^{-10}$ | $\alpha = 2.62, \bar{\alpha} = 3.04$<br>$\beta = 4.58, K = 1.45$ |
|  | SK1B* | [R · H] + (NaCl + NaOH) |
|  | $\bar{D}_{\mathrm{H}} = 1.18 \times 10^{-10}$<br>$\bar{D}_{\mathrm{Na}} = 1.54 \times 10^{-10}$ | $\alpha = 6.98, \bar{\alpha} = 7.66$<br>$\beta = 3.99, K = 1.77$ |

*Resin, see Table 1

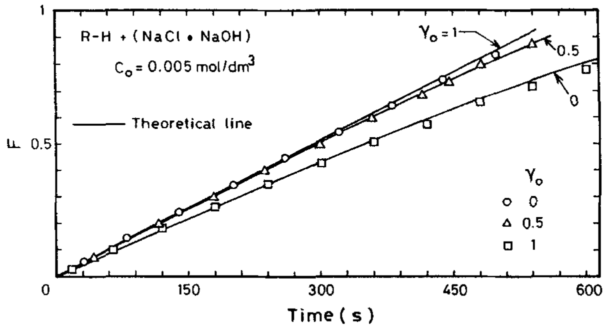

**Figure 9. Experimental and theoretical uptake curves.**
$\theta = 0.0312; \alpha = 6.98; \beta = 3.99; \bar{\alpha} = 7.66; K = 1.774$

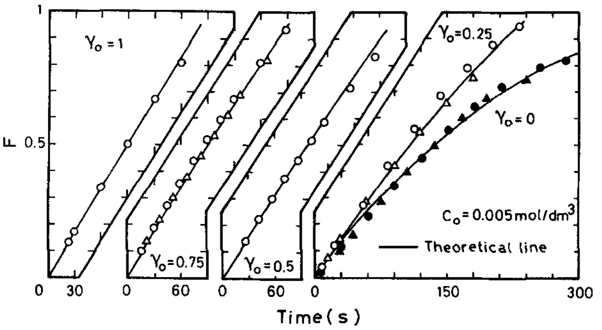

**Figure 10. Experimental and theoretical uptake curves.**
$\theta = 0.2; \alpha = 2.62; \beta = 4.58; \bar{\alpha} = 3.04; K = 1.45$

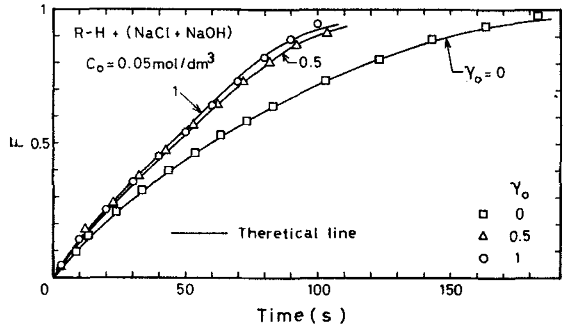

**Figure 11. Experimental and theoretical uptake curves.**
$\theta = 0.35; \alpha = 6.98; \beta = 3.99; \bar{\alpha} = 7.66; K = 1.774$

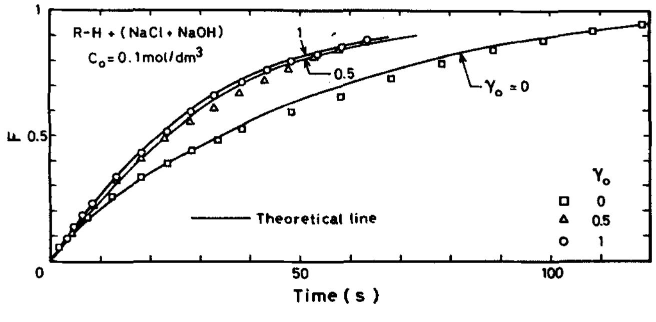

**Figure 12. Experimental and theoretical uptake curves.**
$\theta = 0.7; \alpha = 6.98; \beta = 3.99; \bar{\alpha} = 7.66; K = 1.774$

where $G$ is the gram-equivalent weight of ion species (atomic weight/electric charge) and $\lambda$ is the degree of crosslinking of the resin (%). The above equations were obtained for isotopic ion exchange. We confirmed that when the volume changes little while the ion exchange progresses ($V_H^W/V \simeq$ constant), the self-diffusivity for each counterion can be estimated according to the above equations (Kataoka and Yoshida, 1975).

In Figures 9 and 10, since the liquid-phase solution is relatively low ($C_o$ = 0.005 mol/dm³), liquid-phase diffusion is the dominant contribution to the mass transfer resistance. Figures 11 and 12 show the results for $C_o$ = 0.05 and 0.1, respectively. The higher the liquid-phase solution concentration, the smaller the effect of liquid film diffusion and the faster the ion exchange rate. The smaller the value of $\gamma_o[=C_{OH,o}/C_o$ in the R · H + (NaCl + NaOH) system and $C_{H,o}/C_o$ in the [R · OH] + (NaCl + HCl) system], the slower the exchange rate. When $\gamma_o > 0.5$, the ion exchange rate may be approximated by the line for $\gamma_o = 1$ (pure acid or pure base solution) and the reaction plane is located at the solid/liquid interface. This is independent of the value of $\theta$. When $\gamma_o < 0.5$, the ion exchange rate is affected by the value of $\gamma_o$. From these results, it appears that when $\gamma_o < 0.5$, the reaction plane is not located at the solid/liquid interface and the proposed model may be used to predict the ion exchange rate. Since the situation for $0 < \gamma_o < 0.5$ is encountered especially in the case where a neutral salt flows through a mixed bed of OH-form and H-form resins such as an industrial system for production of pure water, it is actually necessary to consider the mobile reaction plane. When a multivalent ion such as $CaCl_2$ flows through the mixed bed, we should develop a more general theory for heterovalent ion exchange. Since the effect of the electric charge on the ion exchange rate is probably much smaller than the effect of the diffusivity ratio, the proposed theory may be used approximately for heterovalent ion exchange systems. When mixed salt solutions are treated by the mixed bed, multiple reaction schemes should be considered. A more general theory may be developed by extending the model proposed here.

## Notation

$a = \bar{D}_A/\bar{D}_B - 1$
$\underline{C}$ = liquid phase concentration, kmol/m³
$\bar{C}$ = liquid phase concentration at solid/liquid interface, kmol/m³.
$C_o$ = bulk solution concentration of counterion, kmol/m³
$\underline{D}$ = liquid-phase diffusivity, m²/s
$\bar{D}$ = resin-phase diffusivity, m²/s
$D_e$ = liquid-phase effective diffusivity, m²/s
$d_p$ = particle diameter, m
$F$ = fractional attainment of equilibrium
$\mathcal{F}$ = Faraday's constant
$G$ = gram equivalent weight of ion species, g
$h = \delta_R/\delta$
$J$ = flux of ion species in resin phase, kmol/m² s
$j$ = flux of ion species in liquid phase, kmol/m² s
$j_{Bo}$ = flux of ion B in liquid phase without reaction, m² s
$K$ = equilibrium constant
$k$ = liquid-phase mass transfer coefficient of ion species including the effect of the electric field caused by the difference in the diffusivities, m/s
$k_{Bo}$ = liquid-phase mass transfer coefficient of ion B without the effect of the electric field caused by the difference of the diffusivities, m/s
$Q$ = exchange capacity, kmol/m³
$q$ = resin phase concentration, kmol/m³
$\bar{q}$ = resin phase concentration at solid/liquid interface, kmol/m³
$R$ = gas constant

$Re' = d_p u_f \rho/(1-\epsilon)\mu$
$r$ = radial dimension of resin particle, m
$r_o$ = radius of resin particle, m
$Sc_B = \mu/D_B\rho$
$Sc_e = \mu/D_e\rho$
$T$ = temperature, K
$u_f$ = superficial velocity, m/s
$V$ = volume of a resin particle, m$^3$
$V_H^W$ = volume of the resin particle of H-form in water, m$^3$
$X = C/C_o$
$\bar{X} = \bar{C}/C_o$
$Y = q/Q$
$\bar{Y} = \bar{q}/Q$
$Z$ = ionic valence

### *Greek letters*

$\alpha = D_A/D_B$
$\bar{\alpha} = \bar{D}_A/D_B$
$\beta = D_D/D_B$
$\gamma_o = C_{Do}/C_o$
$\delta$ = film thickness, m
$\delta_R$ = distance from solid/liquid interface to reaction plane, m
$\epsilon$ = void fraction of bed
$\theta = r_o k_{Bo} C_o/\bar{D}_A Q$
$\lambda$ = degree of crosslinking, wt. %
$\mu$ = viscosity, kg/ms
$\nu = j_B/j_{Bo}$
$\xi = (D_e/D_B)^{1/3}$
$\rho$ = density, kg/m$^3$
$\sigma = r/r_o$
$\sigma_R = \delta_R/r_o$
$\sigma_\delta = \delta/r_o$
$\tau = D_A t/r_o^2$
$\phi$ = electric potential

### *Subscripts*

$A$ = counterion in the resin phase at $t = 0$
$B$ = counterion in the liquid phase
$D$ = noncounterion that reacts with A ion instantaneously
$E$ = noncounterion that does not react with any ions

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