

Ion-Exchange Kinetics Based on Film Theory

Masashi Hatanaka, Makoto Hoshi

Department of Green and Sustainable Chemistry, School of Engineering, Tokyo Denki University, 5 Senju-Asahi-Cho, Adachi-Ku, Tokyo 120-8551, Japan

Correspondence to: M. Hatanaka (E-mail: mhatanaka@xug.biglobe.ne.jp)

ABSTRACT: The ion-exchange kinetics in polymer complexes was theoretically formulated. The regeneration of metal species from an ion-exchange or chelate resin was described as a competitive reaction between metal ions and protons. We considered the ion-exchange terms and the Langmuir terms to describe the rate of reaction, and film diffusion was also taken into account to describe the profile of the kinetics. In contrast to early methods, the surface concentrations were determined so that the rates of the chemical reactions and diffusion were self-consistent. Although in the initial stage ion exchange was controlled by diffusion, in the last stage ion exchange was controlled by chemical reactions, particularly under excess acid. The kinetics were supported by experimental data for an iminodiacetic acid chelate resin and amidinourea resins. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39358.

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INTRODUCTION

Ion exchange is one of the most important unit operations in modern chemical industry. Ion-exchange resins have a wide variety of applications in the preparation of ultrapure water, effluent treatment, separation and purification of chemical products, decolorization, recycling of rare metals, and medical care. In particular, chelate resins are used as functional polymers to analyze metal contents, control water purity, and take advantage of the metal adsorption and complexation phenomena. Recently, the research and development of these resins has been focused on mineral-resource and environmental issues, and the reuse of rare metals is expected as sustainable chemistry.^{1–3}

Adsorption and desorption in liquid phase are complex phenomena, and the theoretical formulation is often difficult due to the diversity of parameters to be considered. For adsorption, however, chemical engineering analysis has been done with classical isotherms. Isotherms in the liquid phase are quite different from those in the gas phase, for example, the Langmuir isotherm. So, empirical formulas such as the Freundlich expression have been applied by many chemists. Metal-loaded ion-exchange resins or chelate resins are, on the other hand, reusable through their treatment with mineral acids such as hydrochloric acid. The reversibility plays an important role in the recycling of the resins and the extraction of rare metals. The recovery of metal species from ion-exchange or chelate resins is usually regarded as a competitive reaction between metal ions

and protons. However, few theoretical studies have been done on the kinetics from the early stage, except for some cases that have described the rate of chemical reactions or diffusion separately.^{4–11}

Boyd et al.⁴ theoretically studied the ion-exchange kinetics for the first time. However, they calculated the rate of the chemical reaction under an approximation that was limited to stationary ion concentrations, and the rate of diffusion was calculated by another expression. Helfferich and coworkers^{6,7} obtained the rate of diffusion within the particles of ion-exchange resins (particle diffusion) with the Nernst–Plank expression and resolved the nonlinear diffusion equation. Their method was rigorous in that the diffusion potential was taken into account, and this basic concept has been inherited until now.^{8,9} However, they did not consider the rate of the chemical reactions explicitly. Even when the combinative kinetics on the rates of the chemical reactions and diffusion are analytically obtained, the expressions are probably very complex and not suitable for practical use. For diffusion problems in ion-exchange resins, the importance of diffusion within the boundary film (film diffusion) was also pointed out by early workers.⁴ The kinetics of film diffusion are, however, often difficult because of the many factors that should be taken into account in the expression. Until now, only a few formulations have been done under limited conditions that suppose simple equilibria at the surface.^{10,11}

Although the total rate of ion-exchange processes is often controlled by diffusion, there are some cases that seem to be

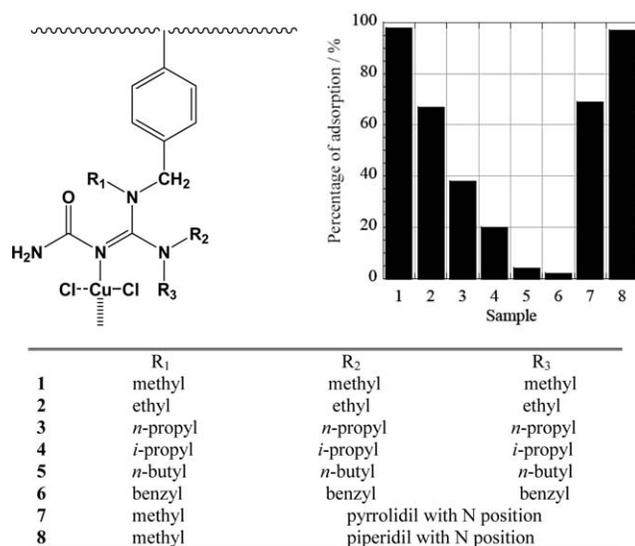


Figure 1. Substituent effect on the Cu(II) adsorption of the amidinoureia resins (reused from ref. 13).

controlled by chemical reactions. Turse and Rieman⁵ concluded experimentally that the ion exchange in chelate resins apparently obeyed second-order chemical kinetics. This is meaningful in that the total rate of ion-exchange processes is not always controlled by diffusion. However, the kinetics that they used were still separated into two expressions corresponding to the rate of the chemical reactions and diffusion, and thus, the interpretation of the experimental plot had somewhat ambiguous aspects. Anyway, although there have been many studies on the equilibria of ion exchange, practical kinetics have not been established yet. Even nowadays, ion-exchange resins are designed in view of the density of crosslinking or spacer effects¹² to control the metal-adsorption efficiency.

Recently, we showed that the metal-adsorption efficiency of amidinoureia resins are strongly effected by substituents around the ligands. As shown in Figure 1, the percentage of Cu(II) adsorption is very sensitive to the arrangement of hydrophilic and hydrophobic substituents around the amidino group.¹³ These resins adsorb Cu(II) selectively at the Schiff-base moiety.¹⁴ Although substitution by alkyl and benzyl groups (resins 1–6) leads to a decrease in the adsorption efficiency because of the corresponding steric hindrance and hydrophobic regions, substitution by pyrrolidil and piperidil groups (resin 7 and 8) leads to an increase in the adsorption efficiency, in which the spread of hydrophilic region overcomes the steric-hindrance effects. Moreover, it was found that the adsorption efficiency was approximately proportional to the water solubility of the corresponding substituted amidinoureias.¹³ These facts show that boundary films are formed at the surface of resins, and the importance of film diffusion in polymer complexes is implied. In view of chemical engineering, we should recognize that there is a nontrivial difference between the overall mass-transfer coefficient and the liquid-film mass-transfer coefficient. Therefore, in the research and development of ion-exchange resins, both the chemical-reaction and diffusion rates should be considered. Nowadays, the time dependence of the ion concentrations can be pursued by titration, ion chromatography, atomic absorption spectrometry, and inductively

coupled plasma (ICP) analysis. However, profiles for the theoretical kinetics of combination between chemical reactions and film diffusion are not clear, even at the qualitative level. So, we were interested in formulating the kinetics with not so complicated expressions.

In this study, we formulated the theoretical kinetics of a polymer ion exchanger in view of the chemical reactions and film diffusion simultaneously, and we suggest a simple method to estimate the degree of chemical-reaction control or diffusion control. In contrast to early methods that suppose equilibrium at the surface, the ion concentrations at the surface were self-consistently determined between the chemical-reaction terms and the diffusion terms. As an application, the boundary-film effects on ion exchange of a commercial iminodiacetic acid chelate resin and amidinoureia resins were studied. The expression is quite simple, and we think it will be useful in the design of general ion-exchange resins.

THEORETICAL

Langmuir Adsorption of Single Components

In polymer complexes, such as chelate resins, there exist pure adsorption and desorption processes between the ions and ligands.¹⁴ So, we first introduced the time dependence of simple Langmuir terms. Although the Langmuir isotherm is well known, the time dependence of the ion concentration is somewhat complex. Hereafter, M is the concentration of metal ions; θ is the coverage of active sites; N is the concentration corresponding to the total sites; and k and k' are the rate constants for adsorption and desorption, respectively. Strictly speaking, we should consider the reaction ratio between the ion and the ligand. However, we consider only one-to-one adsorption for simplicity. Adsorption with a ratio of 1: x ($x \neq 1$) is considered later. The net rate of the chemical reaction is described as usual:

$$\frac{dM}{dt} = -kMN(1-\theta) + k'N\theta. \quad (1)$$

The material balance is

$$M + N\theta = M_0 = \text{Constant} \quad (2)$$

where M_0 corresponds to the total amount of the metal ion, not always the initial concentration. We obtain

$$\frac{dM}{dt} = -kM(M - M_0 + N)/N + k'(M_0 - M). \quad (3)$$

We note that the sign of dM/dt is positive with respect to the desorption. In eq. (3), when the second term is small, we can neglect it, and the equation is elementarily integrated to a second-order kinetics expression containing logarithms. Usually, metal species, once adsorbed to ion-exchange resins or chelate resins, are not desorbed with ease, and the adsorption efficiencies are close to 100% under excess metals. Therefore, the neglect of the second term is reasonable under the usual conditions.

Adsorption of Two Components

As an expansion of the simplest adsorption, we considered a competitive system containing two kinds of metal ions, which were

subject to only adsorption and desorption. Here, we consider a model system with metal ions and protons corresponding to the reuse of ion-exchange resins, where H is the concentration of protons; θ_M and θ_H are the coverages of active sites by metal ions and protons, respectively; and n and n' are the rate constants for the adsorption and desorption of protons, respectively. The time dependence of each concentration is as follows:

$$\frac{dM}{dt} = -kMN(1-\theta_M-\theta_H) + k'N\theta_M \quad (4)$$

$$\frac{dH}{dt} = -nHN(1-\theta_M-\theta_H) + n'N\theta_H \quad (5)$$

Both expressions are described by the Langmuir terms. The material balance is calculated as follows:

$$M + N\theta_M = M_0 = \text{Constant} \quad (6)$$

$$H + N\theta_H = H_0 = \text{Constant} \quad (7)$$

These are simultaneous ordinary differential equations and extend to more complicate systems with multiple components. For example, the adsorption of many heavy metal ions by chelating resins can be described by these equations. However, this is a special case of an ion-exchange process, as described later.

Adsorption and Ion Exchange of Two Components

Next, we extend the previous Langmuir expression and consider ion-exchange processes in which two kinds of ions react at the same active site. Here, we consider a cation-exchange resin. The active sites can be anionic or neutral. For now, we consider neutral resins, which generally have high ion-exchange efficiencies. Figure 2 shows the schematic interactions between the ions and active sites (Rs), where $k, l, m, n, k', l', m',$ and n' are the respective reaction rate constants. The dashed lines correspond to adsorption and desorption reactions between the ions and active sites, and the solid lines correspond to ion-exchange reactions between the ions and the metal- or proton-adsorbed sites. We assume that ion exchange occurs only at the surface, and each ion diffuses at once within the liquid phase. Ion exchange between the metal ions and protons in the solid phase is not considered. Because the two schematic ion-exchange reactions in Figure 2 are essentially same except for the directions, they contribute to the time dependence of the ion concentrations twice as much as the single scheme (i.e., $m = l', m' = l$). The time dependence of each ion is described with the ion-exchange reaction rate constants (m and m'):

$$\frac{dM}{dt} = -kMN(1-\theta_M-\theta_H) + k'N\theta_M + 2mHN\theta_M - 2m'MN\theta_H \quad (8)$$

$$\frac{dH}{dt} = -nHN(1-\theta_M-\theta_H) + n'N\theta_H + 2m'MN\theta_H - 2mHN\theta_M \quad (9)$$

In both expressions, the first and second terms are the usual Langmuir types, and the others are the ion-exchange terms. The material balance is similar to the previous equations:

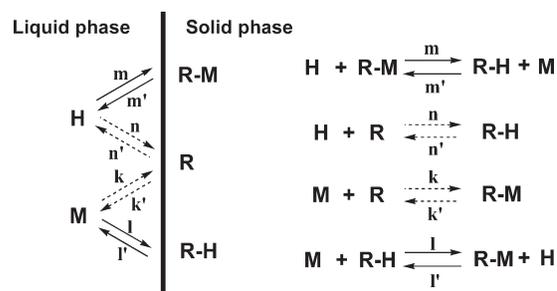


Figure 2. Chemical-reaction scheme of the adsorption/desorption and ion-exchange systems, where $m = l'$ and $m' = l$.

$$M + N\theta_M = M_0 = \text{Constant} \quad (10)$$

$$H + N\theta_H = H_0 = \text{Constant} \quad (11)$$

Then, we can obtain expressions without θ_M and θ_H with the material balance.

The rates of the ion-exchange reactions between the metal ions and protons are usually much larger than those of pure adsorption and desorption reactions. Although the activation energy of the bond cleavage between the ion and active site is approximately close to the dissociation energy between the metal and ligand, the transition state of the ion-exchange reaction resembles a binuclear complex. Therefore, the energy of the ion-exchange transition state is much lower than that of the dissociated states. (In this case, the proton affinity to the ligand R is much larger than the metal-ion affinity to R. Under Hammond's postulate, the structure of the ion-exchange transition state is close to R—M rather than R—H, and M and H do not interact so strongly. Thus, the transition state should be much more stable than the dissociated states.) This situation is shown in Figure 3. Thus, in many cases, the first and second terms in eqs. (8) and (9) can be neglected. Then, by eliminating θ_M and θ_H through eqs. (10) and (11), we obtain the following:

$$\frac{dM}{dt} \cong 2mH(M_0 - M) - 2m'M(H_0 - H) \quad (12)$$

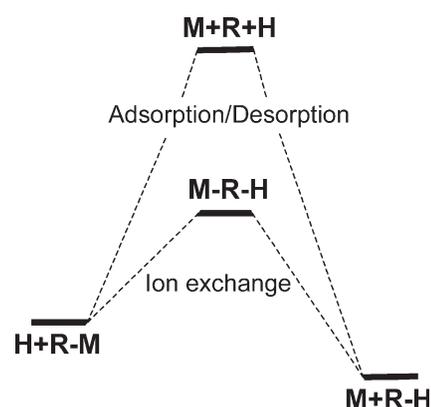


Figure 3. Activation energies for the adsorption/desorption and ion-exchange reactions.

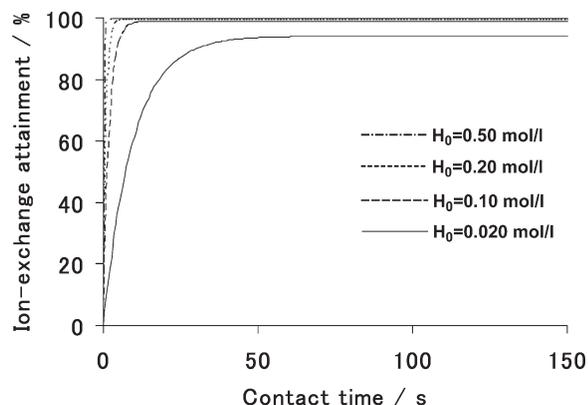


Figure 4. Theoretical curves for the ion exchange between the metal ions and protons without the boundary films.

$$\frac{dH}{dt} \cong -2mH(M_0 - M) + 2m'M(H_0 - H) \cong -dM/dt \quad (13)$$

However, when the pH is quite high, a neutralization reaction between the acid and base occurs,¹⁵ or the electronic states of the ligands sometimes change into other types.¹⁶ Then, the approximation cannot be applied. Although $2m$ and $2m'$ can be rewritten as m and m' , we left them unchanged for the deduction of the expressions. These expressions do not contain θ_M and θ_H explicitly, but the concentrations in the solid phase are also taken into account implicitly by eqs. (10) and (11).

Equations (12) and (13) are also simultaneous ordinary differential equations. Under the previous approximation, the explicit square terms of M and H do not appear, and the product term MH appears, in contrast to the previous case. The solutions can be obtained by numerical calculations. One important case is the ion exchange of maximally metal-adsorbed resins by excess acids (e.g., hydrochloric acid) with the initial concentration of acid (H_0). The numerical solutions, in this case obtained by the fourth-order Runge–Kutta method, are shown in Figure 4. M_0 was set to 100 ppm,¹⁴ and H_0 was made to vary. m and m' were set 5×10^{-5} and 3×10^{-5} ppm⁻¹ s⁻¹, respectively, to approximately reproduce the case of the amidinourea resins.

EFFECTS OF THE BOUNDARY FILM

Classical Theory of Film Diffusion

As introduced previously, the adsorption efficiencies of ion-exchange resins are highly dependent on the hydrophilic and hydrophobic properties of substituents around the ligands.¹³ Moreover, the adsorption efficiencies are also affected by the polarization of the polymer chain.¹⁶ Because these aspects do not come from the electronic states of the ligand itself, it is reasonable that there exist boundary films of the ion concentrations at the surface of the resin bead. Once the concentration at the surface is determined, the diffusion constant D_M is reflected to the rate of reaction through the surface concentration. Therefore, in principle, if one can estimate the length of the boundary films (δ_M), the total rate of reaction is described as a function of the bulk-phase concentrations.

Because the regeneration of ion exchangers is usually performed with resins with considerably high metal coverage and excess

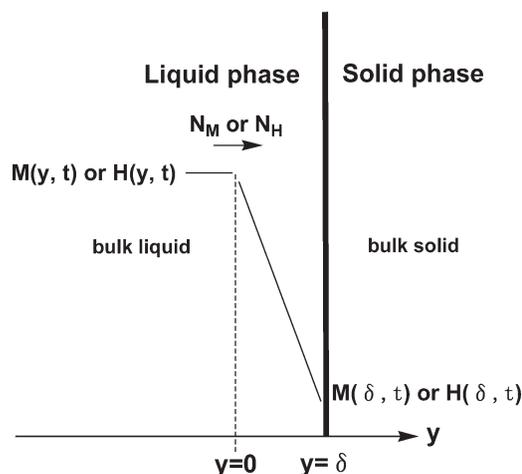


Figure 5. Boundary film of the ion-exchange resins.

acids, the process is akin to mutual diffusion between the metal ions and protons through the double films. In fact, when we take into account eqs. (12) and (13), the sum of the molar flux of the metal ions (N_M) and protons (N_H) should be zero. That is

$$N_M = -N_H \quad (14)$$

Thus, from the diffusion equation, we can calculate the molar flux within the boundary films, obtain the total rate of reaction, and eliminate the surface concentrations.

Figure 5 shows a schematic model of the boundary films in the liquid phase. As mentioned previously, the sum of N_M and N_H with respect to the fixed coordinate is zero. Therefore, the bulk flux term of the Fickian equation diminishes, and thus

$$\begin{aligned} N_M &= -D_M \frac{\partial M(y,t)}{\partial y} + \frac{M(y,t)}{M(y,t) + H(y,t)} (N_M + N_H) \\ &= -D_M \frac{\partial M(y,t)}{\partial y} \end{aligned} \quad (15)$$

where the y axis is directed from the bulk liquid phase to the surface, M and H are rewritten as $M(y,t)$ and $H(y,t)$ as functions of the distance (y) and time (t), and D_M is the mutual diffusion coefficient for the concentration of metal ions, which should be the same value as that of H . When M is much smaller than H , D_M is almost same as the individual diffusion coefficient of the metal ion.⁶ Therefore, in usual conditions, eq. (15) is satisfactory enough, even when a diffusion potential exists. Because no chemical reactions occur inside the boundary films, N_M is independent of y within the film, and thus, the differential of the concentration is also independent of y . Denoting the surface concentration of the metal ions as $M(\delta_M, t)$, we obtain the following:

$$N_M = D_M [M(0, t) - M(\delta_M, t)] / \delta_M \quad (16)$$

Similarly, for protons, we obtain the following:

$$N_H = D_H [H(0, t) - H(\delta_H, t)] / \delta_H \quad (17)$$

With the classical methods, early workers hypothesized the equilibrium of ion exchange at the surface of the boundary

films.^{10,11} That is, the left-hand-side terms in eqs. (12) and (13) are replaced with zero, and we obtain

$$2mH(\delta_H, t)[M_0 - M(\delta_M, t)] - 2m'M[H_0 - H(\delta_H, t)] = 0 \quad (18)$$

When the surface concentrations are eliminated, N_M becomes

$$N_M = \frac{(\delta_M/\delta_H)D_M D_H [M(0, t)\theta_H(t) - KH(0, t)\theta_M(t)]}{D_H \delta_M \theta_H(t) + K D_M \delta_H \theta_M(t)} \quad (19)$$

where K is the equilibrium constant of the ion exchange and can be calculated as follows:

$$K = \frac{m}{m'} \quad (20)$$

In particular, when $\delta_M = \delta_H$, eq. (19) is identical to that of the Adamson–Grossman method.¹⁰ In view of the bulk scale, dM/dt and N_M correspond to the space velocity and line velocity, respectively. Therefore, there is a constant of proportionality with the dimension of length, which should consist of the surface area of the resins (S) and the volume of the liquid (V). Thus, if we pay attention to the sign of the reaction rate, it follows that

$$\frac{dM}{dt} = -(S/V)N_M \quad (21)$$

Here, we consider the initial rate of reaction. When only acids are present in the initial liquid phase, the initial rate is obtained by the substitutions of $M(0,0) = 0$, $\theta_H(t) = 0$, and $H(0,0) = H_0$:

$$\left. \frac{dM}{dt} \right|_{t=0} \cong (S/V)(\delta_M/\delta_H^2)D_H H_0 \quad (22)$$

This is a linear function of H_0 . The initial rate is independent of K , the reaction rate constants, and M_0 . The independence is due to the hypothesis of equilibrium at the surface of the boundary films. As a result, the kinetics are essentially described by diffusion control. In general, the acid-concentration dependence on the initial rate of ion exchange is not linear. So, in many cases, this is not a sufficient approximation, as shown later.

Self-Consistent Surface Concentration

In contrast to the classical methods, in this study, we determined the surface concentrations so that the rates of the chemical reactions and diffusion were self-consistent. Substituting M and H in eqs. (12) and (13) with $M(\delta_M, t)$ and $H(\delta_H, t)$, respectively, we proportionally identify dM/dt with N_M and dH/dt with N_H with eq. (21). From the symmetry of the expressions, only dM/dt is needed:

$$\frac{dM}{dt} = 2mH(\delta_H, t)[M_0 - M(\delta_M, t)] - 2m'M(\delta_M, t)[H_0 - H(\delta_H, t)] \quad (23)$$

We note that the surface concentrations in the solid-phase film are also determined implicitly from eqs. (10) and (11). Eliminating $M(\delta_M, t)$ and $H(\delta_H, t)$ by eqs. (16) and (17), we obtain a quadratic equation of N_M , and the total rate of reaction is

obtained as a function of the bulk concentrations $M(0, t)$ and $H(0, t)$:

$$\frac{dM}{dt} \cong -(S/V)[1/(2p)][-q + (q^2 - 4pr)]^{0.5} \quad (24)$$

where

$$p = 2(m - m')\delta_M \delta_H / D_M D_H \quad (25)$$

$$q = 2(m - m')[H(0, t)\delta_M / D_M - M(0, t)\delta_H / D_H] + (S/V)[1 + 2(V/S)(mM_0\delta_H / D_H + m'H_0\delta_M / D_M)] \quad (26)$$

$$r = 2[mM_0H(0, t) - m'H_0M(0, t)] - 2(m - m')M(0, t)H(0, t) \quad (27)$$

This expression contains both $M(0, t)$ and $H(0, t)$ and is a somewhat complex differential equation. However, the initial rate is easily estimated as follows. That is, putting $H(0,0) = H_0$ and $M(0,0) = 0$ and neglecting the high order terms with respect to δ_M and D_M , we can calculate the initial rate as follows:

$$\left. \frac{dM}{dt} \right|_{t=0} \cong \frac{2mH_0M_0}{1 + (2mV/S)(\delta_M H_0 / D_M + \delta_H M_0 / D_H)} \quad (28)$$

If H_0 is not so large, this can be expanded by the power of H_0 :

$$\left. \frac{dM}{dt} \right|_{t=0} \cong 2mH_0M_0[1 - (2mV/S)(\delta_M H_0 / D_M + \delta_H M_0 / D_H)] \quad (29)$$

Thus, when the system is controlled by the chemical reactions, the initial rate is of the first order with respect to H_0 . On the other hand, when the system is controlled by diffusion, the initial rate is of the second order with respect to H_0 , which is a convex function of H_0 . If H_0 is quite large, the rate converges to a constant because of the higher order terms:

$$\lim_{H_0 \rightarrow \infty} \left. \frac{dM}{dt} \right|_{t=0} \cong (S/V)M_0(D_M/\delta_M) \quad (30)$$

Because this asymptotic form consists of a diffusion term independent of chemical-reaction constants, we can obtain a ratio between D_M and δ_M . In both eqs. (29) and (30), the magnitude of the diffusion terms depend on δ_M and D_M . Thus, the total rate of ion exchange is affected by the hydrophilic and hydrophobic atmosphere around the ligands and the viscosity of the solvent. In particular, a high-viscosity solvent easily leads to diffusion control because of the reduction in D_M ; this is consistent with common sense. Equation (29) is also a convex quadratic function of m . Therefore, even when m increases because of the substituent effects or temperature, the initial rate is saturated by diffusion control through the same functional type as H_0 .

Here, we consider the related cases in which the ion-exchange ratio is not a one-to-one type. Generally, in these cases, the bulk-flux term in Fick's law is not zero. However, when the acid is in excess and the molar ratio of metal ions is small enough, the term can also be neglected. The initial rate is similarly estimated with the same formulation. For example, when the ion and active sites react with a ratio of 1:2, one ion is exchanged with two protons. Thus, the initial rate is estimated by the

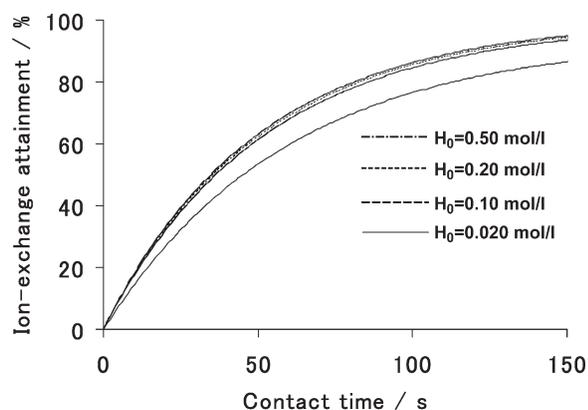


Figure 6. Theoretical curves of the ion exchange between the metal ions and protons with the boundary films.

substitution of H_0 in eqs. (28) or (29) by H_0^2 . Then, the functional type of eq. (29) becomes concave not convex under both chemical-reaction and diffusion control. In this case, the linearity with respect to H_0 is not obtained. Conversely, we can guess the ion-exchange ratio from the initial rate analysis. In general, when the ion and proton react with a ratio of 1: x in the chemical rate-determining step, the initial ratio is as follows:

$$\left. \frac{dM}{dt} \right|_{t=0} \cong 2mH_0^x M_0 [1 - (2mV/S)(\delta_M H_0^x / D_M + \delta_H M_0 / D_H)] \quad (31)$$

When the concentration of metal ions is smaller than that of acid, the ion-exchange rate in the last stage is also simple to analyze. That is, when $H(0, \infty) \cong H_0$, the rate of reaction is expanded by the power of H_0 as follows:

$$\left. \frac{dM}{dt} \right|_{t=\infty} \cong 2mH_0(M_0 - M) [1 - (2V/S)(m\delta_M H_0 / D_M + m'\delta_H M_0 / D_H)] \quad (32)$$

Because it generally holds that $m > m'$, the boundary-film effect in the last stage is always smaller than that in the initial stage. In particular, when the regeneration efficiency of metal ions is large and m' can be neglected, the boundary-film effect in the last stage becomes quite small. Then, however, the term $M_0 - M$ becomes very small, and thus, confirmation of the boundary-film effect from the experimental data in the last stage will be difficult.

As shown previously, ion exchange in usual use is generally subject to diffusion control in the initial stage and chemical-reaction control in the last stage. This is consistent with early empirical speculation. Numerical solutions for an ion-exchange system with boundary films can be calculated by the Runge–Kutta method. m and m' were set to be the same as the values in the previous section, and typical conditions for the batch experiments that we studied were used as follows:

$$\begin{aligned} M_0 &= 100 \text{ ppm} = 1.6 \times 10^{-3} \text{ mol/L} \\ H_0 &= 0.020, 0.10, 0.20, \text{ and } 0.50 \text{ mol/L} \\ D_M = D_H &= 1 \times 10^{-12} \text{ m}^2/\text{s} \\ \text{Specific surface} &= 50 \text{ m}^2/\text{g dry} \end{aligned}$$

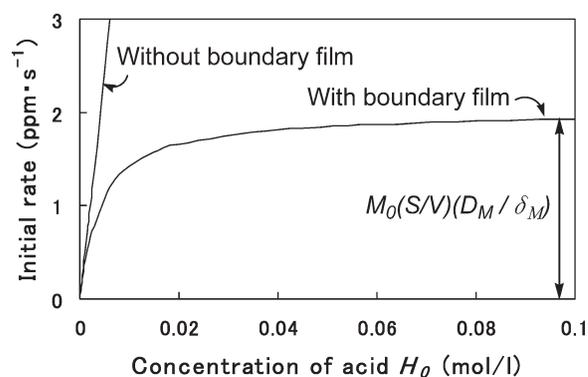


Figure 7. Initial reaction rates versus H_0 in the ion exchange between the metal ions and protons.

Resin = 50 mg ($\therefore S = 50 \text{ m}^2/\text{g} \times 50 \text{ mg} = 2.5 \text{ m}^2$).
Volume of liquid (V) = 25 mL.

D_M corresponds to typical values of multivalent cations.^{5,9,15} Strictly speaking, this is not determined uniquely by this formulation, as shown later. The effective δ_M was set to $5 \times 10^{-6} \text{ m}$ ($5 \mu\text{m}$) for both the metal ions and protons. Figure 6 shows the theoretical curves based on the results. In comparison to Figure 4, we could clearly observe the time delay of ion exchange due to the film diffusion. Figure 7 shows the initial rate corresponding to Figures 4 and 6. We observed that the initial rate was a linear function for the chemical-reaction control without boundary films and a quadratic function for the diffusion control with boundary films. We noted that the two graphs contacted each other at the origin. In the high-concentration region, the rate with boundary films increased very slowly because of the terms over the third order and converged to the asymptotic value. The initial rate of the diffusion-controlled system was much suppressed compared with that of the chemical-reaction controlled system. In this parametrization, the initial rate was saturated at $H_0 \cong 0.05 \text{ mol/L}$. In eq. (28), when H_0 is equal to M_0 , the contribution ratio of chemical reactions and diffusion becomes about 1:1. In this system with excess acids, the contribution of diffusion was over 80%, and the graph reproduced the asymptotic region and the quadratic region. In classical theory, K and the reaction rate constants do not appear in the initial rate expression, and the degree of chemical-reaction control or diffusion control is not determined. In this sense, this method is more advanced and shows reasonable kinetics.

APPLICATION

The simplest method for justifying the theory was to analyze the ratio of the initial rates under different acid concentrations. Experimental data on a typical ion exchanger were found in our previous work,¹⁴ in which Cu^{2+} on iminodiacetic acid bisodium chelate resins (MURO-Chelate A-1', Muromachi Kagaku Kogyo, Ltd.) were exchanged with H^+ . Initial rates of 0.1 and 1.0 mol/L were obtained by polynomial fitting (e.g., the fourth order) of the fractional attainments versus the contact time. The polynomial fitting was the best method to reduce the errors because the curves so obtained could be easily differentiated

Table I. Initial Rates of Ion Exchange on an Iminodiacetic Acid Chelate Resin

H_0	Iminodiacetic acid-Cu(II)/HCl		
	0.1 mol/L	1.0 mol/L	
Initial rate ^a versus the maximum capacity	2.39 (%)(s ⁻¹)	11.4 (%)(s ⁻¹)	
Ratio of the initial rate ^b			
Observed	$x = 1.0,$ calculated	$x = 1.5,$ calculated	$x = 2,$ calculated
4.8	10.0	31.6	100.0

^aBased on the fourth-polynomial fitting of the experimental data.¹⁴

^bRatio of the initial rate = $dM/dt|_{H=1.0\text{ mol/l}}, t=0 / dM/dt|_{H=0.1\text{ mol/l}}, t=0$. $dM/dt \approx 2mM_0H_0^x(1 - \text{Diffusion terms})$.

and immediately gave the initial rates at the origin. As summarized in Table I, the ratio of the initial rate was calculated to be 4.8. This was much lower than those of the nonfilm value, $(1.0\text{M}/0.1\text{M})^x = 10.0^x$, where x is the ratio $\text{H}^+/\text{Cu}^{2+}$ per exchange reaction. On the basis of the chemical compositions, $x \approx 1-2$ because Cu^{2+} was adsorbed at $\text{pH} \approx 4$; this was followed by ion exchange at $\text{pH} < 2$. In the chemical rate-determining step, probably $x \approx 1$. These data clearly show that the rate process could not be described only by chemical-reaction-controlled kinetics nor by Adamson-Grossman's classical diffusion methods. This supported the nonlinearity of the acid-concentration dependence and the existence of boundary film.

As another application, we analyzed an ion-exchange reaction of an amidinourea resin. The resin was loaded with CuCl_2 , and the copper ions were exchanged with hydrochloric acid at various concentrations.¹⁴ The copper ions were exchanged with protons at the Schiff-base site to form a stable 1:1 hydrochlorate. Figure 8 shows the experimental data. The sample was trimethylaminourea resin with a polystyrene skeleton. Details of the synthesis and ion-chromatograph measurements were given in a previous article.¹⁴ The resins used were globularized into about 50 mesh by suspension polymerization under poly(vinyl alcohol).¹⁷ The experiment was not a case of particle diffusion with a disc-type resin¹⁸ but a batch-type contact-filtration method with an agitation speed of 300 rpm. The experiment was done at room temperature, in which $M_0 = 100$ ppm, $V = 25$ mL, and resin = 50 mg. The ion exchange was almost attained within 300 s of the contact time. The initial slope of the reaction rate was close to that shown in Figure 6 with boundary films rather than that shown in Figure 4 with no boundary films. The diffusion effect became clear through analysis of the acid-concentration dependence on the initial reaction rate.

As shown in Figure 7, the initial reaction rate with no boundary films should be proportional to the concentration of acid. However, with boundary films, the proportionality should be broken into a quadratic function of the acid concentration. Thus, we

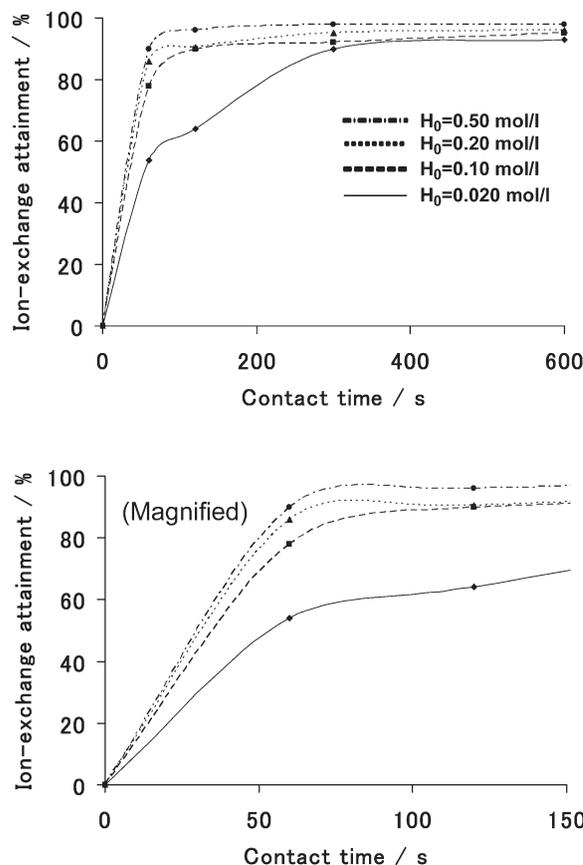


Figure 8. Experimental curves for the ion exchange between the Cu(II) ions and protons in the trimethylaminourea resin.

analyzed the experimental initial rate from curve fitting by a fourth-polynomial approximation. As shown in Figure 9, the plot of the initial rates versus H_0 was not linear but was a convex function. Strictly speaking, in this polymer complex, the ratio between the copper ions and active sites was not an integer. It consisted of a mixture of 1:1 and 1:2 complexes, in which the mean ratio was 1:1.59.¹⁴ However, as mentioned previously, when the ratio of the reaction at the chemical-rate-determining step is 1:2, the curve should be concave. Therefore, we could regard the ratio at the chemical-rate-determining step as 1:1. The convex curve observed was consistent with the previous

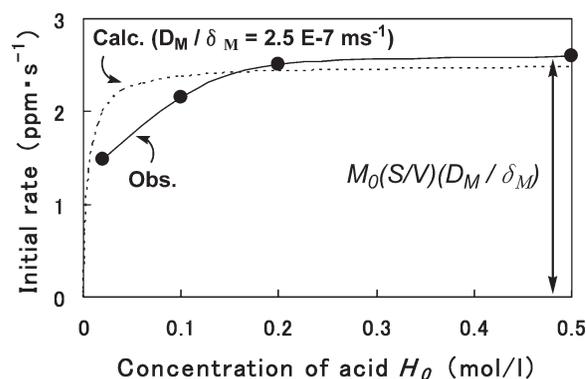


Figure 9. Initial reaction rate versus H_0 in the ion exchange between the Cu(II) ions and protons in the trimethylaminourea resin.

theoretical formula, and thus, the total ion exchange was subject to film-diffusion control. Such analyses cannot be done with classical theory. It is not until the surface concentrations are determined so as to be self-consistent that the degree of chemical reaction or diffusion control is estimated. The shape of the curve is essentially determined by the Sherwood number, and thus, the ratio between the diffusion constant and δ_M is not determined uniquely. However, the previous theoretical analysis will be sufficient for practical use as an approximate solution. In fact, from the asymptotic behavior of the initial rate, we could reproduce the ratio D_M/δ_M to be 2.5×10^{-7} m/s, which was consistent with the theoretical simulation (dashed line in Figure 9). That is, when the diffusion constant of metal ions was determined by another experiment, we could estimate the corresponding δ_M .

In relation to the previous ion-exchange reaction, the adsorption of amidinourea resins introduced in the first section was also reinterpreted in view of film diffusion. Because metal ions are always hydrated, an increase in the hydrophilic region around the active sites decreased δ_M . As a result, the adsorption efficiency increased kinetically. An increase in the hydrophobic region, on the other hand, increased δ_M , and thus, the hydrated ions tended to escape to the bulk liquid phase. Then, the mass transfer coefficients became very small, which was consistent with the previous formulation.

Thus, the diffusion process is essential for describing the total rate of ion exchange. We formulated approximately reasonable solutions with the chemical-reaction terms and the diffusion equation within the boundary films. In particular, the ion-exchange reactions were subject to the diffusion control in the initial stage of the reaction. By analyzing the initial rate, we could grasp the degree of control by chemical reactions or diffusion. The resulting kinetics are usable for the estimation and molecular design of novel ion exchangers.

CONCLUSIONS

The kinetics of ion-exchange reactions were formulated on the basis of boundary-film theory. In contrast to classical methods, the surface concentrations were determined so that the rates of chemical reactions and diffusion were self-consistent each other. The expression is available for both chemical-reaction-controlled systems and diffusion-controlled systems. In particular, under excess acid, the reaction was subject to diffusion control in the initial stage and chemical-reaction control in the last stage. The numerical solutions reproduced the experimental

data of ion-exchange curves well. From the initial rate analysis, the diffusion control in the initial stage was confirmed.

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