

Ion-adsorption Kinetics in Polymers

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Abstract

A useful formulation of ion-adsorption kinetics is introduced based on our recent researches. The chemical reaction kinetics and diffusion kinetics are simultaneously analyzed combining with the Einstein's viscosity formula. The rate-determining steps are quantitatively determined by estimating the relative magnitude of the kinetics resistances in the boundary film and the particle. The key concept of this method is an addition theorem of film-diffusion kinetic resistance and the particle-diffusion kinetic resistance. While in hydrophilic polymers, the thickness of boundary film decreases due to the attractive force between the ion and the surface, in hydrophobic polymers, it increases with the amount of hydrophobic components. This is confirmed by using chitosan resins with hydrophilic/hydrophobic components. The experiments are based on the batch method, and degree of film-diffusion control and particle-diffusion control is determined simultaneously. The film mass-transfer coefficient in the boundary film is also determined from a simple plotting of the experimental data. This method is also applicable to ion-exchange kinetics by summing the kinetic resistances at each step in the ion-exchange reaction and the mutual diffusion. Our method will serve as a guiding tool for designing of adsorption agents and ion-exchangers. Copyright © VBRI Press.

Keywords: Adsorption, kinetics, rate-determining steps, diffusion, boundary film.

Introduction

Adsorption is one of the fundamental phenomena in the field of physical chemistry and chemical engineering [1]. Our modern life owes a great deal to adsorption technique through chelate resins, activated carbons, chromatography, optical resolution agents, and so on. Ion exchangers are also commonly used for water purification, decoloring, metal recycling, medicine, etc. [2]. These techniques are usually performed by the batch method or column method, and the efficiency of adsorption has often been evaluated in view of equilibrium between the ion (molecule) and the ligand that is often fixed to polymers.

The kinetics of adsorption is, on the other hand, another important aspect to determine the efficiency of adsorption. Above all, for industrial applications, the actual efficiency of the adsorption agents is often determined by kinetics, rather than the equilibrium. In this sense, adsorption kinetics is more important for actual designing of adsorption agents, because the time to be required for adsorption should not be infinite.

Smoluchowski developed the first classical theory of the adsorption kinetics based on diffusion theory. The actual kinetics of adsorption phenomena consists of diffusion and chemical reaction processes. This is very important aspects of the adsorption kinetics in that both diffusion control and chemical-reaction control kinetics is possible, depending on the experimental conditions. Therefore, modern theory of adsorption kinetics is based on both diffusion and chemical reaction process. The conventional formulations are, however, generally complex due to many terms to be considered.

In this proceeding, a concise and intuitive kinetics of general adsorption processes is introduced based on our recent researches. After brief reviewing of the classical kinetics of adsorption, our method is introduced as an extension of the law of addition theorem of kinetic resistances. Our method is based on film theory and ordinary chemical-reaction rate process, combining with the Einstein's viscosity expression. By analyzing the initial rate of the adsorption process, the rate-determining step is quantitatively evaluated through simple plotting of the effective rate constant versus the initial rate. The present method is also available to analyze ion-exchange processes, and widely applicable to designing for adsorption agents, ion exchangers, and optical resolution agents.

Theoretical

The most classical kinetics of diffusion process was formulated by Smoluchowski [3]. The gist of it is hypothesis that molecule A as 'sink' with radius R reacts with molecule B by diffusion only. A and B immediately react at the sink in which the rate constant of the chemical reaction is infinity. Outside the adsorbent, however, the diffusion constant is a finite value, and thus, there should be a diffusion rate constant as a parameter describing the whole process. From elementary fluid dynamics, the diffusion rate constant k_d is given as:

$$k_D = 4\pi RD, \quad (1)$$

where D is the diffusion constant. This simple formula is independent of the chemical-reaction rate constant k_c ,

and thus, the whole process is entirely controlled by diffusion only.

In 1949, Collins and Kimball introduced a boundary condition on the surface of the adsorbent so that flow of the molecule B is connected to the chemical reaction rate between A and B at the surface through the balance of materials [4]. From elementary differential equations, one can deduce the effective rate constant k as follows:

$$k = \frac{k_C k_D}{k_C + k_D}, \quad (2)$$

or by reciprocal of the expression, we obtain a very important formula:

$$\frac{1}{k} = \frac{1}{k_C} + \frac{1}{k_D}. \quad (3)$$

This is the addition theorem of the kinetic resistance [5]. The meaning of this expression is that time to be required for the diffusion $1/k_d$ and time to be required for the chemical reaction $1/k_c$ is simply summed in series. Therefore, the rate determining step of the system depends on the magnitude of each kinetic resistance $1/k_d$ and $1/k_c$.

After such fundamental construction of the kinetics, some refinements of diffusion kinetics were done by Ovchinnikov [5] to include fluctuation of the concentration of the molecule. As for the ionic particles, effect of diffusion potential was considered by using the Nernst-Planck equation, which has been applied for analyzing the ion-exchange kinetics [6]. Ion-exchange process has been basically described by simple exchange chemical reaction or diffusion within a boundary film [7]. Nowadays, detail calculation of the ion-exchange kinetics is performed by computation programs including diffusion potential and mutual diffusion coefficients [8].

Recently, we extended the addition theorem of the kinetic resistance so that the particle resistance inside the adsorbent is included in series. As shown in Fig. 1, the kinetic resistance is then sum of three terms in units of k_c [9]:

$$\frac{1}{k} = \frac{1 + \alpha + \beta}{k_c}, \quad (4)$$

where α is film-diffusion kinetic resistance within the boundary film (①), and β is particle-diffusion kinetic resistance inside the adsorbent (②), and the chemical-reaction kinetic resistance (③) is set to be unity in the numerator. From the elementary fluid dynamics, the concrete expression of α becomes:

$$\alpha = \frac{\delta k_C}{sD}, \quad (5)$$

where δ is the thickness of boundary film, and s is specific area of the adsorbent as an aggregate of sphere particles. We note that α is proportional to δ , and anti-proportional to mass transfer coefficients D/δ . On the other hand, β is regarded to be a constant on average,

which is considered to be kinetic resistance inside the particle with micro-pores:

$$\beta = \beta(M, R). \quad (6)$$

β can be, however, slightly dependent of adsorbate concentration (such as metal ion) M and adsorbent radius R , but independent of adsorbent concentration (such as resins) N . Hereafter, M and N represents bulk concentration of metal ion and resin concentration, respectively. Above all, the initial concentrations are represented by M_0 and N_0 .

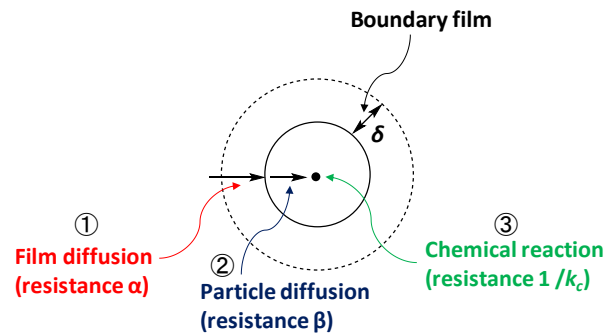


Fig. 1. Construction of kinetic resistances in adsorption.

The diffusion constant generally depends on viscosity of the suspension, which is well known as the Stokes' formula:

$$D = \frac{k_B T}{6\pi\eta R}, \quad (7)$$

where k_B and T is the Boltzmann constant and temperature, respectively. Viscosity η of a given suspension has been formulated by many workers. In the present treatment, we adopt the Einstein's expression:

$$\eta = \eta_0 \left(1 + \frac{5}{2}\phi\right), \quad (8)$$

where ϕ is volume fraction of the adsorbent.

By combining the expressions above, we obtain the initial rate $v_0 (> 0)$ as [9]:

$$v_0 = -\frac{dM}{dt} \Big|_{(t=0)} = \frac{k_C M_0 N_0}{1 + \frac{\delta k_C}{sD} \left(1 + \frac{5N_0}{2\rho}\right) + \beta} = \frac{k_C M_0 N_0}{1 + \alpha \left(1 + \frac{5N_0}{2\rho}\right) + \beta}, \quad (9)$$

where ρ is density of the adsorbent, and α is rewritten by $\delta k_C/(sD_0)$, corresponding to the diffusion constant D_0 in the pure solvent. We define effective rate constant k_{ex} as:

$$k_{ex} = \frac{v_0}{M_0 N_0}. \quad (10)$$

By deforming it, we obtain a useful form:

$$k_{ex} = \frac{k_C - \alpha \frac{p}{M_0} v_0}{1 + \alpha + \beta}, \quad (11)$$

where $p = 2.5/\rho$. Thus, when we plot k_{ex} versus v_0 , we obtain a straight line by changing N . If kinetics is diffusion control ($1 \ll \alpha, \beta$), from the slope and the intercept, we can obtain a very important ratio β/α , which represents degree of chemical-reaction control or diffusion control. That is, when $\beta/\alpha < 1$, the kinetics is diffusion control, because the diffusion kinetic resistance α is larger than the particle diffusion resistance β . When

$\beta/\alpha > 1$, on the other hand, the kinetics is particle diffusion control, because the particle kinetic resistance β is larger than the film diffusion resistance α . This simple principle is a key concept of our method. For actual designing for adsorption agents, it is useful to grasp the rate-determining step in a given system. The mass transfer coefficient D/δ (or D_0/δ) is also calculated from the experimental results. In the next section, we exemplify some initial rate analyses based on our recent experiments.

Experimental

We chose chitosan resins as adsorbents, which form 1:1 complex with copper ion Cu^{2+} . Firstly, crosslinked chitosans were prepared by using hexamethylene diisocyanate (HMDI), of which crosslinking density was set to be 0, 1, 3, and 5 % [9]. Next, we prepared hydrophilic, hydrophobic, and amphiphilic chitosan resins by copolymerization with 2-hydroxyethyl methacrylate (HEMA) and styrene, in which copolymerization ratio was set to be chitosan-HEMA = 1:1 (1; CH), chitosan-styrene = 1:1 (2; CS), and chitosan-HEMA-styrene = 2:1:1 (3; CHS), respectively, in weight % [10]. The resins were characterized by IR, SEM, XPS, and XRF measurements. As for the synthetic procedures and characterizations, see references [9, 10]. The adsorption measurements were performed by the batch method. As well as the concentration of Cu^{2+} , bulk concentration of the resins was also changed. After real-time electromotive force measurements, the initial rates were evaluated by UV-Visible spectroscopic method. Along the formulations above, the effective rate constant was plotted versus the initial rate, and the ratio β/α was obtained from the slope and the intercept. The rate-determining steps and mass transfer coefficients were determined for each process [9, 10].

As a fundamental model for ion-exchange, desorption process of the chitosan resins was also examined under acidic conditions.

Results and discussion

Fig. 2 shows resin-concentration dependence of the initial rate of the adsorption between the crosslinked-chitosans and Cu^{2+} . We see that all the plots lead to non-straight lines but convex upward curves, which suggest diffusion controlled kinetics. The curvatures of the initial rate versus ion-concentration was also observed (omitted in this proceeding), which was probably due to ion-concentration dependence of the particle kinetic resistance β [9]. The change of the initial rate versus resin concentration were analyzed along Eq. (11) formulated above.

Fig. 3 shows the initial rate analysis along our method. We see that all the lines have negative slope, which represents declining of the initial rate due to the Einstein's viscosity. From the slope and the intercept, we evaluated the ratio β/α and mass transfer coefficients, as summarized in Table 1.

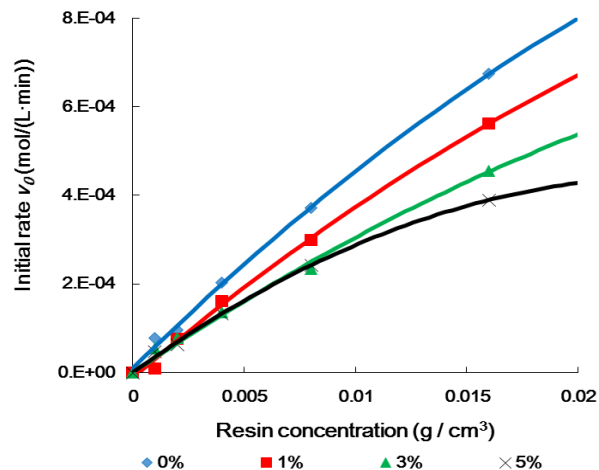


Fig. 2. Resin-concentration dependence of the initial rate of adsorption between the crosslinked chitosans and copper ion Cu^{2+} . Reprinted with permission from Hatanaka, M.; Nishino K.; Miyasaka M.; *J. Appl. Polym. Sci.*, 2017, 134, 44738.

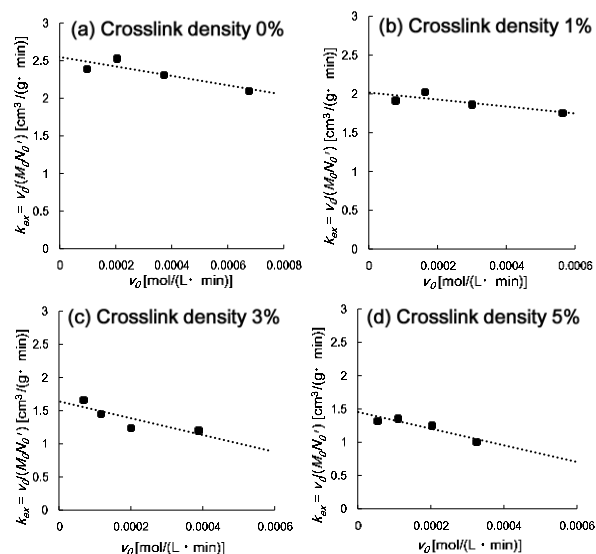


Fig. 3. Initial rate analysis for adsorption between the crosslinked chitosans and copper ion Cu^{2+} . Reprinted with permission from Hatanaka, M.; Nishino K.; Miyasaka M.; *J. Appl. Polym. Sci.*, 2017, 134, 44738.

Table 1. Kinetics parameter for adsorption between crosslinked chitosans and Cu^{2+} . Reprinted with permission from Hatanaka, M.; Nishino K.; Miyasaka M.; *J. Appl. Polym. Sci.*, 2017, 134, 44738.

Crosslink density	Film mass transfer coefficients D_m/δ_m (m/min)	Kinetic resistance ratio β/α	Total Kinetic resistance in $(\text{g}/\text{cm}^3)\text{min}$	Rate determining step
0%	1.3×10^{-4}	1.7	0.39	Particle diffusion
1%	1.4×10^{-4}	2.7	0.50	Particle diffusion
3%	4.8×10^{-5}	0.31	0.52	Film diffusion
5%	4.4×10^{-5}	0.33	0.57	Film diffusion

When crosslinking density is low (0 and 1 %), the rate determining steps lie in particle diffusion, because β/α is larger than unity. On the other hand, when crosslinking density is high (3 and 5 %), the rate determining steps lie in film diffusion, because β/α is smaller than unity. This results suggest that thickness of boundary film increases by the amount of crosslinking agent. The crosslinking agent HMDI is hydrophobic, and thus, the results imply that hydrophilic surface decreases

thickness of boundary film, and hydrophobic surface increases thickness of boundary film. This is a reasonable working hypothesis to design for general adsorption agents. In order to confirm this hypothesis, we further intended to evaluate the rate-determining steps of adsorption between extremely hydrophilic or hydrophobic chitosan resins and copper ion Cu^{2+} .

Fig. 4 shows resin-concentration dependence of the initial rate and the initial rate analysis for adsorption between the hydrophilic (1)/hydrophobic (2) /amphiphilic (3) chitosan resins and Cu^{2+} . Similar to the previous case, all the slopes in the initial rate analysis are negative, and thus, Einstein's viscosity declines the effective rate constant through the increase of the concentration of resins.

Table 2 shows summary of the ratio β/α and mass transfer coefficients. We can clearly see that rate-determining step for the hydrophilic resin 1 lies in particle diffusion, and for the hydrophobic resin 2, it lies in film diffusion. For the amphiphilic resin 3, the kinetics has moderate character, in which both particle diffusion and film diffusion are important. The order of mass transfer coefficients are also reasonable, that is, hydrophilic > amphiphilic > hydrophobic, which suggests existence of long-range interaction between the surface of the resins and ion. Thus, from our experiments, general tendency of rate-determining steps in polymers is confirmed: For hydrophilic resins, thickness of boundary film is small, and the rate-determining step is particle diffusion. For hydrophobic resins, thickness of boundary films is large, and the rate-determining step is film diffusion. For amphiphilic resins, the kinetics has moderate character.

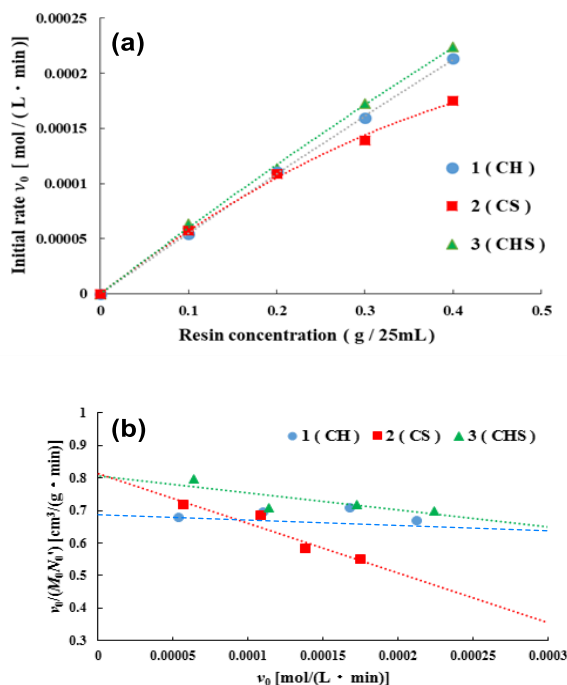


Fig. 4. Resin-concentration dependence of the initial rate and the initial rate analysis for adsorption between hydrophilic/hydrophobic chitosan resins and Cu^{2+} . Reprinted with permission from Sayama D.; Hatanaka, M.; Miyasaka, M.; *J. Appl. Polym. Sci.*, **2018**, *135*, 46493.

Table 2. Kinetics parameter for adsorption between the hydrophilic/hydrophobic chitosan resins and Cu^{2+} . Reprinted with permission from Sayama D.; Hatanaka, M.; Miyasaka, M.; *J. Appl. Polym. Sci.*, **2018**, *135*, 46493.

Resin	D_M/δ_M (m/min)	β/α	Rate determining step
1 (CH)	1.78×10^{-3}	103	Particle diffusion
2 (CS)	2.22×10^{-5}	0.09	Film diffusion
3 (CHS)	6.45×10^{-5}	2.2	Particle and film diffusion

Our initial-rate analysis is also applicable for ion-exchange processes. The addition theorem for kinetic resistances works well for constructing the kinetics of general ion-exchange processes. As a typical reaction, let us consider desorption of metal ion M from polymer ligand L by proton H. **Fig. 5** shows schematic diagram for addition theorem of the kinetic resistances for this reaction. The whole resistance is sum of the five processes; ① film diffusion resistance of H, ② particle diffusion resistance of H, ③ ion-exchange reaction resistance, ④ particle diffusion resistance of M, and ⑤ film diffusion resistance of M. Referring the scheme, further explanation will be not necessary to grasp the principle of construction of the whole kinetics.

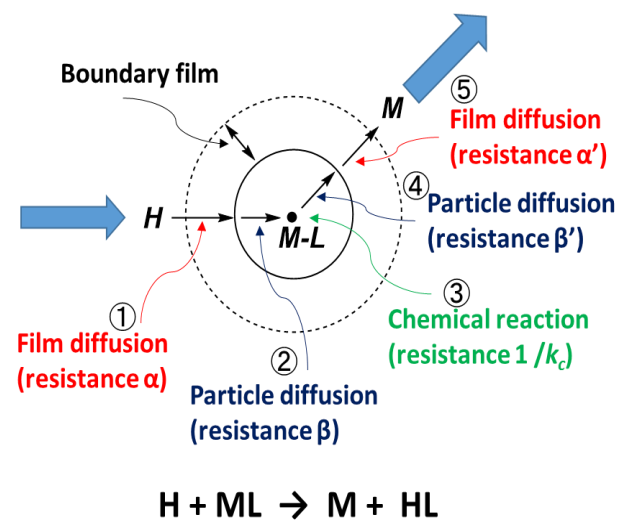


Fig. 5. Construction of kinetics in ion-exchange processes.

Let us exemplify an ion-exchange kinetics by analyzing desorption of Cu^{2+} from the cross-linked chitosans above. For simplicity, we tentatively neglect the particle diffusion terms, and only diffusion resistances of ions are considered [11]:

$$\frac{dM}{dt} \Big|_{(t=0)} = \frac{k_C H_0 M_0}{1 + \frac{V k_C}{S} \left(\frac{\delta_M H_0}{D_M} + \frac{\delta_H M_0}{D_H} \right)}, \quad (12)$$

where V is volume of the system, and S is the total surface area. Subscripts M and H also represent the metal ion and proton. The most important feature of such a case is that there should be an upper limit for the initial rate

with respect to the concentration of the incident ion (proton) H_0 . The limit is:

$$\lim_{H_0 \rightarrow \infty} \frac{dM}{dt} \Big|_{(t=0)} = \frac{S}{V} M_0 \frac{D_M}{\delta_M}. \quad (13)$$

Thus, we should observe an upper limit of the initial rate in ion-exchange kinetics, if the system is controlled by film diffusion.

Fig. 6 shows proton concentration dependence of the initial rate of the ion-exchange (desorption) process in the chitosan-Cu²⁺ system. We clearly see that the initial rate asymptotically closes to a limit, which is proportional to the mass transfer coefficient D/δ , and thus, the kinetics is subject to film-diffusion control. This is consistent with the initial hypothesis. Other examples of ion-exchange kinetics are given in our previous works [10, 11].

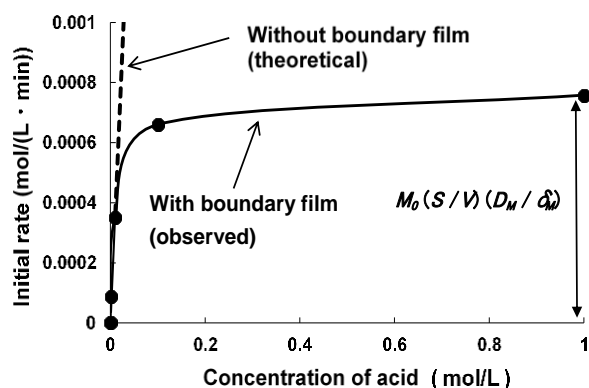


Fig. 6. Initial rate analysis on desorption of the chitosan-Cu²⁺ resin as an ion-exchange system. Reprinted with permission from Hatanaka, M.; Nishino K.; Miyasaka M.; *J. Appl. Polym. Sci.*, **2017**, *134*, 44738.

Our results are also fully consistent with Debye's formula of kinetics under a given potential between the adsorbent surface and ion [10, 12], in which thickness of boundary film is approximately estimated by a definite integral containing the potential. This consistency is a robust evidence for the interaction between the surface and ion [13].

As a further application, a strategy for kinetic optical resolution is suggested. According to the theory above, thickness of boundary film on the hydrophobic adsorbents is large. Then, combining with chiral solvents, the optical resolution is controlled by film diffusion, and difference in the diffusion constant for each enantiomer leads to effective kinetic optical resolution. This will be worth examining by the batch method. In the case of hydrophilic adsorbents, thickness of boundary film is trivial, and kinetics in chiral adsorbents plays a key role in the selectivity of optical resolution. In view of physical chemistry, designing for such adsorption agents based on hydrophilicity / hydrophobicity will be further sophisticated by considering permittivity of the adsorbents. Above all, in the column method, kinetic aspects of adsorption becomes more important than the batch method, and thus,

our analysis will be helpful for practical use of general adsorption agents.

Conclusion

A useful method to evaluate rate-determining steps in ion-adsorption kinetics was introduced. Based on the extended addition theorem of kinetic resistances, contributions of film diffusion and particle diffusion are evaluated by analyzing the initial rate. Our initial rate analysis takes the Einstein viscosity into account to scrutinize the curb on the initial rate versus the adsorbent concentration. Our method is concise and intuitive to chemists in that degree of film-diffusion and particle diffusion control is quantitatively estimated. The method is also applicable to ion-exchange processes, and further application to optical resolution is expected.

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