

Sorption Behavior of Ga(III) and In(III) into a Microcapsule Containing Long-Chain Alkylphosphonic Acid Monoester

Eiji Kamio,[†] Michiaki Matsumoto,[†] Fernando Valenzuela,[‡] and Kazuo Kondo^{*,†}

Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto, 610-0321, Japan, and Faculty of Chemical and Pharmaceutical Sciences, Chile University, P.O. Box 233, Santiago, Chile

The sorption behavior of gallium and indium into a microcapsule containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester is investigated. The effects of pH and metal concentration on sorption rate are investigated to estimate the sorption mechanism. The initial sorption rates are compared to the corresponding initial extraction rates measured for the solvent extraction system. The initial sorption rate varied with pH and metal concentration, following the solvent extraction system. Furthermore, the rate-determining step was evaluated from the activation energy. The activation energy of sorption is obtained as 48.9 kJ/mol for gallium and 30.7 kJ/mol for indium. These values indicate that both chemical reaction and diffusion processes affect the rate-determining step. These results suggest that metal sorption proceeds following sequential processes: diffusion of metal ions through aqueous film, complex formation on the surface of microcapsule, and diffusion of metal complexes through the pores. That is, the global sorption rates were controlled by both complex-formation reaction and intraparticle diffusion.

Introduction

In recent years, separation and recovery of metal using solvent impregnated resins (SIRs) and microcapsules have been investigated as an alternative technique to solvent extraction.^{1–5} SIRs and microcapsules can be easily prepared. Furthermore, it is easy to make them have great selectivity between metals because selection of the extractant is possible. Solvent impregnated resin is prepared by evaporation of organic solvent, which is used as a diluent of the extractant.^{6–8} Porous styrene–divinylbenzene polymeric resin and porous ion-exchange resin are used as supports of the extractants. On the other hand, microcapsules are prepared by polymerization of the O/W emulsion.^{9–10} There are few types of microcapsules such as single-core type, multicore type, and matrix type. There are some microencapsulation techniques such as the coacervation method, interfacial polymerization method, phase separation method, and in situ radical polymerization method. The microcapsule treated in this study is a matrix type prepared by an in situ radical polymerization method. Monomers of capsule wall such as styrene and divinylbenzene are dissolved in the dispersed phase. By heating, the monomer is polymerized and the diluent is evaporated. For both SIRs and matrix type of microcapsule, the wall materials are hydrophobic polymer resins and the extractants are commercial ones. The physicochemical properties of SIRs prepared without using ion-exchange resins as the polymeric supports are the same as those of the matrix type microcapsule.

These SIRs and microcapsules would act as the granular adsorbents containing a liquid extractant, so they would have the characteristics of both ion-exchange

resin and extractant used in a liquid–liquid extraction system. Several researchers have attempted to simulate the metal sorption rate behavior with SIRs by using a kinetics model derived for a metal adsorption system with solid ion-exchange resins, such as the homogeneous particle diffusion model and shrinking core model. Gonzalez-Luque and Streat¹¹ investigated the sorption kinetic of the UO_2^{2+} ion with the Levextrel type SIRs containing the mixture of bis-2-ethylhexyl phosphoric acid (D2EHPA) and trioctyl phosphate oxide. They analyzed the obtained kinetics data with both the homogeneous particle diffusion model and shrinking core model, and they concluded that the rate-determining step of the sorption process is the intraparticle diffusion step. Cortina et al.¹² carried out the sorption kinetics experiments of Zn, Co, and Cd with SIRs containing *O*-methyldiethylphosphine *O'*-hexyl-2-ethylphosphoric acid as extractant. They also analyzed the experimental results with both models, and they suggested that the rate-controlling step would change from a liquid-film diffusion controlling step to an intraparticle diffusion controlling step as the metal concentration increased in the bulk. Serarols et al.¹³ analyzed the sorption rate behavior of Au with an SIR containing triisobutylphosphine sulfide (Cyanex 471) by using homogeneous particle diffusion model and reported that the rate-determining step is the intraparticle diffusion step. They also concluded that the effective intraparticle diffusion coefficient varies with increasing metal concentration in the bulk. In other communication, they also investigated the kinetics data of Zn sorption with an SIR containing D2EHPA with a novel kinetics model that considers a local equilibrium between liquid and solid phases as it occurs in an ion-exchange adsorption process.¹⁴ From the investigation, the rate-determining step would change from a liquid-film diffusion controlling step to an intraparticle diffusion controlling step as the metal concentration increased in the bulk, too. It was also determined that the effective intraparticle

* To whom correspondence should be addressed. Tel/Fax: +81-774-65-6656. E-mail: kkondo@mail.doshisha.ac.jp.

[†] Doshisha University.

[‡] Chile University.

diffusion coefficient varies with increasing metal concentration in the bulk. However, considering the physical meaning of intraparticle diffusivity, it is thought that the intraparticle diffusion coefficient is not affected by external conditions such as metal concentration and bulk pH. Essentially, intraparticle diffusivity is a constant that depends on temperature, pore size of the polymer, and viscosity of the component that diffuses. Then, the variation of intraparticle diffusivity with metal concentration shows that the mechanisms of adsorption into an ion-exchange resin and the sorption into SIR and microcapsules are different. Warshawsky et al. showed the possibility that the effect of pH and metal concentration in an external aqueous phase on sorption rate is caused by the existing state of the metal complex in a polymeric support.¹⁵ That is, they proposed that migration of extractant inside a polymeric support in response to pH and metal concentration variation in the external solution correlates to the morphological properties of the polymeric support and to the mobility of extractant and metal complex. This physical change affects the variation of sorption rate. Formation of metal complex will also contribute to the sorption mechanism. In this study, we have investigated the effect of metal complex formation on sorption rate from another viewpoint.

SIR and microcapsules have the characteristics of both ion-exchange resins and organic extractants used in a liquid-liquid extraction system. Therefore, it is suggested that a complex-formation reaction at the surface would affect the rate-determining step for the metal sorption process with SIRs and microcapsules. Although at present a large number of studies on the sorption kinetics with SIRs and microcapsules have been carried out, to our knowledge, little attention has been paid to an effect of the complex-formation reaction on the rate-determining step. In addition, there are a lot of researchers that have reported the variation of sorption rate with varying aqueous conditions. However, there is no research concerned with the effect of such aqueous conditions on sorption rate behavior.

In the present study, the sorption rate of rare metals with a microcapsule containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) is measured. An effect of complex-formation reaction on rate-determining step is investigated by comparing the initial sorption rate for the microcapsule system and the initial extraction rate for a solvent extraction system. The rate-determining step is also estimated from the activation energy determined from Arrhenius plots.

Experimental Section

Reagents. EHPNA, kindly supplied from Daihachi Chemical Industry Co., Ltd. (Osaka, Japan), was used without further purification. Microcapsules containing EHPNA as an extractant (MC-EHPNA) were prepared by the same procedure as described elsewhere.¹⁰ The amount of EHPNA contained in unit gram of microcapsules is 1.6×10^{-3} mol/g-MC. An appropriate amount of GaCl_3 or $\text{In}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ was dissolved in 0.1 mol/dm³ $(\text{H,Na})_2\text{SO}_4$ aqueous solution. The pH of the aqueous solution was adjusted with a pH meter (Horiba F-23).

Sorption Isotherm. The sorption isotherms of gallium and indium were measured under batch conditions. Before and after metal sorption, the pH of the external aqueous solution changes somewhat. The changes of pH

Table 1. Physical Properties of a Microcapsule Used for Kinetics Experiment

| amount of EHPNA | 1.6×10^{-3} mol/g-MC |
|-----------------|-------------------------------|
| average radius | 75 μm |
| pore radius | 0.3–0.5 μm |
| surface area | 0.054 m ² /g-MC |

under various conditions are checked in a preliminary test. In advance of the sorption experiment, we have adjusted the pH of the aqueous solution so it takes the same value after equilibration. The aqueous solutions having various pH and metal concentrations and 0.1 g of the microcapsules were contacted for over 1 day to attain equilibrium. Then the metal concentration in the aqueous solutions was measured by inductively coupled plasma spectrometer (ICP-OES, Shimadzu ICPS-8000). The amount of metal adsorbed into the microcapsule was determined by mass balance before and after equilibrium.

Rate of Leakage of EHPNA from Microcapsules.

The leak rate of EHPNA was measured by the batch method. A 0.5-g sample of the microcapsules was introduced into 200 cm³ of an aqueous solution whose NaOH concentration was varied in a 0.1–0.2 mol/dm³ range. This concentration range was chosen because it had been found in a previous study¹⁰ in which EHPNA is significantly leaked from microcapsules in an aqueous solution at pH >4. Table 1 shows the physical properties of the microcapsule used in this experiment. Experiments were carried out at 313 K, with the microcapsules and the aqueous solution stirred by using a magnetic stirrer at a velocity of 500 rpm. It was found in preliminary experiments that a stirring speed of 500 rpm was sufficient to ignore liquid-film diffusion resistance surrounding a microcapsule. At the desired periods after introduction of the microcapsules into the aqueous phase, a sample of 1 cm³ of it was collected by using a syringe with filter. The phosphorus concentration in the aqueous sample, which corresponds to EHPNA concentration, was measured by ICP-OES.

Sorption Rates of Gallium and Indium into a Microcapsule. Considering that the microcapsules containing EHPNA exhibit strong hydrophobicity at pH <4 and are not dispersed in an ideal mixing, we measured the kinetic data by the shallow bed method. Figure 1 shows the shallow bed used in this study. A 0.05-g sample of the microcapsules was packed into the bed; their physical properties are shown in Table 1. The bed was conditioned by feeding aqueous solution without metal ion for 30 min. After 30 min, the feed solution containing gallium or indium ion was circulated through the bed during the appropriate periods. It was found in the preliminary experiments that the flow rate, 70 cm³/

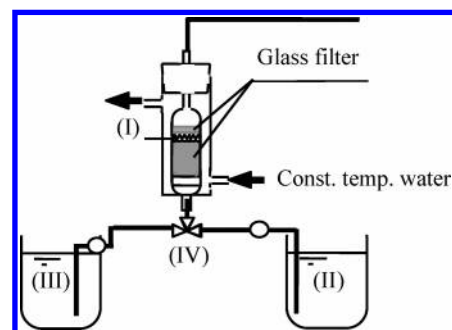


Figure 1. Shallow bed reactor: (I) microcapsule, (II) feed solution, (III) scrubbing solution, and (IV) three-way stopcock.

Table 2. Experimental Conditions for Uptake Curve

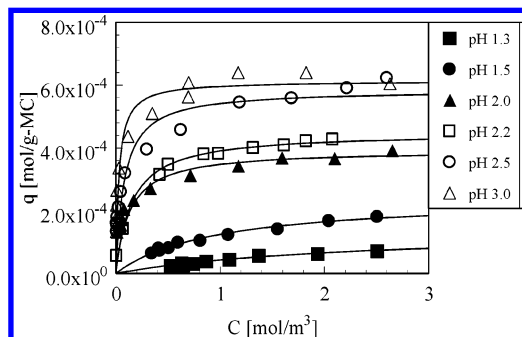
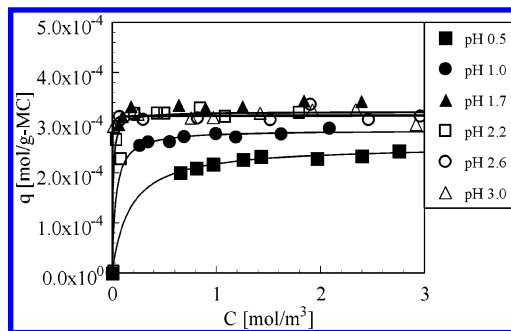
| | |
|----------------------------------|---|
| flow rate | 70 cm ³ /min |
| Reynolds number of feed solution | 3870 |
| microcapsules packed in the bed | 0.05 g |
| pH of the feed | 2.20 |
| metal concentration in the bulk | 0.3 mol/m ³ |
| pH of the scrubbing solution | 3.00 |
| stripping solution | 2.0 mol/dm ³ H ₂ SO ₄ for gallium 5.0 mol/dm ³ H ₂ SO ₄ for indium |
| temperature | 313 K |

min, was enough to ignore liquid-film diffusion resistance surrounding the microcapsule. As soon as the desired time passed, a scrubbing solution of pH 3.0 was introduced into the bed at a fast flow rate to remove the feed solution remaining in the bed. Two minutes was enough to remove completely the metal ion remaining in the bed. Then the obtained microcapsules were collected and contacted with the stripping solution for 1 day. Based on the information communicated previously,¹⁶ as stripping agents 1 and 5 mol/dm³ H₂SO₄ solutions for gallium and indium were used, respectively. It had been found that these concentrations of sulfuric acid can completely strip the metals sorbed in a microcapsule. The metal concentration, in the eluted stripping solution were measured by ICP-OES. The standard experimental condition is described in Table 2. The metal concentration or the pH of the aqueous solution was varied for each experiment.

Kinetics Experiment for Solvent Extraction System. A stirred transfer cell was used to measure the extraction rates of gallium and indium by EHPNA. In this study, undiluted EHPNA was used as the organic phase. The solutions in the cell were stirred at 140 rpm since it was found in preliminary experiments that this stirring speed is fast enough to overwhelm liquid-film diffusion resistance. Aqueous solutions containing no metal ion and undiluted EHPNA were introduced into the lower compartment and higher compartment, respectively. Then the stock solution containing the metal ion was introduced into the aqueous phase in the lower compartment. Small-volume samples were taken at intervals from the aqueous phase. The metal concentration in these samples was measured by ICP-OES. All experiments were carried out at 313 K.

Results and Discussion

Sorption Isotherm. Figures 2 and 3 show the sorption isotherms for gallium and indium at several pHs, respectively. It is shown in these figures that the sorption capacity of metals was increased with increasing pH. Solid lines in these figures correspond to

**Figure 2.** Sorption isotherms for gallium with a microcapsule based on the Langmuir model.**Figure 3.** Sorption isotherms for indium with a microcapsule based on the Langmuir model.

calculated lines using Langmuir isothermal equation as shown in eq 1.

$$q^* = \frac{q_{\infty}KC}{1 + KC} \quad (1)$$

where q_{∞} is the saturation sorption amount of metals and K the Langmuir constants, respectively. C and q^* denote the metal concentration in an aqueous phase and the equilibrium sorption amount of metal sorbed in a microcapsule corresponding to C , respectively. To be exact, the sorption mechanism of metal into a microcapsule does not follow the Langmuir adsorption model. However, the calculated results are correlated with the experimental data for all conditions. Therefore, the equilibrium sorption capacity for a certain concentration of metal ion in an aqueous solution can be calculated from eq 1. In this study, q^* was used for calculation of the fractional attainment of equilibrium of metal sorption, $F(t)$, was determined from eq 1.

Determination of Effective Intraparticle Diffusivity of Metal–Extractant Complex. It is difficult to determine the effective intraparticle diffusivity of a metal–extractant complex in a polymeric support, because there is the possibility that the overall sorption rate will be affected by the complex-formation reaction.¹⁷ In this study, we estimated the effective intraparticle diffusivity of the metal–extractant complex, $D_{s,com}$, as the intraparticle diffusivity of extractant, $D_{s,HR}$. The intraparticle diffusivity of EHPNA can be estimated by the leakage kinetics experiment. If the rate-controlling step of EHPNA leakage is the intraparticle diffusion controlled step, the leakage behavior can be analyzed with a homogeneous particle diffusion model based on Fick's law.¹⁸ Therefore, the fractional attainment of equilibrium of EHPNA leakage, $F'(t)$, can be described with eq 2, where $q_{HR,0}$ and q_{HR} are the amounts of

$$F'(t) = \frac{q_{HR,0} - q_{HR}}{q_{HR,0}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{s,HR}n^2\pi^2t}{r_0^2}\right) \quad (2)$$

EHPNA in the microcapsule at the initial state and random period after the reaction started, respectively. $D_{s,HR}$ is the effective intraparticle diffusivity of EHPNA, and r_0 is the radius of a microcapsule.

Equation 2 can be approximated to the following equation according to Vermulen.¹⁹

$$F'(t) = \left[1 - \exp\left(-\frac{D_{s,HR}\pi^2t}{r_0^2}\right)\right]^{1/2} \quad (3)$$

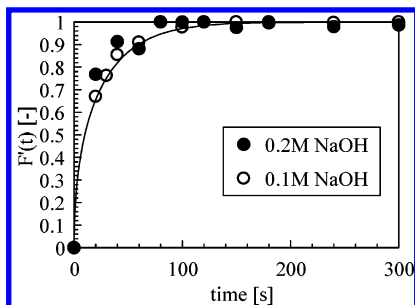


Figure 4. Plots based on eq 2 for extractant leakage from a microcapsule.

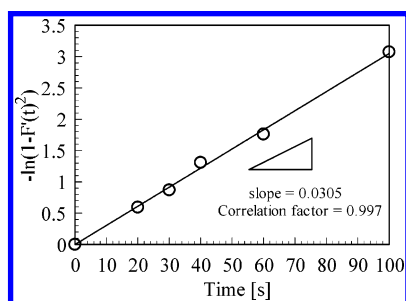


Figure 5. Relationship between $F'(t)$ and t for extractant leakage from a microcapsule.

Figures 4 and 5 show the relationship between $F'(t)$ and t and the plot based on eq 3, respectively. As shown in Figure 4, leaking profiles for both used NaOH concentrations correlate with each other. Then, it is shown that intraparticle diffusion of EHPNA is the rate-determining step for these experimental conditions. In addition, from Figure 5, it is clear that the plot shows linear behavior with a slope of 3.05×10^{-2} . From the slope of the straight line shown in Figure 5, the effective intraparticle diffusion coefficient of EHPNA in a microcapsule is determined as $D_{s,HR} (= D_{s,com}) = 1.74 \times 10^{-11} \text{ m}^2/\text{s}$. The solid line in Figure 4, corresponds to the calculation values from eq 2 using that $D_{s,HR}$ determined, as was mentioned.

When intraparticle diffusion is the rate-determining step, the fractional attainment of equilibrium of metal sorption, $F(t)$, can be expressed as the following equation based on Fick's law:¹⁸

$$F(t) = \frac{q}{q^*} = 1 - \frac{6}{\pi^2 n^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{s,com} n^2 \pi^2 t}{r_0^2}\right) \quad (4)$$

where q denotes the amount of metal sorbed in a microcapsule at a random period of reaction.

Sorption Rate of Metal Ion into a Microcapsule.

Panels a and b in Figure 6 show the effect of pH and metal concentration in the bulk solution on the experimental uptake curves for the sorption of gallium, respectively. In these figures, pH and metal concentration clearly affect to the overall sorption rate. The solid lines described in Figure 6 are the calculated results from eq 4 based on intraparticle diffusion controlled step. If the rate-determining step of gallium sorption were the intraparticle diffusion process, the uptake curve would not be changed by both pH and metal concentration, since the intraparticle diffusivity is not varied with the external condition. However, the obtained uptake curves varied with pH and metal concentration; that is, the overall sorption rate increased with increasing pH and metal concentration. In addition,

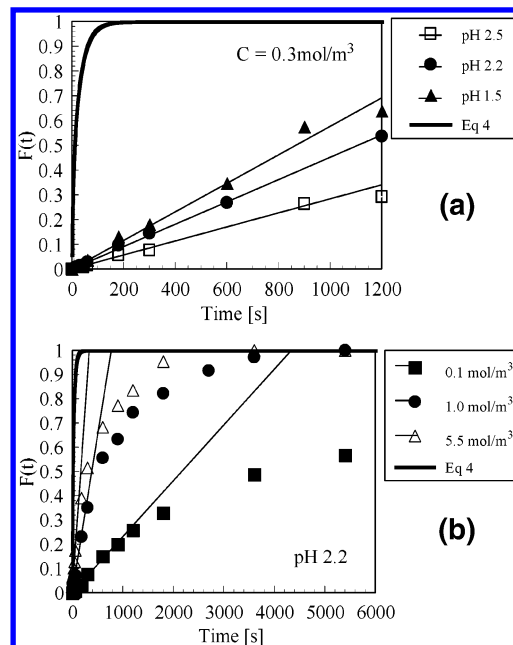


Figure 6. (a) Uptake curves of gallium sorption at various pHs. (b) Uptake curves of gallium sorption at various metal concentrations.

tion, considering that the calculated line shows a faster sorption rate than the experimental result, it is suggested that only intraparticle diffusion would not be the controlling sorption rate. The straight lines shown in Figure 6 mean the tangential line for $t = 0$. The initial sorption rate, $R_{0,MC}$, can be calculated with the slope of the tangential line according to the following equation:

$$R_{0,MC} = \frac{m}{A_{MC}} \left. \frac{dq}{dt} \right|_{t=0} = \frac{q^* m}{A_{MC}} \left. \frac{dF(t)}{dt} \right|_{t=0} \quad (5)$$

where m and A_{MC} are the amount of microcapsule packed in the bed and the effective surface area of a microcapsule, respectively. In this study, A_{MC} was calculated as the spherical surface area with r_0 as its radius, because it can be regarded that EHPNA exists at the surface of a microcapsule. EHPNA has interfacial activity,²⁰ and it adsorbs on the interface between continuous aqueous phase and dispersion organic phase when a microcapsule is formed. Divinylbenzene in the dispersion phase is polymerized in situ,^{10,24} therefore, a monomolecular layer of EHPNA would be formed on the surface of a microcapsule. The relationship between intraparticle sorption rate for gallium, $R_{0,MC,Ga}$, and pH and metal concentration are shown in panels a and b of Figure 7 with closed square symbols, respectively. It is shown in Figure 7 that $R_{0,MC,Ga}$ depends on the first order for both pH and metal concentration. They have the same tendency as those observed for the solvent extraction system.^{20,21} From these results it is suggested that the complex-formation reaction roughly presents an influence on the rate-determining step of gallium sorption.

The effect of pH and metal concentration on sorption rate of indium was also investigated. Panels a and b in Figure 8 are the observed uptake curves for different pHs and metal concentrations, respectively. Contrary to the tendency observed for gallium sorption, overall sorption rate decreased with increasing pH and indium concentration. This tendency is also different from the result for the solvent extraction system. However, as

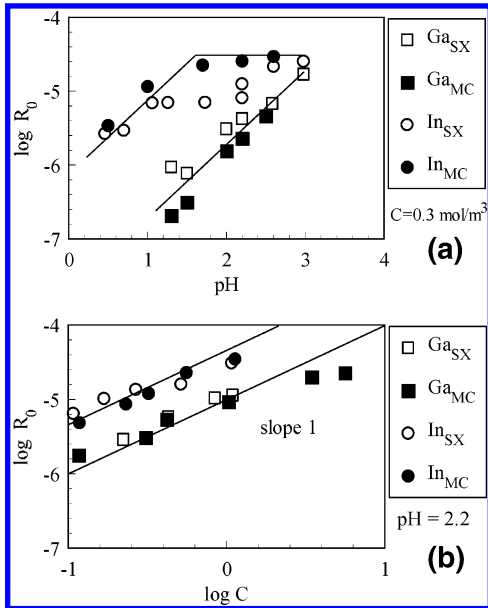


Figure 7. (a) Comparison of initial sorption rate for microcapsule system and initial extraction rate for solvent extraction system in relationship between R_0 and pH. (b) Comparison of initial sorption rate for microcapsule system and initial extraction rate for solvent extraction system in relationship between R_0 and metal concentration.

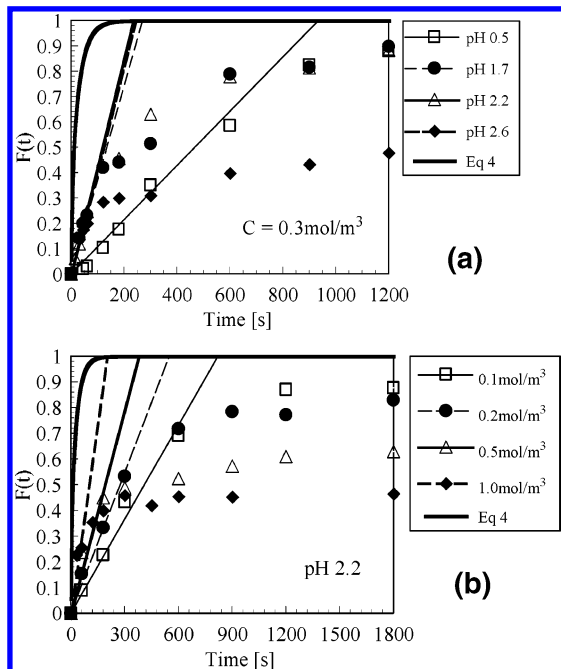


Figure 8. (a) Uptake curves of indium sorption at various pHs. (b) Uptake curves of indium sorption at various metal concentrations.

shown in Figure 8, at the early periods of reaction the initial sorption rate increased with increasing pH and metal concentration. The calculated initial sorption rate for indium, $R_{0,MC,In}$, with eq 5 is also shown in Figure 7a for the effect of pH and 7b for the effect of metal concentration with closed circular symbol. As shown in Figure 7a, the initial sorption rate increased in first order at a lower pH range and did not change at higher pH range ($pH > \sim 2$). Furthermore, as shown in Figure 7b, the initial sorption rate increased in first order within all of the metal concentrations investigated in this study. This is the same tendency as the result for

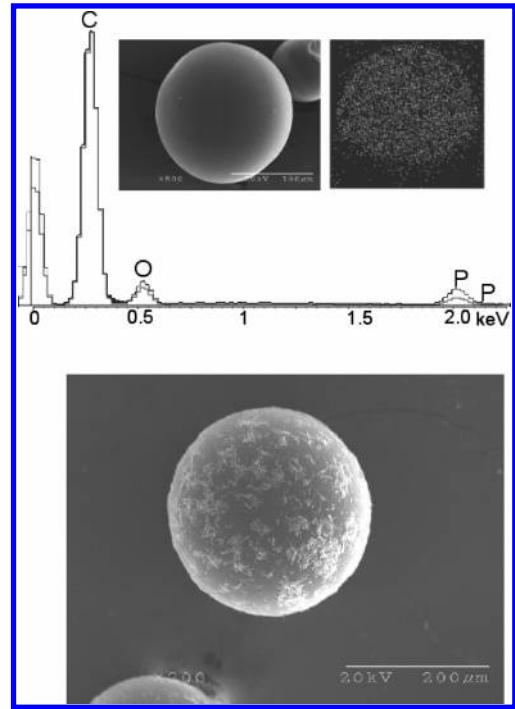


Figure 9. (a) SEM observation of the microcapsule before sorption of indium ($\times 500$). (b) SEM observation of the microcapsule after sorption of indium ($\times 200$)

solvent extraction system.^{20,21} Thus, it is suggested that the complex-formation reaction roughly affects the rate-determining step of indium sorption at the early periods of reaction.

Although it is suggested that complex-formation reaction will contribute to the rate-determining step at the early periods of reaction, the overall sorption rate for indium sorption decreased with increasing pH and indium concentration, as shown in Figure 8. Considering that microcapsules were aggregated in a preliminary test using a batch operation made for the indium sorption system, it could be suggested that a certain variation occurred on the surface of a microcapsule during indium sorption. With this purpose, the surface of a microcapsule after indium sorption was observed by using a scanning electron microscopy (Hitachi, SEM S2460N). Resulted SEM images before and after indium sorption are shown in Figure 9a and b, respectively. From these figures it is clear that many needle aggregates are formed on the surface of a microcapsule after indium sorption. Therefore, the decrease of the overall sorption rate for the indium sorption system could be explained to be due to the needle aggregates closing the pores of a microcapsule. The shape of the aggregates is the same as that formed in extraction of base metals with D2EHPA reported by Neuman and Park.^{22,23} Then it is possible to say that metal species may be extracted as a high loading state in a microcapsule. Thus, the aggregates observed on the surface of a microcapsule would be like a third phase formed in a typical solvent extraction process.

Comparison between Initial Sorption Rate for a Microcapsule System and Initial Extraction Rate for the Solvent Extraction System. To investigate the effect of the complex-formation reaction on the rate-determining step, initial extraction rates of gallium and indium for the solvent extraction system were measured and compared with the initial sorption rates obtained for the microcapsule system. It is con-

sidered that EHPNA exists as an undiluted state in the microcapsule, because toluene used as a diluent in the preparation of the microcapsule would have evaporated from the microcapsule during polymerization.²⁴ Therefore, undiluted EHPNA was used as an organic phase for the measurement of an initial extraction rate for the liquid–liquid extraction system. The effect of pH and metal concentration on initial extraction rate are shown in Figure 7 with open square and circular symbol for gallium and indium, respectively. In Figure 7, the results for the microcapsule system are also shown to compare in both systems. As shown in Figure 7, the initial solvent extraction rate varied almost the same as the initial sorption rate obtained for the microcapsule system for both gallium and indium. In the experimental conditions for these experiments, that is a stirring speed of 140 rpm, it was verified from a preliminary test that diffusion resistance through aqueous and organic phases could be ignored. Thus, it is suggested that the initial extraction rate would be controlled by the complex-formation reaction at the interface between aqueous and organic phases. The fact that the initial solvent extraction and microcapsule-sorption rates are almost the same would also indicate that the complex-formation reaction also affects the rate-controlling step for microcapsule systems. From the EDX measurement shown in Figure 9a, phosphorus in EHPNA exists on the surface of a microcapsule. This indicates that a molecular layer of EHPNA would be formed on the surface of a microcapsule. Therefore it is possible to suggest that the rate-determining step of metal sorption into a microcapsule would be strongly affected by the complex-formation reaction at the surface of a microcapsule.

Estimation of the Rate-Determining Step from the Activation Energy. As mentioned above, the rate-determining step of metal sorption with a microcapsule would be both the intraparticle diffusion and complex-formation reaction on the surface of a microcapsule. In this chapter, to corroborate this suggestion, the rate-determining step was estimated from the activation energy, E_a . It is well known that the rate-determining step is diffusion controlled when $E_a < 30$ kJ/mol and chemical reaction controlled when $E_a > 60$ kJ/mol. Therefore, if the rate-determining step of metal sorption is affected by the complex-formation reaction, the activation energy will be over 30 kJ/mol. The activation energy can be determined from the slope of the Arrhenius plot. Arrhenius temperature dependency for both chemical reaction and diffusion is expressed by the following equation:

$$\ln R_0 \propto -E_a/RT \quad (6)$$

where R ($= 8.314$ J/(K·mol)) is a gas constant. Figure 10 shows the Arrhenius plot based on eq 6 for gallium and indium. In this figure, results for both the microcapsule and solvent extraction systems were plotted altogether. It is shown in Figure 10 that the plots for both systems lie on the same straight line with slope 5.62×10^3 for gallium and slope 4.15×10^3 for indium, respectively. The determined activation energies from these slopes are listed in Table 3. Attention should be paid to the fact that the value of the activation energies for gallium, $E_{a,Ga}$, and indium, $E_{a,In}$, are between 30 and 60 kJ/mol. This fact indicates that both intraparticle diffusion and chemical reaction affect to control the initial sorption rate of metal sorption with a micro-

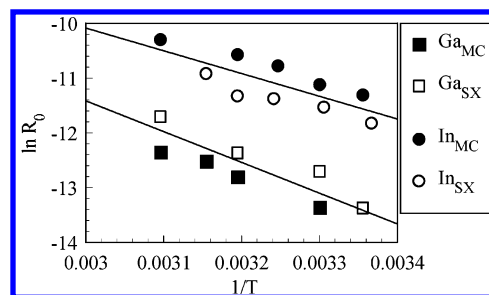


Figure 10. Arrhenius plots of gallium and indium for microcapsule and solvent extraction systems. Experimental condition: pH 2.2; $C = 0.3$ mol/m³.

Table 3. Activation Energy for Initial Extraction Process with EHPNA

| metal | E_a (kJ/mol) |
|-------|----------------|
| Ga | 48.9 |
| In | 30.7 |

capsule. From these results, the sorption mechanism of metal species into a microcapsule can be explained through a number of sequential processes: (a) diffusion of metal ions through the liquid film surrounding a microcapsule, (b) complex-formation reaction of metal ions with extractant on the surface of a microcapsule, and (c) diffusion of metal–extractant complexes through the pores of a microcapsule. In these processes, steps b and c will mainly control the metal sorption rate. Therefore, considering not only the intraparticle diffusion rate but also the complex-formation reaction rate at the surface of a particle is necessary to derive the sorption kinetics model for the microcapsule system.

Conclusion

In this study, we investigated the sorption kinetics behavior of gallium and indium with a microcapsule containing EHPNA. The initial sorption rate for gallium and indium are affected by the external aqueous condition, such as pH and metal concentration. It was found that the initial sorption rate varied in the same way for pH and metal concentration for both metals in a solvent extraction system. Furthermore, the initial sorption rate is almost the same as the initial extraction rate as observed when undiluted EHPNA was used as an organic phase. These facts indicate that (1) the complex-formation reaction controls overall sorption rate and (2) the complex-formation mechanism at the interface between external aqueous phase and EHPNA layer on the surface of a microcapsule is the same as that at the interface between aqueous and organic phases for a liquid–liquid extraction system. From the investigation of rate-determining step by activation energy, the contribution of complex-formation reaction to the rate-determining step has been also confirmed.

As a result, it is clear that not only intraparticle diffusion rate but also complex-formation reaction rate at the surface of a particle must be considered as necessary to derive the sorption kinetics model for a microcapsule system. This combined mechanism of complexation and diffusion processes has not been described in the literature. In the future, studies about metal sorption into a microcapsule will be developed according to the results obtained in this study. We will try to derive a sorption kinetic model based on Fick's diffusion law considering the change in the concentration of diffusible complex at the surface of the microcapsule.

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Nomenclature

A = interfacial area between aqueous phase and organic phase (m^2)
 C = metal ion concentration in aqueous solution (mol/m^3)
 D_s = intraparticle diffusion coefficient (m^2/s)
 E_a = activation energy (kJ/mol)
 $F(t)$ = fractional attainment of equilibrium of metal sorption (–)
 $F'(t)$ = fractional attainment of equilibrium of leaked EHPNA (–)
 K = Langmuir constant (m^3/mol)
 R = gas constant ($J/K\cdot mol$)
 R_0 = initial sorption or extraction rate ($mol/m^2\cdot s$)
 T = temperature (K)
 m = weight of microcapsules (g)
 n = a positive number (–)
 q = amount of metal sorbed in microcapsules ($mol/g\text{-MC}$)
 q_∞ = saturation amount of metal sorbed in microcapsules ($mol/g\text{-MC}$)
 $q_{0,HR}$ = content of EHPNA in microcapsules at initial state ($mol/g\text{-MC}$)
 q_{HR} = content of EHPNA in microcapsules ($mol/g\text{-MC}$)
 q^* = equilibrium sorption amount of metal in microcapsules ($mol/g\text{-MC}$)
 r_0 = radius of a microcapsule (m)
 t = time (s)

Subscript

com = metal–EHPNA complex
 HR = extractant
 MC = microcapsule

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