EXTRACTION KINETICS OF COPPER WITH BENZOYLACETONE DURING DROP RISE

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The authors previously reported the extraction kinetics of copper by benzoylacetone in a stirred transfer cell and during drop formation. The extraction kinetics of the same system during drop rise is discussed in this paper.

To interpret the influence of the concentrations of copper and hydrogen ion in the continuous phase and that of benzoylacetone in the dispersed phase on the extraction rate, a theoretical analysis was carried out, taking account of diffusion in a droplet and that accompanied by (1, 1)-th order irreversible reaction in the continuous phase.

On the basis of the results of this theoretical analysis, the experimental results were examined and it was clarified that the reaction which forms chelating complex in the continuous phase can be treated as a pseudo-first order reaction with respect to benzoylacetone under the present experimental conditions.

Introduction

Today, entering upon the age of exhaustion of resources, we are faced with a decline in the grade of ores of several kinds of metals. To refine these low-grade ores, the hydrometallurgical process in which ores are leached in aqueous acid or ammonia solution and leached metals are separated and purified by solvent extraction is now attaining an important position in the metallurgical industry. Recently, commercial chelating agents such as LIX 64N and Kelex 100 have been developed as extractants for copper, nickel or cobalt and are in extensive use.

The authors studied the extraction kinetics of copper with benzoylacetone as a link in the chain of studies of the extraction mechanism of metals with chelating agents, and have reported about such mechanisms in the stirred transfer cell⁽¹⁾ and during drop formation⁽⁴⁾. In the present paper, the extraction kinetics of the same system during drop rise was studied.

1. Experimental Procedure and Results

The experimental apparatus used is similar to that described in the previous paper⁽³⁾. The preparation of the reagents and the determination of the concentration of copper extracted into the dispersed phase are also described in the previous paper⁽¹⁰⁾. Toluene solution of benzoylacetone was used as the dispersed phase.

As the continuous phase, aqueous copper nitrate solution was used, diluted by 1.0 mol/l ammonium nitrate-ammonia mixture to keep the pH and ionic strength constant.

The extraction rates were measured at 30°C under the conditions listed in Table 1.

The reacted benzoylacetone concentration was calculated from the concentration of copper extracted into a droplet, and the extent of extraction was defined as the fractional conversion of benzoylacetone.

In extraction by a single droplet there are at least three major periods in droplet life during which extraction can take place; (1) during formation of the droplet, (2) during free rise or fall of the droplet through the continuous phase and (3) during coalescence of the droplet at the end of the free-rise period. Therefore, it is of great importance to separate and estimate the extent of extraction during the free-rise period from the overall extent of extraction obtained as experimental results. The procedure to estimate the extent of ex-

Table 1 Experimental conditions

C_{B0} [mol/l]	0.0024, 0.024, 0.048
C_{A0} [mol/l]	0.006, 0.026
pH	4.5-8.5
t_f [sec]	3-30
t_r [sec]	0.5-13
d_p [cm]	0.42 ± 0.01
U [cm/sec]	13.3 ± 0.7
ρ_c [g/cm ³]	1.03
ρ_d [g/cm ³]	0.87
μ_c [c. p.]	0.79
μ_d [c. p.]	0.53

Received December 20, 1978. Correspondence concerning this article should be addressed to K. Inoue. H. Okubo is now with Japan Elastomer Co., Ltd., Oita 870.

Fig. 1 Relationship between extent of extraction and contact time during drop rise

Fig. 2 Relationship between extent of extraction and contact time during drop rise

Fig. 3 Relationship between extent of extraction and contact time during drop rise

traction during the free-rise period was also described in the previous paper⁴⁾.

In Figs. 1, 2 and 3, the experimental results under various conditions obtained in this manner are shown as a plot of $-\ln(1-E_r)$ against the dimensionless contact time of a droplet during free rise based on the

Handlos-Baron model²⁾, τ , as explained in the following section. From these figures, it is obvious that extraction rate increases with decreasing concentration of hydrogen ion in the continuous phase, and it seems that the relations between $-\ln(1-E_r)$ and τ are nearly proportional in the low-pH region.

2. Theoretical Analysis

2.1 The extraction mechanism of copper ion

The extraction of copper ion by benzoylacetone (HR) is described by the following stoichiometric relation.

As reported in the previous papers^{4,10)}, this extraction process proceeds as follows: (1) distribution of HR in the organic phase into the aqueous phase, (2) chemical reaction of HR with copper ion in the aqueous phase to form the copper-chelate (CuR_2) and (3) distribution of CuR_2 produced by the previous step into the organic phase. The chemical reaction rate of benzoylacetone in the aqueous phase is described by Eq. (2), if the formation of the intermediate product, CuR^+ , is rate-determining.

$$r = 2k_R K_2 [\text{Cu}^{2+}][\text{HR}]/[\text{H}^+] - [\text{CuR}_2][\text{H}^+]/K'[\text{HR}] \quad (2)$$

where K_2 is the dissociation constant of HR and K' is the equilibrium constant of the reaction in the aqueous phase. In the region of low extent of extraction, the reverse reaction term of Eq. (2) can be ignored and Eq. (2) is reduced to

$$r = 2k_R K_2 [\text{Cu}^{2+}][\text{HR}]/[\text{H}^+] \quad (3)$$

Furthermore, when the concentration of hydrogen ion is kept constant the system under consideration is reduced to one of mass transfer accompanied by chemical reaction of first order with respect to both copper ion and benzoylacetone in the aqueous phase.

2.2 Mass transfer accompanied by (1,1)-th order irreversible reaction outside a droplet

Mass transfer accompanied by several kinds of chemical reaction from a single droplet, a single bubble or a solid sphere has been studied by many authors^{1,5-8,11,12,14,15,18)}. However, these works take account of only the mass transfer and chemical reaction outside a droplet, a bubble or a solid sphere and there have apparently been no studies reported that take account of the mass transfer process both outside and inside a droplet and the chemical reaction in the continuous phase as the rate-determining steps.

The authors carried out a theoretical analysis of mass transfer in a droplet combined with that accompanied by (1,1)-th order irreversible reaction outside a droplet in series.

Taking account of the value of Reynolds number ($Re \approx 750$) under the present experimental conditions,

the turbulent diffusion model proposed by Handlos and Baron²⁾ was used to interpret the diffusion process in a droplet and film theory was used for the interpretation of that in the continuous phase.

The concentration distribution of benzoylacetone in a droplet can be obtained by solving the following diffusion equation (see Appendix).

$$\frac{\partial Q_B}{\partial \tau} = \frac{1}{x} \cdot \frac{\partial}{\partial x} \left[x(6x^2 - 8x + 3) \frac{\partial Q_B}{\partial x} \right] \quad (4)$$

$$\text{I. C. } \tau=0, 0 \leq x \leq 1 \quad Q_B=1 \quad (5)$$

$$\text{B. C. 1 } \tau > 0, x=0; \partial Q_B / \partial x = 0 \quad (6)$$

$$\text{B. C. 2 } \tau > 0, x=1; \partial Q_B / \partial x = -h\beta \cdot Q_{Bi} \quad (7)$$

where

$$Q_B = C_B / C_{B0} \quad (8)$$

$$\tau = UAt_r / 144\alpha(1 + \mu_d / \mu_c) \quad (9)$$

$$h = 96\alpha \cdot K_1 k_c (1 + \mu_d / \mu_c) / U \quad (10)$$

The parameter h defined by Eq. (10) represents the ratio of the mass transfer rate outside a droplet without reaction to that in a droplet. As to the enhancement factor (β) in Eq. (7), though the approximate equation proposed by van Krevelen¹⁷⁾ is in extensive use, it is too complicated to solve the diffusion equation shown above using this approximate equation since it is expressed by the implicit function. In the present analysis, the following approximate equation proposed by Kishinevskii⁹⁾, which is expressed by the explicit function and is much easier to treat, was used.

$$\beta = 1 + (\gamma/R) \cdot \{1 - \exp(-0.65 \sqrt{R} \cdot \gamma)\} \quad (11)$$

where

$$\gamma = (K_2 k_R C_{A0} D / [H^+])^{1/2} / k_c \quad (12)$$

$$R = \frac{1}{\beta_\infty - 1} + \exp\left(\frac{0.18}{\gamma} - \frac{0.45\gamma}{\beta_\infty - 1}\right) \quad (13)$$

In Eq. (13), β_∞ denotes the limiting value of β for instantaneous reaction and is expressed as follows for the present case.

$$\beta_\infty = 1 + (\varepsilon / Q_{Bi}) \quad (14)$$

$$\varepsilon = 2 \cdot \frac{D_A}{D_B} \cdot \frac{C_{A0}}{K_1 C_{B0}} \quad (15)$$

Extent of extraction during the free-rise period (E_r), which is defined as the fractional conversion of benzoylacetone in a droplet, is obtained from the concentration distribution as follows.

$$E_r(\tau) = 1 - 2 \cdot \int_0^1 x \cdot Q_B(x, \tau) dx \quad (16)$$

Figure 4 shows the numerical results of the relation between $-\ln(1-E_r)$ and τ for instantaneous reaction with various values of h as parameter. In Fig. 4, the relation for lower values of h , for example $h=2 \times 10^{-5}$ or 1×10^{-5} , is expressed by concave curves the location of which depends on the values of h , signifying that the instantaneous reaction takes place outside a droplet. However, for higher values of h , for ex-

Fig. 4 Calculated results of the effect of h on the relation between $-\ln(1-E_r)$ and τ for instantaneous reaction

Fig. 5 Calculated results of the effects of γ on the relation between $-\ln(1-E_r)$ and τ

ample $h=1 \times 10^{-3}$, it is expressed by a single convex curve, which signifies that the instantaneous reaction takes place at the drop surface. For the medium values of h between those mentioned above, for example $h=1 \times 10^{-4}$, 5×10^{-5} or 3×10^{-5} , it is expressed by concave curves in the range of lower extent of extraction and by convex curves in the range of higher extent of extraction, which signifies that the reaction plane of the instantaneous reaction initially located away from the drop surface in the continuous phase moves toward the drop surface in the course of extraction and is located at the drop surface beyond a certain extent of extraction.

Figure 5 shows some examples of the numerical results of the relation between $-\ln(1-E_r)$ and τ with various values of γ as a parameter for the case in which the reaction plane of the instantaneous reaction is located outside a droplet. It is evident that all curves are concave. Figure 6 shows some examples of the numerical results of the relation for the case in which the reaction plane of the instantaneous reaction is located at the drop surface. It is evident that the relation is expressed by straight lines which intersect

Fig. 6 Calculated results of the effects of γ on the relation between $-\ln(1-E_r)$ and τ

Fig. 7 Relationship between dimensionless mass transfer coefficient at stationary state during drop rise and γ

Fig. 8 Relationship between $k_c\beta$ and $k_c\gamma$

the origin for the lower values of γ and by convex curves which asymptotically approach straight lines with the increase of the extent of extraction for the higher values of γ . The slopes of the rectilinear parts of these curves correspond to the dimensionless sta-

tionary-state overall mass transfer coefficients based on the Handlos-Baron model. Figure 7 shows the relation between these slopes and γ with various values of h as a parameter. The curves in Fig. 7 approach the asymptotic values determined by the value of h at small values of γ where physical mass transfer predominates and the reaction has negligible effect. On the other hand, they approach a single asymptotic value ($=0.45$) at greater values of γ where the reaction rate is infinitely rapid and the reaction component in a droplet is completely depleted at the drop surface. In the intermediate region where the reaction is regarded as a pseudo-first order reaction with respect to the reactant in a droplet, the relation between $\log(\text{slope})$ and $\log \gamma$ gives essentially straight lines, the slopes of which are equal to unity.

3. Analysis of the Experimental Results and Discussion

Since the value of K_1 , the partition constant of benzoylacetone to the aqueous phase, is much less than unity ($K_1=7.24 \times 10^{-4}$)¹⁶⁾, the values of β_∞ expressed by Eqs. (14) and (15) are much greater than unity and accordingly the values of β expressed by Eqs. (11) and (13) are considered to be nearly constant regardless of the value of E_{ri} if the values of γ are not so great under the present experimental conditions.

Then, the values of $k_c\beta$ which minimize the standard deviations between the experimental results and the calculated values obtained from Eqs. (4)–(10) were estimated for each experimental condition. As the value of α in Eqs. (9) and (10), the value which had been obtained in the extraction of acetic acid with the cyclohexane solution of Amberlite LA-2³⁾, the physical properties of which resemble those of the present system, i. e. $\alpha=10$, was used. The solid lines in Figs. 1, 2 and 3 are the calculated results obtained by Eqs. (4)–(7) and (10) using the values of $k_c\beta$ estimated in this manner.

In Fig. 8, the values of $k_c\beta$ are plotted against the values of $k_c\gamma$ calculated by Eq. (12) corresponding to each experimental condition and using the following values:

$$K_2=1.86 \times 10^{-12} \text{ mol/cm}^3 \text{ }^{16)}$$

$$k_R=5.2 \times 10^{11} \text{ cm}^3/\text{mol} \cdot \text{sec}^{10)}$$

It is evident that most of the experimental results plotted in Fig. 8 lie on a straight line the slope of which is unity and intersecting the origin, suggesting that the present extraction process can be explained by diffusion accompanied by pseudo-first order irreversible reaction with respect to benzoylacetone in the continuous phase under the present experimental conditions.

Conclusion

The extraction kinetics of copper by benzoylacetone

in toluene solution during the free-rise period of a single droplet was studied. The influence of the concentrations of copper and hydrogen ions in the continuous phase and that of benzoylacetone in the dispersed phase on the extraction rate were interpreted by a model which takes account of the diffusion process in a droplet and that accompanied by pseudo-first order irreversible reaction with respect to benzoylacetone in the continuous phase.

Appendix

The turbulent diffusion model proposed by Handlos and Baron²⁾ is based on the assumption that internal circulation is fully developed and that the circulation pattern is a system of circular tori. It is further assumed that mass transfer in a droplet is caused by mixing between stream lines induced by random radial vibration superposed upon them. Turbulent diffusivity ($\bar{E}$) is used to explain this diffusion process and the diffusion equation in a circular torus is described as follows.

$$\frac{\partial C_B}{\partial t_r} = \frac{16}{d_p^2} \cdot \frac{1}{x} \cdot \frac{\partial}{\partial x} \left[x \cdot \bar{E} \cdot \frac{\partial C_B}{\partial x} \right] \quad (\text{A-1})$$

where x is the dimensionless radial distance from the center of a circular torus defined by Eq. (A-2) and $\bar{E}$ is defined by Eq. (A-3).

$$x = \omega / (d_p/4) \quad (\text{A-2})$$

$$\bar{E} = \frac{d_p U}{384\alpha} \cdot \frac{6x^2 - 8x + 3}{1 + \mu_d/\mu_c} \quad (\text{A-3})$$

where α is the modified parameter of average circulation time along stream lines in a circular torus to compensate the discrepancies from the ideal flow pattern of Hadamard type.

Equation (A-1) is reduced to Eq. (4) using Eq. (A-3) and dimensionless terms defined by Eqs. (8) and (9).

Equation (7), the boundary condition at the drop surface, is easily derived from the following relation.

$$-\frac{\bar{E}}{(d_p/4)} \cdot \frac{\partial C_B}{\partial x} = \beta k_c K_1 C_B \quad \text{at } x=1 \quad (\text{A-5})$$

where $\bar{E}$ at the drop surface is described as follows.

$$\bar{E} = \frac{d_p U}{384\alpha} \cdot \frac{U}{1 + \mu_d/\mu_c} \quad (\text{A-6})$$

Nomenclature

A	= specific area of a droplet	[cm ⁻¹]
C_{A0}	= bulk phase concentration of copper ion in the continuous phase	[mol/cm ³]
C_B	= concentration of benzoylacetone in a droplet	[mol/cm ³]
C_{B0}	= initial concentration of benzoylacetone in a droplet	[mol/cm ³]
D_A	= diffusivity of copper ion in the continuous phase	[cm ² /sec]
D_B	= diffusivity of benzoylacetone in the continuous phase	[cm ² /sec]
d_p	= droplet diameter	[cm]
E_r	= extent of extraction during drop rise	[—]
$\bar{E}$	= turbulent diffusivity defined by Eq. (A-3)	[cm ² /sec]
h	= dimensionless parameter defined by Eq. (10)	[—]
K'	= equilibrium constant of the chelating complex forming reaction in aqueous phase	[—]
K_1	= distribution coefficient of benzoylacetone to aqueous phase	[—]
K_2	= dissociation constant of benzoylacetone in aqueous phase	[mol/cm ³]

k_c	= mass transfer coefficient of benzoylacetone in the continuous phase	[cm/sec]
k_R	= forward reaction rate constant of the chelating complex forming reaction in aqueous phase	[cm ³ /mol·sec]
Q_B	= dimensionless concentration of benzoylacetone in a droplet	[—]
R	= dimensionless term defined by Eq. (13)	[—]
Re	= Reynolds number	[—]
r	= reaction rate of the chelating complex forming reaction in aqueous phase	[mol/cm ³ ·sec]
t_r	= contact time during drop rise	[sec]
U	= velocity of drop rise	[cm/sec]
x	= dimensionless distance from the center of circulation flow in a droplet defined by Eq. (A-2)	[—]
α	= modified parameter of average circulation time in a droplet	[—]
β	= enhancement factor	[—]
β_∞	= enhancement factor for instantaneous reaction	[—]
γ	= dimensionless term defined by Eq. (12)	[—]
ϵ	= dimensionless term defined by Eq. (15)	[—]
τ	= dimensionless contact time during drop rise defined by Eq. (9)	[—]
ρ	= density	[g/cm ³]
μ	= viscosity	[cP]
ω	= radial distance from the center of circulation flow in a droplet	[cm]
[]	= concentration in aqueous phase	[mol/cm ³]
<Subscript>		
c	= continuous phase	
d	= dispersed phase	
i	= interface	

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