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Kinetic Studies of Extraction and Stripping of Copper with Dibenzoylmethane

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Abstract

Kinetic studies of the extraction of copper with dibenzoylmethane and the stripping of copper were carried out in a stirred transfer cell, along with a study of the extraction equilibrium of copper with the extractant at 303 K. The extraction and stripping rates were analyzed by a model of the interfacial reaction between the extractant and the adsorbed 1:1 copper chelate complex accompanied by the mass transfer steps of the species. Furthermore, the extraction rate was simulated by using the equilibrium and reaction rate constants obtained from the analysis.

INTRODUCTION

β-Diketones have been widely used in metal extraction. Acetylacetone, thenoyltrifluoroacetone, and benzoylacetone have attracted special interest from the viewpoint of extraction kinetics. Zolotov et al. (*1*) studied catalytic acceleration by the addition of inorganic salts in the extractions of chromium and iron with acetylacetone. Fomin et al. (*2*) also studied the extraction of iron with acetylacetone and concluded that the extraction rate in the kinetic regime is determined by the rate of a slow reaction in the aqueous solution. The extraction of iron with thenoyltrifluoroacetone (TTA) was carried out by Sekine et al. (*3*). They concluded that the rate-determining step is the formation of a 1:1 complex between TTA and Fe(III) in the aqueous solution. The authors studied the extraction (*4*) of

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copper with benzoylacetone (BA) and the stripping (*5*) of copper. The results were interpreted by a diffusion model accompanied by the complex formation reaction in which the rate-determining step is the 1:1 complex formation between BA and Cu(II). A study on this extraction system was developed by Harada et al. (*6*), in which an interfacial reaction model was proposed.

In the present study, measurements of the extraction rate of copper with dibenzoylmethane in benzene solution and the rate of stripping were carried out by using a stirred transfer cell, and the effect of chelating complex formation on the extraction rate at the interface between aqueous and organic solutions was examined.

EXPERIMENTAL

Materials

All the reagents used were of analytical grade. Dibenzoylmethane (DBM) was purified by distillation under reduced pressure in a nitrogen atmosphere. The copper–DBM chelate complex was synthesized and purified by recrystallization from benzene twice. Benzene was used as the organic diluent for DBM and the copper complex. A stock solution of copper was prepared by dissolving copper nitrate in 1000 mol/m^3 ammonium nitrate aqueous solution. To adjust the pH, 1000 mol/m^3 nitric acid and 1000 mol/m^3 ammonia aqueous solution were used in experiments of the distribution equilibrium and extraction rate of copper, respectively. Hydrochloric acid was used as the stripping agent.

Distribution Equilibrium of Copper

The aqueous solution was prepared by mixing the above-mentioned stock solution of copper and the nitric acid solution so as to keep the pH at a desired value and to keep the ionic strength constant. The copper concentration was adjusted to 1.0 mol/m^3.

Equal volumes of the aqueous and the organic solutions of known concentrations were shaken in a flask and allowed to attain equilibrium in a thermostated bath maintained at 303 K. Then the solutions were separated and analyzed for their copper content. The copper concentration in the aqueous solution was determined directly by atomic absorption spectrophotometry. The copper complex in the organic solution was stripped by 2000 mol/m^3 hydrochloric acid aqueous solution prior to atomic absorption spectrophotometry.

Rates of Copper Extraction and Stripping

A stirred transfer cell (*7*) was used to measure the rate of copper extraction by DBM and the stripping rate of copper by hydrochloric acid at 303 K. The cell consists of two compartments of equal volume (about 1.4×10^{-4} m^3), an upper compartment for the organic solution and a lower one for the aqueous solution. The interfacial area between the two solutions was 1.32×10^{-3} m^2. The solutions in the cell were stirred in opposite directions at 2.5 s^{-1} (150 rpm) by two flat-blade stirrers.

In the experiments for copper extraction, the aqueous solution was prepared by mixing the stock solution of copper and the ammonia aqueous solution mentioned above. In the copper stripping experiments, the organic solution was prepared by dissolving both the copper chelate complex and DBM in benzene.

The aqueous solution was first introduced to the transfer cell from a buret fitted with a constant-temperature jacket, and then the organic solution was placed carefully in such a way as not to disturb the interface. Small samples were taken at intervals from the organic solution. The copper concentration was determined by the same method as mentioned above.

Under various experimental conditions, the initial rate of copper extraction or stripping was obtained from the concentration change of copper chelate complex in the organic solution or of copper in the aqueous solution with time.

RESULTS AND DISCUSSION

Determination of Extraction Equilibrium Constant of Copper

The extraction equilibrium of copper with the extractant, DBM (HR), is expressed as

$$\mathrm{Cu}^{2+}_{\mathrm{aq}} + 2\mathrm{HR}_{\mathrm{org}} \rightleftharpoons \mathrm{CuR}_{2\ \mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}} \tag{1}$$

The extraction equilibrium constant, K_{ex}, is written as

$$K_{\mathrm{ex}} = \frac{C_{\mathrm{CuR2}} C_{\mathrm{H}}^2}{C_{\mathrm{Cu}} C_{\mathrm{HR}}^2} \tag{2}$$

where C is the concentration of the respective species. The distribution ratio of copper, D_{Cu}, is defined as

$$D_{\mathrm{Cu}} = \frac{C_{\mathrm{CuR2}}}{C_{\mathrm{Cu}}} \tag{3}$$

From Eqs. (2) and (3), the following relation is obtained:

$$\log D_{\mathrm{Cu}} = 2 \log (C_{\mathrm{HR}}/C_{\mathrm{H}}) + \log K_{\mathrm{ex}} \tag{4}$$

The experimental data are arranged in Fig. 1 according to Eq. (4). A straight line with a slope of 2 was obtained, from which the value of $K_{ex} = (1.30 \pm 0.24) \times 10^{-4}$ was obtained. The solid line in the figure is the calculated result from using the K_{ex} value and Eq. (4).

Extraction Rate of Copper

Figure 2 shows the relation between the initial extraction rate of copper, J_0, and the pH of the aqueous solution. J_0 was calculated by

$$J_0 = -\frac{V_{aq}}{A}\left(\frac{dC_{Cu}}{dt}\right)_{t=0} \tag{5}$$

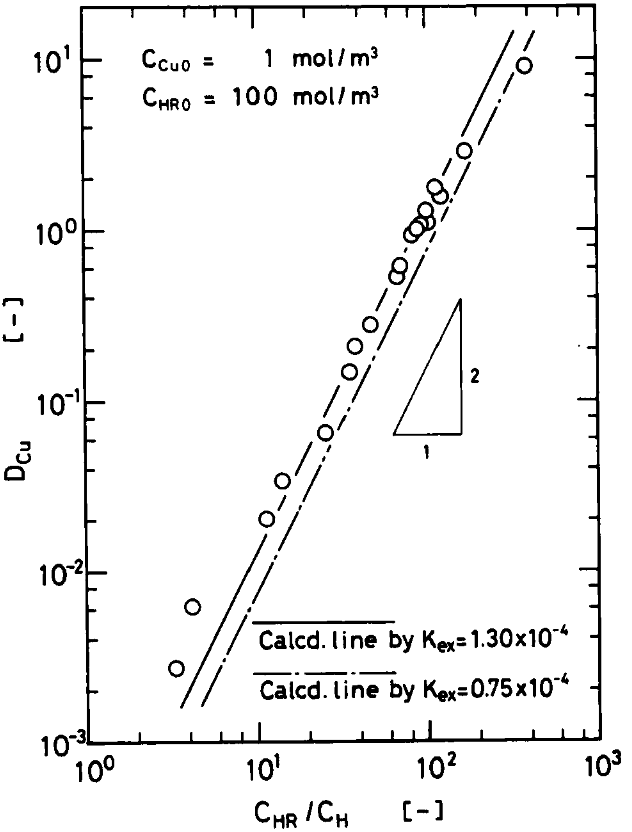

FIG. 1. Relation between D_{Cu} and C_{HR}/C_H.

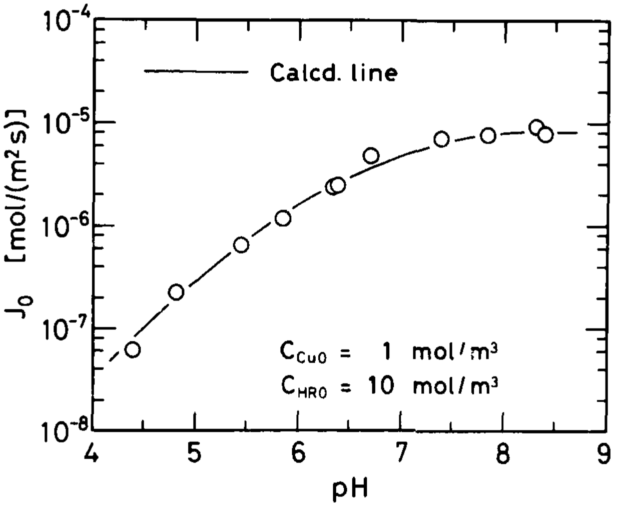

FIG. 2. Relation between initial extraction rate of copper and pH.

where V_{aq} is the volume of the aqueous solution and A is the interfacial area. In the low pH range, the slope is 1, but in the high pH range the slope approaches zero. It is anticipated from these results that the extraction mechanism in the high pH range is different from that in the low pH range where the extraction rate is controlled by the interfacial reaction, as mentioned later.

The relation between J_0 and the initial concentration of copper, C_{Cu0}, is shown in Fig. 3. J_0 is found to be proportional to C_{Cu0} in the low concentration range of copper, but the slope of the relation becomes smaller than 1 in the high concentration range of copper.

Figure 4 shows the relation between J_0 and the initial concentration of DBM, C_{HR0}. In the low concentration range of DBM, the slope of the relation at pH = 6.5 is about 2, but the slope approaches zero in the high concentration range of DBM.

Stripping Rate of Copper

The effect of the initial concentration of hydrogen ion, C_{H0}, on the initial stripping rate of copper, J_0', is shown in Fig. 5. In the low C_{H0} range, the slope of the relation is about 0.5, but the slope approaches zero in the high concentration range of hydrogen ion.

Figure 6 shows the effect of the initial concentration of copper complex,

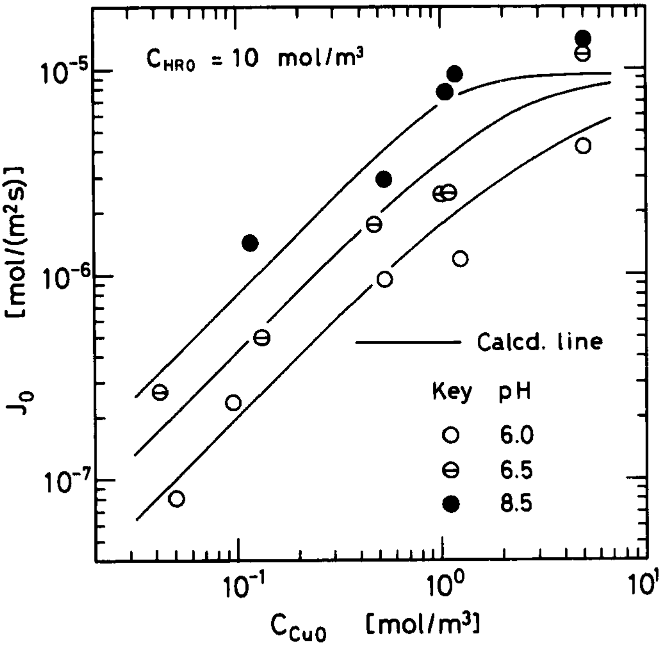

FIG. 3. Relation between initial extraction rate of copper and initial copper concentration.

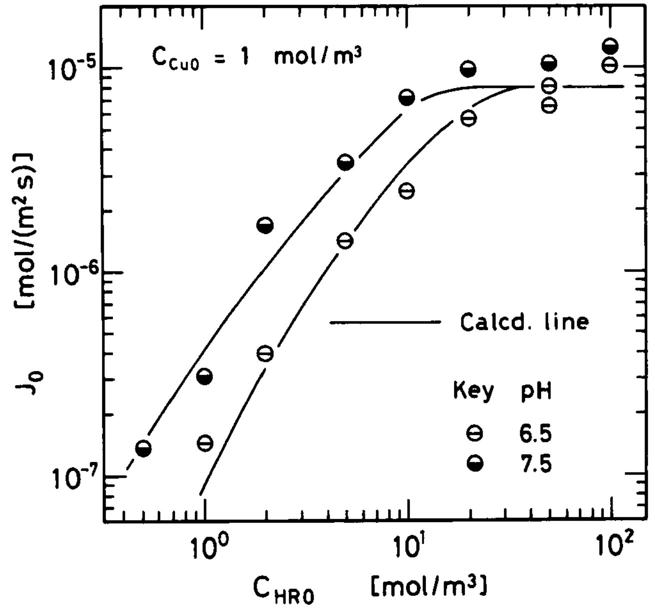

FIG. 4. Relation between initial extraction rate of copper and initial concentration of DBM.

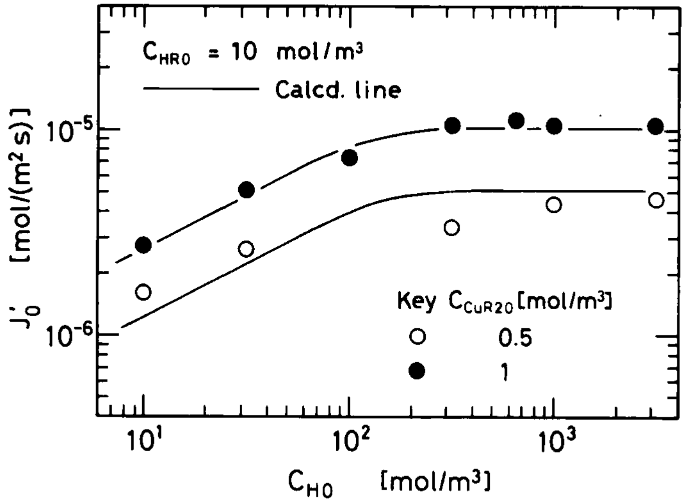

FIG. 5. Relation between initial stripping rate of copper and initial hydrogen-ion concentration.

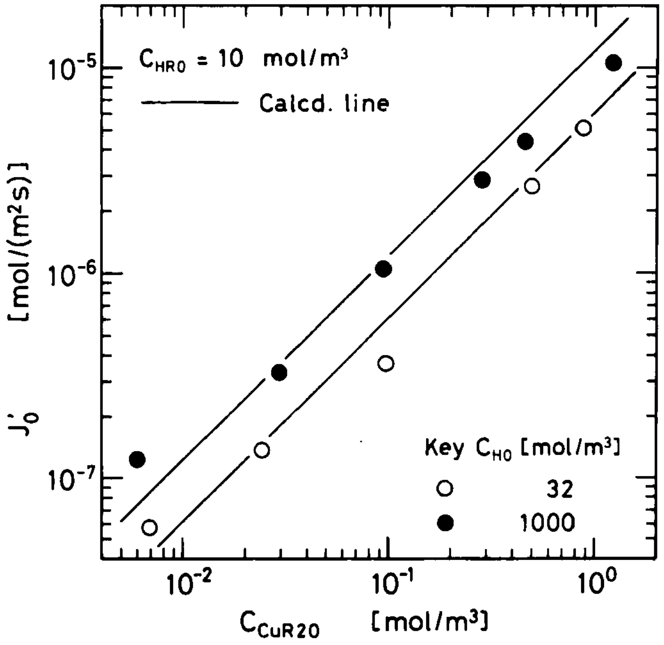

FIG. 6. Relation between initial stripping rate of copper and initial concentration of copper complex.

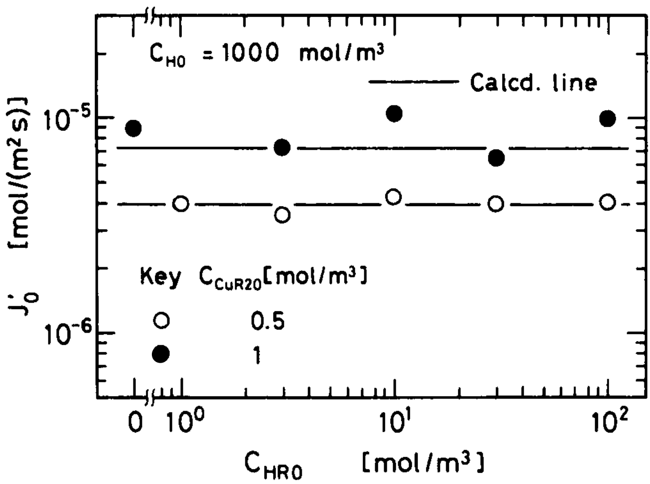

FIG. 7. Relation between initial stripping rate of copper and initial concentration of DBM.

C_{CuR20}, on J_0'. J_0' is found to be proportional to C_{CuR20} over the whole range of C_{CuR20}.

The relation between J_0' and C_{HR0} is shown in Fig. 7. It is found that J_0' is not affected by C_{HR0}.

Interfacial Reaction Model

The extraction reaction is assumed to occur at the interface between the aqueous and organic solutions since the distribution ratio of DBM between the two solutions is very small ($= 1.2 \times 10^{-5}$) (*8*). Moreover, only the undissociated species of DBM is assumed to take part in the extraction reaction under the experimental condition because the pK_a value of DBM is 9.86 (*8*). Since both HR and CuR_2 were found to have no interfacial activity from measurement of the interfacial tension, the following interfacial reaction model is proposed:

$$Cu^{2+}_{aq} + HR_{org} \rightleftharpoons CuR^{+}_{ad} + H^{+}_{aq}: \quad K_1 \tag{6}$$

$$CuR^{+}_{ad} + HR_{org} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuR_{2\,org} + H^{+}_{aq} \tag{7}$$

where K_1 is the equilibrium constant of Reaction (6), k_2 and k_{-2} are the forward and the reverse reaction rate constants of Reaction (7), respectively, and subscript "ad" denotes adsorption state.

Assuming that the second step in the above reaction scheme is the rate-determining step, the interfacial reaction rate, r, is written as

$$r = k_2 \frac{\theta_{\mathrm{CuR}}}{S_{\mathrm{CuR}}} C_{\mathrm{HR}i} - k_{-2} C_{\mathrm{CuR2}i} C_{\mathrm{H}i} \theta_v \tag{8}$$

where θ_{CuR} and θ_v are the fractions of the interfacial area occupied by CuR^+ and vacant sites, respectively, S_{CuR} is the interfacial area occupied by unit mole of CuR^+, and subscript i denotes the aqueous or organic solution adjacent to the interface. Assuming the Langmuir adsorption isotherm, θ_{CuR} and θ_v are expressed as

$$\theta_{\mathrm{CuR}} = K_1 C_{\mathrm{Cu}i} C_{\mathrm{HR}i} S_{\mathrm{CuR}} \theta_v / C_{\mathrm{H}i} \tag{9}$$

$$\theta_v = 1 - \theta_{\mathrm{CuR}} \tag{10}$$

Combining Eqs. (8)–(10), the interfacial reaction rate equation is obtained as

$$r = \frac{k_2 K_1 C_{\mathrm{Cu}i} C_{\mathrm{HR}i}^2 / C_{\mathrm{H}i} - k_{-2} C_{\mathrm{CuR2}i} C_{\mathrm{H}i}}{1 + K_1 S_{\mathrm{CuR}} C_{\mathrm{Cu}i} C_{\mathrm{HR}i} / C_{\mathrm{H}i}} \tag{11}$$

The concentration of the species adjacent to the interface is obtained from the following relation in which the interfacial reaction rate is equal to the mass transfer rate at the steady state.

$$\begin{aligned} J = r &= k_{\mathrm{Cu}}(C_{\mathrm{Cu}} - C_{\mathrm{Cu}i}) \\ &= (k_{\mathrm{HR}}/2)(C_{\mathrm{HR}} - C_{\mathrm{HR}i}) \\ &= k_{\mathrm{CuR2}}(C_{\mathrm{CuR2}i} - C_{\mathrm{CuR2}}) \\ &= (k_{\mathrm{H}}/2)(C_{\mathrm{H}i} - C_{\mathrm{H}}) \end{aligned} \tag{12}$$

where k_{Cu}, k_{HR}, k_{CuR2}, and k_{H} are the mass transfer coefficients of copper, DBM, copper complex, and hydrogen ion, respectively. In our case, however, the concentration of hydrogen ion adjacent to the interface, $C_{\mathrm{H}i}$, is approximated to the bulk concentration, C_{H0}, because the buffer solution was used.

Rate Analyses of Extraction and Stripping

Since in the initial period of copper extraction the second term in the numerator in Eq. (11) can be neglected, the initial rate of copper extraction,

J_0, is expressed as

$$J_0 = \frac{k_2K_1C_{\mathrm{Cu}i}C^2_{\mathrm{HR}i}/C_{\mathrm{H0}}}{1 + K_1S_{\mathrm{CuR}}C_{\mathrm{Cu}i}C_{\mathrm{HR}i}/C_{\mathrm{H0}}} \tag{13}$$

Equation (12) is rewritten as

$$J_0 = k_{\mathrm{Cu}}(C_{\mathrm{Cu0}} - C_{\mathrm{Cu}i}) = (k_{\mathrm{HR}}/2)(C_{\mathrm{HR0}} - C_{\mathrm{HR}i}) \tag{14}$$

By using Eqs. (13) and (14), the relation between J_0 and the bulk concentrations of the species is obtained as an implicit function, that is, the rate of copper extraction corresponding to J_0 is implicitly expressed by the bulk concentrations.

The values of the unknown constants, k_2K_1, K_1S_{CuR}, k_{Cu}, and k_{HR}, were evaluated from the experimental results of J_0 and Eqs. (13) and (14) by nonlinear regression and are listed in Table 1. The solid curves shown in Figs. 2–4 are the results calculated by using the constants and Eqs. (13) and (14).

On the other hand, the initial rate of copper stripping, J_0', can be expressed as follows from Eq. (8):

$$J_0' = k_{-2}C_{\mathrm{CuR2}i}C_{\mathrm{H0}}\theta_v \tag{15}$$

where θ_v is approximated to about 1 because CuR^+ is scarcely formed in the initial period of copper stripping. J_0' at the steady state is equal to the mass transfer rate of copper complex:

$$J_0' = k_{\mathrm{CuR2}}(C_{\mathrm{CuR20}} - C_{\mathrm{CuR2}i}) \tag{16}$$

TABLE 1

The Values of Constants Obtained from the Analyses of the Experimental Results

$k_2K_1 = (2.89 \pm 0.25) \times 10^{-11}\ \mathrm{m^4/(mol \cdot s)}$
$K_1S_{\mathrm{CuR}} = (2.83 \pm 0.03) \times 10^{-5}\ \mathrm{m^3/mol}$
$k_{\mathrm{Cu}} = (8.03 \pm 1.18) \times 10^{-6}\ \mathrm{m/s}$
$k_{\mathrm{HR}} = (1.65 \pm 0.25) \times 10^{-5}\ \mathrm{m/s}$

$k_{-2} = (3.87 \pm 0.59) \times 10^{-7}\ \mathrm{m^4/(mol \cdot s)}$
$k_{\mathrm{CuR2}} = (1.03 \pm 0.08) \times 10^{-5}\ \mathrm{m/s}$

From the above two equations, J_0' can be expressed as

$$J_0' = \frac{k_{-2}C_{\mathrm{CuR20}}C_{\mathrm{H0}}}{1 + k_{-2}C_{\mathrm{H0}}/k_{\mathrm{CuR2}}} \tag{17}$$

The values of the unknown constants, k_{-2} and k_{CuR2}, were evaluated from the experimental results of J_0' and Eq. (17), and they are also listed in Table 1. The solid curves shown in Figs. 5–7 are the results calculated by using the constants and Eq. (17).

The ratio of the overall extraction rate constant, k_2K_1, to the stripping rate constant, k_{-2}, gives a value of the extraction equilibrium constant, K_{ex}. The value thus obtained was $(0.75 \pm 0.18) \times 10^{-4}$, while the K_{ex} value obtained experimentally was $(1.30 \pm 0.24) \times 10^{-4}$. In Fig. 1 the results

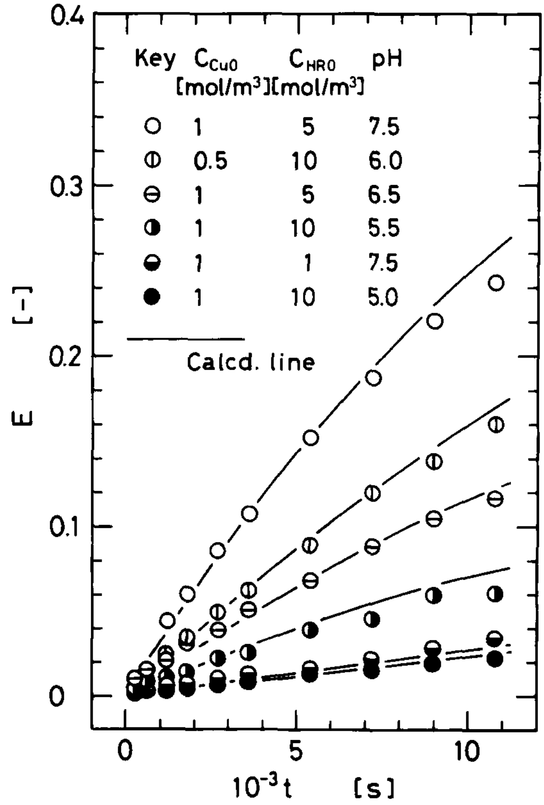

FIG. 8. Simulation of relation between extent of copper extracted and time.

calculated by using both K_{ex} values are shown for the purpose of comparison. A slight difference between them can be seen.

Simulation of Extraction Rate

To confirm the validity of the interfacial reaction model, the change of extent of copper extracted, E, defined by Eq. (18) with time, t, was simulated:

$$E = (C_{\mathrm{Cu0}} - C_{\mathrm{Cu}})/C_{\mathrm{Cu0}} \tag{18}$$

The concentration changes of the species in the aqueous and organic solutions with time are expressed as follows.

$$-V_{\mathrm{aq}}\frac{dC_{\mathrm{Cu}}}{dt} = -\frac{1}{2}V_{\mathrm{org}}\frac{dC_{\mathrm{HR}}}{dt} = V_{\mathrm{org}}\frac{dC_{\mathrm{CuR2}}}{dt} = AJ \tag{19}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic solutions, respectively, and A is the interfacial area, as mentioned before. The extraction rate, J, is expressed by Eq. (11). Given the initial conditions and the constants listed in Table 1, Eqs. (11), (12), and (19) are simultaneously solved by the Runge-Kutta-Gill method to obtain the extent of copper extracted. The calculated results are shown as solid lines in Fig. 8. Approximately good agreements with the experimental results were observed over a wide range of the extent of copper extracted, indicating the validity of the interfacial reaction model.

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