from the Ministry of Education, Science and Culture, Japan.

Nomenclature

A	=	cross-sectional area of sludge bed	[cm^2]
E	=	local strength of electric field in sludge bed	[$V \cdot m^{-1}$]
E_0	=	initial strength of electric field in sludge bed	[$V \cdot m^{-1}$]
H_0	=	initial height of sludge bed	[cm]
H_t	=	height of sludge bed at t	[cm]
h	=	distance from bottom of sludge bed to measuring point	[cm]
i_0	=	constant electric current passing through cross section of sludge bed	[mA]
i_t	=	electric current passing through cross section of sludge bed at t	[mA]
Q_E	=	volume dewatered by electroosmosis	[cm^3]
$Q_{E\infty}$	=	terminal value of Q_E	[cm^3]
Q_T	=	total volume dewatered by electroosmosis and vacuum	[cm^3]
t	=	dewatering time	[min]
V	=	electric potential at height of sludge bed	[V]
V_0	=	constant voltage applied to electrodes	[V]
V_t	=	voltage applied to electrodes at t	[V]
w_l	=	weight of water in sludge	[kg]
w_p	=	weight of particles in sludge	[kg]
ε_w	=	volumetric fraction of water content in sludge	[—]
ε_{w0}	=	initial value of ε_w	[—]
ρ_l	=	density of water	[$kg \cdot m^{-3}$]
ρ_p	=	density of particles	[$kg \cdot m^{-3}$]
ΔP	=	degree of vacuum	[kPa]

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KINETICS OF STRIPPING OF N-8-QUINOLYL-*P*-DODECYLBENZENESULFONAMIDE-COPPER CHELATE COMPLEX WITH HYDROCHLORIC ACID

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Key Words: Extraction, Stripping, Kinetics, Interfacial Reaction, Copper, LIX 34

A kinetic study concerning the stripping of copper chelate complex in toluene with hydrochloric acid was carried out at 303 K, using a stirred transfer cell and pure copper complex prepared from copper and synthesized N-8-quinolyl-*p*-dodecylbenzenesulfonamide.

It was found that the mechanism of copper stripping could not be explained as simply a reverse process of the copper extraction by this extractant from acetate buffer media, due to the reaction between the extractant and hydrochloric acid and the low solubility of the ion pair complex formed by this reaction. Moreover, it was confirmed that the stripping rate was determined by the first step of the interfacial reaction between the copper complex and the acid, and by mass transfer of the copper complex.

Introduction

Research into metal recovery with liquid membranes has rapidly expanded in the last decade, because of practical interest in the development of attractive hydrometallurgical processes.[1,2,4,10] To develop and design the liquid membrane process, it is important to elucidate the mechanism and kinetics of stripping of metal by the stripping solution, as well as extraction of metal by the extractant used as a carrier in the liquid membranes.

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Earlier investigations concerning the kinetics of stripping of copper complex with acid were mainly carried out with commercial extractants, that is, LIX 64N,[13] LIX 65N,[6,8,12] *anti*-2-hydroxy-5-nonylbenzophenone oxime[7] (henceforth *anti*-HNBPO) of the active component of LIX 65N and *anti*-2-hydroxy-5-nonylacetophenone oxime[5,11] (henceforth *anti*-HNAPO) of the active component of SEM 529. Several mechanisms for stripping of the copper complex with acid were proposed to account for each experimental result. Kojima *et al.*[6] measured the stripping rate of copper-loaded LIX 65N in Dispersol solution with sulfuric acid using a dia-

phragm cell which consists of two well-stirred solutions separated by a porous Teflon membrane. They proposed a diffusion model accompanied by a dissociation reaction of the copper complex in aqueous solution adjacent to the interface, in order to explain the experimental results that the stripping rate was proportional to both concentrations of the copper complex and hydrogen ion and inversely proportional to the concentration of free extractant (not bound to copper), after allowing for the mass transfer resistance of the copper complex in the membrane. Komasawa *et al.*[7] carried out measurements of the stripping rate of copper complex in *n*-heptane and xylene with nitric acid in a stirred transfer cell, using *anti*-HNBPO isolated and purified from LIX 65N. They found that the stripping rate was first-order in the concentrations of the copper complex and hydrogen ion and approximately zero-order in the concentration of *anti*-HNBPO. They explained these results by the interfacial reaction model proposed in the previous paper concerning the kinetics of copper extraction with *anti*-HNBPO.[8] Miyake *et al.*[5,11] measured the stripping rate of copper complex in benzene with hydrochloric acid in a stirred transfer cell, using *anti*-HNAPO isolated and purified from SME 529. The results were slightly different from Komasawa's in that the rate was not zero-order in the concentration of *anti*-HNAPO, but decreased with increasing free oxime concentration under the condition of interfacial reaction controlling. They explained this result qualitatively by the shielding effect of the free oxime—that is, by the decrease of effective interfacial area due to adsorption of the free oxime, which is more interfacial-active than the copper complex. Furthermore, they confirmed the shielding effect by using nonionic and cationic surfactants.[11] However, it was very difficult to explain quantitatively the effect of the free oxime on the stripping rate.

In the present work, to elucidate the stripping mechanism, and in particular the effect of the free extractant on the stripping rate, a kinetic study of the stripping of copper complex in toluene with hydrochloric acid was carried out in a stirred transfer cell, using N-8-quinolyl-*p*-dodecylbenzenesulfonamide (henceforth C_{12}phSAQ, abbreviated as HR) synthesized and purified. As shown in a previous paper,[14] C_{12}phSAQ is adsorbed at the interface between the organic and aqueous solutions, but the chelate complex of copper-C_{12}phSAQ (henceforth abbreviated as CuR_2) is not. In addition, C_{12}phSAQ reacts with hydrochloric acid to form an ion pair complex in the range of low pH. Therefore, the solubility and formation equilibrium constant of the ion pair complex were measured to investigate the stripping mechanism.

1. Experimental

1.1 Reagents

The chelate complex, CuR_2, was prepared by adding an aqueous solution of copper acetate to a methanol solution of C_{12}phSAQ at about 333 K, adjusting pH of the solution by ammonium aqueous solution. The complex was purified by recrystallization in a mixture of water and methanol (volume ratio 2 : 1) to obtain a brownish black solid (mp 413–414 K). It was analyzed by elementary analysis; Anal. Calcd. for $C_{54}H_{70}S_2O_4N_4Cu$: C, 67.08; H, 7.30; N, 5.79, Found: C, 67.18; H, 7.29; N, 5.87. The organic solution was prepared by dissolving CuR_2 and HR in toluene. The aqueous solution was prepared with hydroric acid, adding sodium chloride to adjust ionic strength.

1.2 Measurements of solubility and equilibrium constant of C_{12}phSAQ·HCl ion pair complex formation

The organic solution of C_{12}phSAQ and the aqueous solution of hydrochloric acid were mixed and the precipitate of ion pair complex was formed. The precipitate was filtered and rinsed with ethyl ether several times. Then it was analyzed by elementary analysis; Anal. Calcd. for $C_{27}H_{37}SO_2N_2Cl$: C, 66.30; H, 7.62; N, 5.73, Found: C, 66.10; H, 7.55; N, 5.66.

C_{12}phSAQ·HCl was dissolved in toluene to prepare a saturated solution. The concentration of C_{12}phSAQ·HCl in the toluene solution was measured with a Hitachi model 200-10 spectrophotometer ($\varepsilon = 4.18 \times 10^2$ m^2/mol at 310 nm).

The saturated toluene solution of the ion pair complex was shaken with 100 mol/m^3 acetic acid–100 mol/m^3 sodium acetate buffer solution (pH = 5.5–3.5). The concentration of the ion pair complex was also measured with a spectrophotometer and the concentration of chloride ion in the aqueous solution was determined with a chloride ion-selective electrode.

1.3 Measurements of stripping rate

A stirred transfer cell was used to measure the stripping rate of the copper complex by hydrochloric acid at 303 K. The cell was the same as described in the previous paper,[14] except for the material of the partition plate and the impeller of the lower compartment. These parts were made from poly-tetrafluoroethylene in place of stainless steel, to prevent corrosion induced by hydrochloric acid. The volume of each compartment of the cell was about 1.5×10^{-4} m^3, and the interfacial area between the two solutions was 1.54×10^{-3} m^2. Each solution in the cell was stirred in opposite directions by two flat-blade stirrers at 150 rpm. The experimental procedure was the same as described previously.

The concentration change of copper in the aqueous solution with time was measured under various expe-

rimental conditions as follows: the initial concentration of each species, for the copper complex $C_{CuR_2O}=0.1$–5 mol/m^3; for the extractant, $C_{HRO}=0.5$–200 mol/m^3; for hydrochloric acid, $C_{HO}=145$–2370 mol/m^3; and the ionic strength of the aqueous solution was kept at 2370 mol/m^3.

2. Results

2.1 Solubility and formation equilibrium constant of the ion pair complex

The formation of the ion pair complex is considered to proceed as follows:

$$HR_{org}+H^+_{aq}+Cl^-_{aq} \rightleftharpoons H_2R^+Cl^-_{org}: K_f \qquad (1)$$

where $H_2R^+Cl^-$ is the ion pair complex and K_f is the equilibrium constant of the ion pair complex formation. From the concentrations of H^+_{aq}, Cl^-_{aq}, HR_{org} and $H_2R^+Cl^-_{org}$ in equilibrium, the value of K_f was obtained at 303 K, as shown in **Table 1**. The concentrations of HR_{org} and $H_2R^+Cl^-_{org}$ were calculated as follows:

$$\begin{aligned} C_{HR} &= (V_{aq}/V_{org})C_{Cl^-} \\ C_{H_2R^+Cl^-} &= (C_{H_2R^+Cl^-})_0 - C_{HR} \end{aligned} \qquad (2)$$

where V_{aq} and V_{org} are volume of aqueous and organic solution, respectively, and $(C_{H_2R^+Cl^-})_0$ is the initial concentration of the ion pair complex in the organic solution.

The solubility of $H_2R^+Cl^-$ in toluene was 0.60 mol/m^3 at 303 K. Therefore, the precipitate of $H_2R^+Cl^-$ in toluene is formed under the following condition:

$$C_{HR}a_Ha_{Cl} > 3.3\times10^{-2} \quad [(mol/m^3)^3] \qquad (3)$$

where a_H and a_{Cl} are the activity of H^+_{aq} and Cl^-_{aq}, respectively, and the activity coefficient of HR_{org} is assumed to be unity.

In the previous paper,[14] the distribution constant of HR and the dissociation constant of $H_2R^+_{aq}$ were obtained as follows:

$$HR_{org} \rightleftharpoons HR_{aq}: K_D = 2.15\times10^{-6} \quad [—] \qquad (4)$$

$$H_2R^+{}_{aq} \rightleftharpoons HR_{aq}+H^+_{aq}: K_{a1}=33.0 \quad [mol/m^3] \qquad (5)$$

Combining Eqs. (1), (4) and (5) the following equilibrium relation was obtained.

$$H_2R^+Cl^-_{org} \rightleftharpoons H_2R^+_{aq}+Cl^-_{aq}: K_{DC} \qquad (6)$$

where K_{DC} $(=K_D/K_{a1}K_f)=3.6\times10^{-9}$ [mol/m^3]. It is suggested that the solubility of the ion pair complex in water is also very small.

To obtain information concerning the interfacial adsorption of the ion pair complex, the interfacial tension between hydrochloric acid and toluene saturated with the ion pair complex was measured by the drop-weight method. It was found that the ion pair complex had no interfacial activity, because the solubility is too low.

Table 1. Equilibrium constant of ion pair complex formation

$(C_{H_2R^+Cl^-})_0$ [mol/m^3]	pH	C_{Cl^-} [mol/m^3]	$C_{H_2R^+Cl^-}$ [mol/m^3]	K_f [(m^3/mol)^2]
0.60	5.46	0.261	0.99×10^{-2}	18.5
0.59	4.50	0.148	4.76×10^{-2}	18.8
0.60	3.50	0.161	2.80×10^{-1}	17.2
0.60	3.50	0.184	3.18×10^{-1}	19.4
0.59	3.58*)	0.265	3.27×10^{-1}	17.6
				18.3 ± 0.9

*) The toluene solution of the ion pair complex was shaken with deionized water.

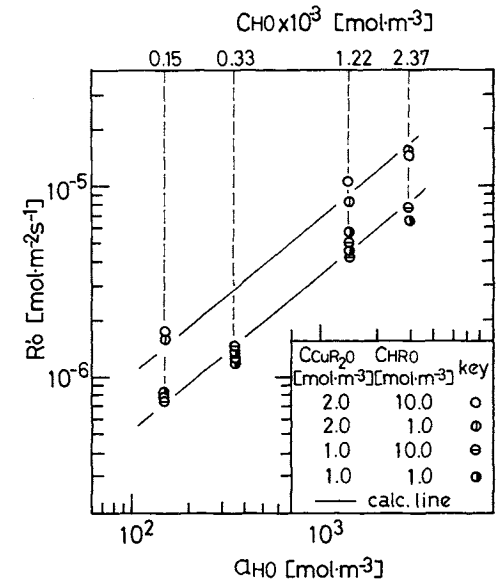


Fig. 1. Effect of activity of hydrogen ion on initial rate of stripping.

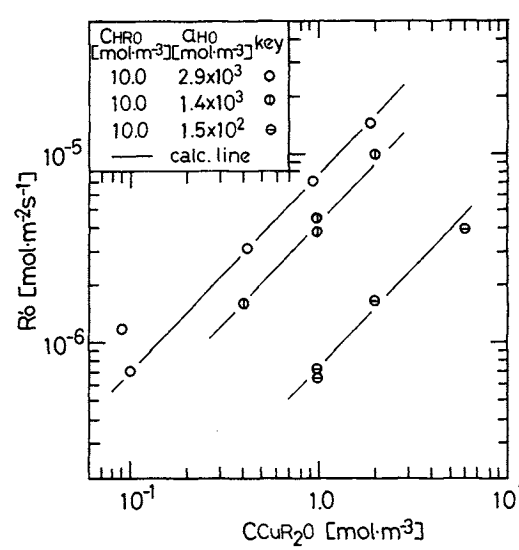


Fig. 2. Effect of initial concentration of copper complex on initial rate of stripping.

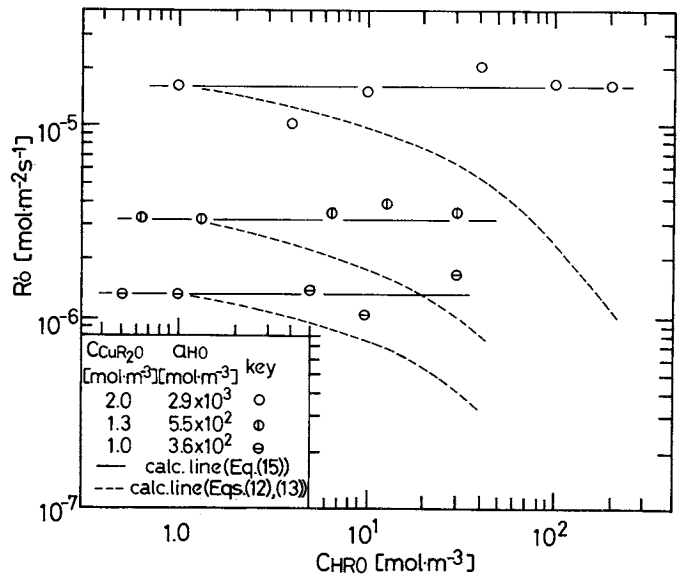


Fig. 3. Effect of initial concentration of extractant on initial rate of stripping.

2.2 Initial rate of stripping

The effects of hydrogen ion, the copper complex and the free extractant on the initial stripping rate, R_0', are shown in **Figs. 1**, **2** and **3**, respectively. The acid concentration used was so high that the activity of hydrogen ion (see **Appendix 1**)[3] was used in place of the concentration, C_{H0}. The experimental results are similar to Komasawa's,[7] except that the slope of the relation between $\log R_0'$ and $\log a_{H0}$ is not unity, but 0.82, due to the mass transfer resistance of the copper complex in the organic solution, as mentioned later. In Fig. 3, no shielding effect caused by the adsorption of the free extractant[5,11] can be observed, although the shielding effect shown by the broken lines is expected from the extraction mechanism proposed in the previous paper,[14] as mentioned later. In the range of high concentration of the free extractant and hydrogen ion, the toluene solution in the upper compartment of the cell became cloudy with the progress of stripping. This was caused by the formation of very small solid particles of the ion pair complex, $H_2R^+Cl^-$. This seems to be main reason why no shielding effect was observed.

3. Discussion

3.1 Analysis of the initial rate of stripping

In the previous paper,[14] the interfacial reaction model was proposed to analyse the initial rate of copper extraction by C_{12}phSAQ and obtain the rate equation used in a wide range of extent of copper extracted. In principle, it should be considered that the rate equation obtained in the previous paper[14] could be applied to the stripping rate of the copper complex in toluene by acid, because it can be considered that extraction and stripping are a reversible reaction. Therefore, the mechanism of stripping was considered to be as follows:

$$CuR_{2\,org} + H^+_{aq} \overset{k_2'}{\rightleftharpoons} CuR^+_{ad} + HR_{ad} \quad K_2^{-1} \tag{7}$$

$$CuR^+_{ad} + H^+_{aq} \rightleftharpoons Cu^{2+}_{aq} + HR_{ad} \quad K_1^{-1} \tag{8}$$

$$HR_{ad} \rightleftharpoons HR_{org} \quad K_{ad}^{-1} \tag{9}$$

where K_1, K_2 and K_{ad} are the equilibrium constants of the reverse reactions, respectively, the subscript *ad* denotes the adsorption state at the interface, and the reaction shown by Eq. (7) is considered as the rate-controlling step among the above reactions. Using the Langmuir adsorption isotherm and assuming that the interfacial area occupied by unit mole of CuR^+ is equal to the value of HR, S_{HR}, the stripping rate at the interface, R', is derived as follows (see **Appendix 2**):

$$R' = \frac{k_2'(C_{CuR_2 i} a_{Hi} - K_{ex} C_{Cui} C^2_{HRi}/a_{Hi})}{(1 + K_{ad} C_{HRi} + K_{ad} K_1 C_{Cui} C_{HRi}/a_{Hi})^2} \tag{10}$$

where k_2' is the reaction rate constant of Eq. (7), the subscript i denotes the organic and aqueous solutions adjacent to the interface, and $K_{ex} = K_1 K_2 (K_{ad}/S_{HR})^2$.

The concentration of each species adjacent to the interface is obtained by assuming that the interfacial reaction rate is equal to the mass transfer rate of each species as follows:

$$\begin{aligned} R' &= k_{CuR_2}(C_{CuR_2} - C_{CuR_2 i}) \\ &= (k_{HR}/2)(C_{HRi} - C_{HR}) \\ &= k_{Cu}(C_{Cui} - C_{Cu}) \end{aligned} \tag{11}$$

where k_j and C_j are the mass transfer coefficient and the concentration of species j in bulk phase ($j = CuR_2$, HR and Cu), respectively. The activity of hydrogen ion adjacent to the interface, a_{Hi}, could be considered to be identical to the activity in the bulk aqueous solution, a_H, because the concentration of the acid is

much higher than the concentrations of the copper complex and the extractant.

Considering $K_{ad}K_1 C_{Cui} C_{HRi}/a_{H0} \ll 1$, the initial rate of stripping, R'_0, is expressed as follows:

$$R'_0 = \frac{k'_2 C_{CuR_2 i} a_{H0}}{(1+K_{ad}C_{HRi})^2} \tag{12}$$

$$R'_0 = k_{CuR_2}(C_{CuR_2 0} - C_{CuR_2 i}) = (k_{HR}/2)(C_{HRi} - C_{HR0}) \tag{13}$$

From Eq. (12) and the value of K_{ad} ($=2.0\times10^{-2}$ m^3/mol) obtained in the previous paper,[14] the shielding effect of HR is expected to appear in the range of high HR concentration. However, no shielding effect can be found from the experimental results, as shown in Fig. 3. As mentioned previously, HR reacts with hydrochloric acid to form an ion pair complex which has very low solubility in toluene and no interfacial activity. Assuming that the reaction between HR_{ad} and hydrochloric acid is very fast compared with the reaction shown by Eq. (7), Eq. (12) becomes as follows (see **Appendix 3**):

$$R'_0 = k'_2 C_{CuR_2 i} a_{H0} \tag{14}$$

Combining Eqs. (13) and (14), R'_0 is expressed as the following equation.

$$R'_0 = \frac{k'_2 k_{CuR_2} C_{CuR_2 0} a_{H0}}{k_{CuR_2} + k'_2 a_{H0}} \tag{15}$$

From Eq. (15), it is suggested that the stripping rate shown in Fig. 1 is affected by the mass transfer resistance of the copper complex. To confirm the validity of Eq. (15), all experimental results are correlated by the following equation, as shown in **Fig. 4**.

$$\frac{C_{CuR_2 0}}{R'_0} = \frac{1}{k_{CuR_2}} + \frac{1}{k'_2}\cdot\frac{1}{a_{H0}} \tag{16}$$

From the slope and intersection of a straight line with the ordinate at $1/a_{H0}=0$, k'_2 and k_{CuR_2} are obtained respectively, as shown in **Table 2**. The solid lines in Figs. 1, 2 and 3 are calculated by Eq. (15), using the values shown in Table 1. The broken lines in Fig. 3 are calculated using Eqs. (12) and (13).

The value of k'_2 agrees approximately with the value of k'_2 ($=3.3\times10^{-9}$ m^4/(mol·s)) calculated from the overall rate and equilibrium constants of copper extraction obtained in the previous paper,[14] in spite of the difference in the interfacial condition of the two studies. The values of k'_2 were obtained by Komasawa *et al.*[7] from the stripping rate of copper-loaded *anti*-HNBPO in *n*-heptane and xylene with nitric acid, as follows: 2.0×10^{-8} m^4/(mol·s) for *n*-heptane and 5.8×10^{-9} m^4/(mol·s) for xylene. The value obtained in this paper is nearly equal to the latter, in spite of the different copper complex.

The value of k_{CuR_2} is considered to be reasonable as

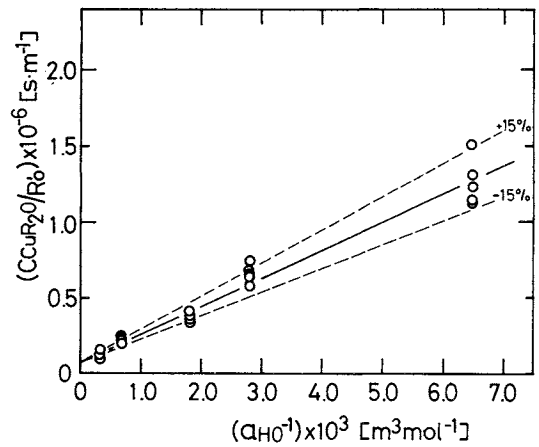


Fig. 4. Correlation between $C_{CuR_2 0}/R'_0$ and $1/a_{H0}$.

Table 2. Values of k'_2 and k_{CuR_2} obtained from Fig. 4

$k'_2=(4.3\pm0.1)\times10^{-9}$	[m^4/(mol·s)]
$k_{CuR_2}=(1.3\pm0.4)\times10^{-5}$	[m/s]

compared with the values of mass transfer coefficient of HR, k_{HR} and that of copper-benzoylacetonate complex, k_{CuB_2} obtained in the previous papers, that is, $k_{HR}=(9.2\pm0.5)\times10^{-6}$ m/s[14] and $k_{CuB_2}=2\times10^{-5}$ m/s,[9] by taking account of the difference in the interfacial condition of the two studies caused by the formation of small solid particles in the organic solution adjacent to the interface.

3.2 Comparison of experimental results with calculated results over the whole range of copper stripping

The relation between the extent of copper stripped and time under various experimental conditions was obtained by using Eqs. (13) and (14) to confirm the validity of the stripping-rate expression proposed. Under the experimental condition, the reverse reaction (extraction) term in Eq. (10) is negligibly small because the concentration of hydrochloric acid is extremely high compared with the concentration of HR, that is, $C_{CuR_2 i}a_{H0} \gg K_{ex}C_{Cui}C^2_{HRi}/a_{H0}$. Therefore, it could be considered that the copper complex in toluene is irreversibly stripped by the acid. The concentration change of the copper complex with time is expressed by the following equation.

$$-V_{org}\frac{dC_{CuR_2}}{dt} = kAC_{CuR_2} \tag{17}$$

where

$$\frac{1}{k} = \frac{1}{k_{CuR_2}} + \frac{1}{k'_2 a_{H0}}, \qquad A = 1.54\times10^{-3}\ \text{m}^2$$

From Eq. (17), the extent of copper stripped, E', is obtained as follows:

$$E' = 1 - e^{-kat} \tag{18}$$

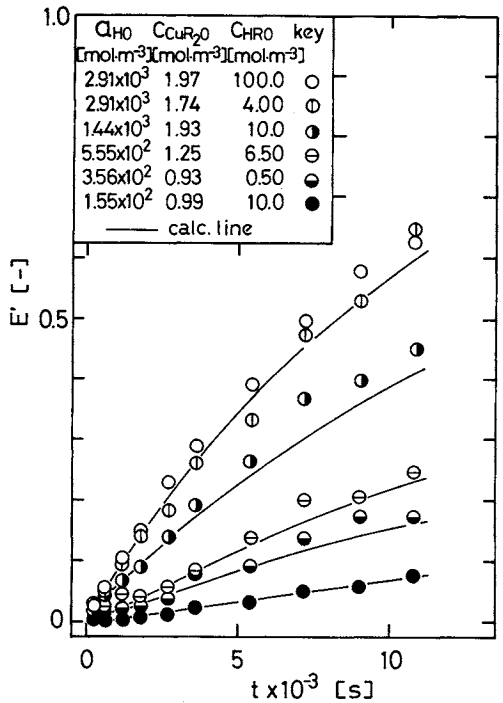


Fig. 5. Simulation of relation between extent of copper stripped and time.

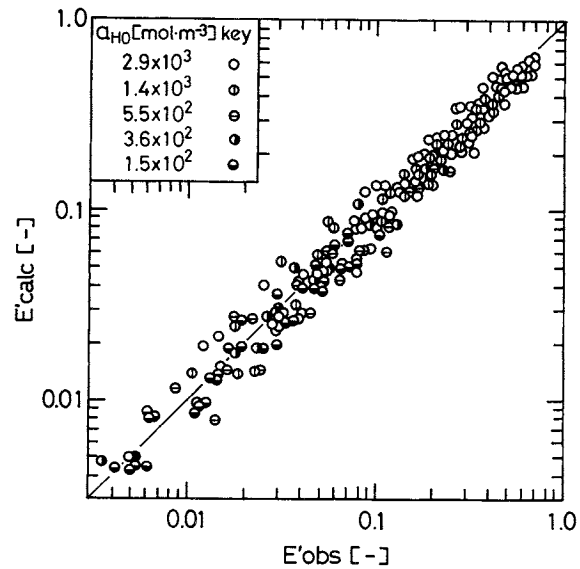


Fig. 6. Comparison of experimental results with calculated results of extent of copper stripped.

where $E'=1-C_{CuR_2}/C_{CuR_2O}$, $a=A/V_{org}$. In **Fig. 5**, E' was calculated from Eq. (18) using the values shown in Table 1. The calculated results agree well with the experimental results over a wide range of the extent of copper stripped. The relation between E'_{calc} and E'_{obs} in all experiments is shown in **Fig. 6**, from which the fit between E'_{calc} and E'_{obs} was confirmed in all conditions.

Conclusion

A kinetic study concerning the stripping of the copper–C_{12}phSAQ complex in toluene by hydrochloric acid was carried out, using a stirred transfer cell. It was concluded that the stripping rate of the copper complex is determined by the first step of the interfacial reaction between the copper complex and hydrogen ion and by mass transfer of the copper complex from the bulk organic solution to the interface, and that the effect of interfacial adsorption of HR or CuR^+ becomes negligibly small due to the formation of an ion pair complex between HR and hydrochloric acid, and the low solubility of the ion pair complex.

The interfacial reaction rate constant of the first step and the mass transfer coefficient were obtained from analysis of the initial rate of copper stripping, and it was confirmed that the values obtained were reasonable as compared with the values reported in the previous papers. Furthermore, the relation between the extent of copper stripped and time was obtained over a wide range of experimental conditions to confirm the validity of the overall rate expression of copper stripping.

Appendix 1

The activity coefficient of hydrochloric acid was calculated as follows:[3]

$$\log\gamma_{\pm}=\log\gamma_{\pm}(0)-\alpha_{HCl}m_{NaCl} \tag{A1}$$

where $\gamma_{\pm}(0)$ is the activity coefficient of the acid in the case of $m_{NaCl}=0$, and α_{HCl} is a parameter expressed by the following equations.

$$\log\gamma_{\pm}(0)=-\frac{0.512C}{1+1.418C}-8.0\times10^{-5}+0.1272C+6.0\times10^{-3}C^2-\log(1+0.03604m_{total}) \tag{A2}$$

$$\alpha_{HCl}=0.0308-8.789\times10^{-4}m_{total}^2 \tag{A3}$$

where

$$C=0.966m_{total}-1.822\times10^{-2}m_{total}^2 \tag{A4}$$

$$m_{total}=m_{HCl}+m_{NaCl} \tag{A5}$$

m_{HCl} and m_{NaCl} are the molalities of hydrochloric acid and sodium chloride, respectively, and their values were calculated from the following equations.

$$m_{HCl}=\frac{8.864+3.356\times10^{-2}C_{HCl}}{Mw_{HCl}\{0.982-(3.356C_{HCl}+4.993C_{NaCl})\times10^{-5}\}} \tag{A6}$$

$$m_{NaCl}=\frac{9.691+4.993\times10^{-2}C_{NaCl}}{Mw_{NaCl}\{0.982-(3.356C_{HCl}+4.993C_{NaCl})\times10^{-5}\}} \tag{A7}$$

where Mw_{HCl} and Mw_{NaCl} are molecular weights of hydrochloric acid and sodium chloride, respectively.

The relation between the mean ionic molar activity coefficient of hydrochloric acid, $y_{\pm}$, and the mean ionic molal activity coefficient, $\gamma_{\pm}$, is expressed as follows:

$$\gamma_{\pm}/y_{\pm}=\frac{d-C_{HCl}Mw_{HCl}-C_{NaCl}Mw_{NaCl}}{d_0} \tag{A8}$$

where d and d_0 are densities at 303 K of mixture and pure deionized water, respectively. Therefore, the activity of hydrogen ion, a_{H0}, is obtained from the concentration and its activity coefficient; that is,

$$a_{H0} = C_{HCl} y_{\pm} .$$

Appendix 2

The interfacial reaction rate, R', is expressed as follows[14]:

$$R' = k_2' \left(\frac{C_{CuR_2 i} C_{HRi} \theta_v^2}{K_2} - \frac{\theta_{CuR} \theta_{HR}}{S_{CuR} S_{HR}} \right) \quad \text{(A9)}$$

where θ_{HR} and θ_{CuR} are the fractions of interfacial area occupied by HR and CuR^+, respectively.

Assuming the Langmuir adsorption isotherm, θ_{HR}, θ_{CuR} and θ_v are expressed as follows:

$$\theta_{HR} = K_{ad} C_{HRi} \theta_v$$

$$\theta_{CuR} = K_1 \theta_{HR} C_{Cui} / C_{Hi} \quad \text{(A10)}$$

$$\theta_v = 1 - \theta_{HR} - \theta_{CuR}$$

Combining Eqs. (A9) and (A10), the stripping rate at the interface, R', is expressed by Eq. (10).

Appendix 3

Combining Eqs. (1) and (9), the following equilibrium relation was obtained:

$$HR_{ad} + H_{aq}^+ + Cl_{aq}^- \rightleftharpoons H_2R^+Cl_{org}^- : K_f/K_{ad} \quad \text{(A11)}$$

where $K_f/K_{ad} = 9.2 \times 10^2$ [m^3/mol]. Therefore, the fraction of interfacial area occupied by HR, θ_{HR}, is expressed as follows:

$$\theta_{HR} = \frac{K_{ad}}{K_f} \frac{C_{H_2R^+Cl^-}}{a_H a_{Cl}} \theta_v \quad \text{(A12)}$$

Considering the solubility of $C_{H_2R^+Cl^-}$, it is found that θ_{HR}/θ_v is very samll in the range of high acid concentration.

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Nomenclature

A	=	interfacial area between organic and aqueous solutions	[m^2]
a	=	specific area ($=A/V_{org}$)	[m^{-1}]
a_H	=	activity of hydrogen ion	[mol/m^3]
C	=	total concentration defined by Eq. (A4)	[mol/m^3]
C_j	=	concentration of species j (j=Cu, HR, CuR)	[mol/m^3]
d	=	density of aqueous solution	[kg/m^3]
d_0	=	density of water	[kg/m^3]
E'	=	extent of copper stripped	[—]
K_{ad}	=	adsorption equilibrium constant	[m^3/mol]
K_{a1}	=	dissociation constant of $H_2R_{aq}^+$ defined by Eq. (5)	[mol/m^3]
K_D	=	distribution constant of HR defined by Eq. (4)	[—]
K_{DC}	=	equilibrium constant of reaction expressed by Eq. (6)	[mol/m^3]
K_{ex}	=	equilibrium constant of copper extraction	[—]
K_f	=	equilibrium constant of ion pair complex formation of Eq. (1)	[(mol/m^3)^2]
K_1	=	equilibrium constant of reverse reaction of Eq. (8)	[—]
K_2	=	equilibrium constant of reverse reaction of Eq. (7)	[m^2]
k	=	overall stripping rate constant	[m/s]
k_j	=	mass transfer coefficient of species j (j=Cu, HR, CuR_2, CuB_2)	[m/s]
k_2	=	reverse reaction rate constant of Eq. (7)	[m^2/(mol·s)]
k_2'	=	forward reaction rate constant of Eq. (7)	[m^4/(mol·s)]
Mw_j	=	molecular weight of species j (j=HCl, NaCl)	[kg/mol]
m_j	=	molality of species j (j=HCl, NaCl)	[mol/kg]
m_{total}	=	molality defined by Eq. (A5)	[mol/kg]
R'	=	stripping rate	[mol/(m^2s)]
R_0'	=	initial stripping rate	[mol/(m^2s)]
S_j	=	interfacial area occupied by unit mole of species j (j=HR, CuR^+)	[m^2/mol]
t	=	time	[s]
V_{org}	=	volume of organic solution in upper compartment of cell	[m^3]
$y_{\pm}$	=	mean ionic molar activity coefficient	[—]
α_{HCl}	=	parameter defined by Eq. (A4)	[—]
$\gamma_{\pm}$	=	mean ionic molal activity coefficient	[—]
θ_j	=	fraction of interfacial area occupied by species j (j=HR, CuR^+)	[—]
ε	=	extinction coefficient	[m^2/mol]

〈Subscripts〉

ad	=	adsorption state at interface
aq	=	aqueous solution
calc	=	calculated value
i	=	adjacent to interface
0	=	initial state
obs	=	observed value
org	=	organic solution

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