

EXTRACTION KINETICS OF COPPER WITH 2-ETHYLHEXYL-PHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER

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Extraction and stripping of copper with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester dissolved in *n*-heptane were carried out at 303 K in both a stirred transfer cell and a membrane extractor using a hollow fiber, along with a study of the interfacial adsorption equilibria of extractant and copper complex between aqueous and organic solutions. These results obtained by use of both the stirred transfer cell and the membrane extractor were explained by a diffusion model with interfacial reaction.

Introduction

Recently, the application of hollow-fiber modules has been attempted for metal recovery^{2,12,21)} and protein extraction processes⁵⁾ as a potentially attractive alternative to solvent extraction. In developing

membrane extraction processes, it is very important to elucidate the kinetics and mechanism of extraction and stripping through the membrane, because the major difference between solvent extraction and membrane extraction processes is that the latter are governed by kinetics rather than equilibrium.

Alkylphosphoric acid has received much attention due to its potential in the reprocessing of nuclear

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fuel and in selective hydrometallurgical recovery of metals.¹⁰ Many studies of metal extraction with alkylphosphoric acid, especially di(2-ethylhexyl)-phosphoric acid (henceforce D2EHPA), have been carried out from the viewpoint of equilibrium and kinetics.^{1,6,8,11,13,14,15,18,20} Studies of extraction kinetics were reviewed by Coleman³ and Danesi *et al.*⁷ In most of the papers reported, it was emphasized that in the extraction kinetics of metal species by D2EHPA, interfacial chemical reactions play a predominant role.^{6,8,15,20} However, too few results are available to draw any generalization about the type of mechanisms, because the interfacial mechanism is strongly dependent on the metal species and the extractants.^{4,7}

In the present study, the extraction and stripping of copper with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (henceforce referred to by the commercial name PC-88A, or abbreviated as HR) are carried out by using both a stirred transfer cell and a membrane extractor made of a hollow fiber, along with measurements of the interfacial adsorption equilibria of the extractant and the copper complex, in order to obtain more definite information on the kinetics and mechanism of copper extraction with PC-88A.

1. Experimental

1.1 Reagents

PC-88A (purity 95.5%) from Daihachi Chemical Industry Co. Ltd. was used without further purification in the extraction experiments because the purity did not affect the extraction efficiency.

n-Heptane of commercial GR grade was used as the organic solvent without purification. All other inorganic reagents used were GR grade.

The copper complex of PC-88A was prepared by adding an aqueous solution of copper acetate to a *n*-heptane solution of PC-88A, adjusting pH of the solution by aqueous ammonia solution. The complex was washed by methanol and purified by recrystallization from diethylether to obtain a bluish solid. The results of elementary analysis were as follows. Anal. Cald. for C₃₂H₆₈P₂O₆Cu: 57.00; H, 10.16; Found: C, 56.80; H, 10.11. For C₁₆H₃₅PO₃(PC-88A): Anal. Cald. C, 62.72; H, 11.51; Found: C, 62.54; H, 11.64.

The organic solution was prepared by dissolving PC-88A in *n*-heptane. The aqueous solution was prepared by dissolving copper nitrate in deionized water and adjusting pH and ionic strength of the solution with 100 mol/m³ sodium acetate-acetic acid buffer solution and/or hydrochloric acid.

1.2 Interfacial tension

Interfacial tension between the organic and aqueous solutions was measured at 303 K by the drop weight or the pendant drop method to determine the

characteristic of the interfacial adsorption equilibria of the extractant and the copper complex. In the case of the pendant drop method, the capillary surface was treated with dimethylsilane and the pointed end was polished like a mirror face. It was confirmed that the experimental results obtained by both the drop weight and the pendant drop methods agreed very well with each other.

1.3 Extraction and stripping rates

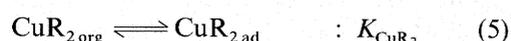
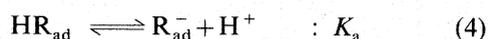
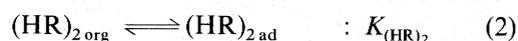
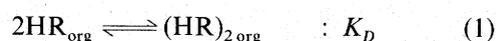
The initial extraction and stripping rates of copper were measured at 303 K using the same transfer cell as described in previous papers,^{16,19} in which the experimental procedure is also explained. The average extraction rates of copper were also measured at 303 K using the same hollow fiber membrane extractor as described in a previous paper.²¹ The organic solution used in the stripping experiment was prepared by adding PC-88A to CuR₂ organic solution based on the relation of extraction equilibrium clarified in a previous paper.¹⁷ The experimental conditions of extraction were as follows: copper concentration was 0.1–10 mol/m³, PC-88A concentration 1–100 mol/m³, pH range 2.5–6.3 and stirring speed 2.5 s⁻¹ in the transfer cell or flow rate of aqueous and organic solution 2.3 × 10⁻⁹ and 4.0 × 10⁻⁹ m³/s in the hollow fiber membrane extractor.

2. Results

2.1 Interfacial tension

The relation between interfacial tension, γ , and concentration of PC-88A, C_{HR}, for various pH values is shown in Fig. 1. The relation between γ and concentration of the copper complex, C_{CuR₂}, is shown in Fig. 2. The results suggest that both PC-88A and copper complex have interfacial activities.

This extractant mainly exists as dimer in *n*-heptane, as shown in the previous paper.¹⁷ The interfacial adsorption equilibria are considered to be:



The relation between γ and the amount of molecules adsorbed at the interface is expressed by Gibbs' adsorption equation. Assuming a Langmuir adsorption isotherm between the amount of molecule adsorbed and its bulk concentration,¹⁹ the relation between γ and the concentration of each species in the organic solution is written as follows:

$$\gamma = \gamma_0 - \{\alpha_1 \ln(\beta_1 C_{\text{HR}} + 1) + \alpha_2 \ln(\beta_2 C_{\text{HR}} + 1)\} \quad (6)$$

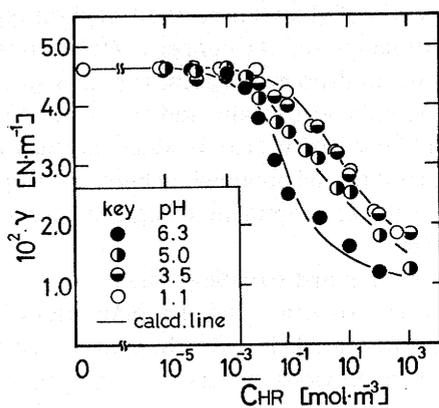


Fig. 1. Interfacial tension of extractant

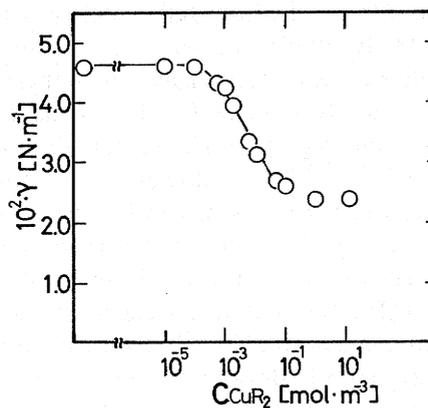


Fig. 2. Interfacial tension of copper complex

Table 1. Values of constants

Adsorption equilibrium constants and interfacial area occupied by unit mole					
K_{HR}	$= 4.65 \pm 1.11$	$[m^3/mol]$	S_{HR}	$= (3.97 \pm 0.91) \times 10^5$	$[m^2/mol]$
$K_{(HR)_2}$	$= 1.80 \pm 0.41$	$[m^3/mol]$	$S_{(HR)_2}$	$= (9.68 \pm 2.22) \times 10^5$	$[m^2/mol]$
K_{CuR_2}	$= 1.60 \pm 0.93$	$[m^3/mol]$	S_{CuR_2}	$= (7.00 \pm 1.86) \times 10^5$	$[m^2/mol]$
K_a	$= 4.79 \pm 1.10$	$[mol/m^2]$	K_D	$= 3.00^{(16)}$	$[m^3/mol]$
K_{ex1}	$= 3.50 \times 10^{-4(16)}$	$[m^3/mol]$	K_{ex2}	$= 1.00 \times 10^{-4(16)}$	$[-]$
Kinetics parameters					
transfer cell		membrane extractor			
k_f	$= (2.44 \pm 2.12) \times 10^{-8}$	$[m/s]$	k_f	$= (5.0 \pm 0.8) \times 10^{-8}$	$[m/s]$
k_r	$= 2.44 \times 10^{-4}$	$[m/s]$	k_r	$= (6.3 \pm 2.7) \times 10^{-4}$	$[m/s]$
k_{Cu}	$= (1.06 \pm 0.21) \times 10^{-5}$	$[m/s]$	D_{Cu}	$= 7.20 \times 10^{-10} *$	$[m^2/s]$
k_{HR}	$= (4.18 \pm 1.56) \times 10^{-5}$	$[m/s]$	$D_{(HR)_2}$	$= 1.62 \times 10^{-9} *$	$[m^2/s]$
k_{CuR_2HR}	$= (1.24 \pm 0.21) \times 10^{-5}$	$[m/s]$	D_{CuR_2HR}	$= 7.07 \times 10^{-10} *$	$[m^2/s]$
Physical properties of hollow-fiber membrane used polytetrafluoroethylene (Japan Goretex Co., Ltd.)					
$2r_1$	$= 9.83 \times 10^{-4} [m]$,	$2r_2$	$= 1.84 \times 10^{-3} [m]$,	$2r_3$	$= 2.40 \times 10^{-3} [m]$
L	$= 0.25 [m]$,	ϵ	$= 0.45 [-]$,	τ	$= 1.60 [-]$
Q_{aq}	$= 2.3 \times 10^{-9} [m^3/s]$,	Q_{org}	$= 4.0 \times 10^{-9} [m^3/s]$		

* Estimated value by the Wilke-Chang correlation.

$$\alpha_1 = \frac{RT[\beta_1 K_{HR}(1 + K_a/C_H)/S_{HR} - K_D K_{(HR)_2}/S_{(HR)_2}]}{\beta_1 \{K_{HR}^2(1 + K_a/C_H)^2 - 4K_D K_{(HR)_2}\}^{1/2}} \quad (7)$$

$$\alpha_2 = \frac{RT[K_D K_{(HR)_2}/S_{(HR)_2} - \beta_2 K_{HR}(1 + K_a/C_H)/S_{HR}]}{\beta_2 \{K_{HR}^2(1 + K_a/C_H)^2 - 4K_D K_{(HR)_2}\}^{1/2}}$$

$$\beta_1 = [K_{HR}(1 + K_a/C_H) + \{K_{HR}^2(1 + K_a/C_H)^2 - 4K_D K_{(HR)_2}\}^{1/2}]/2 \quad (8)$$

$$\beta_2 = [K_{HR}(1 + K_a/C_H) - \{K_{HR}^2(1 + K_a/C_H)^2 - 4K_D K_{(HR)_2}\}^{1/2}]/2$$

In deriving Eq. (6), S_R is assumed to be equal to S_{HR} . As to the copper complex, the relation between γ and C_{CuR_2} in the organic solution is written as follows:

$$\gamma = \gamma_0 - (RT/S_{CuR_2}) \ln(1 + K_{CuR_2} C_{CuR_2}) \quad (9)$$

The values of K_j and S_j were obtained from experimental results of interfacial tension and Eq. (6) or (9) by nonlinear regression using the modified Marquardt method, and are shown in Table 1. The solid curves in

Figs. 1 and 2 were calculated by Eqs. (6) and (9) using the respective constants obtained.

2.2 Initial rates of extraction and stripping in stirred transfer cell

2.2.1 Initial rate of extraction

The initial extraction rate, J_{M0} , was obtained from the relation between extent of copper extracted and extraction time. The effect of pH on J_{M0} is shown in Fig. 3. It is found that J_{M0} varies in inverse proportion to the approximate square of hydrogen-ion activity in the low pH range, but in the high pH range J_{M0} is not affected by a_{H^+} . Therefore, it is anticipated that the extraction mechanism in the high pH range was different from that in the low pH range, namely that the extraction rate was controlled by interfacial reaction in the low pH range and by diffusion of chemical species in the high pH range. The effect of copper concentration, C_{Cu0} , on J_{M0} is shown in Fig. 4. It is found that J_{M0} is proportional to C_{Cu0} . The effect of PC-88A dimer concentration, $C_{(HR)_2,0}$, on J_{M0} is shown in Fig. 5. In the low pH and $C_{(HR)_2,0}$ ranges, J_{M0} varies in proportion to the approximate square of

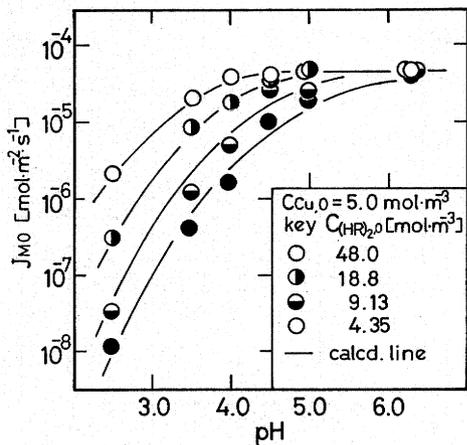


Fig. 3. Effect of pH on initial extraction rate of copper

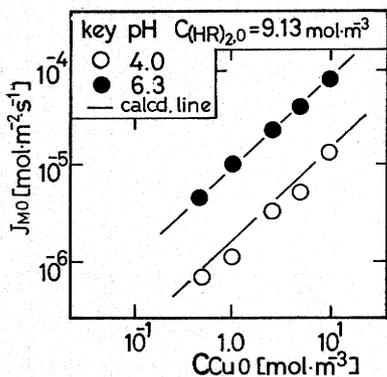


Fig. 4. Effect of initial concentration of copper on initial extraction rate of copper

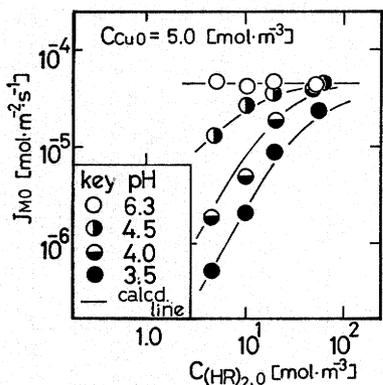


Fig. 5. Effect of initial concentration of extractant dimer on initial extraction rate of copper

$C_{(HR)2,0}$ but is scarcely affected by $C_{(HR)2,0}$ in the high pH and $C_{(HR)2,0}$ ranges.

2.2.2 Initial rate of copper stripping

The effects of a_{H^+} , $C_{CuR_2,2HR_0}$ and $C_{(HR)2,0}$ on the initial stripping rate, J'_{M0} , are shown in Figs. 6 to 8, respectively. From the results, it is evident that the initial stripping rate is proportional to $C_{CuR_2,2HR_0}$ but that J'_{M0} is not affected by either a_{H^+} or $C_{(HR)2,0}$.

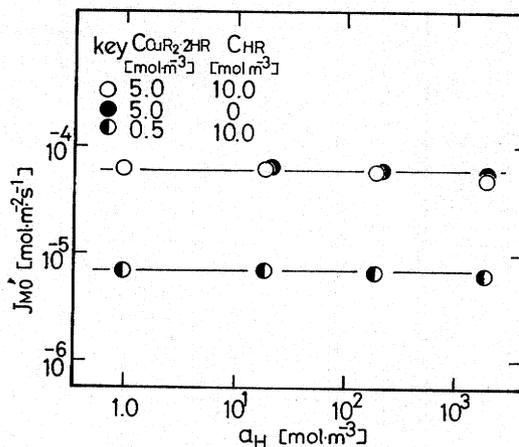


Fig. 6. Effect of activity of hydrogen ion on initial stripping rate of copper

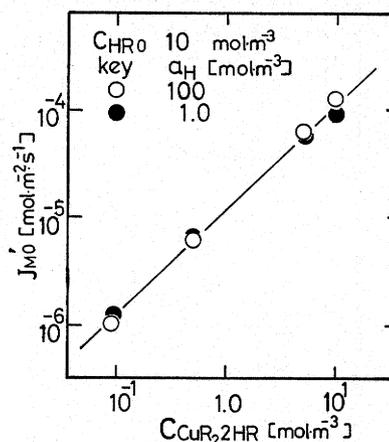


Fig. 7. Effect of initial concentration of copper complex on initial stripping rate

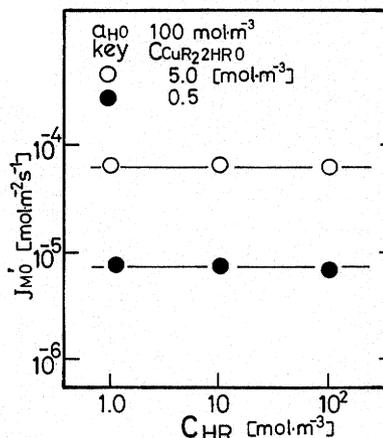


Fig. 8. Effect of initial concentration of free extractant on initial stripping rate

2.3 Extraction and stripping rates of copper in hollow fiber membrane extractor

2.3.1 Extraction rate

The effects of pH, C_{Cu0} and $C_{(HR)2,0}$ on the average extraction rate of copper, \bar{J}_M , which is defined by Eq. (10), are shown in Figs. 9 to 11, respectively.

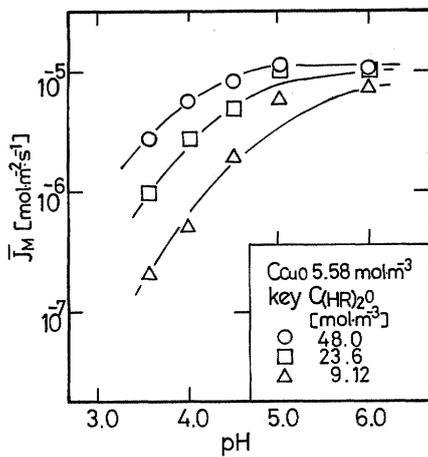


Fig. 9. Effect of pH on \bar{J}_M

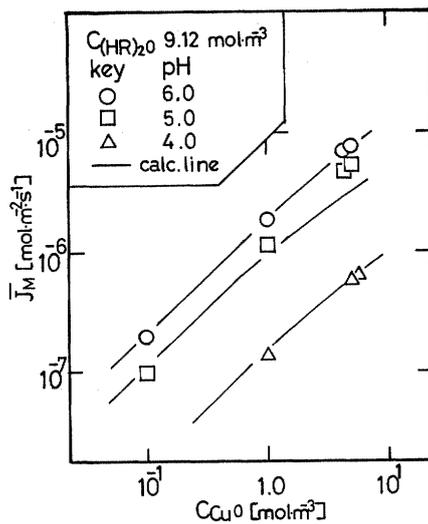


Fig. 10. Effect of initial concentration of copper on \bar{J}_M

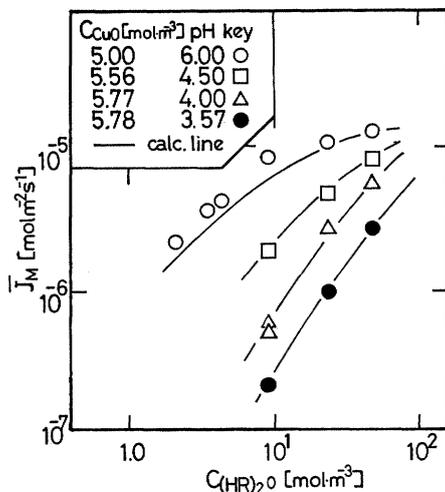


Fig. 11. Effect of initial concentration of extractant dimer on \bar{J}_M

$$\bar{J}_M = C_{Cu0} E Q_{aq} / (2\pi r_1 L) \quad (10)$$

The experimental results are similar to those using the transfer cell except that \bar{J}_M is somewhat small because

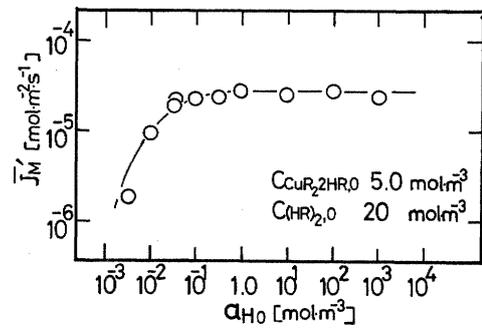


Fig. 12. Effect of activity of hydrogen ion on \bar{J}'_M

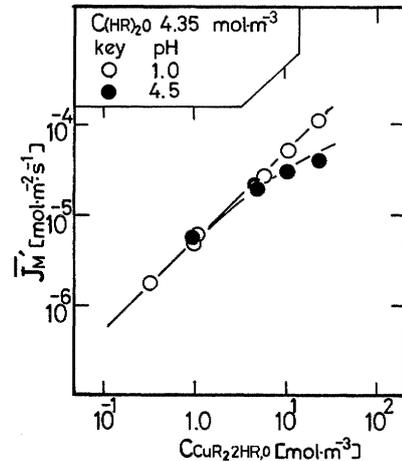


Fig. 13. Effect of initial concentration of copper complex on \bar{J}'_M

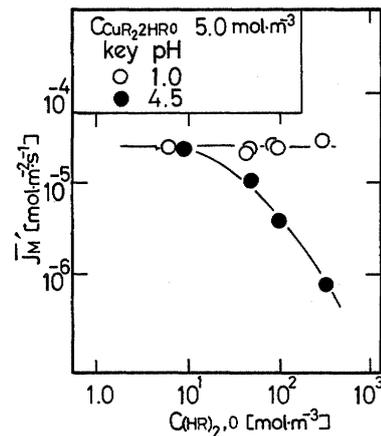


Fig. 14. Effect of initial concentration of free extractant dimer on \bar{J}'_M

of the membrane resistance.

2.3.2 Stripping rate

The effects of a_{H0} , $C_{CuR_22HR_0}$ and $C_{(HR)_2,0}$ on the average stripping rate of copper, \bar{J}'_M , which is defined by Eq. (11), are shown in Figs. 12 to 14.

$$\bar{J}'_M = C_{CuR_22HR_0} E' Q_{aq} / (2\pi r_1 L) \quad (11)$$

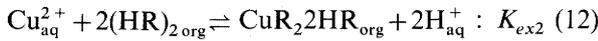
From the result in Fig. 12, it is evident that \bar{J}'_M is not affected by a_{H0} in the range of high a_{H0} , but in the range of low a_{H0} , \bar{J}'_M decreases as a_{H0} decreases, being

affected by the extraction equilibrium. It is also found that \bar{J}'_M is not affected by either $C_{\text{CuR}_2\text{2HR}_0}$ or $C_{(\text{HR})_2\text{O}}$ at pH 1.0, but that at pH 4.5 \bar{J}'_M decreases as $C_{\text{CuR}_2\text{2HR}_0}$ and $C_{(\text{HR})_2\text{O}}$ increase, because of the shielding effect caused by the adsorption of free extractant and/or CuR_2 .

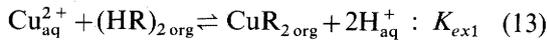
3. Discussion

3.1 Extraction mechanism

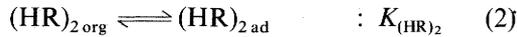
In the previous paper,¹⁷⁾ the extraction equilibrium of copper by PC-88A was shown as follows.



and in the region of low ratio of extractant to copper concentration;



In this paper, the following extraction mechanism is deduced from the experimental results of the extraction equilibrium, the interfacial adsorption equilibrium and the extraction and stripping rates.



From the fact that the reaction order with respect to $C_{(\text{HR})_2}$ was 2.0 power in the low $C_{(\text{HR})_2}$ range, the interfacial reaction step shown by Eq. (15) could be considered as rate-controlling among the interfacial rate steps.¹⁵⁾ Therefore, interfacial reaction rate, R , is written as follows:

$$R = \frac{k_2 K_1 K_{(\text{HR})_2} / S_{\text{CuR}_2} (C_{\text{Cu}_i} C_{(\text{HR})_2\text{i}}^2 / a_{\text{H}_i}^2 - C_{\text{CuR}_2\text{2HR}_i} / K_{\text{ex}})}{(1 + K_{\text{HR}}(1 + K_a / a_{\text{H}_i}) C_{\text{HR}_i} + K_{(\text{HR})_2} C_{(\text{HR})_2\text{i}} + K_{\text{CuR}_2} C_{\text{CuR}_2\text{i}})} \quad (16)$$

Since the extraction rate at steady state is considered to equal the mass transfer rate of each species in the aqueous and organic stagnant layers, the extraction rate is expressed as follows:

$$\begin{aligned} J_M &= k_{\text{Cu}}(C_{\text{Cu}} - C_{\text{Cu}_i}) \\ &= (k_{(\text{HR})_2} / 2)(C_{(\text{HR})_2} - C_{(\text{HR})_2\text{i}}) \\ &= k_{\text{CuR}_2\text{2HR}}(C_{\text{CuR}_2\text{2HR}} - C_{\text{CuR}_2\text{2HR}_i}) \end{aligned} \quad (17)$$

The activity of hydrogen ion adjacent to the interface, a_{H_i} , is considered to be equal to the bulk concentration, a_{H} , on account of the buffer solution.

3.2 Analysis of initial rates of extraction and stripping in stirred transfer cell

Since in the initial period of copper extraction the term of reverse reaction in Eq. (16) is negligibly small as compared with that of forward reaction, the initial extraction rate, R_0 , is expressed as follows:

$$R_0 = \frac{k_2 K_1 K_{(\text{HR})_2} / S_{\text{CuR}_2} (C_{\text{Cu}_i} C_{(\text{HR})_2\text{i}}^2 / a_{\text{H}_0}^2)}{1 + K_{\text{HR}}(1 + K_a / a_{\text{H}_0}) C_{\text{HR}_i} + K_{(\text{HR})_2} C_{(\text{HR})_2\text{i}}} \quad (16')$$

$$\begin{aligned} J_{M0} &= k_{\text{Cu}}(C_{\text{Cu}0} - C_{\text{Cu}_i}) \\ &= (k_{(\text{HR})_2} / 2)(C_{(\text{HR})_20} - C_{(\text{HR})_2\text{i}}) = R_0 \end{aligned} \quad (17)'$$

The values of k_f , k_{Cu} , $k_{(\text{HR})_2}$ and $k_{\text{CuR}_2\text{2HR}}$ could be evaluated from the experimental results of J_{M0} and the equations above by non-linear regression, and are shown in Table 1. The solid curves shown in Figs. 3 to 5 and Figs. 6 to 8 are calculated by using Eqs. (16)' and (17)'. The calculated results agree with the experimental ones.

3.3 Simulation of relation between extent of copper extracted and time in stirred transfer cell

To confirm the validity of the diffusion model with interfacial reaction in the range of high extent of copper extracted, the relation between extent of copper extracted and time was calculated by using Eqs. (16) and (17). Mass balances of the species in the aqueous and organic solutions are expressed as follows:

$$\begin{aligned} -V_{\text{aq}} dC_{\text{Cu}}/dt &= -(V_{\text{org}}/2) dC_{(\text{HR})_2}/dt \\ &= V_{\text{org}} dC_{\text{CuR}_2\text{2HR}}/dt = A \cdot J_M \end{aligned} \quad (18)$$

Using the initial conditions and the values shown in Table 1, Eqs. (16), (17) and (18) were simultaneously solved by the Runge-Kutta-Gill method to obtain the extent of copper extracted.

Figures 15 and 16 show the fit between E_{calc} and E_{obs} , and that between E'_{calc} and E'_{obs} for the experimental results of extraction and stripping, respectively, confirming close agreement between the observed and calculated results over a wide range of the extent of copper extracted and stripped.

3.4 Application of diffusion model with interfacial reaction to hollow fiber extractor

As mentioned above, it is important to know what affects the permeation rate through the porous membrane of the hollow fiber. To obtain k_f and k_r , the experimental results for the hollow fiber membrane extractor were analyzed by the diffusion model with interfacial reaction, taking account of the laminar velocity distributions of the aqueous and organic solutions which flow along the hollow fiber.^{21,22)} The solid curves shown in Figs. 9 to 14 are the calculated results. Close agreement between the observed and the calculated results is obtained over a wide range of experimental conditions. The ratio of k_f to k_r gives a value of the extraction equilibrium constant. The value thus obtained k_f/k_r , is 0.8×10^{-4} and it agrees with K_{ex} , 1×10^{-4} , shown in Table 1. Also, the values of both k_f and k_r agree with those for the transfer cell, shown in Table 1, within experimental error.

Conclusion

Kinetic studies of extraction and stripping of copper with 2-ethylhexyl phosphonic acid mono-2-

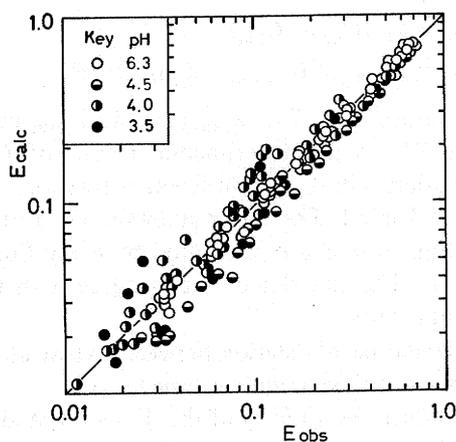


Fig. 15. Comparison of experimental results with calculated results of extent of copper extraction in stirred transfer cell

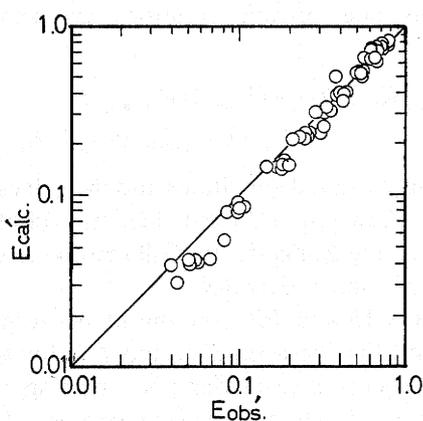


Fig. 16. Comparison of experimental results with calculated results of extent of copper stripped in stirred transfer cell

ethylhexyl ester were carried out by using both the stirred transfer cell and the hollow fiber membrane extractor, along with a study of the interfacial adsorption equilibria of the extractant and the copper complex between the aqueous and organic solutions.

From the experimental results of the interfacial adsorption equilibrium, it was concluded that both monomer and dimer species of the extractant are adsorbed at the interface, and the interfacial adsorption equilibrium constants and the interfacial area occupied by unit mole of the extractant and the copper complex were obtained.

From the experimental results of the kinetic study, a diffusion model with interfacial reaction was presented, where the step in which the extraction species, $\text{CuR}_2\text{2HR}$ is formed at the interface and diffuses to the bulk organic solution is the rate-determining one. The values of constants in the rate equations were obtained from the experimental results at the early stage of extraction by non-linear regression. Furthermore, the relations between the extent of copper extracted and time were simulated over a wide

range of experimental conditions to confirm the fit between the observed and calculated results.

Similarly, the experimental results for the hollow fiber membrane extractor were explained by the same diffusion model with interfacial reaction as in the transfer cell, taking account of the laminar velocity distributions of the aqueous and organic solutions which flow along the hollow fiber.

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Nomenclature

A	= interfacial area	$[\text{m}^2]$
a_{H}	= activity of hydrogen ion	$[\text{mol}/\text{m}^3]$
C_j	= concentration of species j ($j = \text{Cu}, (\text{HR})_2, \text{CuR}_2\text{2HR}$)	$[\text{mol}/\text{m}^3]$
D_j	= Diffusivity of species j	$[\text{m}^2/\text{s}]$
$E^{(s)}$	= extent of copper extracted (stripped)	$[-]$
$J_M^{(s)}$	= extraction (stripping) rate of copper	$[\text{mol}/\text{m}^2 \text{ s}]$
K_a	= acid dissociation constant of extractant	$[\text{mol}/\text{m}^3]$
K_D	= dimerization constant of extractant	$[\text{m}^3/\text{mol}]$
K_{ex}	= extraction equilibrium constant	$[-]$
K_j	= adsorption equilibrium constant of species j	$[\text{m}^3/\text{mol}]$
K_1	= equilibrium constant defined by Eq. (12)	$[\text{mol}/\text{m}^3]$
k_f	= overall extraction rate	$[\text{m}/\text{s}]$
k_r	= overall stripping rate	$[\text{m}/\text{s}]$
k_j	= mass transfer coefficient of species j	$[\text{m}/\text{s}]$
k_2	= forward reaction rate constant of Eq. (13)	$[\text{m}^2/\text{mol}]$
L	= effective length of hollow fiber	$[\text{m}]$
Q	= volumetric flow rate	$[\text{m}^3/\text{s}]$
$R^{(s)}$	= interfacial extraction (stripping) rate	$[\text{mol}/\text{m}^2 \text{ s}]$
r_1	= inner radius of hollow fiber	$[\text{m}]$
r_2	= outer radius of hollow fiber	$[\text{m}]$
r_3	= inner radius of membrane extractor	$[\text{m}]$
S_j	= interfacial area occupied at interface by unit mole of species j	$[\text{m}^2/\text{mol}]$
V	= volume	$[\text{m}^3]$
α	= constant defined by Eq. (7)	$[\text{N}/\text{m}]$
β	= constant defined by Eq. (8)	$[\text{m}^3/\text{mol}]$
γ	= interfacial tension	$[\text{N}/\text{m}]$
ε	= porosity of hollow fiber	$[-]$
τ	= tortuosity of hollow fiber	$[-]$

<Subscripts>

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

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