

EXTRACTION KINETICS OF COPPER WITH LIQUID SURFACTANT MEMBRANES CONTAINING LIX65N AND NONIONIC SURFACTANT

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Using a newly synthesized surfactant, a kinetic study of copper extraction by liquid surfactant membranes containing anti-2-hydroxy-5-nonylbenzophenone oxime was carried out in a stirred tank, along with studies of the extraction equilibrium of copper with the extractant organic solution containing the surfactant and adsorption equilibrium of the surfactant between the organic and aqueous solutions at 303 K.

The extraction rate by liquid surfactant membranes was analyzed by an interfacial reaction model between the carrier adjacent to the interface and the 1:1 copper chelate complex adsorbed at the interface. Furthermore, the change of extent of copper extracted with time was simulated by use of the constants of adsorption equilibrium and the interfacial reaction rate obtained from the analysis.

Introduction

Separation by liquid membranes is an attractive approach to the recovery of valuable substances from very dilute solutions. For the recycling of industrial resources or energy conservation in the field of hydrometallurgical and waste water treating processes, practical application of the membrane process is anticipated.^{1,10,23} Among them, the liquid surfactant membrane (LSM) process has already been applied as an industrial process to remove zinc from low-concentration waste water at a textile plant in Austria.⁵

Though it is well known that the surfactant plays an important role in the LSM process,¹⁹ the effects of the surfactant on the process have not been made clear. Teramoto *et al.*²² and Lorbach *et al.*¹⁵ developed an excellent mass transfer model for a LSM system which took into account complex elementary processes, but there is no model that considers the adsorption of surfactant. In general, as the con-

centration of the surfactant is increased to stabilize the LSM the rate of metal extraction is decreased.^{8,21} Mikuchi and Osseo-Asare reported that Span 80 causes a decrease in the rate of interfacial chemical reaction by its preferential adsorption at the interface of W/O emulsion.¹⁷ Gu also reported that the interfacial surfactant layer formed by ECA 4360 (Polyamine) becomes a barrier to mass transfer.⁷ However, the effect of surfactant on the extraction rate in the LSM process has not been clarified. One of the main reasons is that commercial surfactants (e.g., Span 80 or Polyamine), which are mixtures of more than one compound,¹⁶ have been used in all experiments, and besides their properties are not known. So it is desirable to use pure surfactant to elucidate the effect of surfactant on the extraction rate. In a previous paper,⁶ we reported the development of new surfactants, and it was confirmed that a derivative of glutamic acid dioleylester (abbreviated as 2C₁₈A⁹GE) formed the most suitable emulsion. In the present paper, the extraction of copper by LSM containing the active component of LIX65N, 2-hydroxy-5-nonylbenzophenone oxime (abbreviated as HNBPO),

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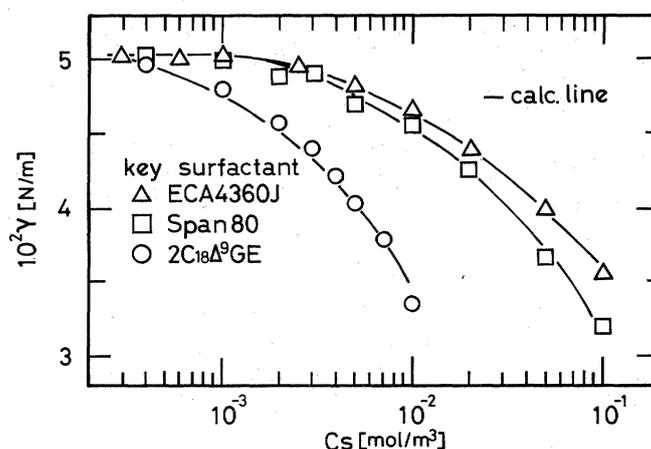


Fig. 2. Interfacial tension of surfactants

adsorption equilibrium of surfactant is expressed as

$$Sf_{org} \rightleftharpoons Sf_{ad} : K_s \quad (1)$$

The relation between interfacial tension and the amount of surfactant adsorbed at the interface is expressed by Gibbs' adsorption equation. Assuming a Langmuir adsorption isotherm between the amount of surfactant adsorbed and the bulk concentration of surfactant, C_s , the relation between interfacial tension, γ , and C_s at temperature T is expressed as

$$\gamma = \gamma_0 - (\mathcal{R}T/S_{Sf}) \ln(1 + K_s C_s) \quad (2)$$

where γ_0 is the interfacial tension between *n*-heptane and the aqueous solution (in this study, $\gamma_0 = 0.0502$ N/m). The values of K_s and S_{Sf} are obtained from the experimental results for the interfacial tension and Eq. (2) by nonlinear regression. The results are listed in Table 2. The solid curves in Fig. 2 were calculated by Eq. (2) using the constants in Table 2.

2.2 Extraction equilibrium of copper with LIX65N *n*-heptane solution containing surfactants

Extraction equilibrium of copper with the extractant LIX65N is expressed as follows.¹⁴⁾



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

$$K_{ex} = C_{CuR_2} C_H^2 / C_{Cu} C_{HR}^2 \quad (4)$$

where C_{Cu} is the concentration of free cupric ion, which can be calculated by considering the formation of copper-acetate complex.¹⁴⁾ The distribution constant of copper, D , is defined as

$$D = C_{CuR_2} / C_{Cu} \quad (5)$$

From Eqs. (4) and (5), the following relation can be obtained.

$$\log D = 2 \log(C_{HR} / C_H) + \log K_{ex} \quad (6)$$

The experimental data are arranged in Fig. 3 accord-

Table 2. Adsorption equilibrium constant and interfacial area occupied by unit mole of each surfactant in *n*-heptane

Surfactant	K_s [m ³ /mol]	S_{Sf} [m ² /mol]	(Å/molecule)
Span 80	52 (±6.3)	2.41 (±0.31) × 10 ⁵	(40.2)
ECA4360J	49 (±8.1)	3.13 (±0.26) × 10 ⁵	(52.2)
2C ₁₈ A ⁹ GE	187 (±31)	2.16 (±0.71) × 10 ⁵	(36.0)

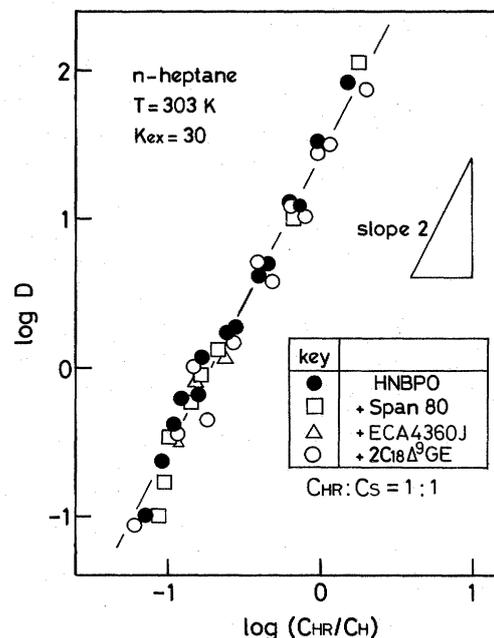


Fig. 3. Effect of surfactants on extraction equilibrium

ing to Eq. (6). Extraction equilibrium was not affected by the surfactants added, so a straight line with a slope of 2 was obtained. From the intercept of this line, the value of $K_{ex} = 30$ was obtained.

However, in the sole case of addition of Polyamine (ECA4360J), the amount of copper extracted in the organic phase tends to decrease if the contact time is more than 3 days. This phenomenon is due to decomposition of oxime in the extractant by Polyamine

surfactant as reported by Draxler *et al.*¹⁾

2.3 Measurement of diameters of W/O emulsion drop and internal water droplet

The measurement results of W/O emulsion drop and internal water droplet diameters are shown in **Table 3**. The mean diameter of W/O emulsion globules obtained in this experiment almost agrees with the value obtained by Kataoka *et al.*⁹⁾ for the system of Span 80 and ECA4360J.

The distribution curves of drop diameters obtained for each surfactant showed logarithmic normal distribution. One emulsion globule contains about 10^5 internal water droplets, and the interfacial area formed by the internal droplets was about one hundred times that formed by the W/O emulsion globules.

2.4 Extraction of copper by LSM

1) Stability of emulsion To estimate of liquid membrane stability, a break-up rate constant, k_b , is defined by Eq. (7) according to the previous paper.⁶⁾

$$\ln(1-\varepsilon) = -k_b \cdot t \quad (7)$$

where ε is the break-up ratio of LSM defined by Eq. (8).

$$\varepsilon = (V_{w,e} \cdot C_{Ni,e}) / (V_{w,in}^0 \cdot C_{Ni,in}^0) \quad (8)$$

The experimental results were arranged by Eq. (7) and the relation between k_b and the concentration of surfactant, C_s , for each surfactant is shown in **Fig. 4**. As is evident from Fig. 4, $2C_{18}\Delta^9GE$ forms a more stable emulsion even in a lower concentration range than do the commercial surfactants Span 80 and ECA4360J. In the previous paper,⁶⁾ it was confirmed that a break-up rate constant remains constant above a critical concentration of surfactant, but it rapidly increases below that concentration. From Fig. 4, it is found that the critical concentrations in this system are about 3 mol/m^3 , 3 wt% (39 mol/m^3) and 5 wt% (42 mol/m^3) for $2C_{18}\Delta^9GE$, Span 80 and ECA4360J respectively.

2) Effect of sulfuric acid concentration in internal aqueous solution on extraction rate **Figure 5** shows the effect of sulfuric acid concentration on the extraction of copper.

From Fig. 5, it is found that the concentration of H_2SO_4 in the internal aqueous phase does not affect the extraction rate if the concentration of acid in the internal aqueous phase is more than 400 mol/m^3 . When the stripping rate at the interface of internal water droplets is much larger than the extraction rate at the interface of emulsion globules, the membrane penetration rate of copper by LSM is determined by the following factors: the mass transfer rate of copper in the external aqueous solution, the rate of interfacial chemical reaction between the extractant and copper at the interface of emulsion globules, and the mass transfer rate of the copper complex in the membrane.

Table 3. Diameters of W/O emulsion drop and internal water droplet

Surfactant	$d_{E32} [10^3 \text{ m}]$	$d_{p32} [10^6 \text{ m}]$
$2C_{18}\Delta^9GE$	$0.308 (\pm 0.081)$	$4.7 (\pm 0.32)$
Span 80	$0.279 (\pm 0.053)$	$4.6 (\pm 0.26)$
ECA4360J	$0.338 (\pm 0.061)$	$7.5 (\pm 0.81)$

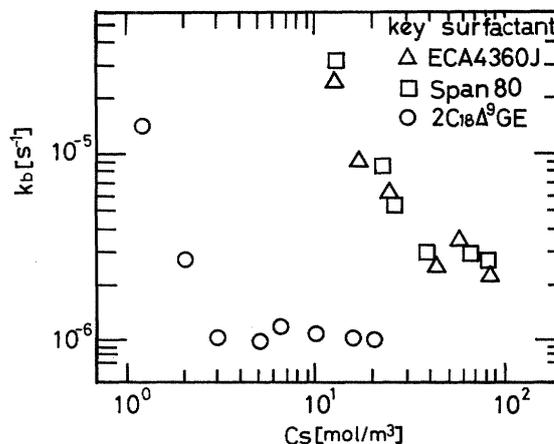


Fig. 4. Effect of surfactant concentration on break-up

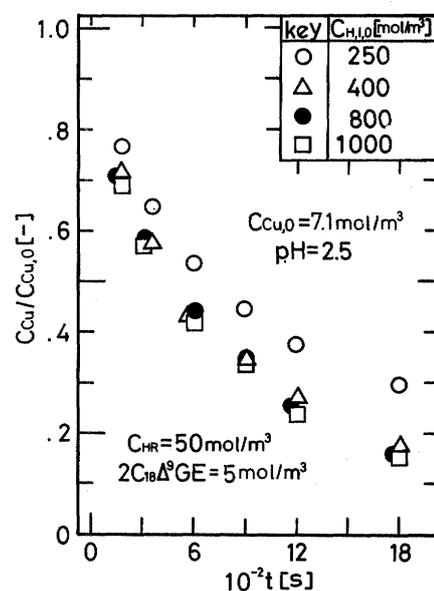


Fig. 5. Effect of sulfuric acid concentration in internal aqueous solution on extraction rate

3) Extraction rate of copper by LSM Assuming uniform dispersion of the water droplets in the emulsion phase, the apparent membrane thickness is considered to be much thinner than $1 \mu\text{m}$ ¹³⁾ in this study. So the mass transfer resistance in the membrane is negligibly small compared with that of the interfacial reaction. Furthermore, assuming a rapid stripping rate as described above, the extractant concentration in the membrane is considered to be equal to the initial concentration. Takahashi *et al.*²¹⁾ investigated the extraction rate of copper by LSM

using Span 80 under the condition that the hydrogen-ion concentration in the external solution is so high that the interfacial reaction is the rate-determining step, and it was confirmed that the concentration of copper complex in the membrane and the diffusion resistance of copper in the external solution are negligibly small. The extraction rates of copper with LIX65N have been already measured by many investigators,^{2,11,14,20,21} and it was elucidated that the rate is proportional to C_{Cu}/a_H . So the extraction rate of copper is assumed to be described by the following expression:

$$R = k_f' \cdot C_{Cu}/a_H \quad (10)$$

The change of concentration of copper ion in the external solution in the stirred tank with time can be shown by the following equation:

$$-dC_{Cu}/dt = a \cdot R \quad (11)$$

If the change of activity coefficient of hydrogen ion, γ_H , is small, and the break-up and swelling of emulsion are negligibly small, the hydrogen-ion activity in the external solution can be expressed as follows:

$$a_H = a_{H,0} + 2\gamma_H(C_{Cu,0} - C_{Cu}) \quad (12)$$

Equation (13) is derived from Eqs. (11) and (12).

$$\begin{aligned} (a_{H,0}/\gamma_H + 2C_{Cu,0}) \ln(C_{Cu}/C_{Cu,0}) + 2(C_{Cu,0} - C_{Cu}) \\ = -(a/\gamma_H)k_f't \end{aligned} \quad (13)$$

The activity coefficient was experimentally determined by Eq. (12) and the value was about 0.86–1.07. In analyzing the experimental results by Eq. (13), the average value of γ_H (for each experiment) and the value of emulsion diameter obtained in 2.3. were used for each experiment. Some results arranged according to Eq. (13) are shown in **Fig. 6**. In all experiments, break-up was measured by using Ni(II) as a tracer, but the break-up was quite small, especially when using 2C₁₈Δ⁹GE, and was less than 0.5%/hr.

The relation between the apparent extraction rate constant, k_f' , and the hydrogen-ion concentration is shown in **Fig. 7**. **Figure 8** shows the relation between k_f' and the initial copper concentration. From Figs. 7 and 8, the validity of Eq. (10) was confirmed.

3. Discussion

3.1 Interfacial reaction model in copper extraction by LSM

In general, the extractant used as a carrier of LSM has a long alkyl chain to suppress dissolution loss to the feed aqueous solution, so it commonly has interfacial activity and the distribution into the aqueous solution is extremely small. For such an extractant, it has been found that the complex formation between a metal ion and the extractant occurs at the oil–water interface.^{3,11,14,18,20,24}

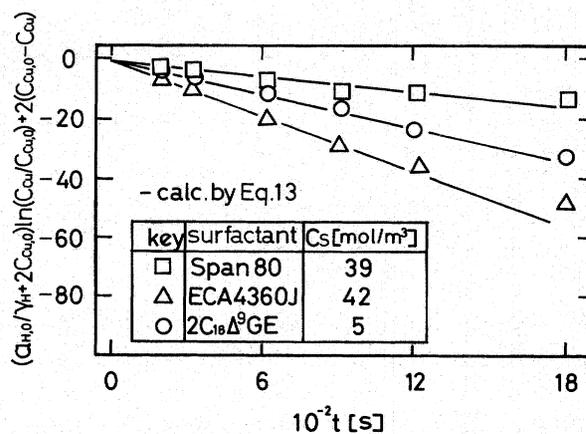


Fig. 6. Determination of k_f' in Eq. (13)

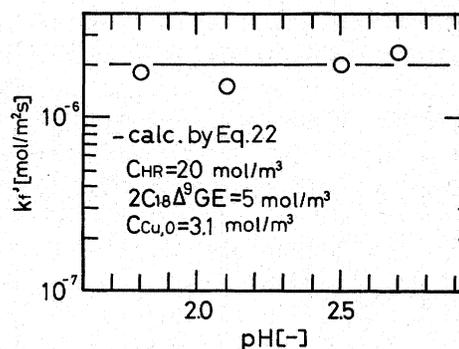


Fig. 7. Relation between k_f' and pH

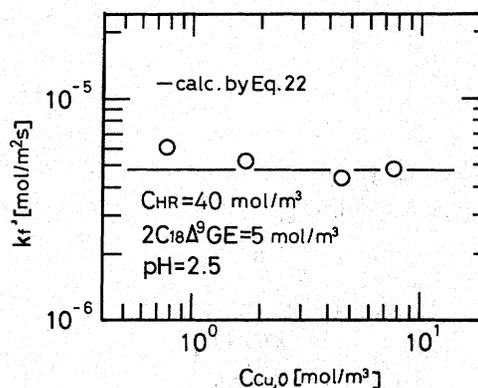


Fig. 8. Relation between k_f' and initial copper concentration

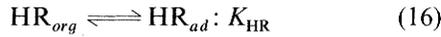
However, in the extraction by LSM, a surfactant that is more interfacially active than such a carrier coexists with the carrier. This is different from solvent extraction. Therefore, the relation between the amounts of carrier and the surfactant adsorbed at the oil–water interface should be determined. The mass balances of carrier and surfactant are expressed as follows.

$$V_{org}C_{HR,org}^0 = V_{org}C_{HR,org} + AC_{HR,ad} \quad (14)$$

$$V_{org}C_{s,org}^0 = V_{org}C_{s,org} + AC_{s,ad} \quad (15)$$

In addition to the adsorption of surfactant, that of

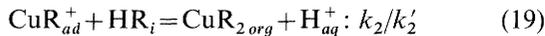
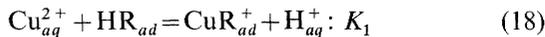
carrier is also taken into account, as follows.



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

$$\left. \begin{aligned} \theta_{HR} &= K_{HR} C_{HR,org} \theta_v \\ \theta_s &= K_s C_{s,org} \theta_v \\ \theta_v + \theta_{HR} + \theta_s &= 1 \end{aligned} \right\} \quad (17)$$

The adsorption equilibrium constant of the carrier was obtained as described in the previous paper,¹⁴⁾ and is $K_{HR} = 1.86[\text{m}^3/\text{mol}]$. The fractions occupied by both the carrier and the surfactant were calculated on the basis of Eq. (17), and the relation between θ_s/θ_{HR} and C_{HR} is shown in Fig. 9 for the case of $2\text{C}_{18}\Delta^9\text{GE}$. As is evident from Fig. 9, the fraction of the surfactant adsorbed at the interface is larger than that of the carrier. We could explain the extraction rate of copper with HNBPO by the interfacial reaction model in which a reaction between the adsorbed extractant and the adsorbed 1:1 copper chelate complex was the rate-determining step. However, in the LSM system the surfactant is preferentially adsorbed at the interface, so it seems difficult for the 1:1 copper chelate complex adsorbed to react with the adjacent adsorbed carrier. So in the extraction by LSM, the following interfacial reaction model shown by Eq. (19) is proposed.



Assuming that the second step in the above reaction scheme is a rate-determining one, the interfacial reaction rate is written as follows:

$$R = \frac{k_2 K_1 (K_{HR}/S_{HR}) C_{HR,org}^2 C_{Cu,i}/C_{H,i} - k'_2 C_{CuR,org} C_{H,i}}{1 + K_{HR} C_{HR,org} + K_{CuR} C_{CuR,org} + K_s C_{s,org}} \quad (20)$$

3.2 Analysis of extraction rate of copper by LSM

Assuming that the stripping rate at the interface of internal water droplets is extremely fast compared with the extraction rate at the interface of emulsion globules and that the carrier in the liquid membrane is considered to be almost constant at the initial concentration, Eq. (20) is rewritten as follows.

$$R = \frac{k_f C_{HR,org}^2 \cdot C_{Cu,i}/C_{H,i}}{1 + K_{HR} C_{HR,org} + K_s C_{s,org}} \quad (21)$$

where $k_f = k_2 K_1 (K_{HR}/S_{HR})$.

An apparent interfacial reaction rate constant, k'_f , previously defined by Eq. (10) can be expressed as a function of the concentration of carrier and surfactant.

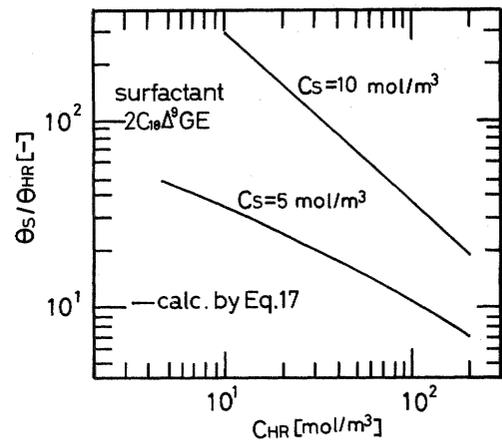


Fig. 9. Fraction occupied by carrier and surfactant at interface

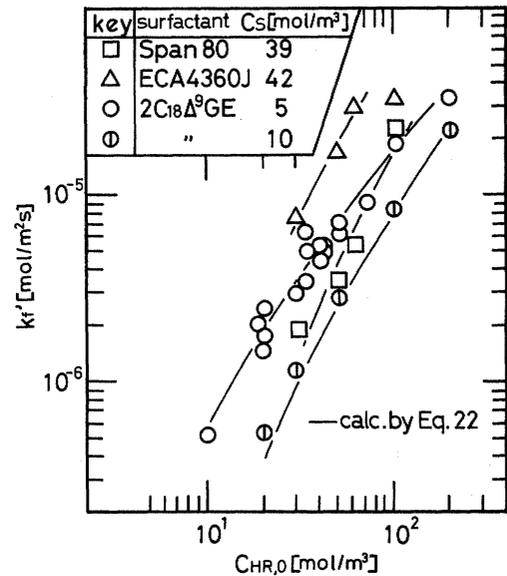


Fig. 10. Relation between k'_f and initial carrier concentration

$$k'_f = \frac{k_f C_{HR,org}^2}{1 + K_{HR} C_{HR,org} + K_s C_{s,org}} \quad (22)$$

The relation between the apparent interfacial reaction rate constant, k'_f , and the carrier concentration is shown in Fig. 10. Figure 11 shows the relation between k'_f and the surfactant concentration. Figure 12 shows the relation of k'_f vs $C_{HR,org}^2/(1 + K_{HR} C_{HR,org} + K_s C_{s,org})$ according to Eq. (22). The value of the unknown constant, k_f , can be evaluated from Fig. 12 by the least squares method, as follows;

$k_f (= k_2 K_1 (K_{HR}/S_{HR}))$ was $(0.90 \pm 0.39) \times 10^{-6} [\text{m}^4/(\text{mol} \cdot \text{s})]$ in the case of $2\text{C}_{18}\Delta^9\text{GE}$. The value of k_f for the commercial surfactants is considered to depend on the lot of the surfactants. The values of k_f of Span 80 and ECA4360J used in this experiment were $(2.1 \pm 0.32) \times 10^{-6}$ and $(1.1 \pm 0.36) \times 10^{-5}$, respectively. The values of k_f obtained become smaller in the order $\text{ECA4360J} > \text{Span 80} > 2\text{C}_{18}\Delta^9\text{GE}$. The main

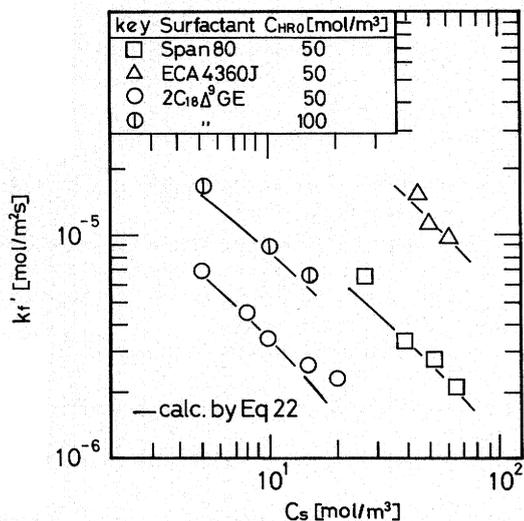


Fig. 11. Relation between k_f' and surfactant concentration

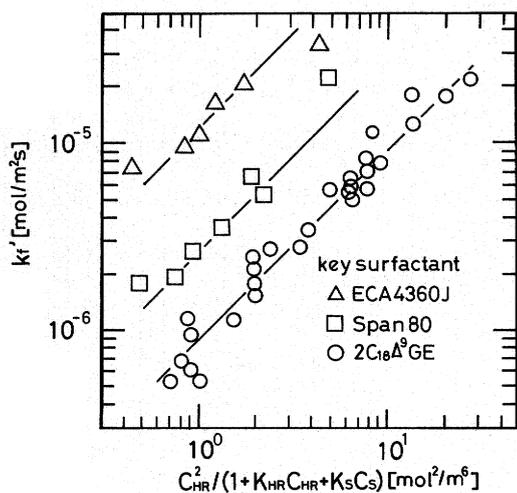


Fig. 12. Determination of k_f in Eq. (22)

reason for the difference in k_f' is that a molecular packing of the surfactant at the interface, that is, an interfacial orientation of the surfactant, affects the reaction rate of Eq. (19). As seen from Table 2, the values of S_{Sf} become smaller in the same order as k_f' . In addition, the degree of interaction between the surfactant and copper was also observed in the order ECA4360J > Span 80 \gg 2C₁₈A⁹GE.¹⁶⁾ Using this value, the change of extent of copper extracted, E , defined by Eq. (23) with time, t , was simulated.

$$E = (C_{Cu,0} - C_{Cu}) / C_{Cu,0} \quad (23)$$

The relation between E and t is rewritten as follows from Eq. (13).

$$-(a_{H,0} + 2C_{Cu,0}) \ln(1 - E) - 2C_{Cu,0} \cdot E = a \cdot k_f' \cdot t \quad (24)$$

where $\gamma_H = 1$ is assumed to simplify the calculation. Using Eqs. (14), (15) and (17), the bulk concentrations of the carrier and the surfactant are obtained, and using these values and the constant, k_f' , an

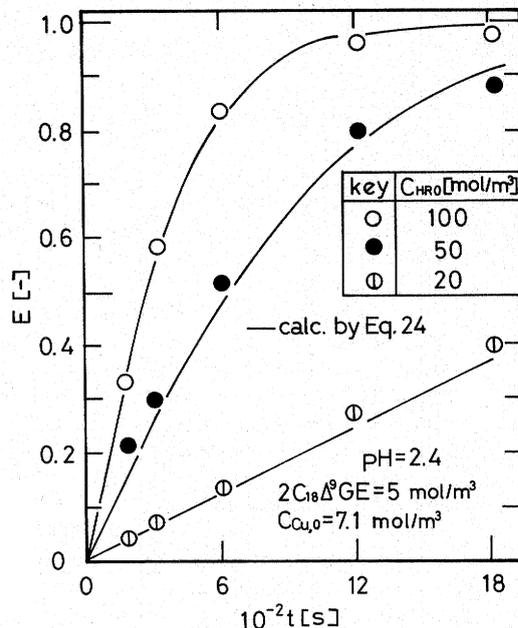


Fig. 13. Simulation of change of copper extracted with time

apparent interfacial rate constant, k_f' , is obtained from Eq. (22). If an initial condition and the interfacial area, a , are given, Eq. (24) is solved by the Newton-Raphson method to obtain the extent of copper extracted.

The calculated results are shown in Fig. 13 as solid lines. Good agreement between the experimental results and the calculated values was obtained over a wide range of extent of copper extracted.

Conclusion

The kinetic studies of the extraction of copper by LSM containing anti-2-hydroxy-5-nonylbenzophenone oxime as the carrier were carried out in the stirred tank, along with the studies of the extraction equilibrium of copper by the extractant organic solution containing the surfactant and the adsorption equilibrium of the surfactants. It was concluded that the rate of copper extraction by LSM is determined by the interfacial reaction between the 1:1 copper chelate complex adsorbed and the carrier adjacent to the interface. The values of constants in the rate equation were obtained from the experimental results. Using these values, the change of extent of copper extracted with time was simulated. It was found that the extraction rate by the LSM is considerably decreased by the preferential adsorption of the surfactant at the interface, so hereafter the improvement of this point should be done by other method.

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Nomenclature

A	= total interfacial area	$[m^2]$
a	= interfacial area defined by $(V_E/V_{w,e})(6/d_E)$	$[1/m]$
a_H	= activity of hydrogen ion	$[mol/m^3]$
C_j	= concentration of species j	$[mol/m^3]$
$C_{j,ad}$	= concentration of species j adsorbed	$[mol/m^2]$
D	= distribution ratio of copper	$[-]$
d_E	= diameter of emulsion globule	$[m]$
d_p	= diameter of internal water droplets in W/O emulsion	$[m]$
K_1	= equilibrium constant of reaction expressed by Eq. (18)	$[-]$
K_{ex}	= equilibrium constant of copper extraction	$[-]$
K_s	= adsorption equilibrium constant of surfactant	$[m^3/mol]$
K_{HR}	= adsorption equilibrium constant of HNBPO	$[m^3/mol]$
k_2	= reaction rate constant of Eq. (19)	$[m^3/mol \cdot s]$
k'_2	= reverse reaction rate constant of Eq. (19)	$[mol \cdot s/m^4]$
k_f	= interfacial reaction constant	$[m^2/mol \cdot s]$
k'_f	= apparent interfacial reaction constant defined by Eq. (10)	$[mol/m^2 \cdot s]$
R	= extraction rate	$[mol/m^2 \cdot s]$
\mathcal{R}	= gas constant	$[Nm/mol \cdot K]$
S_{sf}	= interfacial area occupied by unit mole of surfactant	$[m^2/mol]$
T	= temperature	$[K]$
t	= extraction time	$[s]$
V	= volume of solution	$[m^3]$
ϵ	= break-up ratio of LSM	$[-]$
γ	= interfacial tension	$[N/m]$
γ_H	= activity coefficient of hydrogen ion	$[-]$
θ_j	= fraction of interfacial area occupied by species j	$[-]$
θ_v	= fraction of vacant site	$[-]$
<Subscripts>		
E	= emulsion phase	
e	= external aqueous solution	
HR	= extractant	
i	= bulk solution close to interface	
in	= internal aqueous solution	
j	= species (= Cu^{2+} , H^+ , HR , CuR_2 etc.)	
0	= initial value	
org	= organic phase	
s	= surfactant	
w	= aqueous solution	

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