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EFFECT OF HYDROPHOBICITY OF EXTRACTANT ON EXTRACTION KINETICS OF COPPER WITH *N*-8-QUINOLYLSULFONAMIDE

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Using four kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamides of different alkyl-chain length and their copper chelate complexes, kinetic studies concerning the extraction of copper with extractant and the stripping of copper with sulfuric acid were carried out in a membrane extractor using a hollow fiber.

It was found that the interfacial reaction between the adsorbed copper complex (CuR_{ad}^+) and the adsorbed extractant (HR_{ad}) is a rate-controlling step among the interfacial reaction steps of the extraction and stripping processes, regardless of the alkyl-chain length of the extractants, and that the reaction rate constant of the rate-controlling step is proportional to the equilibrium constant of this reaction for each of the four kinds of extractants.

The validity of a diffusion model with the interfacial reaction was confirmed by agreement of the observed extents of copper extracted and stripped with those calculated over a wide range of experimental conditions.

Introduction

Extractants used for metal extraction in hydro-metallurgical processes are generally amphiphile, having a hydrophobic long alkyl chain to lower the solubility loss into water and a hydrophilic coordinating group to metal. Due to this property, the extractant exhibits interfacial activity and is adsorbed at the oil-water interface. It is well known that the interfacial reaction between the adsorbed extractant and metal very strongly influences the extraction rate.^{1-3,5,6)} However, no systematic investigation concerning the influence of interfacial activity of extractant on the extraction kinetics has been carried out so far.

In a previous paper,⁷⁾ it was reported that the distribution and interfacial adsorption equilibria of five kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamides (henceforth RphSAQ, abbreviated as HR) having different alkyl-chain length were examined. It was found that the equilibrium constants

of the distribution and the interfacial adsorption of these extractants between the aqueous and organic solutions were remarkably affected by the hydrophobicity of the extractant.

In the present study, using the same RphSAQ as those used in the previous paper,⁷⁾ the extraction and stripping rates of copper were measured in a membrane extractor consisting of a hollow fiber. The experimental results were analyzed by a diffusion model for metal extraction with an interfacial reaction, taking account of the velocity distributions of the aqueous solution in the inner part of the hollow fiber and the organic solution in the annulus between the inner surface of the glass tube and the outer surface of the hollow fiber.⁹⁾ The influence of the hydrophobicity of the extractant on the extraction kinetics was examined quantitatively.

1. Experimental

Four kinds of RphSAQ — *N*-8-quinolyl-*p*-*n*-octadecylbenzenesulfonamide, $\text{nC}_{18}\text{H}_{37}\text{phSAQ}$ (henceforth $\text{nC}_{18}\text{phSAQ}$), $\text{nC}_{12}\text{phSAQ}$, $\text{C}_{12}\text{phSAQ}$ and nC_6phSAQ , and their copper chelate complexes (ab-

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breviated as CuR₂)— were synthesized and purified by the same method as described in the previous paper.^{7)*}

The organic solution was prepared by dissolving HR and/or CuR₂ in toluene. The aqueous solution used in the extraction experiment was prepared by dissolving copper nitrate in water and pH of the solution was adjusted by 100 mol/m³ acetic acid-sodium acetate buffer solution. In the range of low pH (pH < 2.8), 100 mol/m³ nitric acid was added to the solution to adjust the pH. The aqueous solution used in the stripping experiment was prepared with sulfuric acid.

The membrane extractor consisting of a hollow fiber and the experimental procedure used in both the experiments were the same as described in the previous paper.⁹⁾

To evaluate the experimental results, the apparent permeabilities of copper in the extraction and the stripping, P_M and P'_M , were defined by the following equations:

$$P_M (= J_M / C_{Cu0}) = E \cdot Q_{aq} / (2\pi r_1 L) \quad (1)$$

$$P'_M (= J'_M / C_{CuR20}) = E' \cdot Q_{org} / (2\pi r_1 L) \quad (2)$$

2. Results

2.1 Extraction rate of copper with RphSAQ

Figure 1 shows the relation between the apparent permeability of copper in the extraction, P_M , and the pH of the aqueous solution. Regardless of the alkyl-chain length of the extractants, the slopes of this relation are 1.0 in the range of low pH, while they approach zero in the range of high pH. As described in the previous papers,^{6,9)} the extraction rate is controlled by the interfacial reaction in the range of low pH and by diffusion of the extractant or copper in the range of high pH. The results shown in Fig. 1 suggest that the effect of the alkyl-chain length of the extractants on the interfacial reaction is more remarkable than those on diffusion.

A similar dependency is seen in Fig. 2; that is, at high pH the effect of the alkyl-chain length of the extractant on P_M is very small, while at low pH the effect becomes large. For nC₁₈phSAQ, the slope of the relation between P_M and C_{HR0} becomes smaller as compared with other extractants in the range of low C_{HR0} . This suggests that the extraction rate is affected by the adsorption of the extractant at the interface.

The experimental results also showed that P_M was independent of C_{Cu0} in the range of low pH, where P_M decreased with increasing alkyl-chain length of the extractant.

* C₁phSAQ, used in the previous equilibrium study, could not be utilized in the present kinetic study because its solubility in toluene is too low to carry out the experiment.

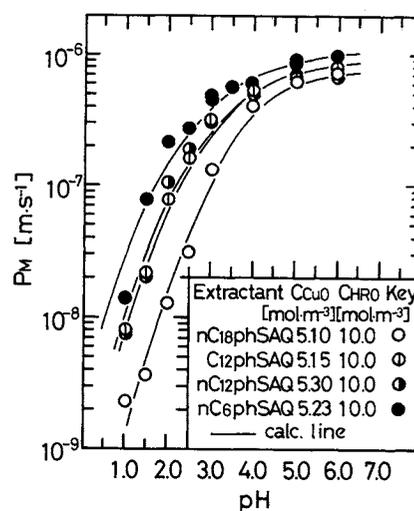


Fig. 1. Relation between P_M and pH of aqueous solution.

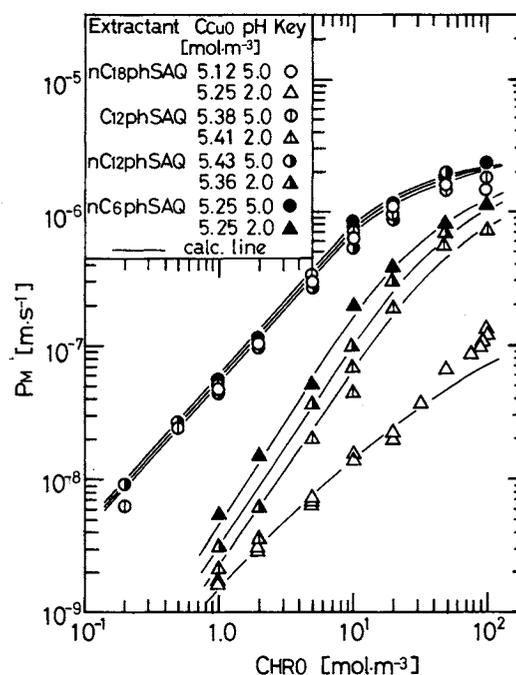


Fig. 2. Relation between P_M and initial concentration of extractant.

2.2 Stripping rate of copper with sulfuric acid

Figure 3 shows the relation between the apparent permeability of copper in the stripping, P'_M , and the initial concentration of the free extractant, C_{HR0} . For the extractants other than nC₁₈phSAQ, P'_M is independent of C_{HR0} in the range of low C_{HR0} , while in the range of high C_{HR0} the slopes of this relation were about -1.0 . However, for nC₁₈phSAQ, the slopes of this relation were about -2.0 under the experimental conditions. This suggests that the shielding effect caused by the adsorption of the free extractant is remarkable.

The experimental results also showed that P'_M was proportional to the initial activity of hydrogen ion, a_{H0} , and that P'_M was independent of C_{CuR20} . These

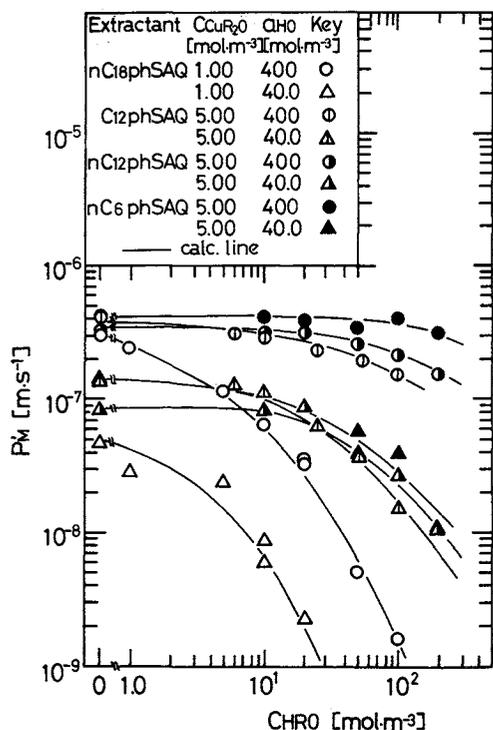
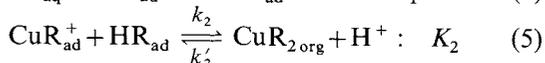
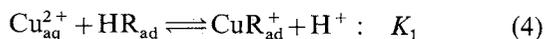
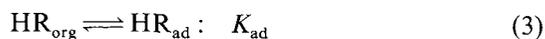


Fig. 3. Relation between P'_M and initial concentration of free extractant.

results agree with those mentioned in the previous paper.¹⁰⁾

3. Discussion

In the previous paper for the extraction and stripping rates in the membrane extractor,⁹⁾ it was clear that the experimental results should be analyzed by using a diffusion model with an interfacial reaction, taking account of the velocity distributions of the aqueous and organic solutions through the inner and outer sides of the hollow fiber. Moreover, as described in previous papers,^{6,10)} the mechanism of copper extraction with RphSAQ and that of stripping of copper with sulfuric acid are expressed by the following interfacial reaction steps:



Using the Langmuir adsorption isotherm and assuming $S_{\text{CuR}} = S_{\text{HR}}$, the rates of interfacial reactions of copper extraction and stripping, R and R' , are expressed as follows:

$$R = \frac{k_f(C_{\text{Cu}}C_{\text{HR}}^2/a_{\text{H}_2\text{O}} - C_{\text{CuR}_2}a_{\text{H}_2\text{O}}/K_{\text{ex}})}{(1 + K_{\text{ad}}C_{\text{HR}} + K_{\text{ad}}K_1C_{\text{Cu}}C_{\text{HR}}/a_{\text{H}_2\text{O}})^2} \quad (6)$$

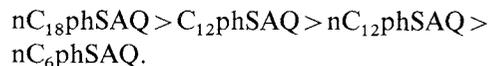
$$R' = \frac{k'_2(C_{\text{CuR}_2}a_{\text{H}_2\text{O}} - K_{\text{ex}}C_{\text{Cu}}C_{\text{HR}}^2/a_{\text{H}_2\text{O}})}{(1 + K_{\text{ad}}C_{\text{HR}})^2} \quad (7)$$

where $k_f (= k_2K_1(K_{\text{ad}}/S_{\text{HR}})^2)$ is the overall reaction rate constant and $K_{\text{ex}} (= K_1K_2(K_{\text{ad}}/S_{\text{HR}})^2)$ is the equilibrium constant of copper extraction shown in previous papers.^{4,8)} In Eq. (7), the term $K_{\text{ad}}K_1C_{\text{Cu}}C_{\text{HR}}/a_{\text{H}_2\text{O}}$ expressing the extent of CuR^+ adsorbed at the interface can be neglected, due to the extremely high concentration of sulfuric acid used as a stripping agent. Since the extents of copper extracted and stripped, E and E' , can be calculated by using the diffusion model with the interfacial reaction of which the rates are expressed by Eqs. (6) and (7), the apparent permeabilities of copper in the extraction and stripping, P_M and P'_M , can be obtained from Eqs. (1) and (2). The values of constants used in the calculation are listed in Table 1.

The unknown constants in Eqs. (6) and (7) are the forward and reverse reaction rate constants, k_2 and k'_2 , and the equilibrium constant of Eq. (4), K_1 . These constants were obtained by the trial-and-error method. The standard deviation, σ , was calculated by the following equation:

$$\sigma = \sqrt{\sum \{(P_{\text{Mobs},i} - P_{\text{Mcalc},i})/P_{\text{Mobs},i}\}^2 / (N-1)} \quad (8)$$

The relation between σ and the estimated overall reaction constant, k_f , and that between σ and the estimated reverse reaction rate constant, k'_2 , are shown in Fig. 4 in the case of nC₁₈phSAQ. From this figure, it is found that σ becomes the minimal value of 0.23 when $k_f = 1.0 \times 10^{-8} \text{ m}^4/(\text{mol} \cdot \text{s})$ and that σ becomes 0.20 when $k'_2 = 1.8 \times 10^{-9} \text{ m}^4/(\text{mol} \cdot \text{s})$. However, K_1 could not be determined by the trial-and-error method. This suggests that the term $K_{\text{ad}}K_1C_{\text{Cu}}C_{\text{HR}}/a_{\text{H}_2\text{O}}$ in Eq. (6) is negligibly small. The constants, k_f and k'_2 , obtained for each RphSAQ are listed in Table 2 along with the minimal values of σ . Solid lines in Figs. 1–3 show the results calculated by using these constants. It is found that the calculated results agree well with the experimental results within the range of experimental error. From Table 2, it is found that the k_f and k'_2 values for each extractant are nearly equal to others. However, in Figs. 2 and 3, the apparent permeabilities of copper in the extraction and stripping, P_M and P'_M , are affected by the adsorption of the extractant at interface, and the extent of influence becomes greater in the order



Considering both the present kinetic study and the equilibrium study in the previous paper,⁷⁾ it is found that RphSAQ having 6–12 carbon atoms in the alkyl group are suitable for extraction of copper, while RphSAQ having 18 carbon atoms in the alkyl group is not a good extractant because of the low solubilities of the extractant and its copper chelate complex in toluene and the shielding effect caused by adsorption

Table 1. Values of constants used for analysis

Extractant	$K_{ad}^{(7)}$ [m ³ /mol]	$S_{HR}^{(7)}$ [m ² /mol]	D_{HR}^* [m ² /s]	$\mathcal{D}_{CuR_2}^*$ [m ² /s]
nC ₁₈ phSAQ	2.25×10^{-1}	3.68×10^5	8.16×10^{-10}	4.99×10^{-10}
C ₁₂ phSAQ	1.98×10^{-2}	3.18×10^5	9.28×10^{-10}	5.67×10^{-10}
nC ₁₂ phSAQ	4.10×10^{-3}	2.97×10^5	9.28×10^{-10}	5.67×10^{-10}
nC ₆ phSAQ	1.58×10^{-3}	2.88×10^5	1.09×10^{-9}	6.66×10^{-10}

$\mathcal{D}_{Cu} = 7.20 \times 10^{-10}$ m²/s, $r_1 = 4.69 \times 10^{-4}$ m, $r_2 = 9.18 \times 10^{-4}$ m, $r_3 = 1.20 \times 10^{-3}$ m, $\varepsilon = 0.45$,⁹⁾ $\tau = 1.60$,⁹⁾
 $L = 0.125, 0.25, 0.50$ m, $Q_{aq} = 0.8 \times 10^{-8} - 3.3 \times 10^{-8}$ m³/s, $Q_{org} = 1.7 \times 10^{-8} - 6.7 \times 10^{-8}$ m³/s

* Estimated value by Wilke-Chang correlation.

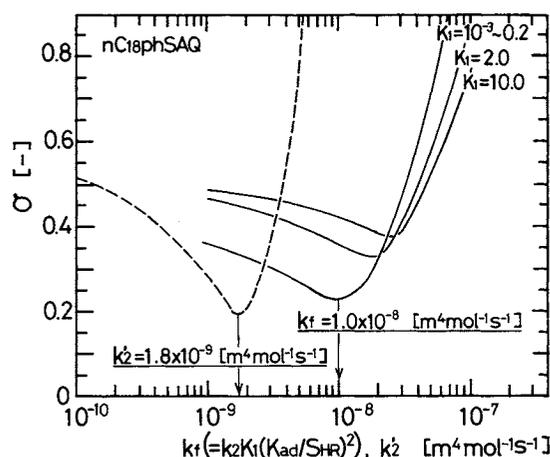


Fig. 4. Relation between standard deviation and estimated overall and reverse reaction rate constants.

Table 2. Reaction rate constants obtained from analysis

Extractant	k_f [m ⁴ /(mol·s)] (σ value)	k_2' [m ⁴ /(mol·s)] (σ value)	k_f/k_2' [—] ($K_{ex}^{4,8}$) [—]
nC ₁₈ phSAQ	1.0×10^{-8} (0.23)	1.8×10^{-9} (0.20)	5.6 (4.6 ± 0.2)
C ₁₂ phSAQ	1.1×10^{-8} (0.14)	4.9×10^{-9} (0.19)	2.3 (3.3 ± 0.3)
nC ₁₂ phSAQ	1.2×10^{-8} (0.19)	2.5×10^{-9} (0.15)	4.8 (5.4 ± 0.2)
nC ₆ phSAQ	3.1×10^{-8} (0.26)	4.6×10^{-9} (0.19)	6.7 (5.2 ± 0.2)
C ₁₂ phSAQ*	$(1.1 \pm 0.1) \times 10^{-8}$	$(4.3 \pm 0.1) \times 10^{-9}$	2.6 ± 0.3

* Values obtained from kinetic study using a stirred transfer cell.^{6,10)}

of extractant at the interface. Thus C₁₂phSAQ, which is the active component of the commercial extractant LIX 34, is considered to be a suitable extractant for hydrometallurgical processing of copper.

The ratio of the overall reaction rate constant, k_f , to the reverse reaction rate constant, k_2' , is considered to be equal to the equilibrium constant of copper extraction, K_{ex} . As was expected, it was found that the K_{ex} value obtained from the extraction equilibrium of copper agrees approximately with the ratio of k_f to k_2' .

Figure 5 shows the relation between the $k_2 K_1$ value calculated by using k_f , K_{ad} and S_{HR} , and the $K_1 K_2$ value calculated by using K_{ex} , K_{ad} and S_{HR} . It is found that the $k_2 K_1$ value is proportional to the $K_1 K_2$ value. This relationship suggests that the k_f value for homologues of *N*-8-quinolylsulfonamide having different alkyl-chain length can be estimated by using K_{ex} , K_{ad} and S_{HR} obtained from equilibrium studies of copper extraction and adsorption of the extractant at the interface.

Figure 6a and **b** respectively compare E_{calc} with E_{obs} and E'_{calc} with E'_{obs} for all experimental data.

Conclusion

Kinetic studies concerning the extraction of copper with four kinds of *N*-8-quinolylsulfonamide of different alkyl-chain length and the stripping of copper with sulfuric acid were carried out in a membrane extractor consisting of a hollow fiber. The following results were obtained.

(1) The experimental results for both the extraction and stripping rates can be explained by a diffusion model for metal extraction with an interfacial reaction, taking account of the velocity distributions of the aqueous and organic solutions in the extractor.

(2) The overall reaction rate constant, k_f , and the reverse reaction rate constant, k_2' , are not influenced by the hydrophobicity of the extractant, while the $k_2 K_1$ value calculated by using k_f , the adsorption equilibrium constant, K_{ad} , and the interfacial area occupied by unit mole of extractant, S_{HR} , is proportional to the $K_1 K_2$ value calculated by using the extraction equilibrium constants, K_{ex} , K_{ad} and S_{HR} .

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Nomenclature

- a_{H^+} = activity of hydrogen ion [mol/m³]
- C_j = concentration of species j ($j = Cu^{2+}$, HR, CuR₂) [mol/m³]
- \mathcal{D}_j = diffusivity of species j ($j = Cu^{2+}$, HR, CuR₂) [mol/m³]

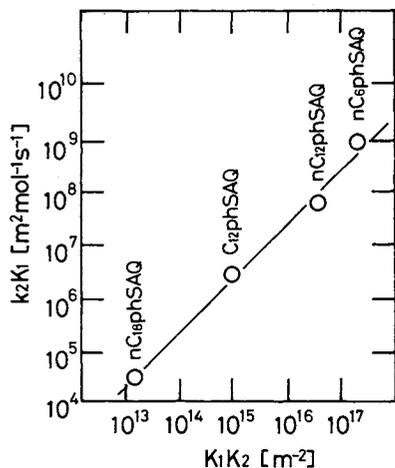


Fig. 5. Relation between k_2K_1 value and K_1K_2 value.

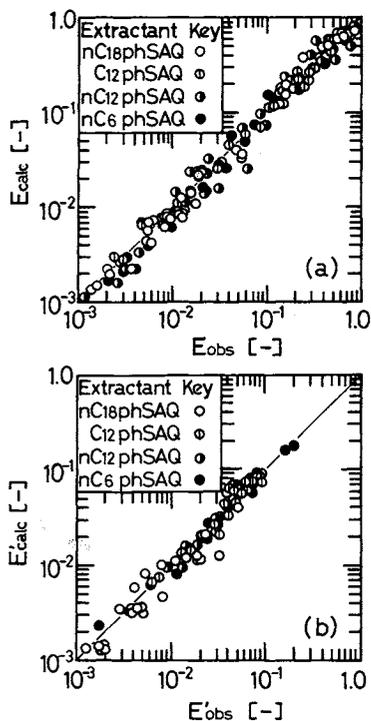


Fig. 6. Comparison of experimental results with calculated results of extent of copper extracted (a) and stripped (b).

E	= extent of copper extracted	[—]
E'	= extent of copper stripped	[—]
K_{ad}	= adsorption equilibrium constant of HR	[—]
K_{ex}	= equilibrium constant of copper extraction	[m ³ /mol]
K_1	= equilibrium constant of Eq. (4)	[—]
K_2	= equilibrium constant of Eq. (5)	[1/m ²]

k_f	= overall extraction rate constant	[m ⁴ /(mol·s)]
k_2	= rate constant of forward reaction of Eq. (5)	[m ² /(mol·s)]
k'_2	= rate constant of reverse reaction of Eq. (5)	[m ⁴ /(mol·s)]
L	= length of membrane extractor	[m]
N	= number of data	[—]
P_M	= apparent permeability of copper in extraction	[m/s]
P'_M	= apparent permeability of copper in stripping	[m/s]
Q	= volumetric flow rate	[m ³ /s]
R	= interfacial extraction rate	[mol/(m ² ·s)]
R'	= interfacial stripping rate	[mol/(m ² ·s)]
r_1	= inner radius of hollow fiber	[m]
r_2	= outer radius of hollow fiber	[m]
r_3	= inner radius in membrane extractor	[m]
S_{HR}	= interfacial area occupied by unit mole of HR	[m ² /mol]
ε	= porosity of hollow fiber	[—]
τ	= tortuosity of hollow fiber	[—]
σ	= standard deviation	[—]

<Subscripts>

ad	= adsorption state
aq	= aqueous solution
calc	= calculated value
0	= initial state
obs	= observed value
org	= organic solution

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