CATALYTIC EFFECT OF BISOLEYLPHOSPHORIC ACID ON COPPER EXTRACTION WITH *N*-8-QUINOLYLSULFONAMIDE

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The extraction kinetics of copper with *N*-8-quinolyl-*p*-hexylbenzenesulfonamide was studied in the presence of acidic and neutral organophosphorus compounds using a hollow-fiber membrane extractor. It was found that in the presence of bisoleylphosphoric acid the permeation rate of copper through the membrane is significantly accelerated, while in the presence of the other organophosphorus compounds, i.e., bis-2-ethylhexylphosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester and trioctylphosphate, the permeation rate was not enhanced except at high concentration of the additive agents. From the kinetic data, the catalytic mechanism of the copper extraction was inferred.

Introduction

Solvent extraction is used widely in hydrometallurgy and waste water treatment from the viewpoint of energy saving. The success of LIX 64N, which is a mixture of LIX 65N, an aromatic β -hydroxyoxime, with a small amount of LIX 63, an aliphatic α -hydroxyoxime, as a commercial extractant for copper is due to the high selectivity against iron and the high extraction rate of copper. As is well known, LIX 65N alone has a slower extraction rate than the other extractants such as organophosphorus compounds and high molecular-weight amines. Thus LIX 63 was added to LIX 65N to enhance the extraction rate.

The enhancement effects on the rate of extraction of copper with β -hydroxyoximes were studied, using α -hydroxyoxime^{1-3,5,6,15)} and cation exchangers

having strong interfacial activity such as bisalkylphosphoric acid⁷⁾ and alkylcarboxylic acid^{4,14)} as an additive. Although many works have been reported, disagreement exists about the catalytic extraction mechanism. The main reason is that the extractants used contain a small amount of impurities. Though it is well known that addition of a small amount of the compounds influences the extraction rate, commercial reagents have been used without purification.

Komasawa and Otake⁷⁾ studied the catalytic effect of bis(2-ethylhexyl)phosphoric acid (D2EHPA) on the extraction kinetics of copper with purified LIX 65N and proposed a catalytic extraction mechanism in which D2EHPA acts as a phase-transfer catalyst.

In a previous paper,¹⁷⁾ the extraction rate of copper with *N*-8-quinolylalkylbenzenesulfonamides was measured by use of a hollow-fiber membrane extractor. The experimental results were explained by the diffusion model accompanied by an interfacial reaction, and it was concluded that the rate-

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determining step was the reaction between adsorbed extractant and adsorbed intermediate complex. In the present work, the rate of extraction of copper with *N*-8-quinolyl-*p*-hexylbenzenesulfonamide (abbreviated as nC₆phSAQ and denoted as HR) in the presence of some neutral and acidic organophosphorus compounds was measured, using a hollow-fiber membrane extractor at 303 K, together with measurements of the extraction equilibrium of copper and the interfacial adsorption equilibrium of bisoleylphosphoric acid. The effect of organophosphorus compounds on the extraction kinetics of copper was examined.

1. Experimental

N-8-quinolyl-*p*-hexylbenzenesulfonamide was prepared according to the procedure mentioned previously.¹¹⁾ Additives (denoted as HL) used were bisoleylphosphoric acid (hereafter abbreviated as DOLPA), bis-2-ethylhexylphosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexylester (PC-88A) and trioleylphosphate (TOLP). DOLPA was synthesized from phosphoryl chloride and oleyl alcohol. The other organophosphorus compounds were used without further purification.

The apparent molecular weight of DOLPA in toluene diluent was measured by vapor-phase osmometry. The equilibrium studies on the interfacial adsorption of HL and on copper extraction from acetate buffer solution with DOLPA were carried out by the usual method^{11,16)} at 303 K.

The membrane extractor for measuring the extraction rate of copper consists of a glass tube and a hollow fiber made of polytetrafluoroethylene (Japan Goretex Co. Ltd.). The inner and outer diameters, porosity and tortuosity factor of the hollow fiber were measured¹⁰⁾ and are shown in Table 1. The kinetic study of copper extraction with HR in the presence of HL was carried out by the same procedure as described previously.¹⁷⁾ The apparent permeability of copper through the membrane, P_M , is expressed as follows:

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

where J_M is the average extraction rate of copper, E is the extent of copper extracted and Q_{aq} is the volumetric flow rate of aqueous solution. And r_1 and L are the inner diameter and the contact length of the hollow fiber.

2. Results

2.1 Dimerization of DOLPA

Acidic organophosphorus compounds are well known to dimerize in nonpolar solvents.¹²⁾ The dimerization of DOLPA in toluene is expressed by Eq. (2).

Table 1. Characteristic values of membrane extractor

inner diameter of hollow fiber $2r_1$	$=9.83 \times 10^{-4}$ m
outer diameter of hollow fiber $2r_2$	$=1.84 \times 10^{-3}$ m
inner diameter of membrane extractor $2r_3$	$=2.40 \times 10^{-3}$ m
length of hollow fiber L	$=0.25$ m
porosity of hollow fiber ε	$=0.45$
tortuosity factor of hollow fiber τ	$=1.60$

Fig. 1. Determination of dimerization constant of DOLPA in toluene

Fig. 2. Interfacial tension between toluene solution containing DOLPA and aqueous solution

Total concentration of DOLPA, $\bar{C}_{HL}$, and the sum of monomer and dimer concentrations in the diluent, C^* , which is obtained experimentally,¹³⁾ are expressed as follows.

$$\bar{C}_{HL} = C_{HL} + 2C_{(\text{HL})_2} \quad (3)$$

$$C^* = C_{HL} + C_{(\text{HL})_2} \quad (4)$$

From Eqs. (3) and (4), the dimerization constant, K_d , is obtained by the following equation.

$$K_d = C_{(\text{HL})_2}/C_{HL}^2 = (\bar{C}_{HL} - C^*)/(2C^* - \bar{C}_{HL})^2 \quad (5)$$

The experimental result is shown in Fig. 1. From the slope of Fig. 1, $K_d = 1.84 \text{ m}^3/\text{mol}$ was obtained.

2.2 Interfacial tension of DOLPA

The relation between interfacial tension, γ , and total concentration of DOLPA is shown in Fig. 2 for various pH values. The result suggests that DOLPA has interfacial activity.

The interfacial adsorption equilibria are expressed as follows:

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 molecules adsorbed and their bulk concentration in toluene, γ is written as follows.⁹⁾

$$\gamma = \gamma_0 - (RT/S_{HL}) \ln \{1 + (1 + K'_a/a_H)K_{HL}C_{HL}\} \quad (8)$$

The values of K_{HL} , S_{HL} and K'_a obtained from Eq. (8) and the experimental results shown in Fig. 2 by non-linear regression are listed in Table 2. The solid curves in Fig. 2 were calculated by Eq. (8) using the constants obtained. From Table 2, it is found that the adsorption equilibrium constant of DOLPA is 3000 times that of nC₆phSAQ.

2.3. Extraction equilibrium of copper with DOLPA and effect of DOLPA on extraction equilibrium of copper with nC₆phSAQ

The extraction equilibrium of copper with acidic organophosphorus extractant is expressed as follows.¹¹⁾

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

$$K_{ex} = C_C a_H^2 / C_{Cu} C_{(HL)_2}^2 \quad (10)$$

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

$$D = C_C / C_{Cu} \quad (11)$$

From Eqs. (10) and (11), the following relation can be obtained.

$$\log D = 2 \log (C_{(HL)_2}/a_H) + \log K_{ex} \quad (12)$$

The experimental data are arranged in Fig. 3 according to Eq. (12). The extraction equilibrium constant of copper with DOLPA is listed also in Table 2, along with that with nC₆phSAQ.

Figure 4 shows the effect of DOLPA on the extraction equilibrium of copper with nC₆phSAQ. It is confirmed that DOLPA has no influence on the extraction equilibrium of copper with nC₆phSAQ. This is due to the large difference in K_{ex} between the extractant and the additive.

Table 2. Values of constants used for analysis

—DOLPA—	
$K_{HL} = (1.19 \pm 0.05) \times 10^4 \text{ m}^3/\text{mol}$	
$S_{HL} = (3.39 \pm 0.18) \times 10^5 \text{ m}^2/\text{mol}$ ($56 \pm 3 \text{ \AA}^2/\text{molecule}$)	
$K'_a = (8.32 \pm 0.69) \times 10^{-2} \text{ mol/m}^3$ ($\text{p}K'_a = 4.08$)	
$K_d = 1.84 \pm 0.16 \text{ m}^3/\text{mol}$	
$K_{ex} = (1.65 \pm 0.17) \times 10^{-3}$	
—nC ₆ phSAQ— ^{16,17)}	
$k_f = 3.1 \times 10^{-8} \text{ m}^4/(\text{mol} \cdot \text{s})$	
$K_{HR} = (1.58 \pm 0.38) \times 10^{-3} \text{ m}^3/\text{mol}$	
$S_{HR} = (2.88 \pm 0.44) \times 10^5 \text{ m}^2/\text{mol}$ ($48 \pm 7 \text{ \AA}^2/\text{molecule}$)	
$K_{ex} = 5.21 \pm 0.20$

Fig. 3. Determination of extraction equilibrium constant of copper with DOLPA

Fig. 4. Effect of DOLPA on copper extraction with nC₆phSAQ

2.4 Kinetics of copper extraction with nC₆phSAQ in the presence of additive

Figure 5 shows the effect of total concentration of HL on P_M . From this figure, it is found that no

Fig. 5. Effect of additives on apparent permeability of copper

enhancement of P_M with the addition of HL appears at pH=5, where the extraction rate is controlled by the diffusion of the extractant or copper.¹⁷⁾ On the other hand, at pH=2, where the rate is controlled by the interfacial reaction, P_M increases with C_{HL} . Especially, at pH=2 in the presence of DOLPA, P_M is enhanced by a factor of 4 when the concentration ratio of DOLPA to nC₆phSAQ, C_{HL}/C_{HR} , is 0.1, while in the presence of D2EHPA, PC-88A and TOLP, P_M is not influenced by the additives until $C_{HL}/C_{HR}=0.1$. The extent of the enhancement of P_M at pH=2 is in the order:

$$\text{DOLPA} \gg \text{TOLP} = \text{D2EHPA} = \text{PC-88A}$$

It seems that enhancement of the copper extraction rate is related to the molecular structures of the additives.

Figure 6 shows the effect of pH on P_M in the presence of DOLPA. The slopes of the relation between log P_M and pH are unity in the low pH range whether DOLPA is added or not.

Figure 7 shows the effect of concentration of HR on P_M in the presence of DOLPA. It is found that under the condition of interfacial reaction rate control (pH=2), the apparent reaction order with respect to C_{HR} changes from 1.5 to 1.1 by the addition of HL. This suggests that HL takes part in the extraction of copper with HR.

3. Discussion

The extraction kinetics of copper with nC₆phSAQ in the presence of DOLPA, the system that gave the largest extraction rate, will be discussed hereafter.

As reported in the previous paper,¹⁷⁾ the extraction mechanism of copper with nC₆phSAQ alone is expressed by the following interfacial reaction steps in which Eq. (14) is the rate-determining step.

Fig. 6. Effect of pH on apparent permeability of copper

Fig. 7. Effect of concentration of nC₆phSAQ on apparent permeability of copper

It is anticipated from the equilibrium study mentioned above that DOLPA plays the role of a catalyst in the extraction kinetics.

Komasawa and Otake⁸⁾ suggested the formation of an intermolecular complex between the P→O group of D2EHPA and the oxime-hydroxyl group of the oxime extractant. In this system, it is expected to form an intermolecular complex between nC₆phSAQ and DOLPA. This means that the intermolecular complex functions as a kind of ligand.

The catalytic extraction mechanism of copper with nC₆phSAQ in the presence of DOLPA is expressed

as follows.

Among the above reaction steps, the reaction of Eq. (18) is considered to be the rate-determining step as well as the non-catalytic reaction mechanism.

Taking account of two parallel reactions (catalytic and non-catalytic), the following interfacial reaction rate is derived.

$$R_i = \frac{k_f(C_{Cu}C_{HR}^2/a_{H0} - 1/K_{ex}C_{CuR2}a_{H0})(1 + \beta C_{HL}^2)}{(1 + K_{HR}C_{HR} + K_s K_{RL} C_{HL} C_{HR} + K_{HL} C_{HL})^2} \quad (19)$$

where $k_f (= k_2 K_1 (K_{HR}/S_{HR})^2)$ and K_{ex} are the overall interfacial reaction rate constant and the equilibrium constant of copper extraction with HR alone, respectively, and a_{H0} is the activity of hydrogen ion in aqueous solution, which can be assumed to be constant, β is the enhancement factor expressed by Eq. (20) assuming $S_{CuRHL} = S_{HRHL}$.

$$\beta = k_3 K'_1 (K_s K_{RL} S_{HR} / K_{HR} S_{HRHL})^2 / k_2 K_1 \quad (20)$$

In Eq. (19), the product of the equilibrium constants of Eqs. (15) and (16), $K_s K_{RL}$, and the enhancement factor of interfacial reaction rate by HL, β , are the unknown parameters. The extraction rate of copper with nC₆phSAQ in the presence of DOLPA was analyzed on the basis of the diffusion model accompanied by the interfacial reaction rate expressed by Eq. (19), using the values listed in Table 1. First, from the experimental results shown in Figs. 6 and 7 where C_{HLO} is kept constant, $K_s K_{RL}$ was evaluated as 0.021, and then the enhancement factor was evaluated using all data as $\beta = 7.2$. The solid lines in Figs. 5–7 represent the calculated results using these values. The calculated curves are in good agreement with the experimental results.

Conclusion

Kinetic and equilibrium studies were conducted on copper extraction with nC₆phSAQ in the presence of some neutral and acidic organophosphorus compounds. It was found that the apparent permeability of copper was significantly accelerated by the addition of DOLPA compared with the addition of D2EHPA, PC-88A and TOLP. The experimental results of copper extraction by nC₆phSAQ in the presence of DOLPA indicated that DOLPA played the role of catalyst in the extraction kinetics. A mechanism of copper extraction with nC₆phSAQ catalyzed by

DOLPA was proposed. The extraction model explained the experimental data reasonably.

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Nomenclature

a_H	= activity of hydrogen ion	[mol/m ³]
C_j	= concentration of species j	[mol/m ³]
C^*	= total concentration of monomer and dimer	[mol/m ³]
D	= distribution ratio of copper	[—]
E	= extent of copper extracted	[—]
J_M	= average extraction rate	[mol/m ² s]
K_1	= equilibrium constant of Eq. (13)	[—]
K'_1	= equilibrium constant of Eq. (17)	[—]
K_{HL}	= adsorption equilibrium constant of HL	[m ³ /mol]
K_{HR}	= adsorption equilibrium constant of HR	[m ³ /mol]
K_{RL}	= adsorption equilibrium constant of HRHL	[m ³ /mol]
K'_a	= acid dissociation constant at interface	[mol/m ³]
K_d	= dimerization constant	[m ³ /mol]
K_{ex}	= extraction equilibrium constant of copper	[—]
K_s	= equilibrium constant of Eq. (15)	[m ³ /mol]
k_2	= rate constant of forward reaction of Eq. (14)	[m ² /(mol·s)]
k_3	= rate constant of forward reaction of Eq. (18)	[m ² /(mol·s)]
k'_2	= rate constnt of reverse reaction of Eq. (14)	[m ⁴ /(mol·s)]
k'_3	= rate constant of reverse reaction of Eq. (18)	[m ⁴ /(mol·s)]
L	= effective length of hollow fiber	[m]
P_M	= apparent permeability of copper	[m/s]
Q_{aq}	= volumetric flow rate of aqueous solution	[m ³ /s]
R	= gas constant	[N·m/(mol·K)]
r_1	= inner radius of hollow fiber	[m]
r_2	= outer radius of hollow fiber	[m]
r_3	= inner radius of membrane extractor	[m]
S_j	= interfacial area occupied by species j	[m ² /mol]
T	= temperature	[K]
β	= enhancement factor	[m ⁶ /mol ²]
γ	= interfacial tension	[N/m]
ε	= porosity of hollow fiber	[—]
τ	= tortuosity of hollow fiber	[—]

<Subscripts>

<i>ad</i>	= adsorption state
<i>aq</i>	= aqueous solution
<i>org</i>	= organic solution
0	= initial state

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