EFFECT OF ANIONIC SURFACTANT ON COPPER EXTRACTION WITH E-2-HYDROXY-5-Nonyl-BENZOPHENONEOXIME

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The effect of the anionic surfactant sodium dioleylsulfosuccinate on the extraction rate of copper with E-2-hydroxy-5-nonylbenzophenoneoxime in n-heptane was studied.

The extraction rate of copper was remarkably enhanced by the addition of the anionic surfactant under appropriate conditions and it was found that the electrostatic interaction between copper and the anionic surfactant and the binding between the extractant and surfactant in the interfacial zone played an important role in the extraction kinetics of copper with the extractant.

An extraction mechanism of copper with E-2-hydroxy-5-nonylbenzophenoneoxime in the presence of the surfactant was proposed.

Introduction

As is well known, the addition of a surface-active agent to a metal extraction system is one means of enhancing the extraction rate. In most studies of the extraction kinetics of metal by a commercial extractant it has been asserted that the rate-determining step of the metal extraction is a reaction taking place at the interface due to the amphiphilic property of the extractant. When a surface-active agent is present in the metal extraction system, the interfacial reaction steps are considered to be remarkably affected by the agent.

Tarasov et al. and Harada et al. reported that sodium dodecylsulfate (water-soluble anionic surfactant) accelerated the extraction rate of copper by LIX 64N and benzoylaceton, respectively. They concluded that the electrostatic effect between the metal cation and ionic surfactants plays an important role in the kinetics of metal extraction in the presence of ionic surfactant. Contrary to these findings, Nitsch et al. showed that sodium dodecylsulfate retarded the extraction rate of zinc by dithizone and that dodecyltrimethylammonium chloride (water-soluble cationic surfactant) accelerated the extraction rate. They suggested that the acceleration effect is caused by the promotion of acid dissociation of the extractant at the interface in the presence of the cationic surfactant. When the surfactants used are water-soluble, the recovery of surfactant from the raffinate is necessary for practical use. Though the acceleration effect of oil-soluble additives on copper extraction with \( \beta \)-hydroxyoxime is well known, the kinetics of metal extraction in the presence of a surfactant has not been clarified.

The effect of Span 80 (oil-soluble nonionic surfactant) on the metal extraction kinetics was studied by Takahashi et al. and Imai and Furusaki in relation to liquid surfactant membrane technique. They reported that the extraction rate of metal was retarded by the addition of Span 80 to the organic solution.

In a previous paper, it was found that an anionic oil-soluble surfactant, sodium dioleylsulfosuccinate (2C18A3SA), accelerated the permeation rate of
copper in a liquid surfactant membrane containing purified LIX 65N as a mobile carrier and L-glutamic acid dioleylester ribitol (nonionic surfactant, henceforth 2C_{18}Δ^9GE) as an emulsifier.

In the present work, the effect of 2C_{18}Δ^9SA on extraction rate of copper with E-2-hydroxy-5-nonylbenzophenoneoxide (abbreviated as E-HNBPO) in n-heptane was studied to obtain fundamental information about the acceleration of the metal permeation rate in the liquid surfactant membrane system. The mechanism of copper extraction with E-HNBPO in the presence of 2C_{18}Δ^9SA is proposed.

1. Experimental

E-HNBPO was isolated from LIX 65N according to the procedure mentioned by Preston et al. Molecular structures of the surfactants used are shown in Fig. 1, along with the formulas of the surfactants. The surfactants were prepared as described in previous papers.

Interfacial tension between n-heptane solution of the surfactants and deionized water was measured at 303 K by the pendant-drop method. A stirred transfer cell was used to measure the rate of copper extraction with E-NHBPO in the presence of the surfactant. Each compartment had a volume of 130 ml and the area of the interface was 12.0 cm². The aqueous and organic phases in the two compartments were stirred independently by two flat-blade stirrers rotating in opposite directions at 150 rpm.

The aqueous solution was prepared according to the following procedure. When pH < 2.7, copper nitrate and sodium nitrate (1 mol/m³) were dissolved in 100 ml/m³ nitric acid and 100 ml/m³ acetic acid aqueous solutions. When pH > 4, copper nitrate was dissolved in 100 mol/m³ acetic acid and 100 mol/m³ sodium acetate aqueous solutions. The pH of the aqueous solution was adjusted by use of the above two aqueous solutions. The organic solution was prepared by dissolving E-HNBPO and the surfactant in n-heptane. The initial rate of copper extraction was obtained from the concentration change of copper chelate complex with time. Copper in the organic solution was stripped by 2 × 10⁻² mol/m³ hydrochloric acid solution prior to concentration measurement by atomic absorption spectrophotometry.

2. Results

2.1 Interfacial tension

The relation between interfacial tension, γ, and the concentration of surfactant, C_s, is shown in Fig. 2.

Interfacial adsorption equilibrium of the surfactant is expressed by Eq. (1).

\[ S_{org} \rightarrow S_{ad} : K_s \]  

Assuming a Langmuir adsorption isotherm between the amount of molecules adsorbed and its bulk concentration in heptane, the interfacial adsorption equilibrium constant, \( K_s \), is defined by Eq. (2).

\[ K_s = \theta_s / \left( C_s \left( 1 - \theta_s \right) \right) \]  

where \( \theta_s \) is the fraction of interfacial area occupied by the surfactant.

The relation between γ and the amount of molecules adsorbed at the interface, \( \Gamma_i \), is expressed by Gibbs' adsorption equation.

\[ -d\gamma = \sum_j \Gamma_j d\mu_j = RT \sum_j (\theta_j / S_j) d\ln C_j \]  

where \( \mu_i \) is the chemical potential of species \( i \) and \( S_j \) is the interfacial area occupied by unit mole of species \( j \). By substituting Eq. (2) into Eq. (3) and then integrating Eq. (3), the following equation was
obtained.

\[ \gamma = \gamma_0 - (\partial T/S_0) \ln(1 + K_i C_i) \]  

(4)

where \( \gamma_0 \) is the interfacial tension between \( n \)-heptane and deionized water. The values of \( K_i \) and \( S_0 \) obtained from Eq. (4) and the experimental results for interfacial tension by non-linear regression are listed in Table 1. Table 1 indicates that the adsorption equilibrium constant of the surfactants is about 100–700 times greater than that of \( E \)-HNBPO. The solid curves in Fig. 2 were calculated by Eq. (4), using the constants in Table 1.

2.2 Extraction rate of copper

Figure 3 shows typical relations between the extent of copper extracted, \( E \), and time. The initial extraction rate, \( R_0 \), was obtained from the following equation.

\[ R_0 = C_{Cu0} \left( \frac{dE}{dt} \right)_{t=0} \left( \frac{V_{eq}}{A} \right) \]  

(5)

Figure 4 shows the effect of the surfactant concentration, \( C_s \), on \( R_0 \). From Fig. 4, \( R_0 \) increases with \( 2C_{18}A^9SA \) concentration at pH = 2 where the rate is controlled by the interfacial reaction. \( R_0 \) is enhanced by a factor of 5 when \( C_s > 10^{-2} \) mol/m³. The other surfactants retard the extraction rate of copper. This is similar to the results obtained by Tarasov et al. \(^{15} \) and Harada et al. \(^{8} \) using watersoluble surfactants.

Figure 5 shows the relation between \( R_0 \) and pH when \( 2C_{18}A^9SA \) is used as the surfactant. In the figure, the dotted line is the line calculated by the interfacial reaction model without surfactant. \(^{8} \) The apparent reaction order is unity in the low pH range, while it approaches zero in the high pH range whether \( 2C_{18}A^9SA \) is added or not. As described in the previous paper, \(^{8} \) the extraction rate is controlled by interfacial reaction in the low pH range and by diffusion of the extractant or copper in the high pH range.

The relation between \( R_0 \) and the initial copper concentration, \( C_{Cu0} \), is shown in Fig. 6. In the presence of \( 2C_{18}A^9SA \), \( R_0 \) is proportional to \( C_{Cu0} \) in the range of low copper concentration and the apparent reaction order approaches zero with respect to \( C_{Cu0} \) in the range of high copper concentration, while that without surfactant \(^{8} \) was 1.0.

Figure 7 shows the relation between \( R_0 \) and the initial concentration of HR, \( C_{HR0} \). In the presence of \( 2C_{18}A^9SA \), the apparent reaction order in Fig. 7 is slightly greater than unity in the range of low \( C_{HR0} \), while that without surfactant \(^{8} \) approached zero due to saturation of the extractant at the interface. Experimental data in the presence of \( 2C_{18}A^9SA \) and the dotted line intersect at \( C_{HR} = 10 \) mol/m³. Figures 6 and 7 indicate that the enhancement of extraction rate of copper in the presence of \( 2C_{18}A^9SA \) occurs under a definite condition.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( K_i ) [m⁴/mol]</th>
<th>( S_0 ) [m³/mol] (A²/molecular)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C_{18}A^9GE</td>
<td>187</td>
<td>2.16 \times 10^{5}</td>
</tr>
<tr>
<td>2C_{18}A^9GEC,QA</td>
<td>302</td>
<td>1.62 \times 10^{5}</td>
</tr>
<tr>
<td>2C_{18}A^9SA</td>
<td>1340</td>
<td>1.36 \times 10^{5}</td>
</tr>
<tr>
<td>2C_{18}GEC,QA,PA</td>
<td>206</td>
<td>2.40 \times 10^{5}</td>
</tr>
</tbody>
</table>

E-HNBPO \(^{8} \) 1.86 2.48 \times 10^{5} 41.2

Fig. 3. Relation between extent of copper extracted and time.

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

Each solid curve in Figs. 4 to 7 was calculated by a method shown later.

3. Discussion

3.1 Interfacial reaction model in the presence of \( 2C_{18}A^9SA \)

The following interfacial reactions of copper extraction with \( E \)-HNBPO were proposed. \(^{8} \)
$$\text{CuR}_{2\text{ad}} \rightleftharpoons \text{CuR}_{2\text{org}} : K_{\text{CuR}}^{-1}$$ (9)

where $K_1$ is the equilibrium constant of formation of the 1:1 copper chelate complex, $k_2$ and $k_2'$ are rate constants of the forward and reverse reaction of Eq. (8), respectively, and $K_{HR}$ and $K_{CuR}$ are interfacial equilibrium constants of $E$-HNBO and the copper chelate complex, respectively. The interfacial reaction rate, $R_f$, is expressed as follows by assuming that the reaction of Eq. (8) is the rate-determining step among the reactions of Eqs. (6) and (9).

$$R_f = k_f(C_{\text{Cu}}C_{HR}/a_{HR} - 1/K_{HR}C_{\text{CuR}}a_{HR})/2$$ (10)

$$\sigma_{HR} = 1 + K_{HR}C_{HR}(1 + K_1S_{\text{CuR}}C_{\text{Cu}}/S_{HR}a_{HR})$$

$$+ K_{CuR}C_{CuR}/a_{HR}$$ (12)

where $a_{HR}$ is the activity of hydrogen ion and $K_{ex}$ is the extraction equilibrium constant of copper.

In the previous paper, it was noted that $2\text{C}_{1\text{H}}\Delta^3\text{SA}$ itself did not extract copper and that the addition of $2\text{C}_{1\text{H}}\Delta^3\text{SA}$ did not affect the extraction equilibrium of copper with $E$-HNBO.

Because enhancement of the extraction rate of copper is considered to be caused by the enrichment of copper ion at the interface due to electrostatic interaction between $2\text{C}_{1\text{H}}\Delta^3\text{SA}$ and copper ion, it is assumed that the electrostatic interaction at the interface is expressed by the following reaction.

$$\text{Cu}^{2+}_{\text{aq}} + \text{NaS}_{\text{ad}} \rightleftharpoons \text{CuS}_{\text{ad}} + \text{Na}^{+}_{\text{aq}} : K_e$$ (13)

where $K_e$ is the equilibrium constant of the reaction.

From Fig. 4, the extraction rate is kept constant in the high $C_s$ range. This suggests that the ratio of surfactant to extractant at the interface is kept constant, but according to the Langmuir adsorption isotherm the concentration of extractant at the interface decreases with increasing $C_s$. To keep a constant concentration of the extractant at the interface, it is assumed that binding between the extractant and the surfactant occurs, as is well known to occur in the micellar catalyzed reaction. Then the following reaction is derived.

$$\text{HR}_{\text{org}} + \text{NaS}_{\text{ad}} \rightleftharpoons \text{NaSHR}_{\text{ad}} : K_b$$ (14)

where $K_b$ is the 1:1 binding constant.

Considering Eqs. (13) and (14), the interfacial reaction steps are expressed as follows:

$$\text{CuS}_{\text{ad}} + \text{NaSHR}_{\text{ad}} \rightleftharpoons \text{CuRS}_{\text{ad}} + \text{NaS}_{\text{ad}} + \text{H}^{+}_{\text{aq}} : K_1'$$ (15)

$$\text{Na}^{+}_{\text{aq}} + \text{CuRS}_{\text{ad}} + \text{NaSHR}_{\text{ad}} \rightleftharpoons \text{CuR}_2\text{Na}_{\text{ad}} + \text{NaS}_{\text{ad}} + \text{H}^{+}_{\text{aq}} : k_f/k_3$$ (16)

$$\text{CuR}_2\text{Na}_{\text{ad}} \rightleftharpoons \text{CuR}_{2\text{org}} + \text{NaS}_{\text{ad}} : K_4$$ (17)

Among these reaction steps, it is assumed that the
reaction of Eq. (16) is the rate-determining step. Therefore, when $2C_{18}\Delta^8\text{SA}$ takes part in the interfacial reaction, the interfacial reaction rate, $R_i$, is expressed as follows:

$$R_i = k_3 \frac{\theta_{\text{CURS}}}{S_{\text{CURS}}} \cdot \frac{\theta_{\text{NaSR}}}{S_{\text{NaSR}}} \cdot C_{\text{Na}} - k'_3 \frac{\theta_{\text{CUR2NaS}}}{S_{\text{CUR2NaS}}} \cdot \frac{\theta_{\text{NaS}}}{S_{\text{NaS}}} \cdot \theta_{\text{HI}}$$

(18)

where $k_3$ and $k'_3$ are the rate constants of forward and reverse reactions of Eq. (16), respectively. Assuming the Langmuir adsorption isotherm and $S_{\text{CURS}} = S_{\text{NaSR}} = S_{\text{CUR2NaS}} = S_{\text{NaS}} (= \text{constant})$, $\theta_i$ are expressed as follows:

$$\theta_{\text{HR}} = k_{HR} C_{HR} \theta_i,$$

$$\theta_{\text{NaS}} = k_c C_{\text{Na}} \theta_i,$$

$$\theta_{\text{CUR}} = k_c C_{\text{CUR}} \theta_i,$$

$$\theta_{\text{NaS}} = k_c C_{\text{CUR}} \theta_i,$$

$$\theta_{\text{CUR2}} = k_c C_{\text{CUR2}} \theta_i,$$

$$\theta_{\text{CURS}} = k'_1 \theta_{\text{CURS}} / \theta_{\text{NaS}} \theta_{\text{HI}}$$

(19)

$$\theta_{\text{CURNaS}} = k_c C_{\text{CURNaS}} \theta_i / k_c C_{\text{CURNaS}} \theta_i = 1 - \sum \theta_j$$

where the subscript $i$ denotes the organic and aqueous solutions adjacent to the interface.

Combining Eqs. (18) and (19), $R_i$ is obtained as

$$R_i = k_f C_{\text{S}}^2 \left( C_{\text{Cur}} C_{\text{HR}} / \theta_{\text{Hi}} - 1 / k_c C_{\text{CUR2}} \theta_{\text{HI}} \right) / \theta_i$$

(20)

where

$$\sigma_i = 1 + k_{HR} C_{HR} + k_c K_c C_{\text{HR}} + K_c C_{\text{CUR}} C_{\text{Hi}} / C_{\text{NaN}} + k_{\text{CUR2}} C_{\text{CUR2}} / K_c C_{\text{CUR}} C_{\text{Hi}}$$

(21)

$$k_f = k_f K_c (K_c K_c S_{\text{NaSHR}})^2$$

(22)

The overall extraction rate in the presence of $2C_{18}\Delta^8\text{SA}$, $R$, is expressed by the following equation.

$$R = R_i \sigma_{HR} / \sigma_i^2 + R_z$$

(23)

where $R_z$ is the mass transfer rate at the steady state. $\sigma_i$ is defined by Eq. (24).

$$\beta = \left( \frac{\sigma_{HR}}{\sigma_i} \right)^2 \left( 1 + k_f C_{\text{S}}^2 / k_f \right)$$

(24)

The concentration of each species adjacent to the interface is obtained from the following relation, in which the interfacial reaction rate equals the mass transfer rate at the steady state.

$$R = k_{\text{CUR}} (C_{\text{CUR}} - C_{\text{CUR2}}) = (k_f / \theta_{\text{Hi}}) (C_{\text{HR}} - C_{\text{HRi}})$$

(25)

where $k_f$ is the mass transfer coefficient of species $j$. The activity of hydrogen ion adjacent to the interface, $a_{\text{Hi}}$, is assumed to be equal to that in the bulk $a_{\text{H}}$, because buffer solution is used.

### 3.2 Analysis of the initial extraction rate

Since in the initial period of copper extraction the term of reverse reaction in Eqs. (10) and (20) and the sixth and seventh terms in Eq. (21) can be neglected, the initial rate of copper extraction, $R_0$, is expressed as follows.

$$R_0 = k_f (1 + k_f C_{\text{S}}^2) / (k_f C_{\text{CUR}} C_{\text{HR}} / a_{\text{Hi}})$$

$$= k_{HR} C_{\text{HRi}} + k_c K_c K_c C_{\text{HRi}} + k_c K_c C_{\text{CUR}} C_{\text{HRi}}$$

(26)

By using Eqs. (25) where $R = R_0$ and (26), $R_0$ is implicitly expressed by the bulk concentration.

The previous paper, the values of $k_f$ ($= 3.2 \times 10^{-5} \text{m}^4/(\text{mol} \cdot \text{s})$) and $k_{HR}$ ($= 1.6 \times 10^{-5} \text{m} / \text{s}$) were obtained. Values of the unknown constants were evaluated from the experimental results for $R_0$ and the above equations by non-linear regression as follows: $k_f = 8.5 \times 10^{-2} \text{m}^4/(\text{mol}^2 \cdot \text{s})$, $k_{HR} = 0.95 \text{m} / \text{mol}$, $K_c = 9.5$ and $k_{\text{CUR2}} = 8.0 \times 10^{-6} \text{m} / \text{s}$.

The solid curves in Figs. 4 to 7 were calculated by using Eqs. (25) and (26).

When $C_s = 0.01 \text{mol} / \text{m}^3$, $C_{\text{CUR}} = 5.5 \text{mol} / \text{m}^3$, $C_{\text{HRi}} = 20 \text{mol} / \text{m}^3$ and pH = 2, $\beta$ ($= 3.8$) is calculated by Eq. (24).

### 3.3 Effect of other surfactants on copper extraction

From Fig. 4, the extent of the retardation of $R_0$ is in the order:

$2C_{18}\Delta^8\text{GEC}_2\text{QA} > 2C_{18}\Delta^8\text{GE} > 2C_{18}\text{GEC}_2\text{QAC}_2\text{PA}$

In the case of nonionic surfactant, $2C_{18}\Delta^8\text{GE}$, which does not interact electrostatically with metal ion, the reduction of the extraction rate with $C_s$ may be caused by the decrease in effective interfacial area due to adsorption of the surfactant. In addition to the decrease in effective interfacial area, the cationic surfactant $2C_{18}\Delta^8\text{GEC}_2\text{QA}$, electrostatically repulsed the metal ion at the interface. Therefore, it is considered that $2C_{18}\Delta^8\text{GEC}_2\text{QA}$ causes the decrease in extraction rate at a lower concentration compared with $2C_{18}\Delta^8\text{GE}$. Though the adsorption equilibrium constant of amphoteric surfactant $2C_{18}\text{GEC}_2\text{QAC}_2\text{PA}$ is similar to that of $2C_{18}\Delta^8\text{GE}$, the extent of the decrease in $R_0$ by the addition of $2C_{18}\text{GEC}_2\text{QAC}_2\text{PA}$ is smaller than that by the addition of $2C_{18}\Delta^8\text{GE}$. This suggests the formation of the intermolecular complex between the organophosphorus compound and the extractant as described previously. The quantitative analysis of the effect of oil-soluble surfactants (nonionic, cationic and amphoterics) on the metal extraction is a further problem.

### Conclusion

The effect of the anionic surfactant sodium dioleylsulfosuccinate on the extraction rate of copper...
with E-2-hydroxy-5-nonylbenzophenoneoxime in n-heptane was studied.

It was found that the extraction rate of copper was remarkably enhanced by the addition of the anionic surfactant under a specific condition, and that the electrostatic interaction between copper and the anionic surfactant and the binding between the extractant and the surfactant in the interfacial zone played an important role in the extraction of copper with the extractant.

Nomenclature

\( A \) = area of interface \ ([m^2])

\( a_n \) = activity of hydrogen ion \ ([mol/m^3])

\( C_j \) = concentration of species \( j \) \ ([mol/m^3])

\( E \) = extent of copper extracted \ ([\text{--}])

\( K_i \) = equilibrium constant of Eq. (7) \ ([\text{--}])

\( K_{i1} \) = equilibrium constant of Eq. (15) \ ([mol/m^3])

\( K_{i2} \) = equilibrium constant of Eq. (17) \ ([mol/m^3])

\( K_j \) = adsorption equilibrium constant of species \( j \) \ ((j = S, HR, CoR)) \ ([m^3]/mol)

\( K_b \) = binding constant of extractant \ ([m^3]/mol)

\( K_e \) = electrostatic binding constant of copper \ ([\text{--}])

\( K_{ex} \) = extraction equilibrium constant of copper \ ([\text{--}])

\( k_2 \) = rate constant of forward reaction of Eq. (8) \ ([m^3]/(mol s))

\( k_3 \) = rate constant of forward reaction of Eq. (16) \ ([m^3]/(mol s))

\( k_2' \) = rate constant of reverse reaction of Eq. (8) \ ([m^3]/(mol s))

\( k_3' \) = rate constant of reverse reaction of Eq. (16) \ ([m^3]/(mol s))

\( k_f \) = extraction rate constant without surfactant \ ([m^3]/(mol s))

\( k_{fx} \) = extraction rate constant defined by Eq. (22) \ ([m^3]/(mol s))

\( k_j \) = mass transfer coefficient of species \( j \) \ ([m/s])

\( R \) = extraction rate \ ([mol/(m^3 s)])

\( \Delta \) = gas constant \ ([N m/(mol K)])

\( R_f \) = extraction rate without surfactant \ ([mol/(m^3 s)])

\( R_s \) = extraction rate defined by Eq. (18) \ ([mol/(m^3 s)])

\( \delta_i \) = interfacial area occupied by species \( j \) \ ([m^3]/mol)

\( T \) = temperature \ ([K])

\( t \) = time \ ([s])

\( V_{aq} \) = volume of aqueous solution \ ([m^3])

\( \beta \) = enhancement factor \ ([\text{--}])

\( \gamma \) = interfacial tension \ ([N/m])

\( \theta_i \) = fraction of interfacial area occupied by species \( j \) \ ([\text{--}])

\( \sigma \) = adsorption term \ ([\text{--}])

Subscripts

\( ad \) = adsorption state

\( aq \) = aqueous solution

\( org \) = organic solution

\( 0 \) = initial state

\( i \) = adjacent to interface

Literature Cited


