EXTRACTION OF COPPER WITH LIQUID SURFACTANT MEMBRANES CONTAINING BENZOYLACETONE

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A novel technique for separating and concentrating metals with liquid surfactant membranes containing a mobile carrier has recently attracted practical interest through nuclear, hydrometallurgical and waste-water treating processes. In this work, to obtain the basic information for development of a novel separation technique, the extraction of copper was carried out using liquid surfactant membranes containing benzoylacetone as a mobile carrier. The effects of the processes of chelating complex formation and diffusion on extraction rate were examined experimentally and theoretically on the basis of a simple model for facilitated transport. The experimental results could be explained approximately by considering that the overall extraction rates of copper were controlled by the chelating complex formation and diffusion processes in the aqueous phase close to the interface of the liquid membrane.

Introduction

The commercial use of solvent extraction of metals with chelating agents such as LIX or Kelex reagents has recently attracted interest from the point of view of the recycling of industrial resources or energy conservation in the field of hydrometallurgical and waste-water treating processes^{4,5,13,16,18}, and further development in practical applications is assured^{7,9,12}. Using liquid surfactant membranes containing a mobile carrier, which has attracted special interest recently, testing of the practical application of selective separation and concentration of metallic ion in aqueous solution has been carried out^{6,10,14,15,17}.

In the previous paper⁸, the extraction of copper by benzoylacetone was carried out using a stirred transfer cell as a basic study of a novel separation technique, and the authors indicated that the effects of the chelating complex formation and diffusion processes in the aqueous phase close to the interface on the extraction rate of copper were significant.

In this work, the separation and concentration of copper using liquid surfactant membranes containing benzoylacetone as a mobile carrier was carried out. Furthermore, the effects of chelating complex formation and diffusion processes on the extraction rate of copper are discussed, based on a simple model for facilitated transport.

1. Model for Extraction Rate of Copper with Liquid Surfactant Membrane

A liquid membrane consisting of a water-in-oil-in-water emulsion is shown in Fig. 1. Copper ion in the external aqueous phase will diffuse toward interface 1, where chelating complex formation between benzoylacetone (HB) and copper occurs. Diffusion of the complex takes place in the membrane, and on reaching the opposite interface 2, a stripping reaction takes place to liberate copper ion into the internal aqueous phase. As mentioned in the previous paper⁸, the rate-controlling step is considered to be the chelating complex formation and diffusion processes in the aqueous phase close to the interface 1. Thus, liquid membranes can pump copper ion from a low-con-

Fig. 1 Simplified diagram of liquid membrane for copper extraction

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Fig. 2 Effect of hydrochloric acid concentration on extraction rate of copper

Fig. 3 Model of liquid membrane

tration region into a higher one^{2,3,14,15}). One example of the experimental results is shown in Fig. 2.

The change of copper concentration, C_M , in the external aqueous phase with time can be expressed as

$$-V_w(dC_M/dt) = A J_M \quad [\text{mol/sec}] \quad (1)$$

where V_w is the volume of external aqueous phase, A is the total surface area of emulsion droplets, and J_M is the transfer rate of copper ion per unit surface area of emulsion droplet. Taking account of $A = V_E \times (6/d)$, where V_E is the total volume of emulsion droplets and d is their average diameter, Eq. (1) can be rewritten as

$$-(dC_M/dt) = (V_E/V_w)(6/d) J_M \quad (1a)$$

It is anticipated from Eq. (1a) that the copper extraction rate is affected by the volume ratio of emulsion phase to aqueous phase and by emulsion droplet diameter.

There are three types of situations that predict J_M by considering the effects of both reaction and diffusion in the aqueous phase based on the previous paper⁸) (see Appendix).

It is necessary to rewrite the benzoylacetone concentration in the aqueous phase, C_{HB}^* , in terms of total benzoylacetone concentration in the organic phase, that is, the initial concentration, C_{HB0} . To do this, a model of the emulsion droplet must be presented. Assuming that a cluster of small water droplets will disperse uniformly within the emulsion drop-

let, the following two extreme cases can be considered:

(1) Each water droplet within the emulsion droplet occupies a fixed position, as would a catalyst particle in a fixed bed.

(2) The water droplets within the emulsion droplet migrate freely and each droplet has an average composition with respect to copper even if no coalescence and dispersion occur.

In this work, the emulsion droplet is assumed to behave as in model (2), which is acceptable in the region of low copper extraction and is relatively simple to treat¹¹). However, it is necessary in the region of high copper extraction to consider the emulsion droplet of model (1), accounting for the emulsion breakdown¹¹). According to model (2), the actual emulsion droplet system is equivalent to a large liquid membrane droplet, as shown in Fig. 3. In the liquid membrane of thickness δ , it is assumed that copper chelate diffuses across the membrane from the external aqueous phase to the internal aqueous phase, while benzoylacetone diffuses from the internal to the external interface. Furthermore, since the hydrogen-ion concentration in the internal solution is kept higher than that in the external one, the reverse reaction takes place instantaneously at the internal interface, as is evident from Fig. 2. Copper chelate releases copper ion into the internal aqueous phase, exchanging two hydrogen ions. Therefore, it is considered that at the internal interface copper chelate concentration is negligible and that carrier concentration in the organic phase is equal to the initial concentration of benzoylacetone, C_{HB0} . Therefore, quasi-steady state concentration profiles exist in the membrane at all times. With the assumption mentioned above, the flux of benzoylacetone, J_{HB} , and that of copper chelate, J_C , within the membrane are expressed as follows.

$$J_{HB} = (D'_{HB}/\delta)(C_{HB0} - C_{HB}^i) \quad (2)$$

$$J_C = (D'_C/\delta)C_C^i \quad (3)$$

where D'_{HB} and D'_C are the diffusion coefficients of benzoylacetone and copper chelate within the membrane, respectively, and C_{HB}^i and C_C^i are the concentrations of benzoylacetone and copper chelate at the external interface, respectively, as shown in Fig. 3. By using the equilibrium equation

$$C_{HB}^i = C_{HB}^*/K_1 \quad (4)$$

the following equation is derived from Eqs. (2) and (4) by assuming that $J_{HB} = 2J_C = 2J_M$.

$$C_{HB}^* = K_1 \{ C_{HB0} - (2\delta/D'_{HB}) J_M \} \quad (5)$$

By using Eq. (5) three cases for evaluating J_M , which are discussed in Appendix, can be rewritten as follows.

$$(A) \quad J_M = k_M C_M \quad (6)$$

$$(B) \quad J_M = C_{HB0} C_M^{1/2} / \{ (1/k_{w1}) + (C_M^{1/2}/k_f) \} \quad (7)$$

$$J_M = k_{w1} C_{HB0} C_M^{1/2} \quad (1/k_{w1} \gg C_M^{1/2}/k_f) \quad (7a)$$

Table 1 Concentration dependency of extraction rate using liquid surfactant membranes

	<i>l</i>	<i>m</i>	<i>n</i>	Equation
(A) Diffusion control	0	0	1	(6)
(B) Reaction and diffusion control	-0.5-0	1	0.5-0	(7)
(1) Negligible mass transfer resistance in membrane	-0.5	1	0.5	(7a)
(2) Significant mass transfer resistance in membrane	0	1	0	(7b)
(C) Reaction control	-1-0	1	1-0	(8)
(1) Negligible mass transfer resistance in membrane	-1	1	1	(8a)
(2) Significant mass transfer resistance in membrane	0	1	0	(8b)

$$J_M = k_f C_{HB0} \quad (1/k_{W1} \ll C_M^{1/2}/k_f) \quad (7b)$$

$$(C) \quad J_M = C_{HB0} C_M / \{ (1/k_{W2}) + (C_M/k_f) \} \quad (8)$$

$$J_M = k_{W2} C_{HB0} C_M \quad (1/k_{W2} \gg C_M/k_f) \quad (8a)$$

$$J_M = k_f C_{HB0} \quad (1/k_{W2} \ll C_M/k_f) \quad (8b)$$

where

$$\left. \begin{aligned} k_M &= k_L (D_M/D_{HB}), \quad k_f = D'_{HB}/2\delta, \quad a = A/V_W \\ k_{W1} &= (D_{HB} k_3 K_1^2 K_2 / 4 C_H)^{1/2}, \quad k_{W2} = k_3 K_1 K_2 / a C_H \end{aligned} \right\} \quad (9)$$

The extreme cases mentioned above are summarized in Table 1 in terms of the following expression.

$$J_M \propto C_H^l \cdot C_{HB0}^m \cdot C_M^n \quad (10)$$

2. Experimental Apparatus and Procedure

2.1 Experimental apparatus

The experimental apparatus used was a batch-type stirred glass cell with a 10-cm inner diameter and a 15-cm depth. The vessel was fitted with four stainless steel baffles, each of which was 1 cm in width and 15 cm in length. Stirring was carried out using a turbine impeller with six flat blades connected with a speed controller.

2.2 Experimental procedure

The internal aqueous solution was prepared by dissolving commercial GR grade hydrochloric acid in deionized water. The organic solution was prepared by dissolving benzoylacetone as a mobile carrier and Span 80, a nonionic surfactant, in commercial GR grade toluene. A water-in-oil type emulsion was made from equal volumes of the two immiscible phases mentioned above by stirring and ultrasonic irradiation for 10 min. Measured volumes of this emulsion were then added to the third phase in the vessel, which was the external aqueous solution containing copper ion, and stirred at constant speed. The pH of the external aqueous solution was adjusted using acetic acid-sodium acetate buffer solution. The vessel was situated within a bath through which water maintained at $30.0 \pm 0.1^\circ\text{C}$ was circulated. Samples of about 20 ml was taken at intervals. After separation from the emulsion, the copper solution was removed for analysis. Copper concentration was determined by atomic absorption spectrochemical analysis.

Experiments were carried out at varying surfactant concentration, stirring speed, volume ratio of the aqueous phase to the emulsion phase, hydrochloric

Fig. 4 Effect of surfactant concentration on emulsion breakdown

acid concentration in the external and internal aqueous phase, benzoylacetone concentration in the organic phase, and copper concentration in the external aqueous phase. The stability of the liquid surfactant membranes and the effect of various factors mentioned above on the copper extraction rate were studied.

3. Experimental Results

In the practical application of selective separation and concentration of copper ion using liquid membranes, the stability of the membranes is one of the most important factors. First of all, the effect of surfactant on the stability of liquid membranes was investigated. There was no copper ion in the external aqueous phase in this experiment. The relation between degree of emulsion breakdown, ϵ and surfactant concentration, C_s , is shown in Fig. 4. The emulsion breakdown was computed from pH measurements of the external aqueous solution. It is evident from Fig. 4 that no emulsion breakdown takes place at a surfactant concentration of more than 2.0% but that emulsion breakdown becomes significant as concentration decreases. Thus, it is obvious that the surfactant and its concentration play an important role in the stability of liquid membranes. To put into practice the membrane separation technique, it will be necessary to develop a new surfactant which forms more stable emulsions. In this study a surfactant concentration of 2.0% was used.

In Fig. 5, the effect of stirring speed on the extrac-

Fig. 5 Effect of stirring speed on extraction rate of copper

Fig. 6 Effect of volume ratio on extraction rate of copper

Fig. 7 Effect of pH on extraction rate of copper

Fig. 8 Effect of benzoylacetone concentration on extraction rate of copper

tion rate of copper is shown. It is clear from the figure that the initial extraction rate increases as the stirring speed increases, but that in the cases of 250 and 300 rpm the copper concentration in the external aqueous phase increases markedly owing to emulsion breakdown after 60 min stirring. Therefore, a stirring speed of 200 rpm, at which the membrane was relatively stable, was used in subsequent experiments.

The effect of the volume ratio of aqueous phase to emulsion phase on the extraction rate of copper is shown in Fig. 6. It is evident from Fig. 6 that the initial extraction rate is more rapid at higher volume ratios of the emulsion phase than at lower ones. This is predicted by Eq. (1a), shown before.

The effect of hydrogen-ion concentration in the external aqueous phase on the extraction rate of copper is shown in Fig. 7. From the figure, it is clear that the initial extraction rate increases with pH. As mentioned before, this indicates that the transfer of copper ion depends on the hydrogen-ion concentration difference between the internal and the external aqueous phases. The effect of hydrochloric acid concentration in the internal aqueous phase on the extraction rate of copper has already been shown in Fig. 2.

In Fig. 8, the effect of benzoylacetone concentration in the organic phase on the extraction rate of copper is shown. It is evident that the initial extraction rate increases with benzoylacetone concentration. In the case of low benzoylacetone concentration, it is apparent that the copper concentration in the external aqueous phase increases gradually owing to emulsion breakdown after 60 min stirring.

The effect of copper concentration in the external aqueous phase on the extraction rate of copper is

shown in Fig. 9. It is obvious that the slope of each straight line in Fig. 9 depends on the copper concentration. Therefore, it was evident that the extraction rate of copper could not be represented by the relation of pseudo-first order dependency with respect to copper concentration.

The experimental results mentioned above will be discussed in the next section on the basis of the model presented earlier.

4. Discussion Based on the Model

The slope of each straight line for the initial extraction, α , in Figs. 7 and 8 are plotted in Fig. 10. The figure indicates that the exponents in Eq. (10) become -0.5 for l and 1 for m when $n=1$. Therefore, cases (B) and (C) in Table 1 will be considered. It is necessary to examine the values of k_{w1} , k_{w2} and k_f . The values of k_3 , K_1 , K_2 and D_{HB} used in calculating k_{w1} , k_{w2} and k_f were identical to those used in the previous paper⁸. In calculating k_{w2} , the value of surface-to-volume ratio of the emulsion droplet, $a=10\text{ cm}^{-1}$ * was used. The value of δ estimated from the diameters of both the emulsion droplet and the small water droplet within the emulsion droplet was of the order of magnitude of 10^{-2} cm . Then the value of k_f was regarded as 10^{-3} cm/sec , which is the ordinary mass transfer coefficient. As a result**, it was found that the following equations hold under the experimental conditions.

$$1/k_{w1} \gg C_M^{1/2}/k_f \quad (11)$$

$$1/k_{w2} \ll C_M/k_f \quad (12)$$

Therefore, Eq. (7a) in the case (B) or Eq. (8b) in the case (C) seems adequate for the results by considering Eqs. (11) and (12). However, Eq. (8b) is in contradiction with the experimental results as shown in Fig. 10, in which the extraction rate varies inversely as the 0.5 power of the hydrogen-ion concentration. Accordingly, it is anticipated that the experimental results can be explained approximately by Eq. (7a), which is derived by assuming that the extraction rate is controlled by the chelating complex formation and diffusion processes in the aqueous phase close to the interface 1 shown in Fig. 1. The following equation is derived from Eqs. (1a) and (7a).

$$-(dC_M/dt) = (kaC_{HB0}/C_H^{1/2})C_M^{1/2} \quad (13)$$

where

$$k = (D_{HB}k_3K_1^2K_2)^{1/2}/2 \quad (14)$$

* By considering that average diameter of emulsion droplet, d , is 1 mm at maximum, $(V_E/V_W) (6/d)$, that is, a becomes 10 cm^{-1} .

** $1/k_{w1} = 7.1 \times 10^{-4} - 4.0 \times 10^{-2}\text{ mol}^{0.5}\cdot\text{sec}/\text{cm}^{2.5}$
 $C_M^{1/2}/k_f = 1.6 - 3.3\text{ mol}^{0.5}\cdot\text{sec}/\text{cm}^{2.5}$
 $1/k_{w2} = 7.7 \times 10^{-6} - 2.4 \times 10^{-3}\text{ mol}\cdot\text{sec}/\text{cm}^4$
 $C_M/k_f = 2.5 \times 10^{-3} - 1.1 \times 10^{-2}\text{ mol}\cdot\text{sec}/\text{cm}^4$

Fig. 9 Effect of copper concentration on extraction rate of copper

Fig. 10 Effects of pH and benzoylacetone concentration on α

Using the initial condition

$$C_M = C_{M0} ; t = 0 \quad (15)$$

Eq. (13) can be solved to give Eq. (16) under the conditions in which C_{HB0} and C_H are constant.

$$1 - \left(\frac{C_M}{C_{M0}} \right)^{1/2} = \frac{ka}{2C_{M0}^{1/2}} \frac{C_{HB0}}{C_H^{1/2}} t \quad (16)$$

The relation of Eq. (16) is represented in Fig. 11 as a diagram of $1 - (C_M/C_{M0})^{1/2}$ vs. $C_{HB0}t/C_H^{1/2}$ under the condition in which copper concentration is constant. It is evident from Fig. 11 that the experimental results can be explained approximately by Eq. (16). As was stated previously, these results showed that the overall extraction rates of copper were affected by the chelating complex formation and diffusion processes in the aqueous phase close to the interface, in the case of separation and concentration of copper ion by liquid surfactant membranes as well as in a stirred transfer cell⁸. However, the experimental results tend to deviate slightly from the relation of Eq. (16) in the

Fig. 11 Relation between $1 - (C_M / C_{M0})^{1/2}$ and $(C_{H2O} / C_H^{1/2})t$

region of high copper extraction. This is explained by an apparent increase in the membrane thickness, δ , so that the mass transfer resistance in the membrane becomes significant. In such a case the exponent l , with respect to the hydrogen-ion concentration and n , with respect to the copper concentration, should vary with time, as is evident from Table 1. These variations may be explained by model (1), presented earlier, where the water droplets within the emulsion droplet occupy fixed positions. This problem will be dealt with in a later paper.

Conclusion

The following information was obtained.

1) The initial extraction rate of copper varied inversely as the 0.5 power of the hydrogen-ion concentration in the external aqueous phase.

2) The initial extraction rate of copper was proportional to the concentration of benzoylacetone in the organic phase.

3) The initial extraction rate of copper could not be explained by the relation of pseudo-first order dependency with respect to copper concentration.

The experimental results could be explained approximately by considering that the overall extraction rates of copper were controlled by the chelating complex formation and diffusion processes in the external aqueous phase close to the interface.

Appendix

(A) $M \gg E_i$, that is, the reaction is instantaneous and the extraction rate is determined by diffusion alone.

$$J_M = k_L (D_M / D_{HB}) C_M \quad (A-1)$$

(B) $1 < M \ll E_i$, that is, the extraction rate is affected by both reaction and diffusion.

$$J_M = (D_{HB} k_3 K_2 / 4)^{1/2} C_{HB}^* (C_M / C_H)^{1/2} \quad (A-2)$$

(C) $M \ll 1$, that is, the extraction rate is controlled by the reaction which is very slow.

$$J_M = (V_W k_3 K_2 / A) C_{HB}^* (C_M / C_H) \quad (A-3)$$

where C_{HB}^* is the benzoylacetone concentration in the aqueous phase.

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Nomenclature

A	= total surface area of emulsion droplets	[cm ²]
a	= surface-to-volume ratio of emulsion droplet	[1/cm]
C	= concentration of chemical species	[mol/l]
C_{HB}^*	= benzoylacetone concentration in aqueous phase close to interface	[mol/l]
D	= diffusion coefficient in aqueous phase	[cm ² /sec]
D'	= diffusion coefficient in liquid membrane	[cm ² /sec]
d	= average diameter of emulsion droplet	[cm]
E_i	= enhancement factor for instantaneous reaction ($= 1 + 2D_M C_{M0} / D_{HB} C_{HB}^*$)	[—]
J	= flux of chemical species	[mol/cm ² ·sec]
K_1	= partition constant of benzoylacetone	[—]
K_2	= dissociation constant of benzoylacetone	[mol/l]
k	= constant defined by Eq. (14)	[cm/sec]
k_3	= reaction rate constant of copper mono-complex formation	[cm ³ /mol·sec]
k_f	= mass transfer coefficient defined by Eq. (9)	[cm/sec]
k_L	= mass transfer coefficient of benzoylacetone into aqueous phase	[cm/sec]
k_M	= mass transfer coefficient of copper defined by Eq. (9)	[cm/sec]
k_{W1}	= constant defined by Eq. (9)	[cm ^{2.5} /mol ^{0.5} ·sec]
k_{W2}	= constant defined by Eq. (9)	[cm ⁴ /mol·sec]
l	= exponent with respect to hydrogen-ion concentration in Eq. (10)	[—]
M	= dimensionless term defined as ratio of reaction rate to mass transfer rate ($= D_{HB} k_3 K_2 C_{M0} / k_L^2 C_H$)	[—]
m	= exponent with respect to benzoylacetone concentration in Eq. (10)	[—]
N	= stirring speed	[rpm]
n	= exponent with respect to copper concentration in Eq. (10)	[—]
t	= extraction time	[min]
V	= volume of phase	[cm ³]
α	= slope of straight line in Figs. 7 and 8	[1/min]
δ	= thickness of liquid membrane	[cm]
ϵ	= degree of emulsion breakdown	[—]

<Subscripts>

C	= copper-benzoylacetone chelating complex
E	= emulsion phase
H	= hydrogen ion
HB	= benzoylacetone
HCl	= hydrochloric acid
M	= copper
S	= surfactant
W	= aqueous phase
0	= initial value

<Superscript>

i = interface

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GROWTH RATE AND SIZE DISTRIBUTION OF NaClO_3 CRYSTALS FROM AQUEOUS SOLUTION

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To investigate the growth rate of a single crystal of sodium chlorate from an aqueous solution, a flow system and an stirred cell were used in the temperature range of 16–30°C. The linear growth rate was first-order with respect to supersaturation, and the surface incorporation coefficient was found to follow the Arrhenius relationship.

The over-all growth rates of crystals in a cone type fluidized-bed crystallizer were correlated with crystal size. Using the empirical size-dependent growth rate model and the seed size distribution with a sine function, the population balance equation was integrated and the resultant population density was compared with that observed for the time after seeding. As a result, it was found that the predicted size distribution substantiated the behavior of crystals in the fluidized-bed crystallizer.

Introduction

The design of crystallizers requires careful consideration of control of crystal size distribution as well as nucleation rate. In practical crystallization, it is believed that nucleation, especially secondary nucleation, is affected by the number of crystals or the surface area and the size distribution. Although size distribution

is controlled by the rates of secondary nucleation and crystal growth, little is known about the mechanisms and the secondary nucleation rates except for several limited systems¹⁰⁾.

As for crystal growth rate, in the last decade measurements have been made under conditions approximating those in industrial crystallizers⁶⁾. In particular, the population balance technique^{1,7)} has been fruitful in the case of continuous stirred-tank and fluidized-bed type crystallizers. There are, however, few studies comparing theoretical and observed values of size

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