PREPARATION OF COPPER OXALATE FINE PARTICLES USING EMULSION LIQUID MEMBRANE SYSTEM

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The preparation of copper oxalate fine particles was carried out by using an emulsion liquid membrane (W/O/W emulsion) to control the size of particles. Copper ions were extracted from the external water phase and stripped into the internal water phase, and precipitated as copper oxalate. Particles of 0.18–0.50 μm in diameter, which were aggregates of primary particles of about 8 nm, were obtained. The particle size decreased with increasing volume ratio of organic membrane phase to internal water phase of the W/O emulsion (O/A ratio). The number of internal water droplets in which the Cu ions are distributed and precipitated is greater at O/A ratio=1 than at O/A ratio=0.5, since the emulsion droplets are dispersed well in the external water phase at O/A ratio=1. Therefore, the number of Cu ions moved into one droplet, and thus, the number of primary particles are greater at O/A ratio=0.5 than those at O/A ratio=1, resulting in the formation of greater particles by aggregation of the primary particles. The simulation based on the model of transfer mechanism of Cu ions through the emulsion liquid membrane was also carried out, in order to confirm the reasonability of the proposed mechanism of particle formation.

Introduction

An emulsion liquid membrane (ELM) system has been studied for the selective separation and concentration of metals (Nakashio and Goto, 1990). The metal ions in the external water phase are extracted into the organic phase and stripped into the internal water phase. When precipitation reaction occurs in the internal water phase, the diameters of particles produced are expected to be physically influenced by the water droplet diameters. Therefore, the preparation of fine particles using ELM has been attempted (Majima *et al.*, 1991; Yang *et al.*, 1991; Stewart and Davies, 1992).

In the production of fine particles having diameters smaller than 10 μm in the liquid phase, the purity and size distribution of the particles are essential problems. In conventional processes, five succeeding stages are needed: purification of solution, precipitation, solid-liquid separation and washing, classification and comminution. When the particles are obtained from dilute solution, pre-concentration is necessary. By using an ELM system, because of its selectivity, the stage of purification of solution and also the stage of pre-concentration may be eliminated. In addition, since the water droplet as a reactive field is a restricted area, the size of the particles can be controlled, and thus the stages of classification and comminution are not needed.

In this work, the preparation of copper oxalate fine particles has been investigated. The effects of several factors such as concentration of feed Cu ion, surfactant concentration and O/A ratio of the emulsion on the size of the particles have been studied to clarify the mechanism of formation of the particles. A simulation based on the model of transfer mechanism of Cu ion through ELM has been also carried out, in order to estimate the reasonability of the proposed mechanism of particle formation.

1. Experimental

Bis(2-ethylhexyl)phosphoric acid (D2EHPA), supplied by Daihachi Kagaku Kogyo Co. Ltd., Osaka, was used as the extractant and sorbitan monolaurate (Span 20), supplied by Wako Pure Chemical Industries, Ltd., was used as the surfactant. The internal water phase of the emulsion (0.5 mol/l oxalic acid) and the organic membrane phase (kerosene containing 0.5 mol/l D2EHPA and 4 or 5 wt% Span 20) was mixed and emulsified mechanically by using a homogenizer (12000 rpm). The volume ratio of organic membrane phase to internal water phase of W/O emulsion (O/A ratio) was 0.5 or 1. The size of the water droplets was measured by using a microscope (NIKON OPTIPHOT Type 104). The W/O emulsion (10 ml) was added to CuSO_4 aqueous solution (50 ml, $[\text{Cu}^{2+}] = 100 - 1500$ ppm) and stirred vigorously with a magnetic stirrer to make the emulsion droplet sizes smaller than 1 mm. The size of the emulsion droplets dispersed in the external water phase was

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Table 1 Conditions of preparation of copper oxalate particles

	[Span 20] [wt%]	O/A [—]	[Cu ²⁺] ₀ [ppm]	Internal water droplet			Secondary particles		
				Diameter 1 ^{a)} [μm]	Number ^{b)} [—]	Diameter 2 ^{a)} [μm]	Diameter ^{c)} [μm]	Number ^{b)} [—]	Diameter calculated ^{d)} [μm]
(a)	4	0.5	100	1.44	4.3×10 ¹²	1.51	0.29	2.23×10 ¹¹	—
(b)	4	1	100	1.50	2.8×10 ¹²	1.64	0.21	5.88×10 ¹¹	—
(c)	5	0.5	100	1.61	3.1×10 ¹²	1.70	0.41	7.26×10 ¹⁰	—
(d)	5	1	100	1.43	3.3×10 ¹²	1.51	0.18	1.06×10 ¹²	—
(e)	4	0.5	500	1.44	4.3×10 ¹²	1.44	0.50	2.52×10 ¹¹	0.39
(f)	4	1	500	1.50	2.8×10 ¹²	1.51	0.28	1.50×10 ¹²	0.35
(g)	5	0.5	500	1.61	3.1×10 ¹²	1.62	0.41	4.82×10 ¹¹	0.43
(h)	5	1	500	1.43	3.3×10 ¹²	1.45	0.33	9.26×10 ¹¹	0.34
(i)	4	0.5	1500	1.44	4.3×10 ¹²	1.44	0.50	4.69×10 ¹¹	0.43
(j)	4	1	1500	1.50	2.8×10 ¹²	1.51	0.36	1.80×10 ¹²	0.41
(k)	5	0.5	1500	1.61	4.3×10 ¹²	1.62	0.50	4.36×10 ¹¹	0.48
(l)	5	1	1500	1.43	2.8×10 ¹²	1.45	0.37	1.66×10 ¹²	0.40

Reaction time: 2 h for the cases of [Cu²⁺]₀=100 and 500 ppm, 6.6 min for 1500 ppm a) Measured by microscope b) In 10 ml of W/O emulsion c) Measured by SEM d) Calculated from the values of W_p (the greatest value calculated)
Diameter 1: Measured before particle formation Diameter 2: Measured after particle formation

measured by taking pictures of the droplets during the course of stirring. The W/O emulsion was then separated from the external solution, and demulsified electrically (Yamaguchi *et al.*, 1985). The particles formed in the water droplets were separated by a centrifuge, and the size and morphology of the particles was observed by a scanning electron microscope (SEM), a transmission electron microscope (TEM), and an X-ray diffractometer (XRD). To determine the concentration of Cu remaining in the organic membrane phase, the solution was stripped with 1 mol/l HCl. Copper concentration of the resulting aqueous solution was determined with an atomic absorption spectrophotometer. The concentration of Cu in the internal phase was estimated by mass balance.

2. Results and Discussion

2.1 Size and morphology of particles

When the extracted Cu ions have moved from the external water phase to the internal water phase, the reaction shown in Eq. (1) occurs in the internal water phase and copper oxalate particles are then precipitated.

The size and morphology of the particles are expected to be influenced by several factors, such as the concentration of Span 20 in the membrane phase, O/A ratio of the emulsion and the feed concentration of Cu ion in the external water phase. Thus, the particles were prepared under different conditions as

shown in **Table 1**, where [Cu²⁺]₀ was the initial concentration of Cu in the external water phase.

Typical results obtained using the SEM are shown in **Fig. 1**. Particles of spherical or oval-shaped were observed, and XRD analysis showed that the particles were copper oxalate. The particle diameter is slightly affected by the surfactant concentration, but is remarkably decreased by increasing the O/A ratio. To clarify the advantage of the ELM system for particle formation, copper oxalate particles were also prepared in homogeneous solution, by adding the CuSO₄ solution ([Cu²⁺]₀=800 ppm) to oxalic acid solution. This concentration of Cu²⁺ used was made to be comparable to that of 100 ppm in an ELM system, taking the enrichment of Cu²⁺ concentration in the ELM system into consideration. A SEM picture thus obtained is shown in **Fig. 2**. The morphology of the particles is not spherical, but disk- or a leaf-like, and their size is greater than that of the particles obtained using the ELM system. Thus, the ELM system is effective for controlling the particle size.

The particle in the case of (g) in Table 1 was observed with TEM. Primary particles of 8 nm in diameter were found and most of these particles were aggregated, as shown in **Fig. 3**. The size of the aggregates (secondary particles) was sub-micron order, which corresponds to the size of particles observed with SEM. Thus, the primary particles are likely to be formed at the initial stage, and the secondary particles are then formed by aggregation of the primary particles.

The size and number of internal water droplets and the secondary particles prepared are shown in

Fig. 1 Scanning electron micrographs of copper oxalate particles prepared by using ELM system at feed $[\text{Cu}^{2+}] = 500$ ppm

Fig. 2 Scanning electron micrographs of copper oxalate particles prepared in homogeneous aqueous solutions at feed $[\text{Cu}^{2+}] = 800$ ppm

Table 1. The number of internal water droplets was calculated from the total volume of the water and their diameter measured with a microscope, assuming uniform size of the water droplets. The number of secondary copper oxalate particles was calculated from the mole fraction of Cu in the internal water phase, diameter of the particles and density of the solid copper oxalate, assuming that all Cu ions which had moved into the internal water phase were precipitated.

The diameters were smaller than the diameter of the internal water phase in all cases. The number of particles is smaller than that of the water droplets. The size of particles increases with increasing feed Cu concentration and decreases remarkably with increasing O/A ratio in all cases.

2.2 Rate of extraction of Cu ions and mechanism of formation of particles

Figure 4 shows the time-course variation of the concentrations of Cu ion in the external water phase, organic membrane phase and internal water phase for the case of feed $[\text{Cu}^{2+}] = 500$ ppm, where the mole fraction of the initial external water phase was set as 100%. The rate of extraction and stripping of Cu ions is seen to increase with increasing O/A ratio and was not influenced by the surfactant concentration. This result can be attributed mainly to the dispersibility of the W/O emulsion droplets in the external water phase. The diameter of the emulsion droplets decreases linearly with stirring time and it is smaller at an O/A ratio of one, compared to 0.5, as shown in Table 2. With increasing amount of organic phase, a better dispersion of W/O emulsion droplets is obtained. Thus, the interfacial area for the extraction increases and thus the extraction rate increases at O/A ratio=1.

The diameter of the internal water droplet was found to be unchanged during particle formation.

Fig. 3 Transmission electron micrographs of copper oxalate particles prepared by using ELM system at feed $[\text{Cu}^{2+}] = 500$ ppm, $[\text{Span } 20] = 5$ wt% and O/A ratio = 0.5

Fig. 4 Time-course variations of concentrations of Cu ion in external water phase, organic membrane phase and internal water phase for case of feed $[\text{Cu}^{2+}] = 500$ ppm and $[\text{Span } 20] = 5$ wt%. Mole fraction in the initial external water phase is set as 100%

This means that there is no interaction between two or more droplets, and one secondary particle is probably formed from the Cu ions distributed in the water droplet at the initial stage of the precipitation, via the formation of primary particles and aggregation. The particle size is thus controlled by the distribution of Cu

Table 2 Diameter of W/O emulsion droplet dispersed in external water phase at 1 and 10 min after start of stirring

[Span 20] [wt%]	O/A ratio [—]	Diameter	
		at 1 min [mm]	at 10 min [mm]
4	0.5	0.73	0.50
4	1	0.39	0.26
5	0.5	0.70	0.48
5	1	0.40	0.30

ions into the water droplets. Since the number of secondary particles was smaller than that of the internal water droplets, the Cu ions are considered to be distributed into the droplets located near the membrane/external water phase interface (Teramoto *et al.*, 1983).

As for the cases of (g) and (h) in Table 1, the number of internal water droplets was nearly identical. However, the size of particles obtained at O/A ratio=1 (case (h)) was smaller than that at O/A ratio=0.5 (case (g)). The number of internal water droplets in which the Cu ions are distributed is greater at O/A ratio=1 than that at O/A ratio=0.5, since the W/O emulsion droplets at O/A ratio=1 are dispersed well in the external water phase and there is a greater interfacial area than that at O/A ratio=0.5. This interpretation is consistent with the result that the extraction and stripping of Cu ions occur more rapidly at O/A ratio=1. The number of Cu ions in one water droplet is small, and thus the smaller particles are

prepared in the case of O/A ratio=1.

When the concentration of Span 20 was 4 wt%, the number of the internal water droplet was greater at O/A ratio=0.5 than at O/A ratio=1. The number of droplets used for the particle formation was, however, considered to be greater at O/A ratio=1 than that at O/A ratio=0.5, since the rate of extraction and stripping was greater in the former case. Thus, the smaller particles were prepared at O/A ratio=1. The particle formation process was found to be much influenced by the dispersion of the W/O emulsion droplets in the external water phase and the rate of extraction and stripping, rather than by the diameter of internal water phase.

2.3 Model development for simulation of transport and precipitation of Cu ions

The particle formation process was simulated, based on the extraction model for copper in ELM system proposed by Teramoto *et al.* (1983), to which precipitation in the internal water phase was added. In this model, the W/O emulsion droplets and internal water droplets are spherical and the water droplets are located uniformly and immobile in the emulsion droplet. **Figure 5** shows a schematic diagram of ELM system. The elementary steps are as follows.

(1) Diffusion of Cu and hydrogen ions through the stagnant film of the external water phase.

(2) Formation of complex between Cu ion and extractant at the interface between the external/membrane phases.

(3) Diffusion of the complex and extractant in the peripheral oil layer of the emulsion droplet.

(4) Diffusion of the complex and extractant through the membrane phase.

(5) Stripping of Cu ions and precipitation of copper oxalate by reaction between Cu ion and oxalate ion. Dissociation of oxalic acid with the progress of precipitation in the water droplets.

In this model, breakage of the membrane is not considered. The effective diffusivities of extractant and extracted species in the membrane phase are assumed to be constant. The mass transfer resistance in the internal water phase is neglected because this phase is much smaller than the W/O emulsion droplet.

The overall extraction equilibrium is formulated as Eq. (2) where RH denotes D2EHPA. When the concentrations of Cu ion, dimer of free extractant, extracted species and hydrogen ion are shown by A , B , C and H , respectively, the extraction equilibrium constant and the rates of forward and reverse reactions are expressed by Eqs. (3) – (5), respectively.

$$K_{\text{ex}} = CH^2/AB^2 \quad (3)$$

$$r_f = k_f(AB^2/H^2 - C/K_{\text{ex}}) \quad (4)$$

Fig. 5 Schematic diagram of ELM system

$$r_r = k_r(C - AB^2K_{\text{ex}}/H^2) \quad (5)$$

The mass balance equation of Cu ion in the external water phase (phase I) is given by

$$(1 - \phi') \frac{\partial A_I}{\partial t} = -k_A a_0 (A_I - A_{I,i}) \quad (6)$$

where k_A is the mass transfer coefficient of Cu ion through stagnant water film and $\phi' (= (V_{II} + V_{III}) / (V_I + V_{II} + V_{III}))$ is the volume fraction of W/O emulsion droplets. a_0 is the specific surface area of emulsion droplets.

The mass balance equations of extractant and extracted species in the organic membrane phase (phase II) are expressed as Eqs. (7) and (8), respectively.

$$(1 - \phi) \frac{\partial B}{\partial t} = D_{e,B} \left(\frac{\partial^2 B}{\partial r^2} + \frac{2}{r} \frac{\partial B}{\partial r} \right) + \frac{6\phi k_r}{R_\mu} \left(C - \frac{K_{\text{ex}} A_{III} B^2}{H_{III}^2} \right) \quad (7)$$

$$(1 - \phi) \frac{\partial C}{\partial t} = D_{e,C} \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - \frac{3\phi k_r}{R_\mu} \left(C - \frac{K_{\text{ex}} A_{III} B^2}{H_{III}^2} \right) \quad (8)$$

$\phi (= V_{III} / (V_{II} + V_{III}))$ is the volume fraction of the internal water droplets in the emulsion droplet. $D_{e,B}$ and $D_{e,C}$ are the effective diffusivity of each species in the organic membrane phase. R_μ is the diameter of the internal water droplet.

The mass balance equations of Cu ion, hydrogen ion, oxalate ion and oxalic acid in the internal water

phase (phase III) are given by Eqs. (9)–(12), respectively.

$$\phi \frac{\partial A_{\text{III}}}{\partial t} = \frac{3\phi k_r}{R_\mu} \left(C - \frac{K_{\text{ex}} A_{\text{III}} B^2}{H_{\text{III}}^2} \right) - \phi k_p (A_{\text{III}} [\text{C}_2\text{O}_4^{2-}] - K_{\text{SP}})^n \quad (9)$$

$$\phi \frac{\partial H_{\text{III}}}{\partial t} = \frac{6\phi k_r}{R_\mu} \left(C - \frac{K_{\text{ex}} A_{\text{III}} B^2}{H_{\text{III}}^2} \right) + 2\phi k_1 \left([\text{H}_2\text{C}_2\text{O}_4] - \frac{[\text{C}_2\text{O}_4^{2-}] H_{\text{III}}^2}{K_1 K_2} \right) \quad (10)$$

$$\phi \frac{\partial [\text{C}_2\text{O}_4^{2-}]}{\partial t} = \phi k_1 \left([\text{H}_2\text{C}_2\text{O}_4] - \frac{[\text{C}_2\text{O}_4^{2-}] H_{\text{III}}^2}{K_1 K_2} \right) - \phi k_p (A_{\text{III}} [\text{C}_2\text{O}_4^{2-}] - K_{\text{SP}})^n \quad (11)$$

$$\phi \frac{\partial [\text{H}_2\text{C}_2\text{O}_4]}{\partial t} = -\phi k_1 \left([\text{H}_2\text{C}_2\text{O}_4] - \frac{[\text{C}_2\text{O}_4^{2-}] H_{\text{III}}^2}{K_1 K_2} \right) \quad (12)$$

k_p and K_{SP} are the rate constant of precipitation reaction and solubility product of copper oxalate, respectively. $k_p(A_{\text{III}}[\text{C}_2\text{O}_4^{2-}] - K_{\text{SP}})^n$ denotes the rate of precipitation and n is the exponent of degree of supersaturation. In many cases, $n=2$ is applicable (Doremus, 1970). k_1 is the rate constant of dissociation of oxalic acid and $K_1 K_2$ is the dissociation constant. It is assumed here that the dissociation proceeds in one step from $\text{H}_2\text{C}_2\text{O}_4$ to $\text{C}_2\text{O}_4^{2-}$ and only $\text{C}_2\text{O}_4^{2-}$ reacts with Cu ion. In addition, the rate of dissociation is assumed to equal to the rate of precipitation reaction, and thus Eq. (11) equals 0. The mass balance equation of oxalic acid is shown as Eq. (13).

$$[\text{H}_2\text{C}_2\text{O}_4]_0 = [\text{H}_2\text{C}_2\text{O}_4] + [\text{C}_2\text{O}_4^{2-}] + [\text{CuC}_2\text{O}_4] \quad (13)$$

The initial conditions are;

$$A_1 = A_{1,0} \quad \text{for } t = 0 \quad (14)$$

$$B = B_0, \quad C = C_0, \quad A_{\text{III}} = A_{\text{III},0}, \quad H_{\text{III}} = H_{\text{III},0} \\ A_{\text{III},\text{in}} = A_{\text{III},\text{in},0} \quad \text{for } t = 0, \quad 0 \leq r \leq R' \quad (15)$$

$$[\text{H}_2\text{C}_2\text{O}_4] = [\text{H}_2\text{C}_2\text{O}_4]_0, \quad [\text{C}_2\text{O}_4^{2-}] = [\text{C}_2\text{O}_4^{2-}]_0 \quad (16)$$

The boundary conditions are;

$$1. \quad r = 0, \quad \partial B / \partial r = \partial C / \partial r = 0 \quad (17) \\ 2. \quad k_A (A_1 - A_{1,i}) = k_H (H_{1,i} - H_1) / 2$$

$$= k_f (A_{1,i} B_i^2 / H_{1,i}^2 - C_i / K_{\text{ex}}) \\ = k_B (B_{r=R'} - B_i) / 2 = k_C (C_i - C_{r=R'}) \\ = -D_{e,B} (\partial B / \partial r)_{r=R'} / 2 \\ = D_{e,C} (\partial C / \partial r)_{r=R'} \quad (18)$$

where k_B and k_C are the mass transfer coefficient of the free extractant and extracted species through the peripheral oil layer of the W/O emulsion droplet, respectively. R' is assumed to approximately equal R . In this model, the change of hydrogen ion concentration in the external water phase is involved. However, mass transfer resistance of hydrogen ion in the film of the external water phase was neglected because this step is expected not to be the rate-determining step, particularly at the initial stage of the reaction. The above equations were transformed to dimensionless form and solved using an implicit finite difference method.

2.4 Determination of parameters and comparison of calculated results with observed results

The values of k_f and k_r used are 4.0×10^{-9} m/s and 1.0×10^{-5} m/s, respectively, which were reported by Komasaawa and Otake (1983). The value of K_{ex} can be obtained from using the relation $K_{\text{ex}} = k_f / k_r$. The value of k_C was estimated as $k_C = k_B (D_C / D_B)$, and D_C / D_B was assumed to be equal to $D_{e,C} / D_{e,B}$. The values of k_A , k_B and $D_{e,C}$ were determined to fit the observed results of the time-course variations of the mole fraction of Cu ion in the external water phase. The values of n and k_p should be determined from the distribution profile of particles in the emulsion droplet. However, experimental information of particle concentration as a function of location in emulsion droplet was not obtainable. Thus, the value of $W_p (= 2A_{\text{III},p} / H_{\text{III},0})$, dimensionless concentration of the copper oxalate, was calculated from the numbers of internal water droplets and particles assuming that the particles were located near the emulsion droplet surface and one water droplet contained one particle. The values of W_p are shown by dotted lines (rectangle) in Fig. 6, and the parameters n and k_p were determined to simulate the penetration depth of copper oxalate from the surface of the emulsion droplet ($X=1$). $D_{e,B}$ had almost no influence on the results, and was assumed as 1.5×10^{-9} m²/s, which was slightly greater than the reported values for a different extractant, PC-88A ((2-ethylhexyl)phosphonic acid mono-2-ethylhexyl ester), which was 1.5×10^{-10} m²/s (Teramoto *et al.*, 1986) or 6.359×10^{-10} m²/s (Lee *et al.*, 1994).

The calculated results for the case $[\text{Cu}^{2+}]_0 = 500$ ppm are shown in Fig. 6 and Fig. 7 with solid lines, together with the observed results. The parameters determined are shown in Table 3. The value of k_B was roughly estimated by assuming the emulsion droplet as a rigid sphere with no circulation using Eq. (19) where d_p is the diameter of droplet (Treybal, 1963).

Fig. 6 Distribution of Cu ions (W) and copper oxalate particles (W_p) in emulsion droplets at $t = 3.3$ min for case of feed $[\text{Cu}^{2+}] = 500$ ppm. Comparison of calculated data with observed data

Fig. 7 Time-course variations of concentration of Cu ion in external water phase for case of feed $[\text{Cu}^{2+}] = 500$ ppm. Comparison of calculated data (solid lines) with observed data

$$k_B = \frac{2\pi^2 D_B}{3d_p} \quad (19)$$

Thus, k_B is expected to be about $1.4 \times 10^{-5} - 3.8 \times 10^{-5}$ m/s. The simulation was carried out by referring to

Table 3 Values of parameters

$D_{e,B}$	1.5×10^{-9} m ² /s
k_B	3×10^{-5} m/s
k_C	$k_B \times D_C / D_B (=k_B \times D_{e,C} / D_{e,B})$
$k_f^{(*)}$	4.0×10^{-9} m/s
$k_r^{(*)}$	1.0×10^{-5} m/s
n	2
k_P	3.0×10^{-4} (mol/m ³) ⁻³ /s
k_A	1.0×10^{-5} m/s (O/A ratio=0.5) 5.0×10^{-5} m/s (O/A ratio=1)
$D_{e,C}$	6.0×10^{-10} m ² /s (O/A ratio=0.5) 1.0×10^{-9} m ² /s (O/A ratio=1)

*) Komasa and Otake (1983)

these values, and the value of k_B was determined as 3.0×10^{-5} m/s, which was comparable to the value for PC-88A (4×10^{-5} m/s) in the ELM system reported by Teramoto *et al.* (1986). The calculated values of extraction rate of Cu shown in Fig. 7 was heavily influenced by the value of k_A at the initial stage, and then by the value of $D_{e,C}$. Thus, the rate-determining step was the mass transfer of Cu ion in the film of the external water phase at the initial stage, and then switched to the diffusion of extracted species in the membrane phase. The most probable values of $D_{e,C}$ and k_A increase with the O/A ratio. With increasing O/A ratio, the volume of the membrane phase increases as compared to that of internal water droplets. Thus, the tortuosity for the diffusion for the extracted complex becomes lower in the case of O/A ratio=1, and then, the value of $D_{e,C}$ increases. As for k_A , the increase in the volume of the organic membrane phase also causes an increase in the quantities of extractant and surfactant. This is likely to decrease the interfacial tension, and thus to decrease the mass transfer resistance. The value of k_A for extraction of Cu has been reported as 3.4×10^{-5} m/s (Teramoto *et al.*, 1983) or 9.8×10^{-6} m/s (Lorbach *et al.*, 1986). As for $D_{e,C}$, 3.3×10^{-10} m²/s for Cu-Acorga PT 5050 (Lorbach *et al.*, 1986) and 1.12×10^{-10} m²/s for Eu-PC-88A (Lee *et al.*, 1994) have been reported. These are similar to the present values shown in Table 3.

The diameter of the secondary particles can be calculated from the values of W_p shown in Fig. 6. Although the calculated diameters have size distributions, the most probable values (the greatest diameters calculated) are shown in Table 1. They agree fairly well with the observed diameters.

2.5 Limit of the proposed model

The simulation was also carried out for the case of $[\text{Cu}^{2+}]_0 = 1500$ ppm, using the parameters determined at $[\text{Cu}^{2+}]_0 = 500$ ppm. At O/A ratio=1, the calculated results agree well with the observed data as shown in Figs. 8 and 9. However, at O/A ratio=0.5, the observed results can not be simulated. The cal-

Fig. 8 Time-course variations of concentration of Cu ion in external water phase for case of feed $[\text{Cu}^{2+}] = 1500 \text{ ppm}$. Comparison of calculated data (solid lines) with observed data

Fig. 9 Distribution of Cu ions (W) and copper oxalate particles (W_p) in emulsion droplets at $t = 6.6 \text{ min}$ for case of feed $[\text{Cu}^{2+}] = 1500 \text{ ppm}$. Comparison of calculated data with observed data

culated extraction rate is greater than that observed. This may be explained as follows. When the initial concentration of Cu ion in the external water phase is

increased, the greater part of the internal water droplets located near the emulsion droplet surface may be filled immediately with the precipitated copper oxalate at the initial stage. This is likely to cause the expansion of the diameter of the internal water droplets including particles, which enhances the tortuosity for the diffusion of the extracted complex, especially in the case of O/A ratio=0.5 since the particle size is greater than in the case O/A ratio=1. The assumptions that the size of the internal water droplet is homogeneous and constant may be no longer reasonable in this case.

Conclusion

Copper oxalate fine particles were prepared by using an emulsion liquid membrane (ELM, W/O/W emulsion) system. The factor determining the particle size and the formation mechanism of the particles were investigated with the following results.

1) The particle size remarkably decreased with increasing O/A ratio. The number of Cu ions moved into one droplet, and thus, the number of primary particles was greater at O/A ratio=0.5 than that at O/A ratio=1. As a result, greater particles were obtained at O/A ratio=0.5 by aggregation of primary particles.

2) The validity of the proposed mechanism was estimated by simulation. At $[\text{Cu}^{2+}]_0 = 500 \text{ ppm}$, the observed results were successfully simulated by the model based on the model of transfer mechanism of Cu ion through ELM system. Some limitations of the proposed model were seen when $[\text{Cu}^{2+}]_0$ was increased to 1500 ppm.

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Nomenclature

A	= Cu ion concentration	$[\text{mol}/\text{m}^3]$
a_0	= specific interfacial area between external water phase and organic membrane phase	$[\text{m}^{-1}]$
B	= free extractant concentration	$[\text{mol}/\text{m}^3]$
C	= extracted species concentration	$[\text{mol}/\text{m}^3]$
D_B	= diffusivity of extractant in organic membrane phase	$[\text{m}^2/\text{s}]$
D_C	= diffusivity of Cu-extractant complex in organic membrane phase	$[\text{m}^2/\text{s}]$
$D_{e,B}$	= effective diffusivity of extractant in organic membrane phase	$[\text{m}^2/\text{s}]$
$D_{e,C}$	= effective diffusivity of Cu-extractant complex in organic membrane phase	$[\text{m}^2/\text{s}]$
H	= hydrogen ion concentration	$[\text{mol}/\text{m}^3]$
K_1, K_2	= dissociation constant of oxalic acid, 5.6×10^{-1} and	

	5.4×10^{-2} , respectively	[mol/m ³]
K_{ex}	= extraction equilibrium constant	[—]
k_A	= mass transfer coefficient of Cu ²⁺ through external water stagnant film	[m/s]
k_B	= mass transfer coefficient of extractant through peripheral oil layer of W/O emulsion droplet	[m/s]
k_C	= mass transfer coefficient of Cu-extractant complex through peripheral oil layer of W/O emulsion droplet	[m/s]
k_f	= rate constant of forward reaction	[m/s]
k_H	= mass transfer coefficient of H ⁺ through external water stagnant film	[m/s]
k_r	= rate constant of reverse reaction	[m/s]
k_p	= rate constant of precipitation reaction of copper oxalate	[(mol/m ³) ⁻³ /s]
K_{sp}	= solubility product of copper oxalate, 3.0×10^{-2}	[(mol/m ³) ²]
n	= exponent of degree of supersaturation	[—]
R	= radius of W/O emulsion droplet	[m]
R_μ	= radius of internal water droplet	[m]
r	= radial distance	[m]
r_f	= rate of extraction of Cu ion	[mol/m ² s]
r_r	= rate of stripping of Cu ion	[mol/m ² s]
t	= reaction time	[min]
V	= volume	[m ³]
W	= dimensionless concentration of Cu ion in internal water phase, $2A_{III}/H_{III,0}$	[—]
W_p	= dimensionless concentration of copper oxalate in internal water phase, $2A_{III,p}/H_{III,0}$ ($A_{III,p} = [\text{CuC}_2\text{O}_4]$)	[—]
X	= dimensionless length scale of emulsion droplet, r/R	[—]
ϕ	= volume fraction of internal water droplets in W/O emulsion droplet ($= V_{III}/(V_{II} + V_{III})$)	[—]
ϕ'	= volume fraction of W/O emulsion droplet in emulsion liquid membrane system ($=(V_{II} + V_{III})/(V_I + V_{II} + V_{III})$)	[—]
<Subscript>		
0	= initial value	
i	= interface between external water phase and W/O emulsion droplet	
p	= precipitated	

I	= phase I (external water phase)
II	= phase II (organic membrane phase)
III	= phase III (internal water phase)

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