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F. Nakashio[a]; K. Kondo[a]
[a] Department of Organic Synthesis, Kyushu University, Fukuoka, Japan

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EXTRACTION OF COPPER WITH LIQUID SURFACTANT MEMBRANES

F. Nakashio and K. Kondo
Department of Organic Synthesis, Kyushu University,
Fukuoka 812, Japan

ABSTRACT

Studies of the extraction of copper with liquid surfactant membranes containing a mobile carrier were conducted in a stirred transfer cell. It was found that: (1) the resistance of the diffusion step in liquid surfactant membranes is negligible compared with that of the diffusion step accompanied with chelating complex formation in the outer aqueous solution, (2) the initial rate of copper extraction varied inversely as the 0.5 power of hydrogen-ion concentration in the low-pH range, but in the high-pH range was not affected by hydrogen-ion concentration, (3) the initial rate of copper extraction was proportional to the concentration of benzoylacetone, which is the mobile carrier in the membranes, in the low-pH range, but the rate was scarcely affected by benzoylacetone concentration in the high pH and benzoylacetone concentration ranges. These results are consistent with a model of liquid surfactant membranes which is presented.

INTRODUCTION

With the commercial development of metal chelating agents such as LIX 65N (long-chain alkyl aryl oximes) or Kelex 100 (derivatives of 8-hydroxyquinoline) reagents, interest in the application of solvent extraction for the recovery of metals has increased, particularly with regard to the recycling of industrial resources, to hydrometallurgical processes, and in waste-water treatment processes (1-4). One of the most important problems,

inherent in such processes, is the large inventory of expensive chelating agent and solvent (5). An approach which reduces the solvent inventory is the use of liquid membranes (6-9), in particular, the liquid surfactant membranes which were invented by Li (10) and then developed by many other investigators (5, 11-14).

In order to effectively utilize liquid surfactant membranes for the selective separation and concentration of metals, it is necessary to elucidate the mechanism of extraction. Several models for facilitated transport have been presented to date. Hochhauser and Cussler (11) described the concentration of chromium with liquid surfactant membranes containing tridodecylamine by assuming that all reactions in the membrane are so rapid that they are essentially at equilibrium. Martin and Davies (15) have recently described the extraction of copper with liquid surfactant membranes containing SME 529, which is a commercial chelating agent, by assuming that reactions take place at the interface between the membrane and the aqueous solution.

In a previous paper (14), we have described the separation and concentration of copper with liquid surfactant membranes containing benzoylacetone with a diffusion model and considerations of chelating complex formation in the aqueous phase close to the external interface of the membrane. The model assumed that the small water droplets in the emulsion phase dispersed uniformly, and that the effect of the stripping reaction rate on the overall extraction rate was negligible. However, analysis of the experimental data was complicated by several problems, such as difficulty in evaluating the interfacial area and emulsion breakdown, both caused by the use of a batch-type stirred tank. Therefore, it was difficult to elucidate the mechanism of extraction.

In the present work, the experimental problems were eliminated through the use of a stirred transfer cell. This permitted the mechanism of initial extraction of copper with liquid surfactant

membranes to be defined. The experimental results obtained in the batch-type stirred tank were then described in terms of the mechanism defined by analysis of the stirred transfer cell data.

EXPERIMENTAL

Experimental Apparatus

Two types of experimental apparatus were used. A sketch of the stirred transfer cell which was used is presented in Fig. 1. The cell is very similar to that described previously (16). Copper ion concentration could only be determined in the aqueous phases of the lower glass cell; analysis of the emulsion phase was not possible. The transfer cell was immersed in a

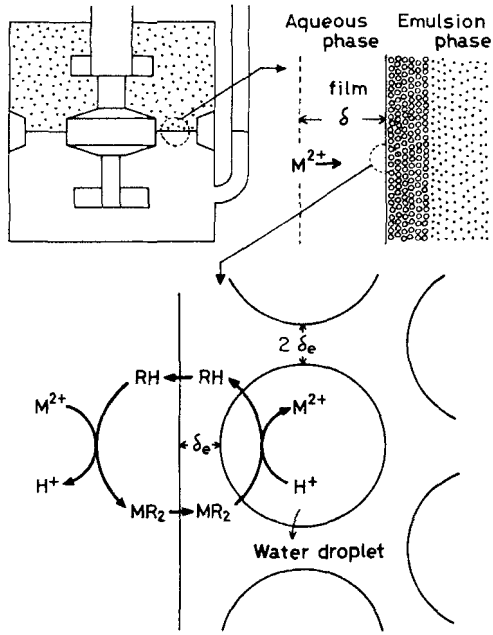

FIGURE 1. Sketch of the stirred transfer cell and description of the model of a liquid surfactant membrane.

constant-temperature (30°C) water bath. The aqueous and emulsion phases in the two compartments were stirred independently by two flat-blade stirrers which operated in opposite directions. The compartments had volumes of 130 ml for the aqueous phase and 115 ml for the emulsion phase. The interfacial area was 15.7 cm^2.

The batch-type stirred tank that was used is shown schematically in Fig. 2. The vessel had an inner volume of about 1200 ml and was fitted with four stainless steel baffles, each of which was 1 cm wide and 15 cm long. The fluids were stirred by a turbine impeller which had six flat blades and which was connected to a speed controller.

Experimental Procedure

The emulsion phase was made from both organic solution and internal aqueous solution by the procedure described previously (14). The organic solution was prepared by dissolving the mobile carrier, benzoylacetone, and Span 80, a nonionic surfactant, in commercial GR grade toluene, and the internal aqueous solution was prepared by dissolving commercial GR grade hydrochloric acid in deionized water. The pH of the external aqueous solution which contained copper ion was adjusted using 0.1 mol/L acetic acid-sodium acetate buffer solution.

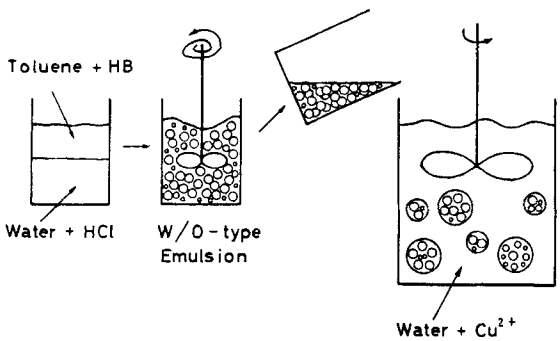

FIGURE 2. Schematic procedure for making liquid surfactant membranes and sketch of the batch-type stirred tank.

In the experiments with the stirred transfer cell, the aqueous phase was first introduced into the cell from a burette which was fitted with a constant-temperature jacket. The prepared emulsion phase was rapidly introduced to the other constant-temperature jacket, and then was placed carefully in the cell in such a way as not to disturb the interface. Stirring was started as soon as the emulsion phase was introduced in the cell. Samples of about 1.2 ml aqueous phase were taken at specified intervals, and then equal volumes of the original aqueous solution were added to the cell to maintain the volume of the aqueous solution at its original value. The effect of the sampling method on extent of copper extracted was negligible up to 120 min stirring. Copper concentration was determined by atomic absorption spectrochemical analysis.

In the experiments with the batch-type stirred tank, measured volumes of the prepared emulsion were added to the third phase in the vessel (the external aqueous solution containing copper ion) and stirred at constant speed. Samples of about 20 ml were taken at specified intervals. After separation from the emulsion, the copper solution was removed for analysis.

Experiments were carried out at varying stirring speed, volume ratio of the organic solution to the internal aqueous solution in the emulsion phase, hydrochloric acid concentration in the internal and external aqueous phases, benzoylacetone concentration in the organic solution, and copper concentration in the external aqueous phase. The effects of these variables on the rate of copper extraction were studied. The extraction rates were measured under the following conditions: pH range, 3.5 to 5.5; benzoylacetone concentration, 0.005 to 0.2 mol/L; and copper concentration, 0.002 to 0.01 mol/L.

Experimental Results with the Stirred Transfer Cell

The stability of the membranes was first examined; this is one of the most important factors in practical applications of membrane processes. Emulsion breakdown was computed from pH

measurements of the external aqueous solution. As a result, it was shown that the degree of emulsion breakdown was very small, e.g., 2 x 10^{-3}% after 180 min stirring at a Span 80 concentration of 2.0 wt %, hydrochloric acid concentration of 0.5 mol/L in the internal aqueous solution, volume ratio (organic solution/aqueous solution in the emulsion phase) of 2, and stirring speeds of 250 rpm in the emulsion phase and 150 rpm in the aqueous phase. In the batch-type stirred tank, the degree of emulsion breakdown was about 1% after 60 min stirring under the same conditions as in the stirred transfer cell, except that the volume ratio was unity and the stirring speed was 200 rpm (14). It is evident that the emulsion breakdown is much lower in the stirred transfer cell than in the batch-type stirred tank (14).

The dependence of the extent of copper extracted, x, on stirring speed in the emulsion phase, N_E, is presented graphically in Fig. 3. The extent of copper extracted is approximately constant at stirring speeds above 250 rpm, whereas the interface

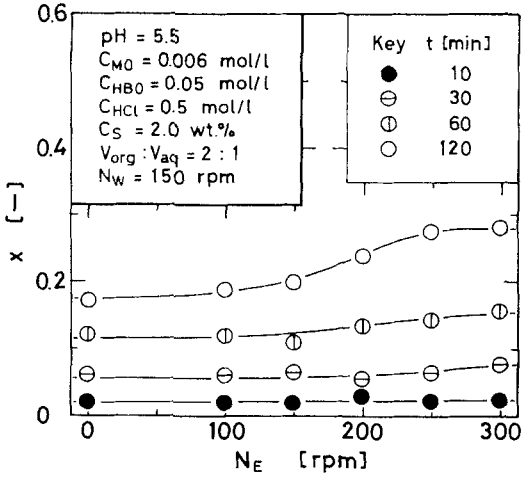

FIGURE 3. Effect of stirring speed in emulsion phase on extent of copper extracted.

between the aqueous and the emulsion phases becomes unstable at stirring speeds above 350 rpm. (In addition, we believe that the mobility of the small water droplets in the emulsion phase is reduced at stirring speeds below 200 rpm.)

The effect of the volume ratio, V_{org}/V_{aq}, on the extent of copper extracted is displayed in Fig. 4. (The value infinity means that only the organic phase is used in place of the emulsion phase.) The extent of copper extracted can be regarded as being roughly independent of volume ratio at ratios above 2. It is possible that the mobility of the small water droplets in the emulsion phase is reduced at ratios less than 2.

The effect of hydrochloric acid concentration, C_{HCl}, in the internal aqueous solution on the extent of copper extracted is presented in Fig. 5. It is evident from these data that the extent of copper extracted is independent of hydrochloric acid concentration. This indicates that the effect of the stripping

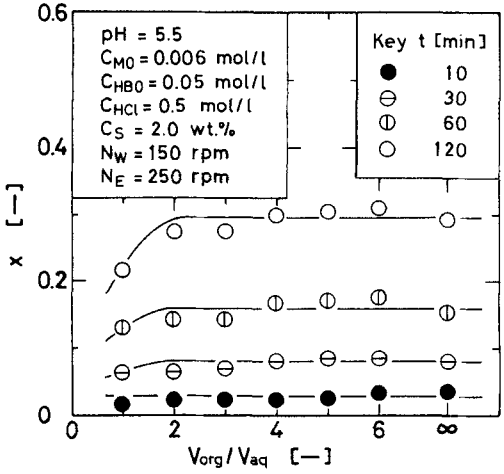

FIGURE 4. Effect of volume ratio of organic solution to aqueous solution in emulsion phase on extent of copper extracted.

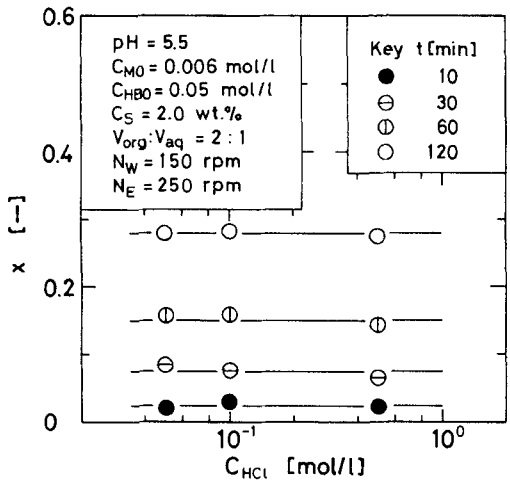

FIGURE 5. Effect of hydrochloric acid concentration in internal aqueous solution on extent of copper extracted.

reaction rate on the overall extraction rate of copper is negligible under the experimental conditions employed.

Typical relations between the extent of copper extracted and time are presented in Fig. 6 as a function of pH. It is evident that the extraction rate increases with pH. These results are similar to those obtained earlier for the extraction of copper with benzoylacetone (17).

As mentioned previously, it is anticipated that the copper extraction reaction occurs in the aqueous phase close to the interface between the aqueous and the emulsion phases. The effect of pH on the initial extraction rate, J_M, is shown in Fig. 7. The initial extraction rate varies inversely as the 0.5 power of hydrogen-ion concentration in the low pH range, but becomes independent of pH in the high pH range.

The effect of initial benzoylacetone concentration, C_{HBO}, on the initial extraction rate is shown in Fig. 8. The initial

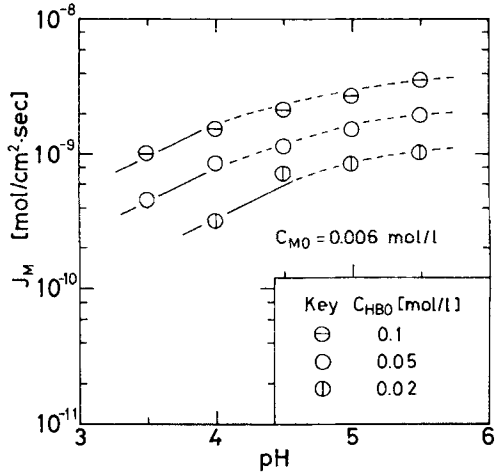

FIGURE 6. Relation between extent of copper extracted and time, as a function of pH.

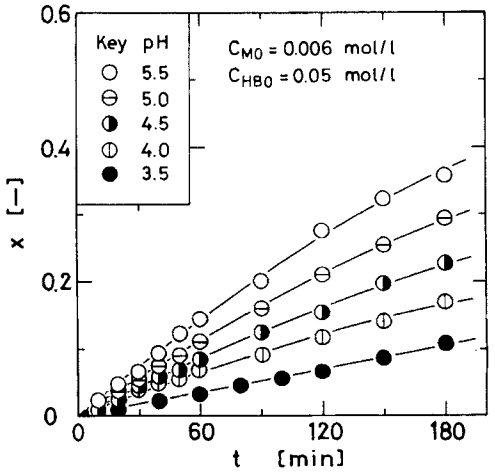

FIGURE 7. Effect of pH on initial extraction rate.

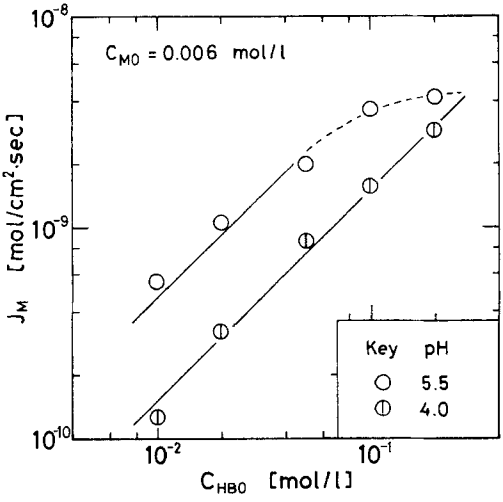

FIGURE 8. Effect of benzoylacetone concentration on initial extraction rate.

extraction rate is proportional to the benzoylacetone concentration in the low pH range. For combinations of high pH and high benzoylacetone concentration, the rate is only slightly affected by benzoylacetone concentration.

The effect of initial copper concentration, C_{MO}, on the initial extraction rate is displayed in Fig. 9. It is evident that the initial extraction rate is proportional to the square root of the copper concentration.

DISCUSSION

In this section we discuss the mechanism for the extraction of copper ion with liquid surfactant membranes in a stirred transfer cell. In a previous paper (14), in which a batch-type stirred tank was used, the initial extraction rate could be described approximately by a model in which each water droplet within the emulsion droplet migrates freely and has an average composition with respect to copper ion. From the data presented in Figs. 3

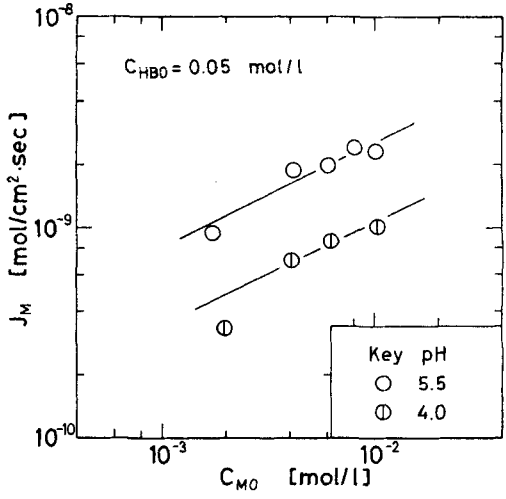

FIGURE 9. Effect of copper concentration on initial extraction rate.

and 4, these assumptions appear to be valid for the stirred transfer cell when operated with a stirring speed of 250 rpm in the emulsion phase and at a volume ratio (organic solution/ aqueous solution in the emulsion phase) of 2.

Consider the average volume, v_{org}, of the organic solution element surrounding a small water droplet in the emulsion phase, assuming uniform dispersion:

$$v_{org} = (\pi/6)[\phi/(1 - \phi)]d_w^3 , \quad (1)$$

where d_w is the diameter of a small water droplet in the emulsion phase, and

$$\phi = V_{org}/(V_{org} + V_{aq}), \quad (2)$$

where V_{org} and V_{aq} are the volumes of organic and aqueous solution in the emulsion phase, respectively. Therefore, the membrane thickness, δ_e, is given approximately by the expression:

$$\delta_e = d_w\{[1/(1 - \phi)]^{1/3} - 1\}. \quad (3)$$

For example, δ_e = 0.78 μm when ϕ = 0.5 and d_w = 3 μm (15).

The thickness of film δ which is in the aqueous phase close to the external interface of membrane can also be estimated. Using the values of the diffusion coefficient of benzoylacetone in the aqueous phase, $D_{HB} = 0.84 \times 10^{-5}$ cm^2/sec, and of the mass transfer coefficient of benzoylacetone in the aqueous phase, $k_L = 9.8 \times 10^{-4}$ cm/sec reported previously (17), the value of δ becomes 8.6×10^{-3} cm based on the film theory. This is about a hundred times the membrane thickness. Therefore, we may consider that the mass transfer resistance in the membrane is negligible in comparison with the resistance in the film of the aqueous phase, which is induced by the chelating complex formation and diffusion processes, as stated earlier (14).

From these considerations, a description of liquid surfactant membranes in a stirred transfer cell which results is that shown schematically in Fig. 1. Copper ion, M^{2+} will diffuse toward the interface to form the chelating complex, MR_2 with chelating agent, RH (benzoylacetone in this case), which will diffuse across the interface from organic solution. The complex will rapidly diffuse across the liquid membrane with a thickness, δ_e, and will liberate copper ion into the small water droplet, exchanging two hydrogen ions. Chelating agent, which is regenerated in the process, will again diffuse toward the interface.

Consider the stripping reaction processes within the small water droplets. According to a previous paper (17), the rate of the chelating complex formation, r_f, in the aqueous phase can be expressed by the relation:

$$r_f = k_3 K_1 K_2 \left(\frac{C_M C_{HB(org)}}{C_H} - \frac{1}{K} \frac{C_{MB2(org)} C_H}{C_{HB(org)}} \right), \qquad (4)$$

where k_3 is the reaction rate constant of copper monocomplex formation, K_1 is the partition constant of benzoylacetone, and K_2 is the dissociation constant of benzoylacetone. C_H and C_{MB2} are the concentrations of the hydrogen-ion and the copper bis-complex with benzoylacetone, respectively. Assuming that the rate-controlling step in the stripping reaction is the same as that in

the chelating complex formation, the expression for the stripping reaction rate, r_s, in the internal aqueous solution is given by

$$r_s = -r_f = k_3 K_1 K_2 \left(\frac{1}{K}\frac{C_{MB2(org)} C_{HCl}}{C_{HB(org)}} - \frac{C_M C_{HB(org)}}{C_{HCl}}\right), \quad (5)$$

where K is the equilibrium constant for the overall extraction reaction of copper, 6.76×10^{-5} (18). We consider a case in which the extent of copper extracted is 15%, with $C_{MO} = 0.006$ mol/L, $C_{HBO} = 0.05$ mol/L, pH = 4.0 and $C_{HCl} = 0.5$ mol/L. The value of the first term in the parentheses of Eq. (4) is 2.6 mol/L, and that of the second term is only 1% of this value. Similarly, the value of the first term in the parentheses of Eq. (5) is 1.3×10^2 mol/L, and that of the second term is only 4×10^{-4}% of this value. Therefore, in the initial period of extraction, the stripping reaction rate is sufficiently larger than the rate of the chelating complex formation, so that the stripping reaction is not considered to be the rate-controlling step of the copper extraction. This result is supported by the experimental results shown in Fig. 5, in which the pH of the internal aqueous phase is seen to have a negligible effect on the reaction rate.

Lastly, the concentration gradient of benzoylacetone in the liquid membrane can be estimated. Since the maximum initial extraction rate is 5×10^{-9} mol/cm^2·sec, the flux of benzoylacetone, J_{HB}, in the membrane can be estimated to be about 10^{-8} mol/cm^2·sec. The expression for J_{HB} can be written (14) as

$$J_{HB} = k'_{HB} (C_{HBO} - C^{i}_{HB}) = k'_{HB} \cdot \Delta C_{HB}, \quad (6)$$

where k'_{HB} is the mass transfer coefficient of benzoylacetone in the membrane, and C^{i}_{HB} is the concentration of benzoylacetone at the external interface. Assuming film theory applies, k'_{HB} can be approximated by D'_{HB}/δ_e, where D'_{HB} is the diffusion coefficient of benzoylacetone in toluene. Using the value of δ_e presented earlier and the value of $D'_{HB} = 1.8 \times 10^{-5}$ cm^2/sec (19), the benzoylacetone concentration difference, ΔC_{HB}, becomes 4.3×10^{-5} mol/L.

This value is only 0.02% of the initial concentration of 0.2 mol/L. Therefore, there appears to be only a very small concentration gradient of copper complex as well as benzoylacetone in the membrane. From the discussion above, it can be assumed that, even at the early stage of extraction, copper ion is accepted into the small water droplets in the emulsion phase.

In developing the mathematical description of the initial extraction rate in the stirred transfer cell, it is sufficient to consider the chelating complex formation and diffusion processes in the aqueous phase close to the external interface of the membrane, as mentioned previously. The experimental results should then be described (see Appendix) by the equation

$$J_M = \frac{1}{(1/K_1 k_L E) + (1/k'_{HB})} \cdot \frac{C_{HBO}}{2}, \qquad (7)$$

where J_M is the flux of copper ion and E is the enhancement factor (which is defined in the Appendix). Assuming that the mass transfer of complex in the membrane is not the rate-controlling step, i.e., $1/K_1 k_L E \gg 1/k'_{HB}$, then Eq. (7) becomes

$$J_M = K_1 k_L E \, (C_{HBO}/2). \qquad (8)$$

Under the conditions of pseudo-first order reaction, i.e., $E_i \gg M > 1$, Eq. (8) can be rewritten in the form

$$J_M = \frac{(D_{HB} k_3 K_1^2 K_2)^{1/2}}{2} \cdot \frac{C_{HBO} C_{MO}^{1/2}}{C_H^{1/2}}. \qquad (9)$$

Equation (9) accurately describes the experimental results at low pH and benzoylacetone concentration.

We can obtain values of the reaction rate constant, k_3, and the mass transfer coefficient, k_L, from the experimental data through the use of Eq. (8). First, the experimental data are summarized as a plot of J_M/C^*_{HB} vs $(C_{MO}/C_H)^{1/2}$. The resultant curve is superposed on a plot of E vs $(M)^{1/2}$ obtained from Eq. (A-1). The value of k_L is then obtained from E, corresponding to J_M/C^*_{HB}, and the value of k_3 is obtained from $(M)^{1/2}$,

corresponding to $(C_{MO}/C_H)^{1/2}$. The values derived in this manner are $k_L = (5.4 \pm 1.5) \times 10^{-4}$ cm/sec and $k_3 = 5.0 \times 10^{12}$ cm^3/mol·sec. In the calculation, the value of the partition constant K_1 used was the same as in the water-benzene system, i.e., 7.2×10^{-4} (18), whereas the values of K_2 and D_{HB} were taken to be identical to those employed in a previous paper (17). The value of k_3 is about ten times the value obtained earlier (17), in which the pH of aqueous phase was adjusted using an ammonium nitrate-ammonium hydroxide solution. This difference is due to the use of acetic acid-sodium acetate buffer solution in the present experiments. Copper ion can form a copper-acetate complex, $Cu(OAc)^+$, in aqueous solution, which can be extracted more rapidly than Cu^{2+}. For example, the addition of acetate ion is reported (20) to enhance the rate of zinc dithiozonate extraction by about a factor of 25. Chloride ion (21), and thiocyanate ion (22) are also reported as chelating agents which accelerate the extraction rates of metals.

On the other hand, the value of k_L is somewhat small in comparison with the value obtained in our previous study (17). This is due to the higher viscosity of the emulsion phase in the present work over that of the organic phase used in the previous study. (It is presumed that the mass transfer coefficient is affected by the mobility of benzoylacetone in the emulsion phase.)

The values of the coefficients k_3 and k_L which were determined in this study were employed in the presentation of the experimental data as a plot of E vs $(M)^{1/2}$ which is shown in Fig. 10. A benzoylacetone concentration of 0.1 mol/L corresponds to $E_i = 150$, whereas a concentration of 0.05 mol/L corresponds to $E_i = 290$. The experimental data appear to be in reasonable agreement with the diffusion model. In other words, the experimental results tend to support the validity of the assumptions which were made in applying the model to the extraction of copper ion in the stirred transfer cell.

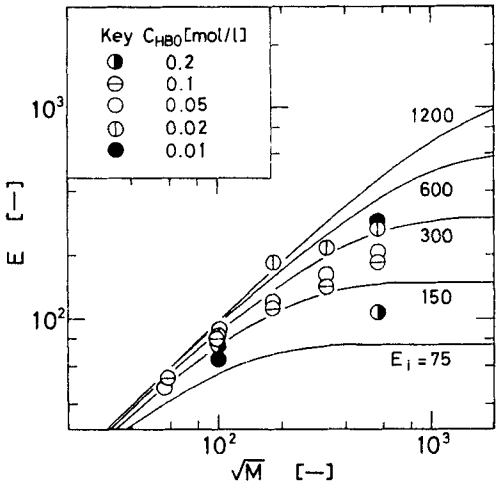

FIGURE 10. Relation between E and $(M)^{1/2}$.

The experimental data obtained with the batch-type stirred tank can now be analyzed in terms of the same extraction mechanism.

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

$$-V_W(dC_M/dt) = AJ_M, \tag{10}$$

where V_W is the volume of external aqueous phase, and A is the total surface area of emulsion droplets. Since $A = V_E(6/d)$, where V_E is the total volume of emulsion droplets and d is their average diameter, the use of Eq. (8) permits Eq. (10) to be rewritten in the form

$$-(dC_M/dt) = k_L a K_1 E\ (C_{HBO}/2), \tag{11}$$

where a is the surface-to-volume ratio of the emulsion droplet, that is, $6\ V_E/dV_W$. Equation (11) can be solved by the Runge-Kutta method, with the initial condition being $C_M = C_{MO}$ at $t = 0$. The value of the constants used in the calculation are

as follows: $D_{HB_4} = 0.84 \times 10^{-5}$ cm^2/sec, $D_{M_3} = 0.72 \times 10^{-5}$ cm^2/sec, $K_1 = 7.24 \times 10^{-4}$, $K_2 = 1.1 \times 10^{-12}$ mol/cm^3, $k_3 = 5.0 \times 10^{12}$ cm^3/mol·sec. Since the values of k_L and $\underline{a}$ are unknown in the stirred tank experiments, Eq. (11) was solved for various combinations of k_L and $\underline{a}$. Comparisons of the experimental data with calculated results are shown in Figs. 11 and 12 for the case $V_W:V_E$ = 700:100. The solid lines represent the calculated results with $k_L = 1.0 \times 10^{-3}$ cm/sec and d = 0.06 cm. The deviations between theory and experiment beyond the 15-min time period are believed to be due to emulsion breakdown.

The same values of k_L and d were then used to construct the theoretical curves for the case $V_W:V_E$ = 750:50 that are

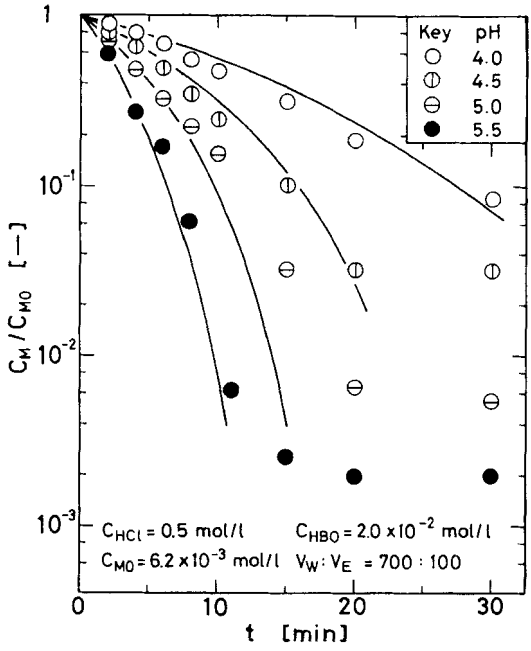

FIGURE 11. Effect of pH on extraction rate of copper in a batch-type stirred tank.

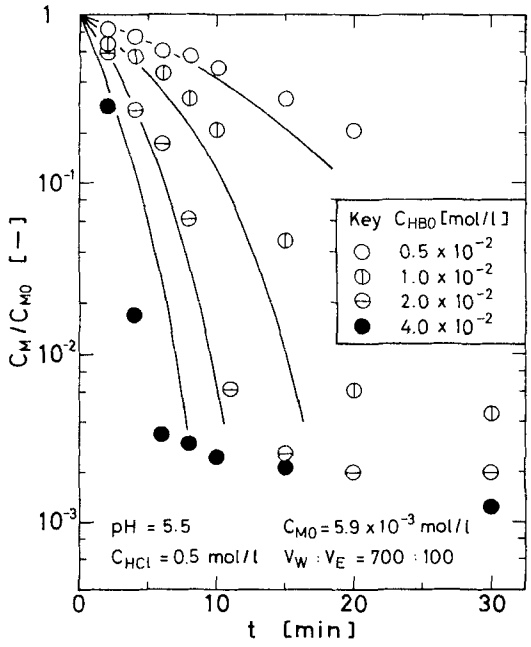

FIGURE 12. Effect of benzoylacetone concentration on extraction rate of copper in a batch-type stirred tank.

shown in Fig. 13. The calculated values are in good agreement with the experimental results over the initial 15-min time period. A primary reason for the divergence over this time interval is the difference in the diameters of the emulsion droplets in the two cases.

The data presented in Figs. 11-13 support the mechanism developed in this paper for the extraction of copper using liquid surfactant membranes. The model as presently developed is applicable only during the early phase of the extraction; further work is necessary to extend the treatment to longer time periods, wherein effects of emulsion breakdown need to be taken into account.

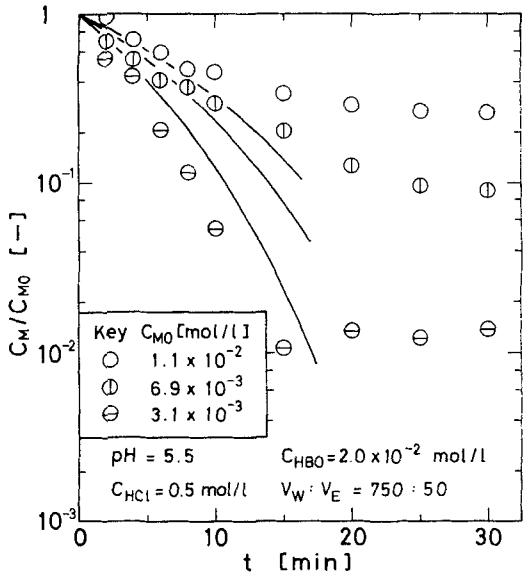

FIGURE 13. Effect of copper concentration on extraction rate of copper in a batch-type stirred tank.

CONCLUSIONS

The extraction of copper with liquid surfactant membranes was carried out in a stirred transfer cell to define the mechanism of extraction. Emulsion breakdown was found to be very small in comparison with that in a batch-type stirred tank. The initial extraction rate of copper varied inversely as the 0.5 power of hydrogen-ion concentration in the low pH range, but tended to become independent of pH in the high pH range. The rate was proportional to the benzoylacetone concentration in the low pH range, but in the high pH range the rate was only slightly affected by the benzoylacetone concentration at high benzoylacetone concentrations. Moreover, the rate was observed to be proportional to the square root of the copper concentration.

A model for facilitated transport was proposed in which the small water droplets in the emulsion phase were assumed to be uniformly dispersed, and the effect of the stripping reaction rate on the overall extraction rate of copper was assumed to be negligible. The experimental data were analyzed in terms of this model to obtain values of the reaction rate constant and the characteristic mass transfer coefficient. The results obtained in this manner were shown to be consistent with experimental data obtained using a batch-type stirred tank.

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APPENDIX

By defining the modulus M as $D_{HB}k_3K_2C_M/k_L^2C_H$, and the enhancement factor E_i as $1 + 2D_MC_M/D_{HB}C^*_{HB}$, E can be expressed (23) as an explicit function of E_i and M.

$$E = 1 + (E_i - 1)[1 - \exp\{-[(M)^{1/2} - 1]/(E_i - 1)\}]. \quad \text{(A-1)}$$

The enhancement factor E is defined by

$$E = 2J_M/k_LC^*_{HB}, \quad \text{(A-2)}$$

where C^*_{HB} is the concentration of benzoylacetone at the interface which is in equilibrium with the concentration in the organic phase;

$$C^*_{HB} = K_1C^i_{HB}. \quad \text{(A-3)}$$

Equation (7) is derived from Eqs. (A-2), (A-3), and (6), and the assumption that $J_{HB} = 2J_M$.