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Masaaki Teramoto[a]; Tsutomu Sakai[a]; Kouyou Yanagawa[a]; Yoshikazu Miyake[a]
[a] DEPARTMENT OF INDUSTRIAL CHEMISTRY, KYOTO INSTITUTE OF TECHNOLOGY, KYOTO, JAPAN

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Modeling of the Permeation of Copper through Liquid Surfactant Membranes by Continuous Operations

MASAAKI TERAMOTO,* TSUTOMU SAKAI,
KOUYOU YANAGAWA, and YOSHIKAZU MIYAKE

DEPARTMENT OF INDUSTRIAL CHEMISTRY
KYOTO INSTITUTE OF TECHNOLOGY
SAKYO-KU, KYOTO 606, JAPAN

Abstract

A model for copper permeation through liquid surfactant membranes in a continuously stirred vessel is presented in which mass transfer resistances both in and around W/O emulsion drops, interfacial reactions at aqueous–organic interfaces, and the residence time distribution of the W/O emulsion drops in the extraction vessel are taken into account. Extraction of copper using SME529 as a carrier was carried out with a continuously stirred vessel. It is shown that the experimental data can be satisfactorily interpreted by the proposed model.

INTRODUCTION

A separation technique using liquid surfactant membranes has been noted as a novel method for separating and concentrating metal ions, weak acids, and weak bases (*1*). In particular, attention has been paid to the concentration of metal ions by means of the active transport mechanism, and several papers on the permeation mechanism of metal ions through liquid surfactant membranes have been presented (*1–3*). The present authors (*4*) have also presented a general model for the extraction of copper using a chelating agent as a carrier in which mass transfer resistances in the W/O emulsion drops and the stagnant aqueous films around the drops, and interfacial reactions at aqueous–organic interfaces are taken into account.

These models have been presented for batch extractions of metal ions where the metal ion concentrations vary with the extraction time and each

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*To whom correspondence should be addressed.

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emulsion drop has the same residence time. However, the continuous operations are more important than the batch operation from the practical point of view. Recently Hatton et al. (*5*) proposed a model for the continuous extraction of ammonia by liquid surfactant membranes.

In the present paper the previous model of the present authors for the batch extraction of copper is extended to the case of the continuous operation by taking into account the dependence of the copper permeation rate on the residence time of the emulsion drop in the continuously stirred vessel.

THEORY

The schematic diagram of the permeation model is shown in Fig. 1. The elementary steps of the copper permeation are as follows.

Steps 1 and 1′: Diffusions of copper and hydrogen ions through the stagnant film of the external aqueous phase.

Step 2: Complex formation between Cu^{2+} and HR, a chelating agent, at the external surface of the W/O emulsion drop.

Steps 3 and 3′: Diffusions of the complex and the chelating agent in the peripheral oil layer of the W/O emulsion drop.

Steps 4 and 4′: Diffusions of the complex and the chelating agent through the interstitial oil membrane phase.

Step 5: Stripping of copper at the interface between the oil membrane phase and the internal aqueous phase droplet containing hydrochloric acid.

It has already been found that R' is approximately equal to R, and the mass transfer resistance of hydrogen ion through the external stagnant film is negligibly small in the present work because buffer solutions were used.

The forward and the stripping reaction rates are represented as follows (*6*):

$$\mathrm{Cu^{2+} + 2HR \rightleftharpoons CuR_2 + 2H^+} \tag{1}$$

$$\mathrm{(A + 2B \rightleftharpoons C + 2H)}$$

$$K_{ex} = (CH^2/AB^2) \tag{2}$$

$$r_f = k_r(AB/H - CH/K_{ex}B) \tag{3}$$

$$r_r = k_r(CH - K_{ex}AB^2/H) \tag{4}$$

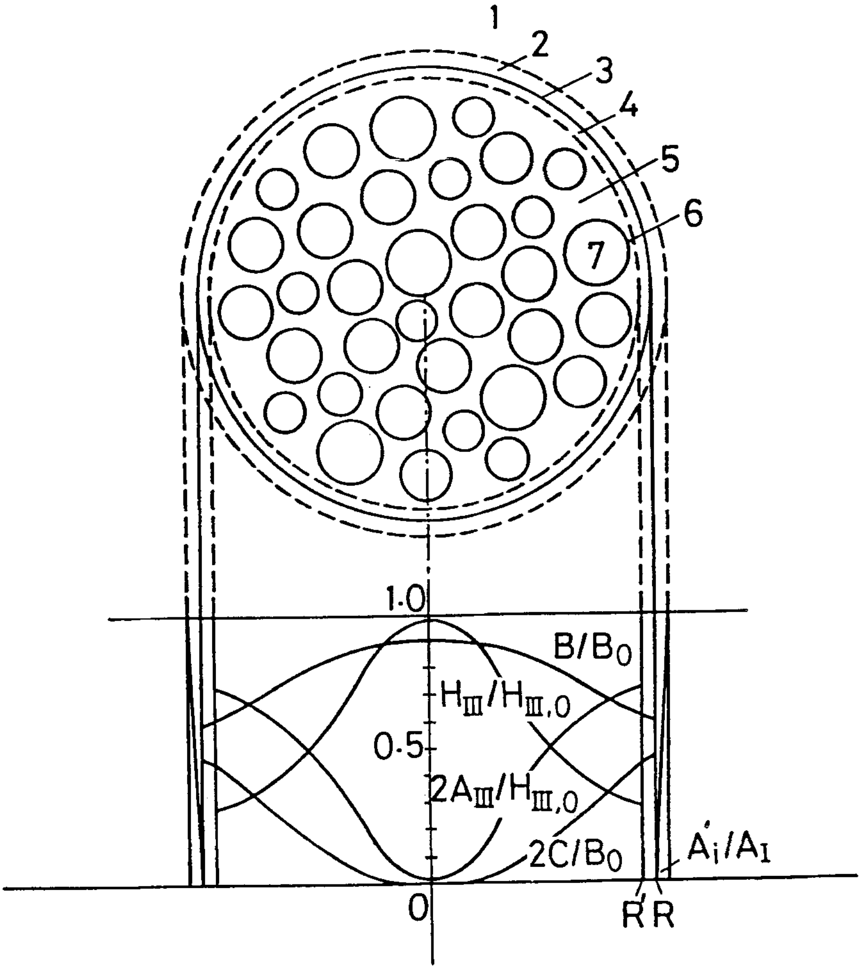

FIG. 1. Schematic diagram of W/O/W multiphase emulsion system. (1) External aqueous phase (Phase I). (2) Stagnant film of Phase I around W/O emulsion drop. (3) Interface between external aqueous phase and W/O emulsion drop. (4) Peripheral oil layer. (5) Oil membrane phase (Phase II). (6) Interface between oil membrane phase and internal aqueous phase. (7) Internal aqueous phase (Phase III).

In the case of continuous operation the copper concentration in the external aqueous phase is maintained at a steady-state value determined by the mass balance equation of copper which contains the term expressing the extraction rate of copper. In this case the basic equations describing the differential mass balances in the emulsion drop are as follows (*4*):

$$(1-\phi)\frac{\partial B}{\partial t}=D_{e,\mathrm{B}}\left(\frac{\partial^2 B}{\partial r^2}+\frac{2}{r}\frac{\partial B}{\partial r}\right)+\frac{6\phi k_r}{R_\mu}\left(CH_{\mathrm{III}}-\frac{K_{\mathrm{ex}}A_{\mathrm{III}}B^2}{H_{\mathrm{III}}}\right) \tag{5}$$

$$(1-\phi)\frac{\partial C}{\partial t}=D_{e,\mathrm{C}}\left(\frac{\partial^2 C}{\partial r^2}+\frac{2}{r}\frac{\partial C}{\partial r}\right)-\frac{3\phi k_r}{R_\mu}\left(CH_{\mathrm{III}}-\frac{K_{\mathrm{ex}}A_{\mathrm{III}}B^2}{H_{\mathrm{III}}}\right) \tag{6}$$

$$\phi\frac{\partial A_{\mathrm{III}}}{\partial t}=\frac{3\phi k_r}{R_\mu}\left(CH_{\mathrm{III}}-\frac{K_{\mathrm{ex}}A_{\mathrm{III}}B^2}{H_{\mathrm{III}}}\right) \tag{7}$$

The initial and the boundary conditions are as follows:

I.C.: $B=B_0,\ C=C_0,\ A_{\mathrm{III}}=A_{\mathrm{III},0},\ (H_{\mathrm{III}}=H_{\mathrm{III},0})$ for $0\leqq r\leqq R,\ t=0$ (8)

B.C.1: $\partial B/\partial r=\partial C/\partial r=0$ for $r=0,\ t\geqq 0$

B.C.2:

$$\begin{aligned} J_A &= k_A(A_{\mathrm{I}}-A_{\mathrm{I},i})\\ &= k_f(A_{\mathrm{I},i}B_i/H_{\mathrm{I},i}-C_iH_{\mathrm{I},i}/K_{\mathrm{ex}}B_i)\\ &= k_B\{(B)_{r=R'}-B_i\}/2\\ &= k_{\mathrm{C}}\{C_i-(C)_{r=R'}\}\\ &= -D_{e,\mathrm{B}}(\partial B/\partial r)_{r=R'}/2\\ &= D_{e,\mathrm{C}}(\partial C/\partial r)_{r=R'} \end{aligned} \tag{9}$$

The charge balance equation in the internal aqueous phase is represented by

$$2A_{\mathrm{III},0}+H_{\mathrm{III},0}=2A_{\mathrm{III}}+H_{\mathrm{III}} \tag{10}$$

In this case, the copper flux is given by

$$J_A = k_A A_I \tag{11}$$

However, the higher the copper concentration is, the larger the mass transfer resistance in the drop becomes because the more rapidly the internal droplets are saturated with copper. Thus when A_I is high, J_A decreases sharply with t as shown in Fig. 2.

When a continuously stirred tank is used, the W/O emulsion drops with different residence times exist in the vessel, and the extraction rate of copper by a W/O emulsion drop varies depending on the residence time of the drop, t. As explained above, the longer the residence time is, the slower the extraction rate becomes. Therefore, it is necessary to consider the residence time distribution of the drops in the vessel. Here the following residence time distribution function for the mixed flow is used.

$$f(t) = \exp(-t/\tau_e)/\tau_e \tag{12}$$

Here τ_e is the mean residence time of the drops and approximately equal to τ, the mean residence time of the feed solution. Then the mean extraction rate of copper in the stirred vessel is expressed by

$$J_{A,av}(\tau_e) = \int_0^\infty J_A(t) \exp(-t/\tau_e)/\tau_e \, dt \tag{13}$$

$J_{A,av}$ can be calculated from Eq. (13) using the relation between J_A and t (Fig. 2).

The mass balance equation of copper in the continuous stirred vessel is represented by

$$\begin{aligned} L(A_{I,in} - A_{I,out}) = L(A_{I,in} - A_I) &= J_{A,av}S \\ &= (3V_e/R)J_{A,av} \end{aligned} \tag{14}$$

where V_e is the total volume of the W/O emulsion, and S is the total interfacial area between the emulsion drops and the external aqueous phase. The dimensionless copper concentration $y = A_I/A_{I,in}$ can be calculated from Eqs. (13) and (14) by a trial and error procedure.

Under the condition that Eq. (11) holds, $J_{A,av}$ is represented by

$$J_{A,av} = k_A A_I \tag{15}$$

Then an analytical solution for y can be obtained from Eqs. (14) and (15).

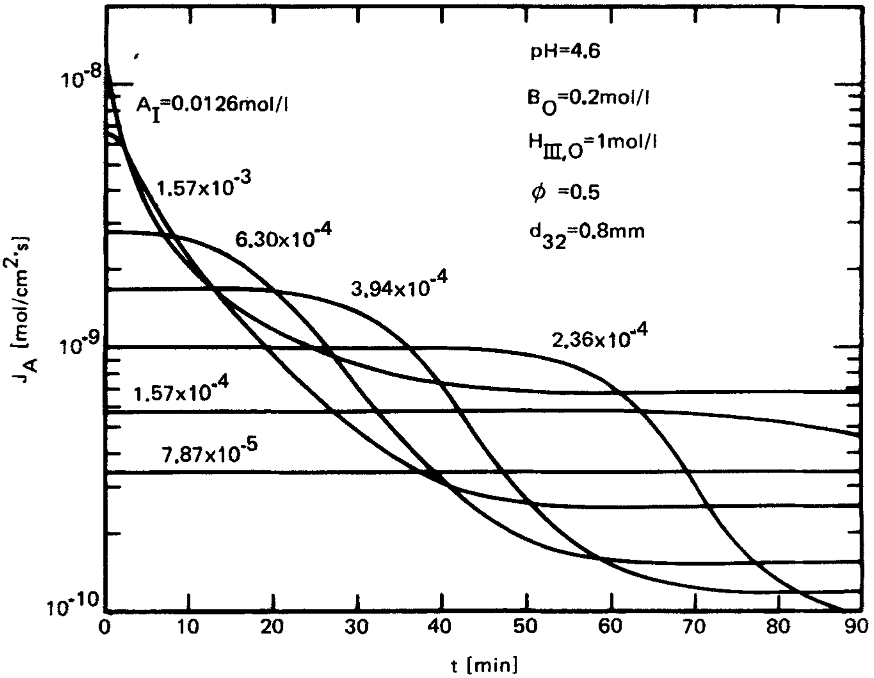

FIG. 2. Effects of the contact time of W/O emulsion drop and the copper concentration on the copper flux. The values of parameters are as follows: $D_{e,B} = 6.1 \times 10^{-7}$ cm^2/s, $k_A = 0.0045$ cm/s, $k_B = 0.0004$ cm/s, $k_C = 0.000264$ cm/s, $k_f = 1.6 \times 10^{-5}$ cm/s, $k_r = 0.044$ cm^4/mol·s, $K_{ex} = 0.6$.

A_I, H_I, B_0, C_0, $A_{III,0}$, $H_{III,0}$, R, R_μ, and ϕ are determined from the experimental conditions, and k_B, k_C, k_f, k_r, $D_{e,B}$, $D_{e,C}$, and K_{ex} have already been reported (*4*). The method to estimate k_A will be described later. If these parameters are given, the basic equations can be numerically solved to give the concentration profiles as a function of t, the contact time between the emulsion drop and the external aqueous phase in which the copper concentration is kept constant at A_I. Then the relation between the copper flux and t is obtained from Eq. (9).

The typical results calculated using the values of the parameters which correspond to the present experimental condition described below are shown in Fig. 2. The values of the parameters are shown in the caption of the same figure. When both A_I and H_I are low, J_A is independent of t because the mass transfer resistance of copper through the external stagnant film is dominant.

$$y = A_{\mathrm{I}}/A_{\mathrm{I,in}} = 1/\{1 + (3k_{\mathrm{A}} V_e/RL)\} \tag{16}$$

On the other hand, if the forward reaction at the external surface of the drop is rate-determining, and is considered to be irreversible, then the following equation holds:

$$y = A_{\mathrm{I}}/A_{\mathrm{I,in}} = 1/\{1 + (3k_f B_i V_e/H_i RL)\} \tag{17}$$

EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 3. The agitation vessel, made of Pyrex glass, is 6 cm in diameter, 8.5 cm in height, and equipped with a six-bladed turbine agitator and four intermediate baffle plates. The pH of copper solution was adjusted using 0.5 mol/L acetic acid–sodium acetate buffer. The W/O emulsion was formulated from the organic and aqueous source as described previously (*4*). The organic membrane phase consisted of Dispersol, a sort of kerosene supplied from the Shell Chemical Co., Ltd., in which were dissolved SME529, a chelating agent (Shell Chemical Co., Ltd.) and Span 80, an emulsifier. The organic solution thus prepared and the same volume of the aqueous solution of hydrochloric acid was agitated for 15 min by a Vibromixer and then sonicated by an ultrasonic homogenizer. The copper solution and the emulsion were supplied to the agitation vessel by a reciprocating pump and a microtubing pump at the flow rates of L and L_e, respectively. The ratio L_e/L was adjusted approximately at 0.1. The liquid volume in the vessel was maintained at 200 cm^3 by a level controller. The stirring speed was 300 rpm. The copper concentration in the effluent external aqueous solution was determined by an atomic absorption spectrophotometer, and each run was continued until a steady-state was attained. The Sauter mean diameter of the W/O emulsion drops and the internal aqueous phase droplets were measured by the photographic and the microscopic methods, respectively. Then the mean copper flux was calculated by

$$J_{\mathrm{A,av}} = L(A_{\mathrm{I,in}} - A_{\mathrm{I}})/S = LR(A_{\mathrm{I,in}} - A_{\mathrm{I}})/3V_e \tag{18}$$

In the present work, the concentrations of Span 80 and SME529 were 5 vol% and 0.2 mol/L, respectively, the temperature was 298 K, the initial concentrations of copper and hydrochloric acid in the internal phase were 0 and 1 mol/L, respectively, and the pH of the feed solution was 4.6. Because of high pH of the feed, the rate of the complexation is very fast. Thus the

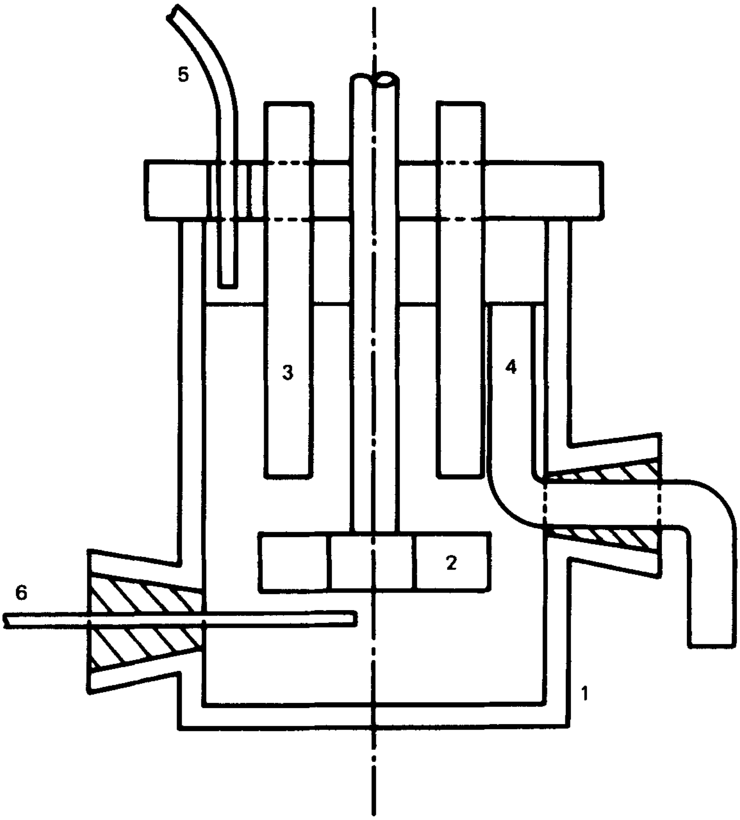

FIG. 3. Schematic diagram of the experimental apparatus. (1) Agitation vessel. (2) Six-bladed turbine agitator. (3) Intermediate baffle plate. (4) Overflow tube (level controller). (5) Inlet tube of feed solution. (6) Inlet tube of W/O emulsion.

resistance of Step 2 could be ignored under the present conditions. R was in the range from 0.35 to 0.45 mm, and R_μ was about 1.6 μm.

RESULTS AND DISCUSSION

(1) Effect of the Flow Rate of the Feed Solution

The effect of the volumetric feed rate of copper solution was examined. The feed rate was varied in the range from 8.3×10^{-3} to 0.55 cm^3/s and the

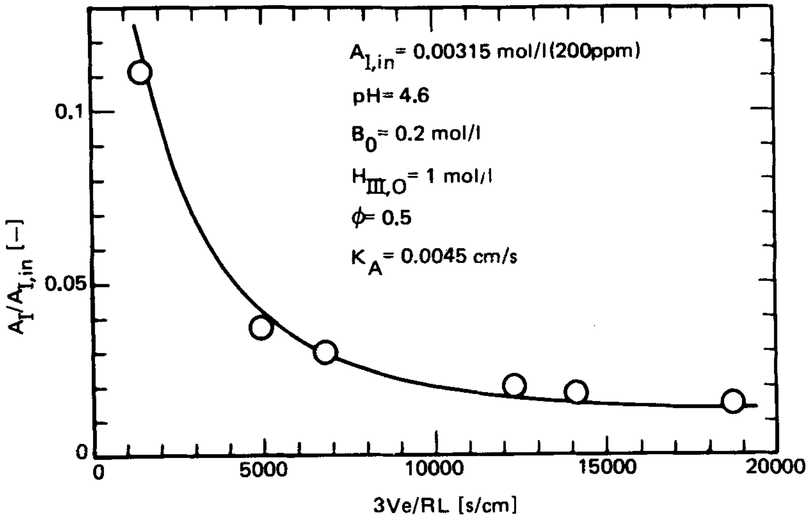

FIG. 4. Effect of the flow rate of the feed solution on the effluent copper concentration.

copper concentration in the feed was kept constant at 3.15×10^{-3} mol/L. Because both A_I and H_I are low, Step 1 is considered to limit the permeation rate. Thus Eq. (16) can be applied to analyze the experimental data. Figure 4 shows the plot of y ($= A_I/A_{I,0}$) against $3V_e/RL$ where the theoretical result calculated from Eq. (16) using 0.0045 cm/s as the value of k_A is also shown by the solid line. This value is higher than that obtained in the previous work (0.0034 cm/s). The cause of this discrepancy may be that a different agitation vessel was used in the present study.

(2) Effect of the Copper Concentration

The effect of the copper concentration in the effluent solution on the mean copper flux is shown in Fig. 5. Here the flow rates were adjusted so that the mean residence time of the liquid might be 6 and 20 min, and the influent copper concentration was varied in the range from 0.0315 to 7.9×10^{-4} mol/L. In the concentration range of copper below 3×10^{-4} mol/L, $J_{A,av}$ is proportional to A_I irrespective of the mean residence time, suggesting that the copper permeation is limited by Step 1 and that $J_{A,av}$ is given by Eq. (15). However, when A_I is high, the concentration dependence of $J_{A,av}$ decreases and $J_{A,av}$ depends on the mean residence time. This behavior can be explained from the relation between J_A and t; i.e., J_A decreases with

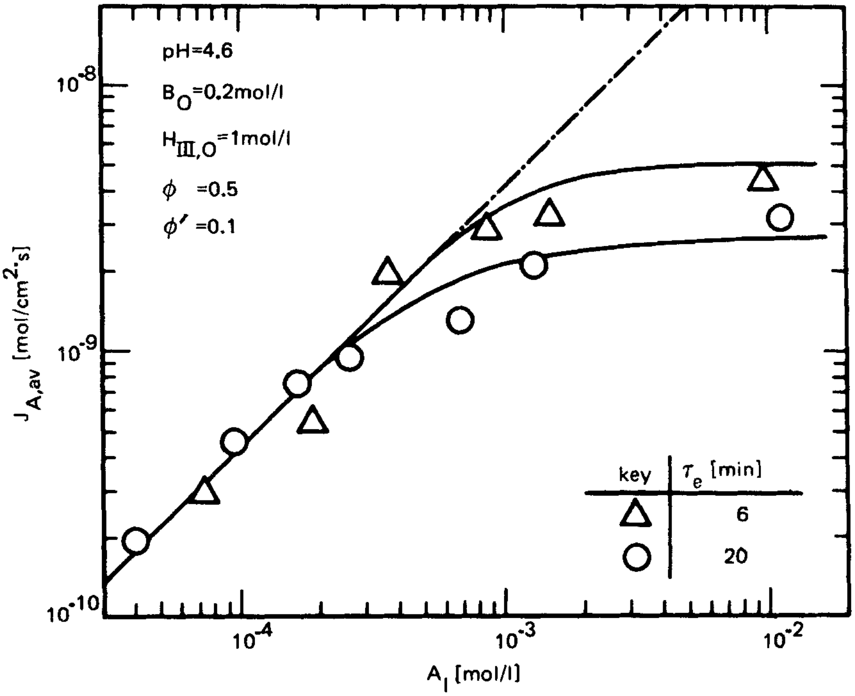

FIG. 5. Effect of the copper concentration in the effluent solution on the mean copper flux.

increasing residence time t when A_I is high, as shown in Fig. 2. The solid lines in Fig. 5 are the theoretical results calculated from Eq. (13). It can be seen that the experimental results are satisfactorily simulated by the proposed model.

The effect of the copper concentration in the feed solution on the effluent copper concentration is shown in Fig. 6. In the range of $A_{I,in}$ below 6×10^{-3} mol/L, y is almost independent of $A_{I,in}$ because Step 1 is rate-determining. The horizontal lines in Fig. 6 are the computed results by Eq. (16).

As $A_{I,in}$ increases, y also increases because the internal diffusion becomes dominant. The solid lines are the theoretical results computed from Eqs. (13) and (14).

CONCLUSION

A general model for the permeation of copper through liquid surfactant membranes in a continuously stirred extraction vessel was developed by

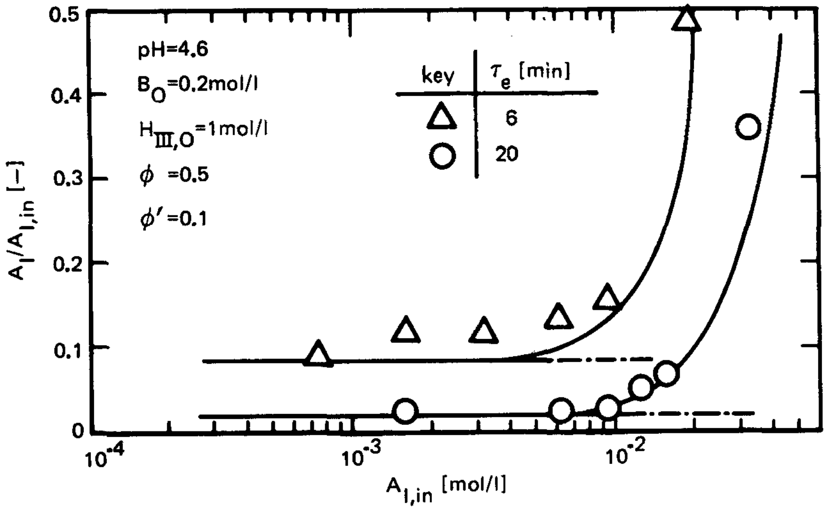

FIG. 6. Effect of the copper concentration in the feed on the effluent concentration of copper.

extending the model which had been developed by the present authors for the batch extraction of copper by liquid surfactant membranes containing a chelating agent as a carrier. The mean copper flux could be calculated from the relation of copper flux vs residence time of the W/O emulsion drop and the residence time distribution function of the drops in the continuously mixed vessel.

It was found that the experimental data obtained with a continuously stirred extraction vessel using SME529 as a carrier could be quantitatively interpreted by the proposed model.

SYMBOLS

A	concentration of copper (mol/cm^3 or mol/L)
B	concentration of chelating agent (mol/cm^3 or mol/L)
C	concentration of chelate (mol/cm^3 or mol/L)
D_e	effective diffusivity (cm^2/s)
$f(t)$	residence time distribution function of W/O emulsion (1/s)
H	hydrogen ion concentration (mol/cm^3 or mol/L)
J_A	copper flux (mol/cm$^2 \cdot$ s)
$J_{A,av}$	mean copper flux (mol/cm$^2 \cdot$ s)
K_{ex}	extraction constant

k_A	mass transfer coefficient of copper through external stagnant film (cm/s)
k_B, k_C	mass transfer coefficients of carrier and chelate through the oil layer around W/O emulsion drop, respectively (cm/s)
k_f, k_r	forward and reverse reaction rate constants, respectively (cm/s), ($cm^4/mol \cdot s$)
L	feed rate of copper solution (cm^3/s)
L_e	feed rate of W/O emulsion (cm^3/s)
R	Sauter mean radius of W/O emulsion drop (cm)
R'	radial distance shown in Fig. 1 (cm)
R_μ	Sauter mean radius of internal droplet (cm)
r	radial distance (cm)
r_f, r_r	forward and stripping reaction rates, respectively ($mol/cm^2 \cdot s$)
t	residence time (s)
V	volume (cm^3)
y	$A_I/A_{I,in}$

Subscripts

A	copper
B	chelating agent
C	chelate
e	emulsion
i	interface between external aqueous phase and W/O emulsion drop
in	inlet
out	outlet
0	initial value
I	Phase I (external aqueous phase)
II	Phase II (organic membrane phase)
III	Phase III (internal aqueous phase)

Greeks

τ	mean residence of copper solution (s)
τ_e	mean residence time of W/O emulsion (s)
ϕ	volume fraction of Phase III in W/O emulsion drop ($= V_{III}/(V_{II} + V_{III})$)
ϕ'	$V_e/(V_I + V_{II} + V_{III}) = (V_{II} + V_{III})/(V_I + V_{II} + V_{III})$

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