EFFECT OF INTERFACIAL REACTION ON RATES OF EXTRACTION AND STRIPPING IN MEMBRANE EXTRACTOR USING A HOLLOW FIBER

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In a membrane extractor using a hollow fiber, the effects of interfacial reaction on the rates of extraction and stripping were studied, using the extraction system of copper and *N*-8-quinolyl-*p*-dodecylbenzenesulfonamide.

It was found that the experimental results could be explained by a diffusion model for metal extraction with an interfacial reaction, taking account of the velocity distributions of the aqueous and organic solutions through the inner and outer sides of a hollow fiber.

It is suggested that the membrane extractor using a hollow fiber can be used as an experimental apparatus for studying the kinetics and mechanism of metal extraction or stripping.

Introduction

Since the mid-1960's, hollow fiber modules have been extensively utilized in many fields, such as desalination of saline water by reverse osmosis, artificial kidney, gas separation and so on.[9] Recently, attractive applications of hollow fiber modules have been attempted in hydrometallurgical processes, i.e., the recovery of uranium with supported liquid membranes[1,2] and the recovery of copper by the membrane extraction process.[7] In the latter process, organic solution containing extractant is circulated between two hollow fiber modules to pick up metal from feed aqueous solution in the extraction module and to release metal into product aqueous solution in the stripping module. To develop and design supported liquid membrane and membrane extraction processes, it is very important to elucidate the mechanisms of both the extraction of metal with extractant and the stripping of metal with stripping agent at both sides of the porous hollow fiber.

Usually, commercial extractants are used in the liquid membrane and membrane extraction processes. In a number of papers concerning the kinetics of metal extraction with commercial extractants, the important role of interfacial reaction on the extraction mechanism has been emphasized.[3,6,8,10,13-15] However, in most papers concerning the coupled transport of metal through the supported liquid membrane of a hollow fiber, it has been shown that the effect of interfacial reaction on the permeation rate was negligibly small.[4,5,11,12]

In the present paper, the effects of interfacial reaction on the rates of extraction and stripping through the porous membrane of a hollow fiber were theoretically and experimentally studied, by using the extraction system of copper and *N*-8-quinolyl-*p*-dodecylbenzenesulfonamide (henceforth C_{12}phSAQ, abbreviated as HR), whose mechanism in a stirred transfer cell was elucidated previously.[14,15]

1. Theory

The extraction of copper with C_{12}phSAQ and the stripping of the complex of copper-C_{12}phSAQ (henceforth CuR_2) with sulfuric acid are represented by a reversible reaction:

$$Cu^{2+}_{aq} + 2HR_{org} \rightleftharpoons CuR_{2org} + 2H^{+}_{aq} \quad K_{ex} \qquad (1)$$

As shown in the previous paper,[14] the reaction of Eq. (1) expresses the following interfacial reactions:

$$HR_{org} \rightleftharpoons HR_{ad} \quad K_{ad} \qquad (2)$$

$$Cu^{2+}_{aq} + HR_{ad} \rightleftharpoons CuR^{+}_{ad} + H^{+}_{aq} \quad K_1 \qquad (3)$$

$$CuR^{+}_{ad} + HR_{ad} \rightleftharpoons CuR_{2org} + H^{+}_{aq} \quad K_2(=k_2/k_2') \qquad (4)$$

Among the interfacial reaction steps, the reaction of Eq. (4) is the rate-determining step. By assuming Langmuir adsorption isotherm to express the adsorption of HR and CuR^+ at the interface, the interfacial extraction rate of Eq. (1), R, is obtained as follows:

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$$R=\frac{k_2K_1(K_{ad}/S_{HR})^2(C_{Cu}C_{HR}^2/a_H-C_{CuR_2}a_H/K_{ex})}{(1+K_{ad}C_{HR}+K_{ad}K_1C_{Cu}C_{HR}/a_H)^2} \quad (5)$$

In the previous paper,[14] the value of each constant in Eq. (5) was obtained as shown in **Table 1**.

It is considered that aqueous solution containing copper or sulfuric acid is flowing through the lumen of a hollow fiber, whereas organic solution containing HR or CuR_2 is cocurrently flowing through the annulus in the membrane extractor shown in **Fig. 1**. In laminar flow, the flow patterns of the aqueous and organic solutions are represented by:

$$u_{aq}(r)=\frac{2Q_{aq}}{\pi r_1^2}\{1-(r/r_1)^2\} \quad (6)$$

$$u_{org}(r)=\frac{2Q_{org}}{\pi r_1^2} \times \frac{(r_3/r_1)^2-(r/r_1)^2+\dfrac{(r_3/r_1)^2-(r_2/r_1)^2}{\ln(r_3/r_2)}\ln(r/r_3)}{(r_3/r_1)^4-(r_2/r_1)^4-\dfrac{\{(r_3/r_1)^2-(r_2/r_1)^2\}^2}{\ln(r_3/r_2)}} \quad (7)$$

The interface between the aqueous and organic solutions is the inner surface of the hollow fiber, because the fiber is hydrophobic. Furthermore, it can be assumed that the activity of hydrogen ion in the aqueous solution is kept constant along the lumen of the hollow fiber, and that in Eq. (5), $K_{ad}K_1C_{Cu}C_{HR}^2/a_{H0} \ll 1+K_{ad}C_{HR}$ under the extraction and stripping conditions discussed in this paper. Therefore, the interfacial extraction rate of copper and the interfacial stripping rate of CuR_2 are simplified to the following equations:

$$R=\frac{k_2K_1(K_{ad}/S_{HR})^2(C_{Cu}C_{HR}^2/a_{H0}-C_{CuR_2}a_{H0}/K_{ex})}{(1+K_{ad}C_{HR})^2} \quad (5a)$$

$$R'=\frac{k_2'(C_{CuR_2}a_{H0}-K_{ex}C_{Cu}C_{HR}^2/a_{H0})}{(1+K_{ad}C_{HR})^2} \quad (5b)$$

From the mass balances of copper, HR and CuR_2 in the membrane extractor, the basic equations and the boundary conditions are as follows:
in the lumen of hollow fiber $(0<r<r_1)$,

$$u_{aq}(r)\frac{\partial C_{Cu}}{\partial l}=D_{Cu}\left(\frac{\partial^2 C_{Cu}}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial C_{Cu}}{\partial r}\right) \quad (8)$$

in the annulus $(r_2<r<r_3)$,

$$u_{org}(r)\frac{\partial C_{HR}}{\partial l}=D_{HR}\left(\frac{\partial^2 C_{HR}}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial C_{HR}}{\partial r}\right) \quad (9)$$

$$u_{org}(r)\frac{\partial C_{CuR_2}}{\partial l}=D_{CuR_2}\left(\frac{\partial^2 C_{CuR_2}}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial C_{CuR_2}}{\partial r}\right) \quad (10)$$

in the porous membrane of the hollow fiber $(r_1<r<r_2)$,

$$D_{eHR}\left(\frac{\partial^2 C_{HR}}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial C_{HR}}{\partial r}\right)=0 \quad (11)$$

$$D_{eCuR_2}\left(\frac{\partial^2 C_{CuR_2}}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial C_{CuR_2}}{\partial r}\right)=0 \quad (12)$$

for the foundary conditions,

$$l=0,\ 0<r<r_1;\quad C_{Cu}=C_{Cu0} \quad (13)$$

$$l=0,\ r_2<r<r_3;\quad C_{HR}=C_{HR0},\ C_{CuR_2}=C_{CuR_20} \quad (14)$$

$$l>0,\quad r=0\ ;\quad D_{Cu}\frac{\partial C_{Cu}}{\partial r}=0 \quad (15)$$

$$l>0,\quad r=r_1\ ;\quad -D_{Cu}\frac{\partial C_{Cu}}{\partial r}=\frac{1}{2}D_{eHR}\frac{\partial C_{HR}}{\partial r}=-D_{eCuR_2}\frac{\partial C_{CuR_2}}{\partial r}=R \quad (16)$$

$$l>0,\quad r=r_2\ ;\quad D_{HR}\frac{\partial C_{HR}}{\partial r}\bigg|_{r_2-0}=D_{eHR}\frac{\partial C_{HR}}{\partial r}\bigg|_{r_2+0}$$

$$D_{CuR_2}\frac{\partial C_{CuR_2}}{\partial r}\bigg|_{r_2-0}=D_{eCuR_2}\frac{\partial C_{CuR_2}}{\partial r}\bigg|_{r_2+0}$$

$$C_{HR}|_{r_2-0}=C_{HR}|_{r_2+0},\quad C_{CuR_2}|_{r_2-0}=C_{CuR_2}|_{r_2+0} \quad (17)$$

Table 1. Values of constants in Eq. (5)

k_2	$=(1.7\pm0.5)\times10^8$	$[m^2/(mol\cdot s)]$
K_1	$=(1.7\pm0.3)\times10^{-2}$	[—]
K_{ad}	$=(2.0\pm0.3)\times10^{-2}$	$[m^3/mol]$
S_{HR}	$=(3.2\pm0.2)\times10^5$	$[m^2/mol]$
K_{ex}	$=3.3\pm0.3$	[—]

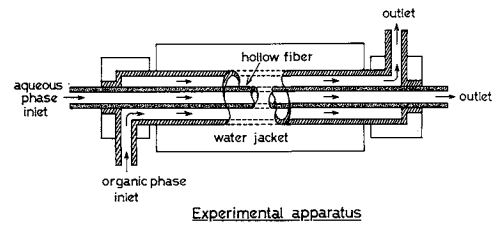


Fig. 1(a). Schematic diagram of membrane extractor using a hollow fiber.

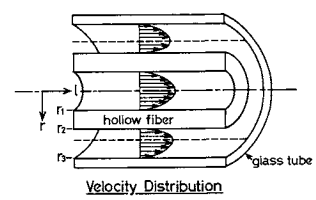


Fig. 1(b). Flow pattern of each solution in membrane extractor.

$$l>0, \quad r=r_3 \quad ; \quad D_{HR}\frac{\partial C_{HR}}{\partial r}=D_{CuR_2}\frac{\partial C_{CuR_2}}{\partial r}=0 \qquad (18)$$

The basic equations can be solved from Eqs. (5a), (5b) (6) and (7) by the numerical method under the boundary conditions to obtain the concentration distributions of copper, HR and CuR_2, i.e., $C_{Cu}(r, l)$, $C_{HR}(r, l)$ and $C_{CuR_2}(r, l)$. The average extraction rate of copper, J_M, and the average stripping rate of CuR_2, $J'_{M'}$, through the membrane extractor are obtained as follows:

$$J_M=Q_{aq}C_{Cu0}E/(2\pi r_1 L) \qquad (19)$$

$$J'_M=Q_{org}C_{CuR_20}E'/(2\pi r_1 L) \qquad (20)$$

E and E' are calculated by:

$$E=1-\left\{2\pi\int_0^{r_1}C_{Cu}(r, L)u_{aq}(r)r\cdot dr/Q_{aq}C_{Cu0}\right\} \qquad (21)$$

$$E'=1-\left\{2\pi\int_{r_2}^{r_3}C_{CuR_2}(r, L)u_{org}(r)r\cdot dr/Q_{org}C_{CuR_20}\right\} \qquad (22)$$

To discuss the effect of the interfacial reaction on the rate of copper extraction or stripping in the membrane extractor, it is rather convenient to rewrite the basic equations and the boundary conditions in dimensionless forms. The basic equations for extraction and stripping are completely the same, but the boundary conditions for the two cases are not all the same. In particular, the feed concentration of each species for extraction is usually different from that for stripping. Therefore, it is necessary to distinguish the definitions of the dimensionless concentration for the two cases, as shown later.

1.1 Extraction of copper

The following dimensionless terms are defined:

$$\left.\begin{aligned}&X_M=C_{Cu}/C_{Cu0}, \quad X_R=C_{HR}/C_{Cu0},\\&X_C=C_{CuR_2}/C_{Cu0},\\&\beta=J_M r_1/D_{Cu}C_{Cu0},\\&\phi=r_1k_2K_1(K_{ad}/S_{HR})^2C_{HR0}^2/D_{Cu}a_{H0}\end{aligned}\right\} \qquad (23)$$

$$\left.\begin{aligned}&\tau_M=D_{Cu}L/Q_{aq}, \ \tau_R=D_{HR}L/Q_{org},\\&\tau_C=D_{CuR_2}L/Q_{org},\\&y=r/r_1, \ z=l/L, \ f_a=u_{aq}(r)r_1^2/Q_{aq},\\&f_o=u_{org}(r)r_1^2/Q_{org},\\&m=K_{ex}(C_{HR0}/a_{H0})^2, \ \sigma=K_{ad}C_{HR0},\\&\gamma_{aR}=D_{eHR}/D_{Cu},\\&\gamma_{aC}=D_{eCuR_2}/D_{Cu}, \ \gamma_{oR}=D_{eHR}/D_{HR},\\&\gamma_{oC}=D_{eCuR_2}/D_{CuR_2}\end{aligned}\right\} \qquad (24)$$

Among the above terms, ϕ is the dimensionless term of interfacial reaction rate, $\tau_M(\tau_R, \tau_C)$ is the dimensionless contact time of each solution and σ is the dimensionless term of adsorption equilibrium constant of extractant at interface, respectively.

Substituting the above dimensionless terms into Eqs. (5a), (6)–(18), the following equations are obtained: in the lumen of the hollow fiber $(0<y<1)$

$$\frac{\partial X_M}{\partial z}=\frac{\tau_M}{f_a}\left(\frac{\partial^2 X_M}{\partial y^2}+\frac{1}{y}\frac{\partial X_M}{\partial y}\right) \qquad (8a)$$

in the annulus $(y_2<y<y_3)$

$$\frac{\partial X_R}{\partial z}=\frac{\tau_R}{f_o}\left(\frac{\partial^2 X_R}{\partial y^2}+\frac{1}{y}\frac{\partial X_R}{\partial y}\right) \qquad (9a)$$

$$\frac{\partial X_C}{\partial z}=\frac{\tau_C}{f_o}\left(\frac{\partial^2 X_C}{\partial y^2}+\frac{1}{y}\frac{\partial X_C}{\partial y}\right) \qquad (10a)$$

in the porous membrane of the hollow fiber $(y_1<y<y_2)$

$$\frac{\partial^2 X_R}{\partial y^2}+\frac{1}{y}\cdot\frac{\partial X_R}{\partial y}=0 \qquad (11a)$$

$$\frac{\partial^2 X_C}{\partial y^2}+\frac{1}{y}\cdot\frac{\partial X_C}{\partial y}=0 \qquad (12a)$$

for the boundary conditions

$$z=0, \ 0<y<1; \quad X_M=1 \qquad (13a)$$

$$z=0, \ y_2<y<y_3; \quad X_R=X_{R0}, \ X_C=X_{C0} \qquad (14a)$$

$$z>0, \quad y=0 \quad ; \quad \frac{\partial X_M}{\partial y}=0 \qquad (15a)$$

$$z>0, \quad y=y_1 \quad ; \quad -\frac{\partial X_M}{\partial y}=\frac{\gamma_{aR}\partial X_R}{2\partial y}=-\gamma_{aC}\frac{\partial X_C}{\partial y}=\phi\frac{\left\{X_M\left(\frac{X_R}{X_{R0}}\right)^2-\frac{X_C}{m}\right\}}{\left\{1+\sigma\left(\frac{X_R}{X_{R0}}\right)\right\}^2} \qquad (16a)$$

$$z>0, \quad y=y_2 \quad ; \quad \left.\frac{\partial X_R}{\partial y}\right|_{y_2-0}=\gamma_{oR}\left.\frac{\partial X_R}{\partial y}\right|_{y_2+0}, \quad X_R|_{y_2-0}=X_R|_{y_2+0}, \quad \left.\frac{\partial X_C}{\partial y}\right|_{y_2-0}=\gamma_{oC}\left.\frac{\partial X_C}{\partial y}\right|_{y_2+0}, \quad X_C|_{y_2-0}=X_C|_{y_2+0}. \qquad (17a)$$

$$z>0, \quad y=y_3 \quad ; \quad \frac{\partial X_R}{\partial y}=\frac{\partial X_C}{\partial y}=0 \qquad (18a)$$

where f_a and f_o are as follows:

$$f_a=(2/\pi)(1-y^2) \qquad (6a)$$

$$f_o=(2/\pi)\left[\frac{y_3^2-y^2+\dfrac{(y_3^2-y_2^2)}{\ln(y_3/y_2)}\ln(y/y_2)}{y_3^4-y_2^4-\{(y_3^2-y_2^2)^2/\ln(y_3/y_2)\}}\right] \quad (7a)$$

Combining Eqs. (19) and (21) gives the following equation:

$$\beta=E/(2\pi\tau_M) \quad (19a)$$

where

$$E=1-2\pi\int_0^1 X_M f_a\, y\,\mathrm{d}\,y\,. \quad (21a)$$

From the above equations, it is suggested that the dimensionless average extraction rate of copper through the membrane extractor, β, will depend on the values of the operating parameters, i.e., τ_M, τ_R, X_{R0}, X_{C0}, ϕ and σ, as well as the size of the membrane extractor (y_2 and y_3), the diffusivity ratio (γ_{aR}, γ_{aC} and γ_{oR} or γ_{oC}), the equilibrium constants and the interfacial reaction rate constant. The effect of the interfacial reaction on the average extraction rate of copper is expressed by the relationship between β and ϕ, in terms of σ as a parameter.

1.2 Stripping of copper

The respective dimensionless concentrations of the species in Eq. (23) are modified as follows:

$$\left.\begin{aligned} &X'_M=C_{Cu}/C_{CuR_20}\,,\quad X'_R=C_{HR}/C_{CuR_20}\,,\\ &X'_C=C_{CuR_2}/C_{CuR_20}\,,\\ &\beta'=J'_M(r_2-r_1)/D_{eCuR_2}C_{CuR_20}\,,\quad \phi'=r_1k'_2a_{HO}/D_{Cu} \end{aligned}\right\} \quad (25)$$

where ϕ' is the dimensionless term of interfacial reaction rate of stripping as mentioned above. By substituting X_j in Eqs. (8a) to (18a) by X'_j ($j=M$, R and C), the basic equations and boundary conditions for stripping of copper are obtained, except for Eqs. (13a), (14a) and (16a).

$$z=0\,,\ 0<y<1;\quad X'_M=X'_{M0} \quad (13b)$$

$$z=0\,,\ y_2<y<y_3;\quad X'_R=X'_{R0}\,,\ X'_C=1 \quad (14b)$$

$$z>0,\quad y=y_1\ ;\quad -\frac{\partial X'_M}{\partial y}=\frac{\gamma_{aR}}{2}\cdot\frac{\partial X'_R}{\partial y}=-\gamma_{aC}\frac{\partial X'_C}{\partial y}$$
$$=-\gamma_{aC}\phi'\frac{X'_C-mX'_M(X'_R/X'_{R0})^2}{\{1+\sigma(X'_R/X'_{R0})\}^2} \quad (16b)$$

Equations (19) and (21) become

$$\beta'=\frac{y_2-1}{2\pi\gamma_{oC}}\cdot\frac{E'}{\tau_C} \quad (19b)$$

where

$$E'=1-2\pi\int_{y_2}^{y_3} X'_C f_0\, y\,\mathrm{d}y \quad (21b)$$

From the above equations, it is suggested that the dimensionless average stripping rate of copper, β', will also depend on the values of the operating parameters, i.e., τ_M, τ_C, X'_{M0}, X'_{R0}, ϕ' and σ, in the same manner as in extraction. The effect of the interfacial reaction on the average stripping rate of copper will be also expressed by the relationship between β' and ϕ', in terms of σ as a parameter.

2. Experimental

An extractant and its copper complex were synthesized and purified by the same method described in the previous papers.[14,15] Organic solutions for the extraction and stripping experiments were prepared by dissolving HR and CuR_2 respectively in toluene. Aqueous solution for the extraction experiment was prepared by dissolving copper nitrate in deionized water and adjusting pH and ionic strength by adding 100 mol/m^3 acetic acid-sodium acetate buffer solution and /or 100 mol/m^3 nitric acid. In the stripping experiment, sulfuric acid was used as the stripping agent.

The membrane extractor shown in Fig. 1 consists of a glass tube and a hollow fiber made of polytetrafluoroethylene (Japan Goretex Co., Ltd.). The inner and outer diameters, porosity and tortuosity factor of the hollow fiber were measured and are shown in **Table 2**. The aqueous and organic solutions were fed cocurrently into the inner and outer sides of the hollow fiber by a microtube pump (Tokyo Rika MP-1001), and the volumetric flow rates were $1\times10^{-9}-3\times10^{-9}$ m^3/s for Q_{aq} and $2\times10^{-9}-6\times10^{-9}$ m^3/s for Q_{org}. At steady state, the concentrations of copper and the copper complex in both the effluent solutions were measured by atomic absorption spectrophotometer (Shimadzu AA-646), and the average extraction rate of copper and stripping rate of copper, J_M and J'_M, were then determined from Eqs. (19) and (20), respectively.

3. Comparison of Experimental Results with Theoretical Results

To obtain the theoretical values of J_M and J'_M, the values given in Tables 1 and 2 were used, together with the diffusivities of copper, HR and CuR_2: $D_{Cu}=7.20\times10^{-10}$ m^2/s, $D_{HR}=9.28\times10^{-10}$ m^2/s and $D_{CuR_2}=5.67\times10^{-10}$ m^2/s.

3.1 Extraction of copper

Figure 2 shows the relationship between β and τ_M for various values of ϕ and X_{R0}. It is found that the calculated curves for $\phi>1.0$ approach an asymptote with increasing τ_M, which is $\beta=0.159\,\tau_M^{-1}$. Since this asymptote indicates that E approaches the equilibrium value at the outlet of the membrane extractor, in this case E approaches 1.0 with increasing contact time of each solution as can be found from Eq. (19a).

Table 2. Characteristic values of membrane extractor

$2r_1=(0.94\pm0.02)\times10^{-3}$	[m]
$2r_2=(1.83\pm0.02)\times10^{-3}$	[m]
$2r_3=2.40\times10^{-3}$	[m]
$L=0.125,\ 0.250,\ 0.500$	[m]
Porosity $=0.45$	
Tortuosity $=1.60\pm0.11$	

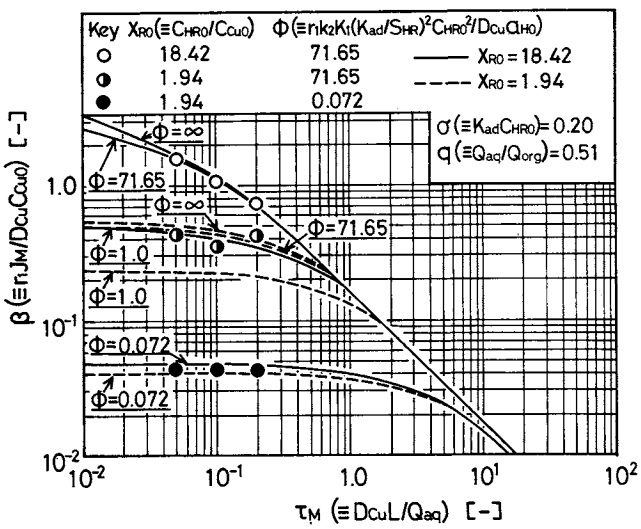


Fig. 2. Relationship between β and τ_M.

The experimental results shown in Fig. 2 were obtained for various volumetric flow rates, keeping the ratio of Q_{aq} to Q_{org}, i.e., the ratio τ_M to τ_R constant. It is found that the effect of the interfacial reaction on the average extraction rate of copper was negligibly small when $\phi=71.7$, i.e., pH$=5.0$, $C_{HR0}=10.0\,mol/m^3$.

Figure 3 shows the relationship between β and ϕ for various values of σ. β tends to become constant with increasing ϕ, which means that the extraction rate is controlled by diffusion of extractant in the organic solution. In the region of small ϕ where the rate is controlled by reaction, the decrease in β tends to be large with increasing σ due to the influence of adsorption of extractant at the interface. A broken line in Fig. 3 was obtained by assuming that $f_a=1/\pi$ and $f_o=1/\pi(y_3^2-y_2^2)$, i.e., the velocity distributions of the aqueous and organic solutions are not expressed by Eqs. (6) and (7), but are those of plug flow. The result suggests that in the calculation of J_M, it is necessary to take account of the velocity distributions of both solutions.

Figure 4 shows the effect of X_{R0} on β for various values of ϕ. In the calculated line for $\phi=\infty$, there are two regions: the region of $X_{R0}>5.3$, where the extraction rate is determined by the diffusion rate of copper in the aqueous solution, and the region of $X_{R0}<5.3$, where the extraction rate is determined by the diffusion rate of the extractant in the organic solution.

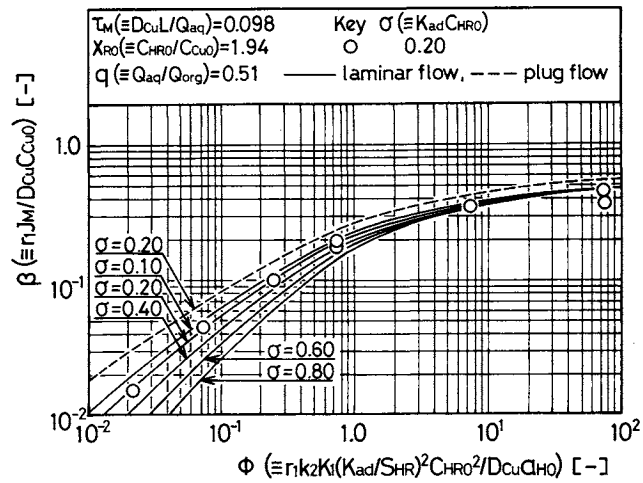


Fig. 3. Relationship between β and ϕ.

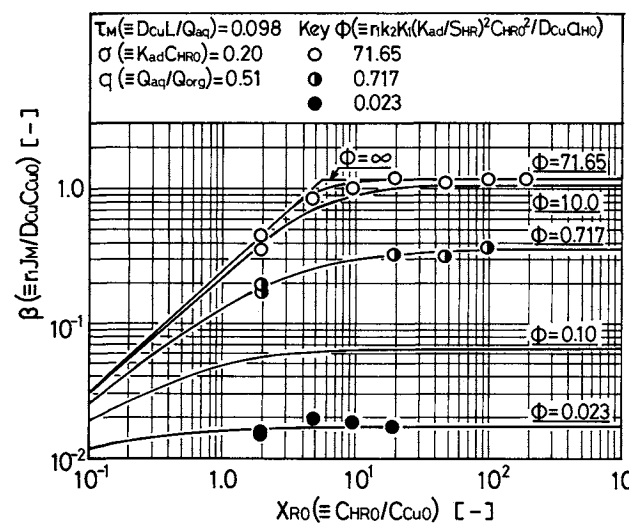


Fig. 4. Effect of X_{R0} on β.

It was confirmed that the calculated curves shown in Figs. 2–4 are not influenced by the ratio of the aqueous to organic volumetric flow rates, $q(=Q_{aq}/Q_{org})$, in the range of $q=0.5$ to 2.0.

From the above figures, agreement between the experimental and respective theoretical curve is very good.

3.2 Stripping of copper

Figure 5 shows the effect of ϕ' on β' for various values of σ. It is found that β' becomes constant with increasing ϕ', which means that the stripping rate is controlled by diffusion of copper complex. In the region of small ϕ' where the rate is controlled by reaction, the decrease in β' with increasing σ is caused by the shielding effect due to adsorption of extractant at the interface.

Figure 6 shows the effect of X'_{R0} on β' for various values of ϕ'. Agreement of the experimental results with respective calculated lines is very good.

To confirm the validity of the present model, the extents of copper extracted and stripped through the

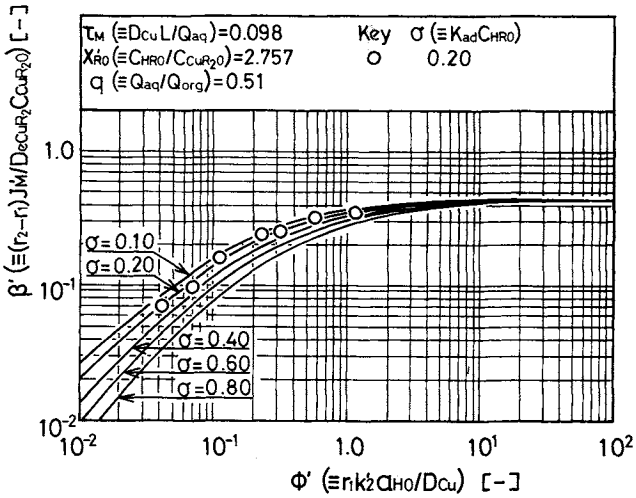


Fig. 5. Effect of ϕ' on β'.

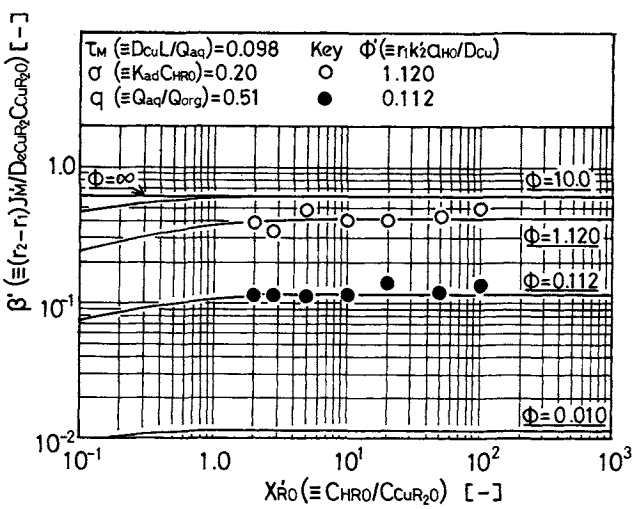


Fig. 6. Effect of X'_{R0} on β'.

extractor were calculated from Eqs. (21) and (22), the results being then compared with E_{obs} and E'_{obs} from all experimental data as shown in Fig. 7. Good agreement between observed and calculated results is obtained over a wide range of E and E' values.

Conclusion

The effects of interfacial reaction on the rates of extraction and stripping in a membrane extractor were theoretically and experimentally studied, using the extraction system of copper and *N*-8-quinolyl-*p*-dodecylbenzenesulfonamide. The following results were obtained.

(1) The experimental results can be explained by a diffusion model for metal extraction with an interfacial reaction, taking account of the velocity distributions of the aqueous and organic solutions which flow along a hollow fiber.

(2) When pH of the aqueous solution is above 5.0, the rate of copper extraction with the extractant is determined by either the diffusion rate of copper in

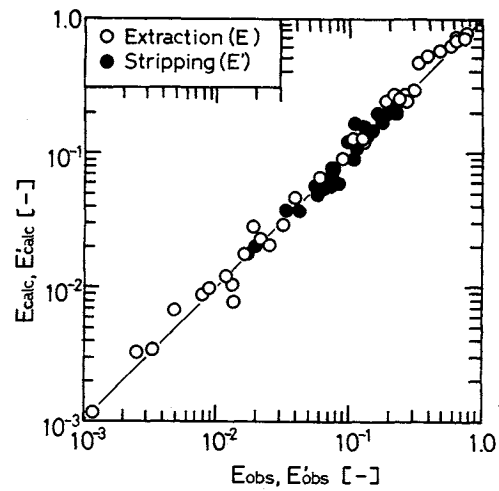


Fig. 7. Comparison of experimental results with calculated results of extents of copper extracted and stripped.

the aqueous solution or of the extractant in the organic solution. However, for lower pH, the role of the interfacial reaction becomes significant in the extraction process.

(3) In the stripping of copper with sulfuric acid, the role of the interfacial reaction becomes important even when $a_{H0} = 400\ \mathrm{mol/m^3}$.

(4) It is suggested that the membrane extractor using a hollow fiber can be used as an experimental apparatus for studying the kinetics and mechanism of metal extraction or stripping, especially in the development of new extractants, because the experiments can be carried out using a small amount of the extractant.

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Nomenclature

a_H	=	activity of hydrogen ion	[mol/m³]
C_j	=	concentration of species j (j=Cu, HR, CuR_2)	[mol/m³]
D_j	=	diffusivity of species j (j=Cu, HR, CuR_2)	[m²/s]
D_{e_j}	=	effective diffusivity of species j (j=HR, CuR_2)	[m²/s]
E	=	extent of copper extracted defined by Eq. (21)	[—]
E'	=	extent of copper stripped defined by Eq. (22)	[—]
f_a	=	dimensionless linear velocity of aqueous solution	[—]
f_o	=	dimensionless linear velocity of organic solution	[—]
J_M	=	average extraction rate of copper	[mol/(m²·s)]
J'_M	=	average stripping rate of copper	[mol/(m²·s)]
K_{ex}	=	extraction equilibrium constant	[—]
K_{ad}	=	equilibrium constant of Eq. (2)	[m³/mol]
K_1	=	equilibrium constant of Eq. (3)	[—]
K_2	=	equilibrium constant of Eq. (4)	[m²]

k_2 = rate constant for forward reaction of Eq. (4) [$m^2/(mol \cdot s)$]
k_2' = rate constant for reverse reaction of Eq. (4) [$m^4/(mol \cdot s)$]
L = contact length between aqueous and organic solutions [m]
l = horizontal distance from point of contact between aqueous and organic solutions [m]
m = dimensionless term defined by Eq. (24) [—]
Q = volumetric flow rate [m^3/s]
q = ratio of aqueous to organic volumetric flow rates ($=Q_{aq}/Q_{org}$) [—]
R = interfacial extraction rate [$mol/(m^2 \cdot s)$]
R' = interfacial stripping rate [$mol/(m^2 \cdot s)$]
r = distance of radial direction of extractor [m]
r_1 = inner radius of hollow fiber [m]
r_2 = outer radius of hollow fiber [m]
r_3 = inner radius of membrane extractor [m]
u = linear velocity [m/s]
X_j, X_j' = dimensionless concentration of j (j=M, R, C) [—]
y = r/r_1 [—]
z = l/L [—]

β = dimensionless average extraction rate [—]
β' = dimensionless average stripping rate [—]
γ = ratio of diffusivities [—]
σ = $K_{ad}C_{HR0}$ [—]
ϕ, ϕ' = dimensionless term defined by Eqs. (23) and (25) [—]
τ = dimensionless term defined by Eq. (24) [—]

〈Subscripts〉
ad = adsorption state
aq = aqueous solution
org = organic solution
0 = initial state

Literature Cited

1) Babcock, W. C., R. W. Baker, D. J. Kelly and E. D. LaChappel: Proc. ISEC '80, 80–90 (1980).
2) Babcock, W. C., D. J. Kelly and D. T. Friesen: Proc. ISEC '83, p. 373 (1983).
3) Danesi, P. R. and C. Chiarizia: CRC Crit. Rev. Anal. Chem., **10**, 1 (1980).
4) Danesi, P. R.: *Solv. Extn. Ion Exchange*, **2**, 115 (1984).
5) Danesi, P. R.: *J. Membrane Sci.*, **20**, 231 (1984).
6) Flett, D. S., D. N. Okuhara and D. R. Spink: *J. Inorg. Nucl. Chem.*, **35**, 2471 (1973).
7) Kim, B. M.: *J. Membrane Sci.*, **21**, 5 (1984).
8) Komasawa, I., T. Otake and T. Muraoka: *J. Chem. Eng. Japan*, **13**, 204 (1980).
9) Lonsdale, H. K.: *J. Membrane Sci.*, **10**, 81 (1982).
10) Miyake, Y., Y. Takenoshita and M. Teramoto: *J. Chem. Eng. Japan*, **16**, 203 (1983).
11) Noble, R. D.: *Ind. Eng. Chem., Fundam.*, **22**, 139 (1983).
12) Noble, R. D.: *Separ. Sci. Technol.*, **19**, 469 (1984).
13) Teramoto, M. and H. Tanimoto: *Separ. Sci. Technol.*, **18**, 871 (1983).
14) Yoshizuka, K., K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **18**, 163 (1985).
15) Yoshizuka, K., K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **18**, 342 (1985).

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