

A NOVEL MEMBRANE EXTRACTOR USING HOLLOW FIBERS FOR SEPARATION AND ENRICHMENT OF METAL

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A novel membrane extractor using hollow fiber module was developed, and extraction and stripping of copper and/or zinc with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester were carried out simultaneously. Separation and enrichment of zinc from aqueous solution containing copper and zinc were also carried out in the membrane extractor. The results were simulated by a diffusion model with interfacial reaction.

Introduction

Membrane separation processes are extensively utilized in many fields, such as desalination of saline water by reverse osmosis and gas separation⁴⁾. Recently, a membrane extraction process was developed for selective removal and recovery of metals

from aqueous solutions. In comparison with the traditional solvent extraction process using mixer-settlers, the membrane extraction process using hollow fibers has several advantages, namely a very large interfacial area per unit extractor volume without direct mixing of the aqueous and organic phases, no need for a difference in phase densities and no problems due to loading and flooding. In the membrane extraction processes developed by Ho *et*

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*al.*²⁾ and Kim³⁾, the organic solution containing extractant is circulated between two hollow fiber modules, one extraction and the other for stripping. Recently, Sengupta *et al.*⁸⁾ proposed hollow fiber-contained liquid membranes (HFCLM) for the separation of phenol or acetic acid from aqueous solutions.

In the present study, a novel membrane extractor of the HFCLM type was theoretically and experimentally verified to be useful for selective separation of zinc from an aqueous solution containing copper and zinc with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (henceforth referred to by the commercial name PC-88A, or abbreviated as HR). The membrane extractor proposed was composed of a single hollow-fiber module, containing n fibers for extraction and n' fibers for stripping. Extraction and enrichment of zinc were carried out simultaneously, as in a liquid-membrane process.

First of all, the extraction and enrichment of copper with PC-88A were carried out in the membrane extractor. The experimental results were compared with calculated results obtained from the basic equations for the membrane extractor. These equations were derived from the diffusion model accompanied by interfacial reaction discussed in previous papers^{5,6,7,9)}. After that, selective separation and enrichment of zinc from an aqueous solution containing copper and zinc were carried out in the membrane extractor and the experimental results at steady state were simulated by the model.

1. Theory

Figure 1 shows a membrane extractor in which $(n+n')$ hollow fibers for extraction and stripping are included. Aqueous solutions of feed and product phases are fed separately and cocurrently into the inner side of n and n' hollow fibers, respectively. An organic solution containing PC-88A is fed cocurrently into the outer side of $(n+n')$ hollow fibers and recirculated through the flow loop shown in Fig. 1. Copper and zinc ions in the feed solution are extracted with PC-88A at the aqueous-organic interface (hereafter interface I). It is located at the inner surface of n hollow fibers for extraction, because the fibers used are hydrophobic. Metal complexes formed at interface I diffuse across the microporous membranes of n hollow fibers, the organic solution on the outer side of $(n+n')$ hollow fibers, and the membranes of n' hollow fibers, to be stripped with hydrochloric acid at the inner surface of n' hollow fibers for stripping (hereafter interface II).

The present membrane permeation process is schematically represented in Fig. 2(a). The extraction side is on the inner sides of n fibers, the stripping side is on the inner sides of n' fibers, and the organic side

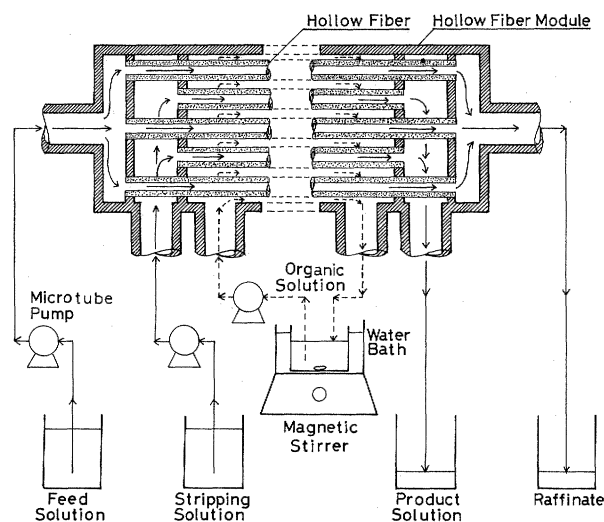


Fig. 1. Schematic diagram of hollow-fiber module

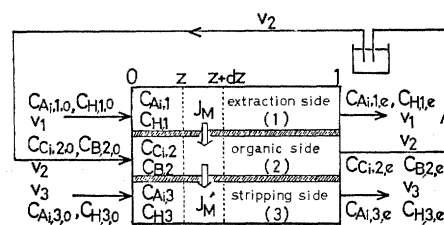
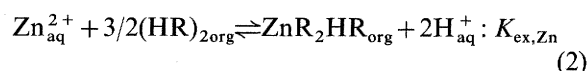
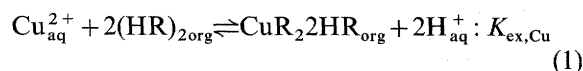


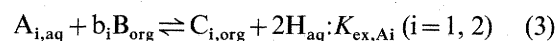
Fig. 2(a). Differential material balances of chemical species in the hollow-fiber module

is the outer side of the fibers.

The extraction of copper and zinc with PC-88A is represented as follows⁵⁾.



where $K_{\text{ex,Cu}}$ and $K_{\text{ex,Zn}}$ are the equilibrium constants for copper and zinc extraction, respectively, and $(\text{HR})_2$ represents the dimer of PC-88A, because PC-88A in a nonpolar organic solution exists mainly as dimers⁵⁾. To simplify notation hereafter, Eqs. (1) and (2) are rewritten as follows.



where A_1 and A_2 denote Cu^{2+} and Zn^{2+} respectively, $b_1 = 2$ and $b_2 = 1.5$.

The basic equations for mass transfer in the membrane extractor at steady state are derived from the differential mass balances of chemical species on each side shown in Fig. 2(a), taking account of the concentration profiles of chemical species shown in Fig. 2(b)* and Fig. 2(c), as follows.

For the metals and complexes:

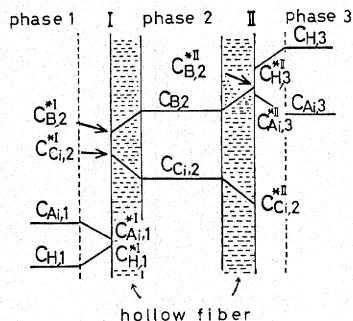


Fig. 2(b). Concentration profiles of chemical species

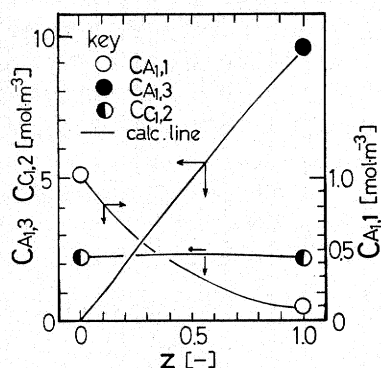


Fig. 2(c). Axial concentration profiles of metal in each phase of the extractor

$$-v_1 \frac{dC_{A,1}}{d(l/L)} = k_{A,1} a_I (C_{A,1} - C_{A,1}^*), \quad (i=1, 2) \quad (4)$$

$$v_2 \frac{dC_{C,2}}{d(l/L)} = k_{C,2}^I a_I (C_{C,2}^I - C_{C,2}) - k_{C,2}^{II} a_{II} (C_{C,2} - C_{C,2}^{II}), \quad (i=1, 2) \quad (5)$$

$$v_3 \frac{dC_{A,3}}{d(l/L)} = k_{A,3} a_{II} (C_{A,3}^{II} - C_{A,3}), \quad (i=1, 2) \quad (6)$$

For the extractant:

$$v_2 \frac{dC_{B,2}}{d(l/L)} = k_{B,2}^{II} a_{II} (C_{B,2}^{II} - C_{B,2}) - k_{B,2}^I a_I (C_{B,2} - C_{B,2}^I) \quad (7)$$

For hydrogen ion:

$$v_1 \frac{dC_{H,1}}{d(l/L)} = k_{H,1} a_I (C_{H,1}^I - C_{H,1}) \quad (8)$$

$$-v_3 \frac{dC_{H,3}}{d(l/L)} = k_{H,3} a_{II} (C_{H,3} - C_{H,3}^{II}) \quad (9)$$

where a_I and a_{II} are the interfacial area of interfaces

* It is assumed that mass transfer of the extractants and complexes in the organic solution is controlled by molecular diffusion of these species in the micropores of the membrane, because the membrane is hydrophobic.

I and II respectively; $a_I = nL\pi d$ and $a_{II} = n'L\pi d$. In the basic equations, $C_{i,j}^*$ and $C_{i,j}^{**}$ ($i=A, C, B, H$, $j=1, 2, 3$) are the concentrations of chemical species at interfaces I and II respectively, which are represented as functions of $C_{i,j}$ ($i=A, C, B, H$, $j=1, 2, 3$) from the following equations based on the mass balance of chemical species at each interface, provided that the equilibrium constants, the interfacial reaction constants and mass transfer coefficients are known. For metals and complexes:

$$k_{A,1} (C_{A,1} - C_{A,1}^*) = k_{C,2}^I (C_{C,2}^I - C_{C,2}) = R_{A,1}^I \quad (i=1, 2) \quad (10)$$

$$k_{A,3} (C_{A,3}^{II} - C_{A,3}) = k_{C,2}^{II} (C_{C,2} - C_{C,2}^{II}) = R_{C,2}^{II} \quad (i=1, 2) \quad (11)$$

For the extractant:

$$k_{B,2}^I (C_{B,2} - C_{B,2}^*) = \sum_{i=1}^2 b_i R_{A,1}^I \quad (12)$$

$$k_{B,2}^{II} (C_{B,2}^{II} - C_{B,2}) = \sum_{i=1}^2 b_i R_{C,2}^{II} \quad (13)$$

For hydrogen ion:

$$k_{H,1} (C_{H,1}^I - C_{H,1}) = 2 \sum_{i=1}^2 R_{A,1}^I \quad (14)$$

$$k_{H,3} (C_{H,3} - C_{H,3}^{II}) = 2 \sum_{i=1}^2 R_{C,2}^{II} \quad (15)$$

where $R_{A,1}^I$ and $R_{C,2}^{II}$ are the reaction rates of extraction at interface I and of stripping at interface II respectively.

In previous paper^{6,7}, $R_{A,1}^I$ and $R_{C,2}^{II}$ are represented as follows:

$$R_{A,1}^I = k_{f,A,1} \sigma^I \left\{ \frac{C_{A,1,1}^I (C_{B,2}^I)^2}{(C_{H,1}^I)^2} - \frac{C_{C,1,2}^I}{K_{exA1}} \right\} \quad (16)$$

$$R_{C,2}^{II} = k_{r,C,2} \sigma^{II} \left\{ C_{C,1,2}^{II} - K_{exA1} \frac{C_{A,1,3}^{II} (C_{B,2}^{II})^2}{(C_{H,3}^{II})^2} \right\} \quad (17)$$

$$R_{A,2}^I = k_{f,A,2} \sigma^I \left\{ \frac{C_{A,2,1}^I (C_{B,2}^I)^2}{(C_{H,1}^I)^2} - \frac{C_{C,2,2}^I (C_{B,2}^I)^{0.5}}{K_{exA2} (K_D)^{0.5}} \right\} \quad (18)$$

$$R_{C,2}^{II} = k_{r,C,2} \sigma^{II} \left\{ C_{C,2,2}^{II} (C_{B,2}^{II})^{0.5} - K_{exA2} \frac{C_{A,2,3}^{II} (C_{B,2}^{II})^2}{(C_{H,3}^{II})^2} \right\} \quad (19)$$

where

$$\sigma^I = \left\{ 1 + K_{HR} (1 + K_a / C_{H,1}^I) (C_{B,2}^I / K_D)^{0.5} + K_{(HR)2} C_{B,2}^I + \sum_{i=1}^2 K_{Ci} C_{C,1,2}^I \right\}^{-1} \quad (20)$$

$$\sigma^{II} = \left\{ 1 + K_{HR} (1 + K_a / C_{H,3}^{II}) (C_{B,2}^{II} / K_D)^{0.5} \right\}$$

$$+ K_{(HR)2} C_{B2}^{*II} + \sum_{i=1}^2 K_{Ci} C_{Ci,2}^{*II} \}^{-1} \quad (21)$$

To obtain the concentration of chemical species at $l=L$, the basic equations were solved numerically by using Eqs. (10) to (21) and the following boundary conditions.

$$l=0, \left\{ \begin{array}{l} C_{Ai,1} = C_{Ai,1,0}, C_{Ci,2} = C_{Ci,2,0}, C_{Ai,3} = C_{Ai,3,0} \\ C_{B,2} = C_{B,2,0}, C_{H,1} = C_{H,1,0}, C_{H,3} = C_{H,3,0} \end{array} \right\} \quad (22)$$

The basic equations can be simplified when a buffer solution is used as the feed solution and the concentration of hydrochloric acid in the stripping solution is very high, because the concentrations of hydrogen ion in the two aqueous solutions then are constant through the membrane extractor. Furthermore, it can be assumed that mass transfer coefficients of metals in both aqueous solutions are equal to each other, and that mass transfer of chemical species in the organic solution is mainly controlled by molecular diffusion of chemical species in the micropores of the membrane, as follows.

$$C_{H,1}^* = C_{H,1} \equiv C_{H,1,0}, \quad C_{H,3}^{*II} = C_{H,3} \equiv C_{H,3,0} \quad (23)$$

$$k_{Ai,1} = k_{A2,1} = k_{A1,3} = k_{A2,3} \equiv k_A \quad (24)$$

$$\left. \begin{array}{l} k_{C1,2}^I = k_{C1,2}^{*II} \equiv k_{C1} (\equiv D_{C1} \varepsilon / \delta \xi) \\ k_{C2,2}^I = k_{C2,2}^{*II} \equiv k_{C2} (\equiv D_{C2} \varepsilon / \delta \xi) \\ k_{B,2}^I = k_{B,2}^{*II} \equiv k_B (\equiv D_B \varepsilon / \delta \xi) \end{array} \right\} \quad (25)$$

To compare the experimental results with the calculated ones, it is rather convenient to express the basic equations in dimensionless form. The following dimensionless terms are defined, taking account of the above assumptions.

$$X_{Ai} = C_{Ai,1} / C_{Ai,1,0} \quad (i=1, 2);$$

$$Y_{Ai} = C_{Ai,3} / C_{Ai,1,0} \quad (i=1, 2)$$

$$X_{Ci} = C_{Ci,2} / C_{Ai,1,0} \quad (i=1, 2); X_B = C_{B,2} / C_{B,2,0}, \quad z = l/L$$

$$N_A = k_A \cdot a_l / v_1; \quad \phi_i = (k_{f,Ai} / k_A) (C_{B,2,0} / C_{H,1,0})^2$$

$$\phi'_1 = k_{rC1} / k_A, \quad \phi'_2 = (k_{rC2} / k_A) (C_{B,2,0} / K_D)^{0.5}$$

$$m_{A1} = K_{exA1} (C_{B,2,0} / C_{H,1,0})^2,$$

$$m'_{A1} = K_{exA1} (C_{B,2,0} / C_{H,3,0})^2$$

$$m_{A2} = K_{exA2} (C_{B,2,0} / C_{H,1,0})^2 (K_D / C_{B,2,0})^{0.5},$$

$$m'_{A2} = K_{exA2} (C_{B,2,0} / C_{H,3,0})^2$$

$$\gamma_B = k_B / k_A, \quad \gamma_{Ci} = k_{Ci} / k_A, \quad f = n' / n$$

$$\lambda_o = v_1 / v_2, \quad \lambda_a = v_1 / v_3$$

$$\sigma^I = \left\{ 1 + K_{HR} (1 + K_a / C_{H1,0}^*) (C_{B2}^* / K_D)^{0.5} (X_B^{*I})^{0.5} \right.$$

$$\left. + K_{(HR)2} C_{B2,0} X_B^{*I} + \sum_{i=1}^2 K_{Ci} C_{Ai,1,0} X_{Ci}^{*I} \right\}^{-1}$$

$$\sigma^{II} = \left\{ 1 + K_{HR} (1 + K_a / C_{H3,0}^*) (C_{B2,0} / K_D)^{0.5} (X_B^{*II})^{0.5} \right.$$

$$\left. + K_{(HR)2} C_{B2,0} X_B^{*II} + \sum_{i=1}^2 K_{Ci} C_{Ai,1,0} X_{Ci}^{*II} \right\}^{-1} \quad (26)$$

Among the above terms, N_A is the reciprocal dimensionless length per transfer unit based on the feed solution, ϕ 's (ϕ_i and ϕ'_i) are the dimensionless terms of the interfacial reaction rate constants, m 's (m_{Ai} and m'_{Ai}) are the dimensionless terms of extraction equilibrium, which correspond to the distribution constant of metals, and σ 's (σ^I and σ^{II}) denote the effect of adsorption of chemical species on the interfacial reaction rate.

By introducing the above dimensionless terms, the basic equations become

$$-\frac{dX_{Ai}}{dz} = N_A (X_{Ai} - X_{Ai}^I), \quad (i=1, 2) \quad (4a)$$

$$\frac{dX_{Ci}}{dz} = \lambda_o \gamma_{Ci} N_A \{ (X_{Ci}^I - X_{Ci}) - f \cdot (X_{Ci} - X_{Ci}^{*II}) \}, \quad (i=1, 2) \quad (5a)$$

$$\frac{dY_{Ai}}{dz} = \lambda_a \cdot N_A \cdot f (Y_{Ai}^{*II} - Y_{Ai}), \quad (i=1, 2) \quad (6a)$$

$$\frac{dX_B}{dz} = \lambda_o \gamma_B N_A \{ f \cdot (X_B^{*II} - X_B) - (X_B - X_B^I) \} \quad (7a)$$

The dimensionless concentrations of chemical species at each interface are obtained numerically as functions of X_{Ai} , X_{Ci} , Y_{Ai} and X_B from the following equations.

$$\begin{aligned} X_{Ai} - X_{Ai}^I &= \gamma_{Ci} (X_{Ci}^I - X_{Ci}) \\ &= \phi_1 \sigma^I \{ X_{Ai}^I (X_B^{*I})^2 - (X_{Ci}^I / m_{A1}) \} \end{aligned} \quad (10a)$$

$$\begin{aligned} X_{A2} - X_{A2}^I &= \gamma_{C2} (X_{C2}^I - X_{C2}) \\ &= \phi_2 \sigma^I \{ X_{A2}^I (X_B^{*I})^2 - (X_{C2}^I (X_B^{*I})^{0.5} / m_{A2}) \} \end{aligned} \quad (10b)$$

$$\begin{aligned} Y_{A1}^{*II} - Y_{A1} &= \gamma_{C1} (X_{C1} - X_{C1}^{*II}) \\ &= \phi'_1 \sigma^{II} \{ X_{C1}^{*II} - m'_{A1} Y_{A1}^{*II} (X_B^{*II})^2 \} \end{aligned} \quad (11a)$$

$$\begin{aligned} Y_{A2}^{*II} - Y_{A2} &= \gamma_{C2} (X_{C2} - X_{C2}^{*II}) \\ &= \phi'_2 \sigma^{II} \{ X_{C2}^{*II} (X_B^{*II})^{0.5} - m'_{A2} Y_{A2}^{*II} (X_B^{*II})^2 \} \end{aligned} \quad (11b)$$

$$\begin{aligned} \gamma_B (X_B - X_B^I) &= b_1 \phi_1 \sigma^I \{ X_{A1}^I (X_B^{*I})^2 - (X_{C1}^I / m_{A1}) \} \\ &+ b_2 \phi_2 \sigma^I \{ X_{A2}^I (X_B^{*I})^2 (X_{C2}^I (X_B^{*I})^{0.5} / m_{A2}) \} \end{aligned} \quad (12a)$$

$$\begin{aligned} \gamma_B (X_B^{*II} - X_B) &= b_1 \phi'_1 \sigma^{II} \{ X_{C1}^{*II} - m'_{A1} Y_{A1}^{*II} (X_B^{*II})^2 \} \\ &+ b_2 \phi'_2 \sigma^{II} \{ X_{C2}^{*II} (X_B^{*II})^{0.5} - m'_{A2} Y_{A2}^{*II} (X_B^{*II})^2 \} \end{aligned} \quad (13a)$$

Eqs. (4a) to (7a) can be solved numerically by the Runge-Kutta-Gill method under the following boun-

dary conditions, considering that the organic solution is recycled as shown in Fig. 2(a).

$$z=0: \begin{cases} X_{Ai}=1.0, X_{Ci}=X_{Ci(z=1)}, Y_{Ai}=0 & (i=1,2) \\ X_B=X_{B(z=1)} \end{cases} \quad (22a)$$

Figure 2(c) shows the axial concentration profiles of metal in the extractor. From the calculated values of the dimensionless concentrations at $z=1$, the extent of metal extracted, E_{Ai} , and the selectivity of metal separated, α , in the membrane extractor are obtained as follows.

$$E_{Ai}=1-X_{Ai}, \quad (i=1,2) \quad (27)$$

$$\alpha=(Y_{A2}/X_{A2})/(Y_{A1}/X_{A1}) \quad (28)$$

where Y_{A1} and Y_{A2} correspond to the enrichment factors of copper and zinc, respectively.

2. Experimental

The membrane extractor used is shown in Fig. 1, where $n=3-7$ and $n'=1-3$. The size of the extractor is shown in Table 1, along with physical properties of the hollow fiber made of polytetrafluoroethylene.

PC-88A delivered from Daihachi Chemical Industry Co. Ltd. was used without further purification. Organic solution was prepared by dissolving PC-88A in *n*-heptane. The feed solution was prepared by dissolving copper nitrate and/or zinc nitrate in deionized water and adjusting pH and ionic strength of the solution with 100 mol/m³ sodium acetate-acetic acid buffer solution and/or hydrochloric acid. The stripping solution was hydrochloric acid aqueous solution.

The concentrations of copper and/or zinc in both effluent and product solutions were measured by atomic absorption spectrophotometry.

3. Results and Discussion

3.1 Extraction and enrichment of copper

Figure 3 shows the effect of ϕ_1 (i.e. $C_{B,2,0}$ and $C_{H,1,0}$) on X_{A1} and Y_{A1} in three membrane extractors of $n=6$ and $n'=1$ ($f=0.17$), $n=3$ and $n'=2$ ($f=0.67$) and $n=4$ and $n'=3$ ($f=0.75$). From these results it is found that copper in the feed solution is extracted in the organic solution and concentrated in the stripping solution. In Fig. 3 the broken, solid and dotted lines are the calculated results corresponding to $f=0.17$, $f=0.67$ and $f=0.75$ respectively, using the kinetic and equilibrium constants shown in Table 2. The value of k_A is estimated by taking account of laminar flow¹⁾, and the values of k_{ci} and k_B are estimated by Eqs. (25) using the estimated values of diffusivity from the Wilke-Chang correlation. Good agreement between experimental and calculated results is obtained for each membrane extractor under various operating

Table 1. Properties of membrane extractor

Inner diameter of membrane extractor	$= 1.00 \times 10^{-2}$	[m]
Effective length of hollow fiber (L)	$= 0.5$	[m]
Outer diameter of hollow fiber (d)	$= 1.84 \times 10^{-3}$	[m]
Inner diameter of hollow fiber (d_i)	$= 9.83 \times 10^{-4}$	[m]
$\varepsilon=0.45$, $\xi=1.60$, $n=3\sim 7$, $n'=1\sim 3$		

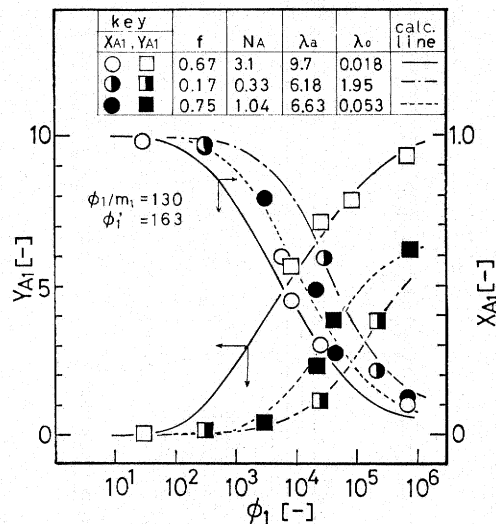


Fig. 3. Effect of ϕ_1 on X_{A1} and Y_{A1}

Table 2. Values of constants

$K_{HR}=4.65$	[m ³ /mol] ⁶⁾		
$K_{(HR)_2}=1.80$	[m ³ /mol] ⁶⁾		
$K_D=3.00$	[m ³ /mol] ⁵⁾		
$K_a=4.79$	[mol/m ³] ($pK_a=2.3$) ⁶⁾		
Zn		Cu	
$k_{fzn}=1.0 \times 10^{-5}$	[m/s] ⁷⁾	$k_{fCu}=5.0 \times 10^{-8}$	[m/s] ⁶⁾
$K_{ZnR2}=0.80$	[m ³ /mol] ⁷⁾	$K_{CuR2}=1.60$	[m ³ /mol] ⁶⁾
$K_{exzn1}=7.1 \times 10^{-4}$	[mol/m ³] ⁷⁾	$K_{exCu1}=3.50 \times 10^{-4}$	[mol/m ³] ⁵⁾
$K_{exzn2}=0.85$	[(mol/m ³) ^{0.5}] ⁵⁾	$K_{exCu2}=1.00 \times 10^{-4}$	[—] ⁵⁾
$\phi'_1=163$	[—],	$\phi'_2=658$	[—]
$\gamma_B=0.49$	[—],	$\gamma_{C1}=0.18$	[—],
		$\gamma_{C2}=0.21$	[—]

conditions.

Figure 4 shows the effect of N_A (i.e. v_1) on X_{A1} and Y_{A1} in the membrane extractor of $f=0.67$. The enrichment factor, Y_{A1} , increases with the flow rate of the feed solution under the condition of constant flow rate of the stripping solution. The solid lines in Fig. 4 are the calculated results.

Figure 5 shows the effect of m'_{A1} (i.e. $C_{H,3,0}$) on X_{A1} and Y_{A1} in the membrane extractor of $f=0.67$. From these results, it is found that X_{A1} and Y_{A1} are scarcely affected by the distribution constant of copper extraction, m'_{A1} , at interface II. This means that the permeation rate of copper from the feed solution to the stripping solution is not influenced by the stripping rate at high $C_{H,3,0}$.

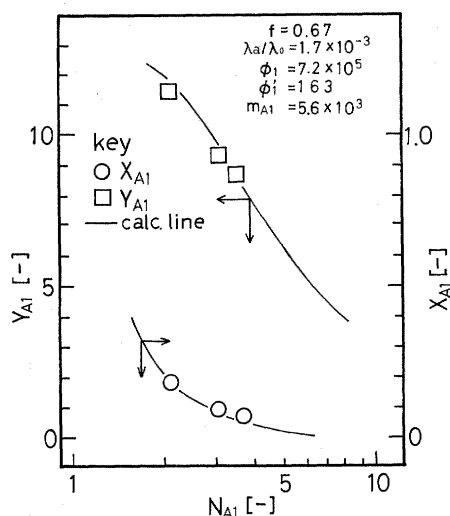


Fig. 4. Effect of N_A on X_{A1} and Y_{A1}

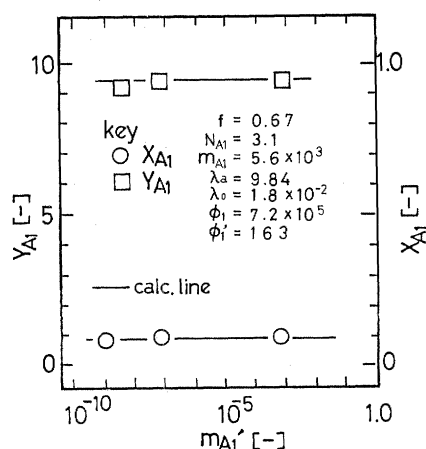


Fig. 5. Effect of m_{A1} on X_{A1} and Y_{A1}

The results shown in Figs. 3 to 5 indicate that the experimental results can be explained by the diffusion model accompanied by the interfacial reaction; that is, the basic equations and the several assumptions used are valid and acceptable.

3.2 Separation and enrichment of zinc

In the membrane extractor of $f=0.67$, the separation and enrichment of zinc from feed solution containing both copper and zinc were carried out under conditions of high concentration of hydrogen ion in the stripping solution. The results show that the concentrations of chemical species at interface II are expressed in terms of the extraction equilibrium conditions.

Figure 6 shows the relationship between α and E_{A2} for various values of N_A (i.e. v_1) and ϕ_1 (i.e. $C_{H,1,0}$ and $C_{B,2,0}$). As the solid lines in Fig. 6 show, the selectivity of zinc to copper, α , increases with decreasing ϕ_1 , that is, decreasing pH in the feed solution and extractant concentration in the organic solution. This indicates that the extraction rate at interface I is controlled by the interfacial reaction. At

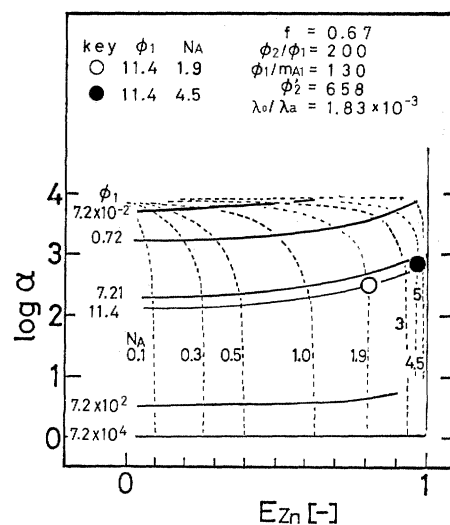


Fig. 6. Relationship between α and E_{Zn}

smaller ϕ_1 , however, a larger value of N_A is required to keep the extent of zinc extracted, E_{A2} , at high level, as shown by the dotted line in Fig. 6. This leads to a larger-scale membrane extractor because the interfacial reaction rate becomes too small. In Fig. 6, the experimental results show good agreement with the calculated ones.

Conclusion

A new type of membrane extractor was proposed for selective separation and enrichment of zinc from feed solution containing copper and zinc with PC-88A. Basic equations for the design of this type of membrane extractor made of a single hollow-fiber module were derived from a diffusion model accompanied by interfacial reaction. The validity of the basic equations was confirmed by comparing the calculated results obtained from the basic equations with experimental results concerning the extraction and enrichment of copper in three membrane extractors. From these basic equations, the relationship between the selectivity of zinc to copper and the extent of zinc extracted was compared with the experimental results. Good agreement between the experimental and calculated results was obtained.

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Nomenclature

A_i	= metal species	[-]
	($i=1$ for copper and $i=2$ for zinc)	
a	= interfacial area	[m ²]
B	= dimer species of extractant	[-]
b_i	= stoichiometric number of species i	[-]

	(i=1 for copper and i=2 for zinc)	
C_i	= metal complex of species i	[—]
C_j	= concentration of species j	[mol/m ³]
	{j=A, B, C, H}	
D	= Diffusivity	[m ² /s]
E_{Ai}	= extent of metal extracted	[—]
f	= n/n'	[—]
K_a	= acid dissociation constant of extractant	[mol/m ³]
K_{Ci}	= interfacial adsorption equilibrium constant of C_i	[m ³ /mol]
K_D	= dimerization constant of extractant	[m ³ /mol]
$K_{ex,M}$	= extraction equilibrium constant for metal M (M= Cu and Zn)	[—]
K_{HR}	= interfacial adsorption equilibrium constant of HR	[m ³ /mol]
$K_{(HR)2}$	= interfacial adsorption equilibrium constant of (HR) ₂	[m ³ /mol]
k_{Ai}	= mass transfer coefficient of A_i	[m/s]
k_B	= mass transfer coefficient of B	[m/s]
k_{Ci}	= mass transfer coefficient of C_i	[m/s]
$k_{f,Ai}$	= interfacial extraction rate constant of A_i	[m/s]
k_H	= mass transfer coefficient of H	[m/s]
$k_{r,Ci}$	= interfacial stripping rate constant	[m/s]
l	= distance from point contact between aqueous and organic solutions	[m]
L	= length of hollow fiber	[m]
$m_{Ai}^{(0)}$	= dimensionless term of extraction equilibrium defined by Eq. (26)	[—]
N_A	= reciprocal dimensionless length per transfer unit based on the feed solution ($=k_{Ai}/v_1$)	[—]
n	= number of hollow fibers for extraction	[—]
n'	= number of hollow fibers for stripping	[—]
R_{Ai}	= interfacial extraction rate of A_i	[mol/(m ² ·s)]
R_{Ci}	= interfacial stripping rate of C_i	[mol/(m ² ·s)]
v	= volumetric flow rate	[m ³ /s]
X	= dimensionless concentration in the feed or organic solution defined by Eq. (26)	[—]
Y	= dimensionless concentration of metal in the product solution defined by Eq. (26)	[—]
z	= dimensionless distance ($=l/L$)	[—]
α	= selectivity of metal separated	[—]
γ	= dimensionless term defined by Eq. (26)	[—]
δ	= thickness of hollow fiber	[m]
ε	= porosity of hollow fiber	[—]
λ	= dimensionless term defined by Eq. (26)	[—]

ξ	= tortuosity of hollow fiber	[—]
σ	= dimensionless term defined by Eq. (26)	[—]
ϕ	= dimensionless term of interfacial reaction rate constant	[—]

<subscript>

A_i	= metal species (i=1 for copper, i=2 for zinc)
aq	= aqueous solution
B	= dimer species of extractant
C_i	= metal complex
H	= hydrogen ion
i	= chemical species
j	= phase
org	= organic solution
0	= initial state
1	= extraction phase
2	= organic phase
3	= stripping phase
I	= interface for extraction
II	= interface for stripping

<superscript>

*I	= interface I of extraction side
*II	= interface II of stripping side

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