

EXTRACTION KINETICS OF ZINC WITH 2-ETHYLHEXYL PHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER USING A HOLLOW-FIBER MEMBRANE EXTRACTOR

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The development of efficient processes for the separation and recovery of valuable metals from low-grade ores and more complex materials has become increasingly important, from the viewpoint of saving natural resources and energy. Recently, the application of a membrane extractor made of hollow fiber has been attempted for recovery of metal as one of the efficient separation processes⁷⁾.

In work described in a previous paper,⁶⁾ the extraction rate of copper with 2-ethylhexyl phosphonic

acid mono-2-ethylhexyl ester (henceforth referred to by the commercial name, PC-88A, or abbreviated as HR) and the stripping rate of copper complex with hydrochloric acid were measured, using a membrane extractor made of a hollow fiber, to elucidate the mechanism of extraction and stripping of copper through the membrane.

In the present paper, experiments on the extraction of zinc with PC-88A and the stripping of zinc complex with hydrochloric acid were carried out with the membrane extractor to elucidate the mechanism of the extraction and stripping of zinc and to develop

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the extraction process using a membrane consisting of hollow fiber modules for the efficient separation of zinc.

1. Experimental

PC-88A (purity 95.5%) delivered from Daihachi Chemical Industry Co., Ltd. was used in the extraction experiment without further purification.

The zinc complex of PC-88A was prepared by the same procedure as that for copper complex⁶⁾. The results of elementary analysis were as follows; Anal. Calcd. for $C_{32}H_{68}P_2O_6Zn$: C, 56.84; H, 10.14; Found; C, 56.59; H, 10.14.

The organic solution was prepared by dissolving PC-88A in *n*-heptane. The aqueous solution was prepared by dissolving zinc nitrate in deionized water and by adjusting pH and ionic strength of the solution with 100 mol/m³ sodium acetate-acetic acid buffer solution and/or hydrochloric acid.

Interfacial tension between the organic and aqueous solutions was measured at 303 K by the pendant-drop method⁶⁾ to obtain information concerning the interfacial adsorption equilibrium of the zinc complex.

The average extraction and stripping rates of zinc, J_M and J'_M , were measured with the same hollow-fiber extractor and experimental procedure as those described in the previous paper⁶⁾. Both rates were defined by the following equations:

$$J_M = C_{M0}EQ_{aq}/(2\pi r_1 L) \quad (1)$$

$$J'_M = C_{MR_2HR_0}E'Q_{aq}/(2\pi r_1 L) \quad (2)$$

2. Results and Discussion

The relation between interfacial tension, γ , and the concentration of the zinc complex, C_{ZnR_2} , is shown in Fig. 1. From the experimental results, it is found that the zinc complex exhibits interfacial activity. The relationship between γ and C_{ZnR_2} is derived from the Gibbs equation for adsorption, assuming a Langmuir adsorption isotherm to express the relation between the amount of ZnR_2 adsorbed at the interface and C_{ZnR_2} , as follows:

$$\gamma = \gamma_0 - (RT/S_{ZnR_2}) \ln(1 + K_{ZnR_2}C_{ZnR_2}) \quad (3)$$

The values of K_{ZnR_2} and S_{ZnR_2} were obtained from the experimental results in Fig. 1 and Eq. (3) by non-linear regression, as shown in Table 1.

Figures 2 and 3 show the effects of pH and $C_{(HR)_2,0}$ on J_M , respectively. The experimental results also showed that J_M was proportional to C_{Zn0} in the range of low pH. From these results, it is suggested that the extraction rate is controlled by interfacial reaction in the low pH range and by diffusion of the extractant or metal in the high pH range. Figures 4 and 5 show the effects of a_{H_2O} and $C_{(HR)_2,0}$ on J'_M . Also, J'_M was

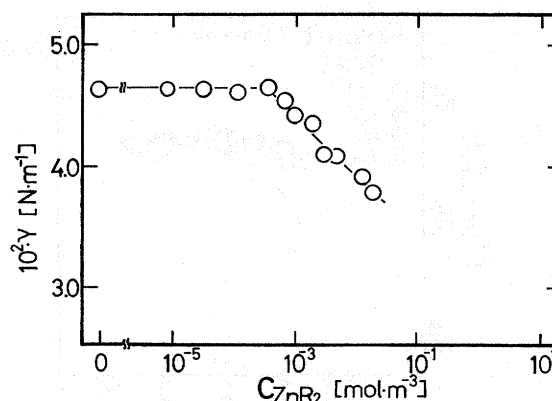


Fig. 1. Interfacial tension of zinc complex (pH=6.3)

Table 1. Values of equilibrium constants

K_{HR}	= 4.65	[m ³ /mol] ⁽⁶⁾	K_{ZnR_2}	= 0.80	[m ³ /mol]
$K_{(HR)_2}$	= 1.80	[m ³ /mol] ⁽⁶⁾	K_{ex}	= 0.79	[(mol/m ³) ^{0.5}] ⁽⁵⁾
K_D	= 3.00	[m ³ /mol] ⁽⁵⁾	K_a	= 4.79	[mol/m ³] ⁽⁶⁾

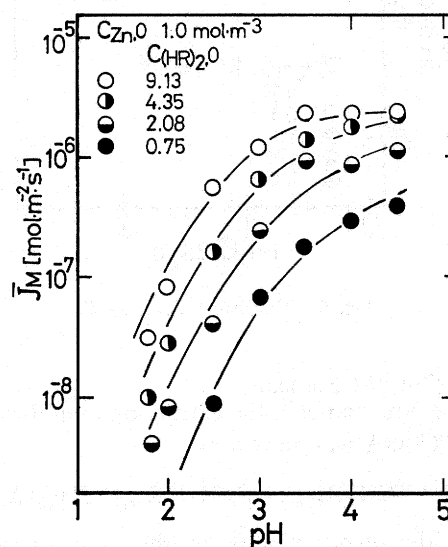


Fig. 2. Effect of pH on J_M

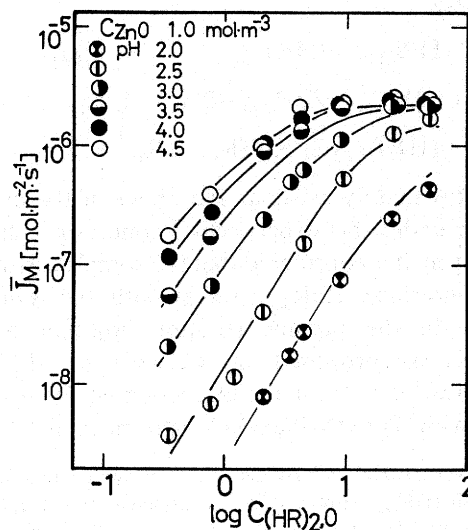


Fig. 3. Effect of $C_{(HR)_2,0}$ on J_M

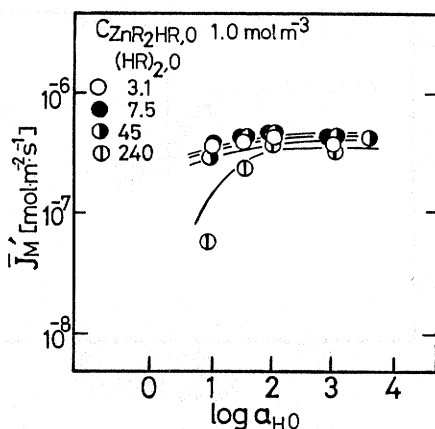


Fig. 4. Effect of a_{HO} on J'_M

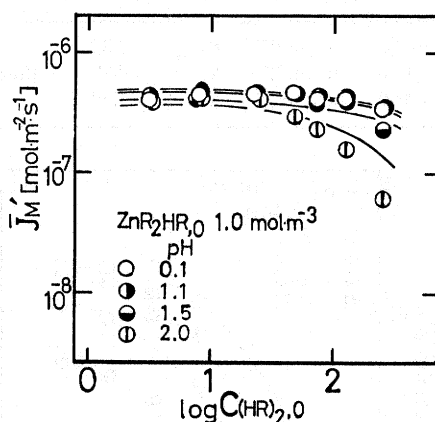


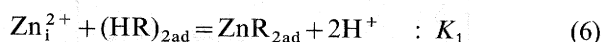
Fig. 5. Effect of $C_{(\text{HR})_2,0}$ on J'_M

proportional to $C_{\text{ZnR}_2\text{HRO}}$.

In a previous paper⁵⁾, the extraction equilibrium of zinc by PC-88A was shown as



From the experimental results, the extraction mechanism of zinc with PC-88A is considered to be as follows.



PC-88A mainly exists as the dimer in the organic solution under this experimental condition⁵⁾. In this mechanism, it is considered that the complex adsorbed at the interface, $\text{ZnR}_{2\text{ad}}$, reacts with the dimer of PC-88A in the organic solution adjacent to the interface, as proposed by Cianetti *et al.*²⁾ and Komasaawa *et al.*⁴⁾ for the extraction of the divalent metals with di(2-ethylhexyl)phosphoric acid.*¹⁾

*¹⁾ Ajawin *et al.*¹⁾ and Huang *et al.*³⁾ proposed that $\text{ZnR}_{2\text{ad}}$ reacts with $(\text{HR})_{\text{ad}}$. However, it is considered from the C.P.K. molecular model that the reaction between $\text{ZnR}_{2\text{ad}}$ and $(\text{HR})_{2\text{i}}$ occurs more easily than the reaction between $\text{ZnR}_{2\text{ad}}$ and $(\text{HR})_{\text{ad}}$.

Table 2. Values of constants

rate constants	
$k_r = 1.0 \times 10^{-5}$ [m/s]	$k_r = 6.4 \times 10^{-4}$ [m ^{2.5} /mol ^{0.5} sec]
character of membrane extractor	
$r_1 = 4.92 \times 10^{-4}$ [m]	$r_2 = 9.20 \times 10^{-4}$ [m]
$r_3 = 1.20 \times 10^{-3}$ [m]	
$L = 0.25$ [m]	$\varepsilon = 0.45$ [—]
$\tau = 1.60$ [—]	
$Q_{\text{aq}} = 2.3 \times 10^{-9}$ [m ³ /s]	$Q_{\text{org}} = 4.0 \times 10^{-9}$ [m ³ /s]
$D_{\text{Zn}} = 7.20 \times 10^{-10}$ [m ² /s]	$D_{(\text{HR})_2} = 1.62 \times 10^{-9}$ [m ² /s]
$D_{\text{ZnR}_2\text{HR}} = 8.40 \times 10^{-10}$ [m ² /s]	
* estimated value by the Wilke-Chang correlation	

As discussed in the previous paper concerning copper extraction with PC-88A⁶⁾, the interfacial reaction step shown by Eq. (7) could be considered as rate-controlling among the interfacial reactions of Eqs. (5) to (7). Assuming that the activity of hydrogen ion is kept constant along the lumen of hollow fiber, the interfacial reaction rate, R , is written as

$$R = (k_r C_{\text{Zn}}^i C_{(\text{HR})_2}^{i2} / a_{\text{H}_2\text{O}}^2 - k_r C_{\text{ZnR}_2\text{HR}}^i C_{\text{HR}}^i) / \sigma_{\text{HR}} \quad (8)$$

$$\sigma_{\text{HR}} = 1 + K_{\text{HR}}(1 + K_a/a_{\text{H}_2\text{O}})C_{\text{HR}}^i + K_{(\text{HR})_2}C_{(\text{HR})_2}^i + K_{\text{ZnR}_2}C_{\text{ZnR}_2}^i \quad (9)$$

The experimental results were analyzed by the diffusion model with interfacial reaction, taking account of the laminar velocity distributions of the aqueous and organic solutions which flow along the hollow fiber⁷⁾.

Solid lines in Figs. 2–5 are the results calculated by using the constants shown in Tables 1 and 2. It is found that the calculated results agree well with the experimental ones*²⁾.

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Nomenclature

a_{H}	= activity of hydrogen ion	[mol/m ³]
C_j	= concentration of species j ($j = \text{Zn}, (\text{HR})_2, \text{ZnR}_2, \text{ZnR}_2\text{HR}$)	[mol/m ³]
D_j	= diffusivity of species j	[m ² /s]
E'	= extent of zinc extracted (stripped)	[—]
J_M'	= extraction (stripping) rate of zinc	[mol/m ² ·s]
K_a	= acid dissociation constant of extractant	[mol/m ³]
K_D	= dimerization constant of extractant	[m ³ /mol]
K_{ex}	= extraction equilibrium constant	[(mol/m ³) ^{0.5}]
K_j	= adsorption equilibrium constant of species j ($j = \text{HR}, (\text{HR})_2, \text{ZnR}_2$)	[m ³ /mol]
K_1	= equilibrium constant defined by Eq. (6)	[mol/m ³]
k_r	= overall extraction rate	[m/s]
k_r	= overall stripping rate	[m/s]

*²⁾ The experimental results were not explained by the diffusion model in which the interfacial reactions of Eqs. (5) to (7) are assumed to attain equilibrium.

k_2	= forward reaction rate constant of Eq. (7)	$[m^2/mol \cdot s]$
L	= effective length of hollow fiber	$[m]$
Q	= volumetric flow rate	$[m^3/s]$
R'	= interfacial extraction (stripping) rate	$[mol/m^2 \cdot s]$
r_1	= inner radius of hollow fiber	$[m]$
r_2	= outer radius of hollow fiber	$[m]$
r_3	= inner radius of membrane extractor	$[m]$
S_j	= interfacial area occupied at interface by unit mole of species j	$[m^2/mol]$
γ	= interfacial tension	$[N/m]$
ε	= porosity of hollow fiber	$[-]$
τ	= tortuosity of hollow fiber	$[-]$

<Subscripts>

ad	= adsorbed state
aq	= aqueous solution
i	= adjacent to interface
org	= organic solution

0 = initial state

Literature Cited

- 1) Ajawin, L. A., E. S. Perez de Ortiz and H. Sawistowski: *Chem. Eng. Res. Des.*, **61**, 63 (1983).
- 2) Cianetti, C. and P. R. Danesi: *Solv. Extr. Ion Exch.*, **1**, 9 (1983).
- 3) Huang, T.-C. and R.-S. Juang: *J. Chem. Eng. Japan*, **19**, 379 (1986).
- 4) Komasaawa, I. and T. Otake: *Ind. Eng. Chem. Fundam.*, **22**, 367 (1983).
- 5) Nakashio, F., K. Kondo, A. Murakami and Y. Akiyoshi: *J. Chem. Eng. Japan*, **15**, 274 (1982).
- 6) Sato, Y., Y. Akiyoshi, K. Kondo and F. Nakashio: *J. Chem. Eng., Japan*, **22**, 182 (1989).
- 7) Yoshizuka, K., K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **19**, 312 (1986).

(Presented at the Kagoshima Meeting of the Society of Chemical Engineers, Japan, at Kagoshima (1987)).