1306 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *55*, *1306—1309 (1982)* [Vol. 55, No. 4

Mechanism of Copper Transport through a Diaphragm-type Liquid Membrane

Takeshi Kataoka, Tadaaki Nishiki,* and Koretsune Ueyama
Department of Chemical Engineering, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591

(Received March 13, 1981)

The permeation mechanism of copper with a liquid membrane process was studied by measuring the permeation rate of copper, which was allowed to permeate through a diaphragm-type liquid membrane with LIX64N as a mobile carrier at various concentrations of carrier and acid. The permeation rate is explained approximately by the diffusional process in the membrane for a chelating complex between copper and carrier and by the succeeding stripping reaction at the interface between the membrane and stripping phase.

A novel technique which can separate and concentrate dissolved solutes and ions in aqueous solution with liquid membranes has attracted special interest recently.[1,2] Especially, the liquid membrane process containing a mobile carrier can be expected to give high selectivity and concentrating effect, so researches have been actively advanced to apply the process to hydrometallurgy and waste water treatment.

The liquid-liquid extraction of copper with LIX reagents has been one of important commercial solvent extractions for practical applications in hydrometallurgical processes. Therefore, a number of studies on equilibria and kinetics of extraction reactions have been reported. However, concentration and separation of copper with liquid membrane containing LIX reagents as a mobile carrier has not sufficiently been studied,[3–6] and the mechanism of permeation through such a membrane has not been elucidated.

The purpose of the present investigation is to clarify the permeation mechanism of copper ion with a liquid membrane. The permeation rate of copper ion through a diaphragm-type liquid membrane was measured by adopting LIX64N as a mobile carrier. The effect of the concentration of carrier and acid on the permeation rate was examined, and the permeation mechanism was discussed.

Theoretical

Model for Permeation of Copper. The permeation mechanism of copper ion through a liquid membrane containing LIX64N as a mobile carrier is shown schematically in Fig. 1. Copper ion M^{2+} in the left cell diffuses to the interface $x=0$, where it undergoes chelating complex formation with the carrier RH. The complex R_2M formed diffuses across the membrane toward the interface $x=L$, reacts with hydrogen ion H^+ and liberates copper ion in the right cell. The regenerated carrier RH diffuses back to the left side of membrane and reacts again with M^{2+} in the left cell. As a result of repetition of such a mechanism, copper ions are permeated and concentrated from the left into the right cell.

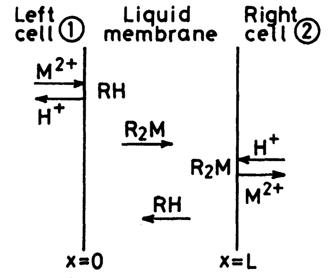

Fig. 1. Permeation mechanism.

Permeation Rate. If the permeation rate is controlled both by the diffusion process in the membrane and by the stripping process at the interface between the membrane and the right cell, the quasi-steady state may be assumed, and the fluxes $\bar{J}$ in the membrane and J in the right cell are respectively given by

$$J_{\mathrm{M}} = \bar{k}_{\mathrm{M}}\{(\bar{C}_{\mathrm{T}}/2)-\bar{C}_{\mathrm{ML}}\}, \tag{1}$$

$$J_{\mathrm{RH}} = -\bar{k}_{\mathrm{RH}}\bar{C}_{\mathrm{RHL}}, \tag{2}$$

$$J_{\mathrm{M2}} = k_{\mathrm{M2}}(C_{\mathrm{ML}}-C_{\mathrm{M2}}), \tag{3}$$

where k is the mass-transfer coefficient and $\bar{C}_{\mathrm{T}}$ the total concentration of mobile carrier. The bar superscript and the subscripts L and 2 denote the membrane phase, the interface $x=L$, and the right cell, respectively.

The following interfacial reaction model[7] may be applied to the stripping reaction at $x=L$:

$$(\overline{\mathrm{R_2M}})_{\mathrm{i}} + (\mathrm{H^+})_{\mathrm{i}} \underset{k_{-\mathrm{r1}}}{\overset{k_{\mathrm{r1}}}{\rightleftarrows}} (\mathrm{RM^+})_{\mathrm{ad}} + (\overline{\mathrm{RH}})_{\mathrm{i}} \quad K_1, \tag{4}$$

$$(\mathrm{RM^+})_{\mathrm{ad}} + (\mathrm{H^+})_{\mathrm{i}} \rightleftarrows (\mathrm{M^{2+}})_{\mathrm{i}} + (\mathrm{RH})_{\mathrm{ad}} \quad K_2, \tag{5}$$

$$(\mathrm{RH})_{\mathrm{ad}} \rightleftarrows (\overline{\mathrm{RH}})_{\mathrm{i}} \qquad K_3, \tag{6}$$

where K is the equilibrium constant, the subscript "ad" denotes the interfacially adsorbed species, and "i" denotes the species adjacent to the interface, either on the membrane side or on the right cell side. If the reaction shown in Eq. 4 is a rate-controlling step, the stripping reaction rate is expressed as

$$\begin{aligned} r &= k_{\mathrm{r1}}[\overline{\mathrm{R_2M}}]_{\mathrm{i}}[\mathrm{H^+}]_{\mathrm{i}} - \frac{k_{-\mathrm{r1}}[\mathrm{M^{2+}}]_{\mathrm{i}}[\mathrm{RH}]_{\mathrm{ad}}[\overline{\mathrm{RH}}]_{\mathrm{i}}}{K_2[\mathrm{H^+}]_{\mathrm{i}}} \\ &= k_{\mathrm{r1}}\bar{C}_{\mathrm{ML}}C_{\mathrm{HL}} - \frac{\alpha C_{\mathrm{ML}}\bar{C}_{\mathrm{RHL}}}{C_{\mathrm{HL}}}, \end{aligned} \tag{7}$$

where $\alpha=\bar{k}_{-\mathrm{r1}}[\mathrm{RH}]_{\mathrm{ad}}/K_2$.

From Eqs. 1, 2, 3, and 7, the concentration $\bar{C}_{\mathrm{ML}}$ of the complex at the interface $x=L$ is given by

$$\begin{aligned} \bar{C}_{\mathrm{ML}} = (1/4\alpha\beta\gamma)[&2\alpha\beta\gamma\bar{C}_{\mathrm{T}}+k_{\mathrm{r1}}C_{\mathrm{HL}}^2+\bar{k}_{\mathrm{M}}C_{\mathrm{HL}}+2\alpha\beta C_{\mathrm{M2}} \\ &-\{k_{\mathrm{r1}}C_{\mathrm{HL}}^2(4\alpha\beta\gamma\bar{C}_{\mathrm{T}}+k_{\mathrm{r1}}C_{\mathrm{HL}}^2+2(\bar{k}_{\mathrm{M}}C_{\mathrm{HL}}+2\alpha\beta C_{\mathrm{M2}})) \\ &+(\bar{k}_{\mathrm{M}}C_{\mathrm{HL}}+2\alpha\beta C_{\mathrm{M2}})^2\}^{1/2}], \end{aligned} \tag{8}$$

where $\beta=\bar{k}_{M}/\bar{k}_{RH}$ and $\gamma=\bar{k}_{M}/k_{M2}$.

Consequently, with $\bar{C}_{ML}$ obtained from Eq. 8, the concentration C_{M1} of copper in the left cell can be calculated successively as a function of time by using Eq. 1 and the following equation:

$$-V(\mathrm{d}C_{M1}/\mathrm{d}t) = SJ_{M}, \tag{9}$$

where V and S represent the volume of cell and the area of diaphragm, respectively.

In the initial contact time, the second term on the right-hand side of Eq. 7 may be neglected and the copper concentration with time is expressed as

$$\frac{C_{M1}}{C_{M1,0}} = 1 - \frac{1}{2}\left(\frac{S}{V}\right)\left\{\frac{k_{r1}C_{HL}}{1+(k_{r1}/\bar{k}_{M})C_{HL}}\right\}\left(\frac{\bar{C}_{T}}{C_{M1,0}}\right)t, \tag{10}$$

where $C_{M1,0}$ is the initial concentration of copper in the left cell.

The mass-transfer coefficient k_{M2} was evaluated from the following equation:

$$\frac{kd}{D} = 0.158\left(\frac{\mu}{\rho D}\right)^{1/3}\left(\frac{\omega d^2\rho}{\mu}\right)^{0.63}, \tag{11}$$

where D is the diffusivity, d the diameter of impeller, ρ the density, μ the viscosity, and ω the rotational speed of impeller. This equation is correlated with the mass-transfer coefficients obtained from the following experiment. Namely, benzoic acid was cast in a circular depression corresponding to the membrane in the same apparatus as used in this study. Rates of dissolution of benzoic acid from the flat surface into several liquids were measured for various speeds.

Experimental

Apparatus. The permeation apparatus used is illustrated in Fig. 2. The membrane was clampled between two glass half-cells with inner diameter of 8 cm. A Teflon millipore membrane filter, which has a thickness of 125 μm, a porosity of about 68%, and a pore size of 10 μm, was used as a diaphragm throughout this study. The volume of each cell is 370 cm^3 and the contact area between the membrane and aqueous solution is 33.2 cm^2. The turbine impellers of 4 cm diameter with six flat-blades filtted at the center of cell length were driven in the same direction at a constant speed of 82 min^{-1} with variable-speed motors in both cells. The apparatus was placed in an air bath which was maintained at 25 °C. In addition, all metal surfaces were coated with Teflon.

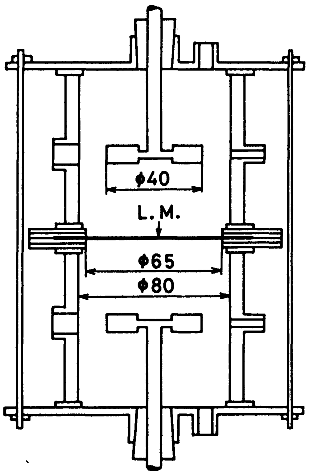

Fig. 2. Permeability cell.

Method. The pores in the membrane were filled up by immersing the membrane filter in the membrane solution. The membrane solution was prepared by dissolving LIX64N as a mobile carrier in kerosene. The concentration of active ingredient of LIX64N in kerosene was determined by measurement of the ultimate copper loading of LIX64N. The aqueous solutions were prepared by saturating degassed deionized water with kerosene.

The aqueous copper sulfate solution containing acetic acid–sodium acetate buffer was carefully poured into the left cell and the aqueous hydrochloric acid or sulfuric acid solution into the right cell so that the liquid levels in both cells might become equal. The time when the aqueous solution had come into contact with whole surface of membrane was taken as the beginning of experiment. After each cell was filled with the solution, both cells were stirred immediately.

Samples were taken from the left cell at regular time intervals by replacing them with fresh solution. The amount of sample was about 5 cm^3 and the number of samples was 5 or 6 in each run. The copper concentration was determined by titration with a standardized EDTA solution.

Results and Discussion

Effects of pH and Initial Concentration of Copper. The effect of pH on the partition equilibrium of copper between LIX64N in kerosene and aqueous solution was investigated by the batchwise method. The result obtained shows that the percent extraction of copper becomes constant around 100% above pH=3.

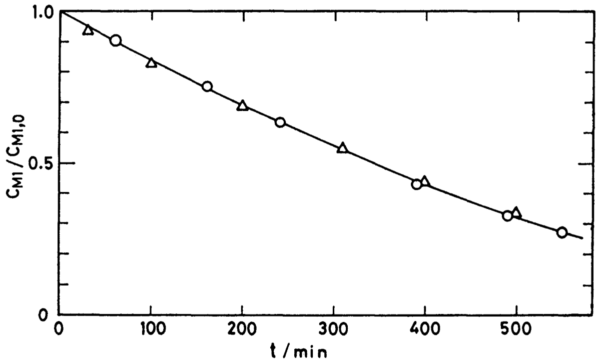

Fig. 3. Effect of pH on permeation rate of copper.
System: 0.01 mol dm^{-3} $CuSO_4$–L.M. ($\bar{C}_T$=0.490 mol dm^{-3})–2 mol dm^{-3} HCl. △: pH=3.5, ○: pH=4.5.

To examine the effect of pH on the permeation rate of copper, the copper concentration in the left cell with time was followed with time by keeping the pH in the left cell at 3.5 and 4.5. These results are shown in Fig. 3. No appreciable difference in permeation rate is detected for the above two pH values. Therefore, all the runs described below were performed for pH=4.5.

Figure 4 shows a result where differences in concentration, *i.e.*, the decreased amounts of copper in the left cell, were plotted against time for the initial copper concentrations of 0.01, 0.02, and 0.05 mol dm^{-3}. There

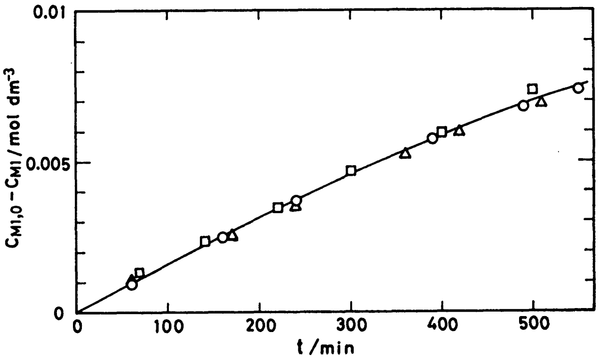

Fig. 4. Effect of initial coper concentration on permeation rate of copper.
System: $CuSO_4$(pH=4.5)-L.M. ($\bar{C}_T$=0.490 mol dm^{-3}) -2 mol dm^{-3} HCl. ○: $C_{M1,0}$=0.01, △: $C_{M1,0}$=0.02, □: $C_{M1,0}$=0.05 mol dm^{-3}.

is no change in concentration difference with the variation of initial concentration and the effect of the initial copper concentration on the permeation rate may be neglected.

From the above results, the foregoing assumption that the permeation rate is controlled both by the diffusion process in the membrane and by the stripping process seems to be reasonable.

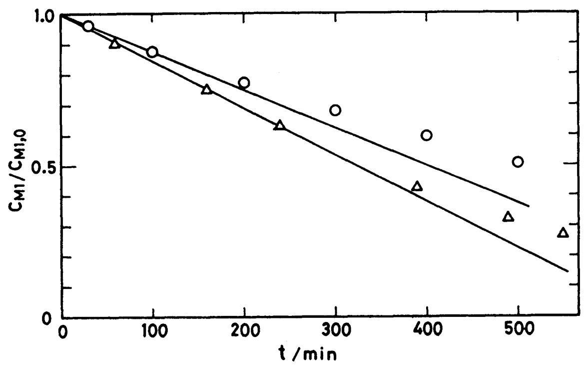

Fig. 5. Copper concentration in left cell *vs.* time (determination of k_{r1}).
System: 0.01 mol dm^{-3} $CuSO_4$(pH=4.5)-L.M.($\bar{C}_T$= 0.490 mol dm^{-3})-2 mol dm^{-3} acid. ○: H_2SO_4, △: HCl.

TABLE 1. ESTIMATED VALUES OF MASS-TRANSFER COEFFICIENTS

$\bar{C}_T$ mol dm^{-3}	$\bar{k}_M$ cm min^{-1}	$\bar{k}_{RH}$ cm min^{-1}
0.490	8.3×10^{-4}	1.3×10^{-3}
0.193	2.1×10^{-3}	3.2×10^{-3}
0.100	2.7×10^{-3}	4.2×10^{-3}

Acid	C_{HL} mol dm^{-3}	k_{M2} cm min^{-1}
HCl	2.0	4.6×10^{-2}
	1.0	4.8×10^{-2}
H_2SO_4	4.0	2.9×10^{-2}
	2.0	3.8×10^{-2}

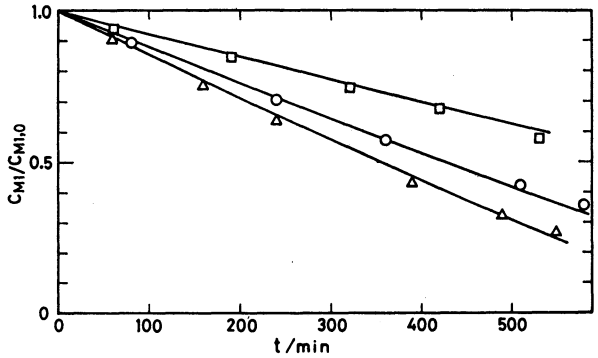

Fig. 6. Copper concentration in left cell *vs.* time (effect of carrier concentration).
System: 0.01 mol dm^{-3} $CuSO_4$ (pH=4.5)-L. M.-2 mol dm^{-3} HCl. α=0.16 cm min^{-1}. □: $\bar{C}_T$=0.100, ○: $\bar{C}_T$=0.193, △: $\bar{C}_T$=0.490 mol dm^{-3}.

Determination of Reaction Rate Constant k_{r1}. Figure 5 shows results of runs in which time-dependent concentrations of copper in the left cell were measured by using 2 mol dm^{-3} hydrochloric acid or sulfuric acid as an acid in the right cell at the carrier concentration of 0.49 mol dm^{-3}. The solid lines are the slopes for each straight region near contact time zero. The values of k_{r1} obtained from each slope and Eq. 10 are 2.5 for HCl and 0.95 cm^4 mol^{-1} min^{-1} for H_2SO_4. The value of $\bar{k}_M$ in the membrane adopted in this calculation was evaluated by the same method as in the case of the concentration of chloride ion[8] and by using the diffusivity estimated from the Wilke-Chang equation. The estimated value of $\bar{k}_M$ is shown in Table 1. In the figure, the experimental values tend to deviate upward from each straight line. This is caused by neglecting the second term on the right hand side of Eq. 7.

Effect of Carrier Concentration. Figure 6 shows the effect of the carrier concentration on the permeation rate at 2 mol dm^{-3} of hydrochloric acid. The solid lines are the concentrations as a function of time for each carrier concentration which were calculated from Eqs. 1, 8, and 9 by using the above value of k_{r1} and those of $\bar{k}_M$ and $\bar{k}_{RH}$ in Table 1. In this case, the mass-transfer coefficient k_{M2} in the right cell was obtained from Eq. 11 by using the diffusivity of copper ion estimated from the Nernst-Einstein equation, and is shown in Table 1. In addition, the value of α, which is constant because the value of $[RH]_{ad}$ becomes the saturated value at the high concentrations of LIX64N used, was determined by the trial and error method. The calculated values agree with the experimental results over the wide range of contact time for each carrier concentration.

The effect of carrier concentration on the permeation rate at 2 mol dm^{-3} of sulfuric acid is shown in Fig. 7. The solid line represents the calculated values for α= 0.20 cm min^{-1} obtained in the same way as in the case of hydrochloric acid by using the k_{r1} obtained above and the mass-transfer coefficients presented in Table 1. The calculated values agree with the observed over the whole range of contact time for all the carrier concentrations. The value of α for H_2SO_4 is a little different

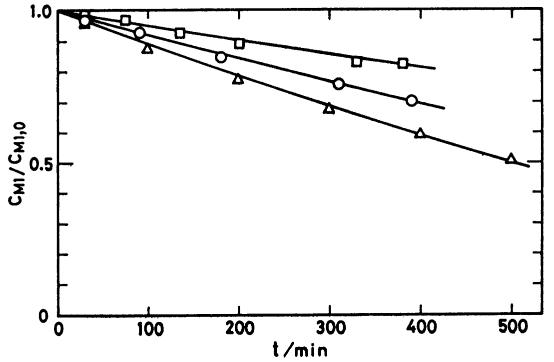

Fig. 7. Copper concentration in left cell *vs.* time (effect of carrier concentration).
System: 0.01 mol dm^{-3} $CuSO_4$ (pH=4.5)-L.M.-2 mol dm^{-3} H_2SO_4. α=0.20 cm min^{-1}. □: $\bar{C}_T$=0.100, ○: $\bar{C}_T$=0.193, △: $\bar{C}_T$=0.490 mol dm^{-3}.

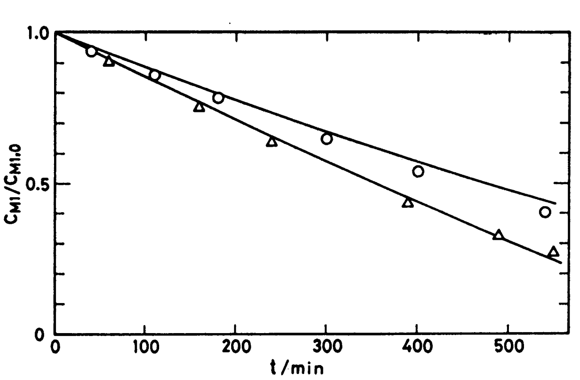

Fig. 8. Copper concentration in left cell *vs.* time (effect of hydrochloric acid concentration).
System: 0.01 mol dm^{-3} $CuSO_4$ (pH=4.5)-L. M. ($\bar{C}_T$= 0.490 mol dm^{-3})-HCl. α=0.16 cm min^{-1}. ○: HCl concn=1.0, △: HCl concn=2.0 mol dm^{-3}.

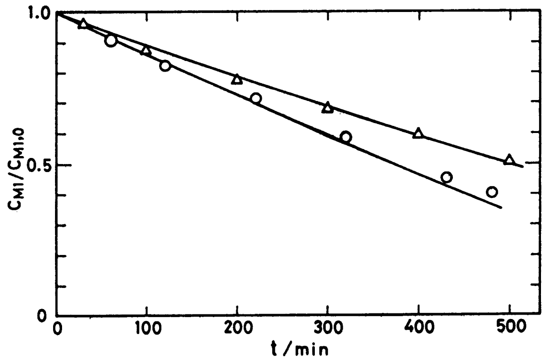

Fig. 9. Copper concentration in left cell *vs.* time (effect of sulfuric acid concentration).
System: 0.01 mol dm^{-3} $CuSO_4$ (pH=4.5)-L. M. ($\bar{C}_T$= 0.490 mol dm^{-3})-H_2SO_4. α=0.20 cm min^{-1}. △: H_2SO_4 concn=2.0, ○: H_2SO_4 concn=4.0 mol dm^{-3}.

from α=0.16 cm min^{-1} for HCl. This may be caused by a difference in k_{-r1} value between the two acids.

Effect of Acid Concentration. To clarify the effect of acid concentration in the right cell on the permeation rate, the copper concentration with time was measured by varying the concentration of hydrochloric acid at a constant carrier concentration of 0.49 mol dm^{-3}. These results are shown in Fig. 8. The solid lines are the calculated values obtained by using the same values of k_{r1} and α as in the case of the variation of carrier concentration. The calculated values agree approximately with the experimental ones, althought there are slight deviations between the calculated and experimental values in the region of long contact time.

Figure 9 shows results of the time-dependent concentration for sulfuric acid of 2 and 4 mol dm^{-3}. The agreement between the calculation and experiment is approximately good to the same extent as in the case of hydrochloric acid.

Conclusion

To clarify the permeation mechanism of copper ion with a liquid membrane, the time-dependent concentration of copper was measured for a diaphragm-type liquid membrane impregnated with LIX64N as a mobile carrier.

The permeation rate of copper ion is affected by the concentration of carrier and of the acid in the stripping phase. It has become apparent that the mechanism for the present permeation can be expressed by the diffusional process in the membrane for a chelating complex between copper and carrier and by the succeeding reaction at the interface between the membrane and stripping phase.

This work was supported by Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Culture, Japan, Grant No. 355406. The authors wish to acknowledge the support leading to the publication of this article.

References

1) N. N. Li and A. L. Shrier, "Recent Developments in Separation Science," ed by N. N. Li, CRC Press, Cleveland (1972), Vol. 1, p. 163.

2) J. W. Frankenfeld and N. N. Li, "Recent Developments in Separation Science," ed by N. N. Li, CRC Press, Cleveland (1977), Vol. 3, p. 285.

3) R. W. Baker, M. E. Tuttle, D. J. Kelly, and H. K. Lonsdale, *J. Membr. Sci.*, **2**, 213 (1977).

4) A. Kopp, R. Marr, and F. Moser, presented at CHISA '78 Conference, 12.6 (1978).

5) K. H. Lee, D. F. Evans, and E. L. Cussler, *AIChE J.*, **24**, 860 (1978).

6) W. Volkel, W. Halwachs, and K. Schügerl, *J. Membr. Sci.*, **6**, 19 (1980).

7) I. Komasawa, T. Otake, and T. Muraoka, *J. Chem. Eng. Jpn*, **13**, 204 (1980).

8) T. Kataoka, T. Nishiki, Y. Tamura, and K. Ueyama, *J. Chem. Eng. Jpn.*, **13**, 35 (1980).