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Mechanism of Copper Permeation through Hollow Fiber Liquid Membranes

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Abstract

A general model for the carrier transport of copper through hollow fiber liquid membranes is presented. A series of experiments on the extraction of copper was carried out with hollow fiber liquid membranes containing SME529 as a carrier under various experimental conditions. It is shown that observed permeation rates can be quantitatively interpreted by the proposed model.

INTRODUCTION

Recently attention has been paid to the separation technique using liquid membranes. The liquid membrane configurations that can be used for practical purpose are liquid surfactant membranes and supported liquid membranes (*1*). Although it is possible to extract solutes very rapidly by liquid surfactant membranes due to the large specific area and the thinness of the membranes, the process is rather complicated because of the necessity of demulsification to recover the concentrated solutes in the encapsulated drops. On the other hand, in the case of supported liquid membranes, the process is very simple, the extractant inventory is very small, and the extractant loss is also very small. However, there are several disadvantages. The first is the low permeation rate compared to the liquid surfactant membrane, and the second is the degradation of membranes mainly due to the dissolution of the organic solution in aqueous solutions.

Hollow fiber liquid membranes have advantages over flat liquid membranes because a large membrane area is available and also degraded

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membranes can be easily regenerated as shown below. From these points of view, Babcock et al. (*2*) used hollow fiber modules to recover and concentrate uranium from synthetic sulfuric acid leach solutions.

Although many papers (*3–7*) have been presented on the mechanism of copper permeation through flat liquid membranes, the mechanism through hollow fiber membranes has not yet been investigated. In this paper a general model for the carrier transport of copper through hollow fiber liquid membranes is proposed. Furthermore, comprehensive experiments were carried out using hollow fiber liquid membranes containing SME529, a chelating agent supplied from Shell Chemical Co. Ltd. as a carrier. The effects of such experimental conditions as concentrations of copper, hydrogen ion and SME529, temperature, and membrane viscosity are discussed on the basis of the proposed model. The behavior of the degradation of liquid membranes and the method of the regeneration of membranes are also presented.

PERMEATION MODEL

It has already been shown that the reaction between Cu^{2+} and *anti* 2-hydroxy-5-tert-nonyl acetophenone oxime, the active species of SME529, occurs at the organic–aqueous interface, and the forward and reverse reaction rates are expressed as (*8, 9*)

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

$$(A + 2B \rightleftharpoons C + 2H)$$

$$K_{ex} = ([CuR_2][H^+]^2/[Cu^{2+}][HR]^2)_{eq} = (CH^2/AB^2)_{eq} \tag{2}$$

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

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

The elementary steps for the permeation of copper through a hollow fiber liquid membrane are shown in Fig. 1. The rates of these steps at steady-state are as follows.

Step 1: Diffusion of copper through the external aqueous film from the external phase (Phase I, feed solution) to the external surface of the membrane:

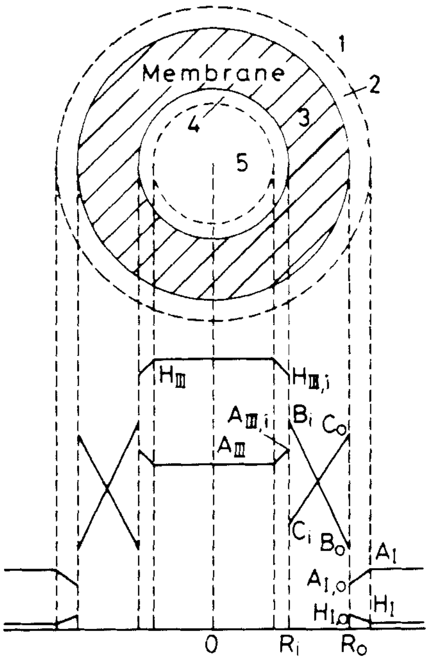

FIG. 1. Model of copper permeation through hollow fiber liquid membrane. (1) Feed solution (external aqueous phase, Phase I). (2) Stagnant film of external aqueous phase. (3) Hollow fiber liquid membrane (Phase II). (4) Stagnant film of internal aqueous phase. (5) Stripping solution (internal aqueous phase, Phase III).

$$N_{A,I} = k_{A,I} S_o (A_I - A_{I,o}) \tag{5}$$

Step 2: Diffusion of hydrogen ion through the external aqueous film:

$$N_{H,I} = k_{H,I} S_o (H_{I,o} - H_I) \tag{6}$$

Step 3: Forward chelating reaction at the external surface of the membrane:

$$N_f = k_f S_o [A_{I,o} B_o / H_{I,o} - C_o H_{I,o} / (K_{ex} B_o)] \tag{7}$$

Steps 4 and 5: Diffusions of the chelating agent and the copper complex through the liquid membrane:

$$N_B = k_B S_{av}(B_i - B_o) \tag{8}$$

$$N_C = k_C S_{av}(C_o - C_i) \tag{9}$$

Step 6: Stripping reaction at the internal surface of the liquid membrane:

$$N_r = k_r S_i\,(C_i H_{III,i} - K_{ex} A_{III,i} B_i^2 / H_{III,i}\,) \tag{10}$$

Steps 7 and 8: Diffusions of copper and hydrogen ion through the internal aqueous film:

$$N_{A,III} = k_{A,III} S_i (A_{III,i} - A_{III}) \tag{11}$$

$$N_{H,III} = k_{H,III} S_i (H_{III} - H_{III,i}) \tag{12}$$

If the dissolution of the carrier and the complex in the aqueous phase is negligibly small, the total quantity of the carrier must be conserved.

$$\pi(R_o^2 - R_i^2)B_f = 2\pi \int_{R_i}^{R_o} (B + 2C) r\, dr \tag{13}$$

Here, B_f is the initial concentration of HR.

The concentration profiles of HR and CuR_2 are expressed as

$$B = B_i + (B_o - B_i)(\ln r - \ln R_i)/\ln (R_o/R_i) \tag{14}$$

$$C = C_i + (C_o - C_i)(\ln r - \ln R_i)/\ln (R_o/R_i) \tag{15}$$

Substitution of Eqs. (14) and (15) into Eq. (13) gives

$$B_f = (1 - p)B_i + pB_o + 2(1 - p)C_i + 2pC_o \tag{16}$$

where p is the geometrical factor of the hollow fiber, and equal to 0.5 for flat membranes.

$$p = R_o^2/(R_o^2 - R_i^2) - 1/\{2 \ln (R_o/R_i)\} \tag{17}$$

At steady-state, the following equation holds:

$$N_{A,I} = N_{H,I}/2 = N_f = N_B/2 = N_C = N_r = N_{A,III} = N_{H,III}/2 \tag{18}$$

If the concentrations A_I, H_I, B_f, A_{III}, and H_{III}, and the rate parameters $k_{A,I}$, $k_{H,I}$, k_f, k_B, k_C, k_r, $k_{A,III}$, and $k_{H,III}$ are given, nine unknowns (eight concentrations $A_{I,o}$, $H_{I,o}$, B_o, C_o, B_i, C_i, $A_{III,i}$, $H_{III,i}$, and N) can be obtained from Eqs. (5)–(12) and (16) by a trial-and-error method.

The copper fluxes for the special cases are as follows.

(1) Diffusion of copper in the external aqueous film is rate-controlling:

$$J_A = k_{A,I}A_I S_o/S_{av} \tag{19}$$

(2) Forward reaction is rate-controlling:

$$J_A = k_f(A_I B_o/H_I)(S_o/S_{av}) \tag{20}$$

(3) Diffusion of the complex in the membrane is rate-controlling:

$$J_A = k_C B_f/[2\{(1-p)q+p\}] \tag{21}$$

$$q = k_C/k_B$$

(4) Stripping is rate-controlling:

$$J_A = k_r(B_f H_{III}/2)(S_i/S_{av}) \tag{22}$$

Here, J_A is the copper flux based on the logarithmic mean of the external and internal membrane areas.

$$J_A = N_A/S_{av},\ S_{av} = (S_o - S_i)/\ln(S_o/S_i) \tag{23}$$

Equation (21) is derived from Eqs. (8), (9), (16), and (18) with both B_o and C_i put at zero.

As described below, in the present experiments the pH of the copper solution was adjusted using an acetic acid–sodium acetate buffer solution when its pH was higher than 3. On the other hand, when the pH was low, the forward reaction rate was slow compared to the diffusion rate through the external aqueous film. Therefore, mass transfer resistance of hydrogen ion through the external aqueous film could be neglected. Furthermore, the resistance in the internal aqueous film was found to be negligibly small. It was also found by stripping experiments using a Lewis cell that the hydrogen ion concentrations in Eqs. (10) and (22) should be replaced by the activities of hydrogen ion (*9*).

$$N_r = k_r S_i(C_i a_{H,III} - K_{ex}A_{III}B_i^2/a_{H,III}) \tag{10'}$$

$$J_A = k_r(B_i a_{H,III}/2)(S_i/S_{av}) \tag{22'}$$

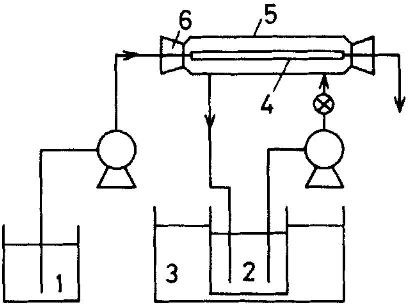

FIG. 2. Schematic diagram of experimental apparatus. (1) Stripping solution (acid solution). (2) Feed solution (copper solution, volume: 3 dm^3). (3) Water bath. (4) Hollow fiber liquid membrane. (5) Glass tube. (6) Rubber stopper.

Thus, the theoretical copper fluxes were calculated using Eqs. (5), (7)–(9), (10′), (16), and (18), and are shown by the solid lines in the following figures.

EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 2. The hollow fiber membranes used are shown in Table 1. The membrane was soaked with the organic solution prepared by diluting SME529 with Dispersol, a sort of kerosene offered by Shell Chemical Co. Ltd., and set in a glass tube, 2.5 cm in inner diameter. The length of the membrane was about 25 cm. Feed solutions were prepared by dissolving cupric sulfate in deionized water, and the pH was adjusted using 0.1 mol/dm^3 acetic acid–sodium acetate buffer solution or sulfuric acid. The feed solution (copper solution) and the stripping solution (aqueous sulfuric acid or hydrochloric acid solution) were supplied to the external and internal sides of the membrane, respectively, and the feed solution (3 dm^3) was circulated. The concentrations of copper at the inlet and outlet of the stripping solution were measured by an atomic absorption spectrophotometer, and the copper flux was calculated by

$$J_A = L_{III}(A_{III,in} - A_{III,out})/S_{av} \qquad (24)$$

Unless otherwise stated, the linear velocity of the feed solution was 4.1 cm/s, and the temperature was 298 K.

TABLE 1
Mass Transfer Characteristics of Hollow Fiber Liquid Membranes[a]

Membranes[b]	1	2	3	4
	Gore-Tex TA-001	KPF-400	—	—
	Junkosha	Mitsubishi Rayon	Asahi Kasei	Asahi Kasei
Material	Teflon	Polypropylene	Polypropylene	Polyacrylonitrile
D_i (cm)	0.1	0.04	0.08	0.08
δ (cm)	0.04	0.0033	0.03	0.03
Porosity	0.5	0.45	0.7	0.81
D_μ (μm)	2.0[c]	0.135	—	—
k_C (cm/s)	4.3×10^{-6}	3.0×10^{-5}	4.1×10^{-6}	3.2×10^{-6}
$D_{e,C}$ (cm^2/s)	1.7×10^{-7}	9.9×10^{-8}	1.2×10^{-7}	9.6×10^{-8}
τ	2.3	3.6	4.5	6.7
J_A (mol/cm$^2 \cdot$ s)	1.8×10^{-9}	1.0×10^{-8}	1.7×10^{-9}	1.3×10^{-9}

[a] Experimental conditions are as follows: $A_I = 0.0153$ mol/dm^3, $H_I = 1.51 \times 10^{-5}$ mol/dm^3, $B_f = 0.752$ mol/dm^3, $H_{III} = 4$ mol/dm^3 (hydrochloric acid). Rate parameters are as follows: $k_{A,I} = 0.0012$ cm/s at $u_I = 4.1$ cm/s, $k_f = 6.0 \times 10^{-7}$ cm/s, $k_r = 0.0355$ cm^4/mol·s for HCl solution, $k_r = 0.0858$ cm^4/mol·s for H_2SO_4 solution, $k_B = 1.5k_C$, $K_{ex} = 0.85$.

[b] $D_{e,C}$: effective diffusivity of chelate, D_i: inner diameter of hollow fiber, D_μ: average pore diameter, δ: membrane thickness, τ: tortuosity factor.

[c] Maximum pore diameter.

RESULTS AND DISCUSSION

(1) Determination of Rate Parameters

It is desirable to determine the values of the parameters included in the proposed model independently. As described below, it was possible to realize the situation that only one step included in the permeation mechanism is rate determining by adjusting the experimental conditions such as the concentrations of copper and hydrogen ions. Then the value of the parameter can be calculated using Eqs. (19)–(21).

The forward reaction rate constant was determined from the flux obtained under the condition of high hydrogen ion concentration in the feed solution where Step 3 is rate determining.

The stripping rate constant was determined by stripping experiments using a Lewis cell (*9*). The mass transfer coefficient of copper through the external aqueous film was determined from the flux measured under the condition of low copper and hydrogen ion concentrations where Step 1 is rate determining. The membrane mass transfer coefficient was obtained as described below. The values of the parameters are summarized in Table 1.

(2) Effect of Hydrogen Ion Concentration

The time courses of the copper flux obtained with two kinds of hollow fiber membranes are shown in Fig. 3. When the thick membrane, TA-001, 0.4 mm in thickness, was used, about an hour was needed to attain a steady-state flux while a few minutes were sufficient for the thin membrane, KPF-400, 33 μm in thickness. In the latter case, J_A decreased with time as will be discussed below. The value of J_A reported in this paper is the maximum flux in each run.

The effect of hydrogen ion concentration on J_A obtained with TA-001 and KPF-400 membranes, with sulfuric acid and hydrochloric acid as the stripping agent, is shown in Fig. 4. When H_I is high, J_A is inversely proportional to H_I, suggesting that the forward reaction is rate-determining. The value of k_f can be calculated from the data in this region using Eq. (20). On the other hand, as H_I decreases, the reaction rate as well as the partition of copper to the membrane increases. Thus, in the region of low H_I, the resistance of the diffusion of the carrier or the complex is important, and J_A is almost independent of H_I. It can be seen that when KPF-400 was used, J_A obtained with HCl solution as the stripping solution is higher than that with H_2SO_4 solution. This is because the activity of hydrogen ion in the former is

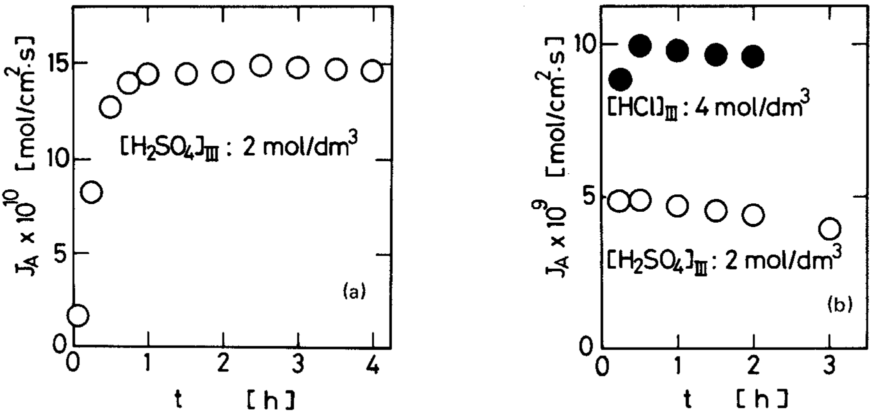

FIG. 3. Time course of copper flux. $A_I = 0.0153$ mol/dm^3, $H_I = 1.5 \times 10^{-5}$ mol/dm^3, $B_f = 0.75$ mol/dm^3. (a) TA-001 membrane. (b) KPF-400 membrane.

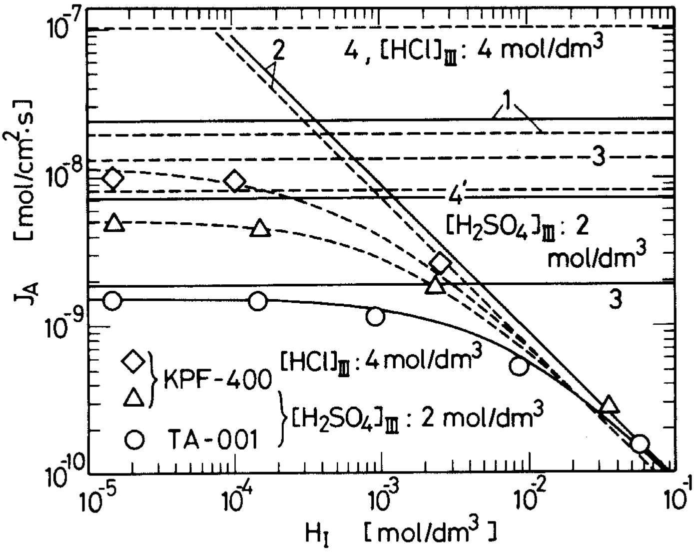

FIG. 4. Effect of hydrogen ion concentration in the feed solution on the permeation rate of copper. $A_I = 0.0153$ mol/dm^3, $B_f = 0.75$ mol/dm^3. The straight lines are the hypothetical copper fluxes when the following steps are rate-determining. (1) Diffusion of copper in the external aqueous film. (2) Forward reaction. (3) Diffusion in the membrane. (4), (4′) Stripping reaction. Solid straight lines: TA-001. Dotted lines: KPF-400.

higher than that in the latter solution when the normalities of these solutions are the same (*10*). Thus, when sulfuric acid was used, the resistance of the stripping reaction contributes considerably to the overall resistance. However, in the case of the TA-001 membrane, such a remarkable difference was not observed under the condition of Fig. 4 because of the large membrane resistance.

The approximate values of k_B and k_C were calculated from the data in the region of membrane diffusion controlling using Eq. (21). The value of q was determined as 0.67 by assuming that the diffusivity is proportional to (molar volume)$^{-0.6}$ (*11*). The copper fluxes calculated by the proposed model are shown by three curves in Fig. 4. The agreement between the computed and the experimental results is fairly good.

(3) Effect of Copper Concentration in the Feed

The effect of copper concentration in the feed solution on the copper flux is shown in Fig. 5. In the region of low copper concentration, J_A is proportional to the copper concentration because the diffusion of copper in the external aqueous film is rate-determining. This was confirmed by the experimental results that J_A depended on u_I, the linear velocity of the feed solution as

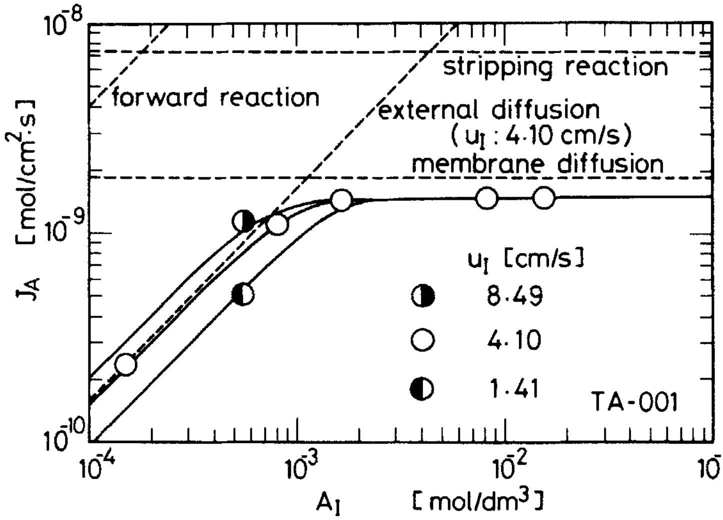

FIG. 5. Effect of copper concentration in the feed solution on the permeation rate of copper. $H_I = 1.5 \times 10^{-5}$ mol/dm^3, $B_f = 0.75$ mol/dm^3, $[H_2SO_4]_{III} = 2$ mol/dm^3.

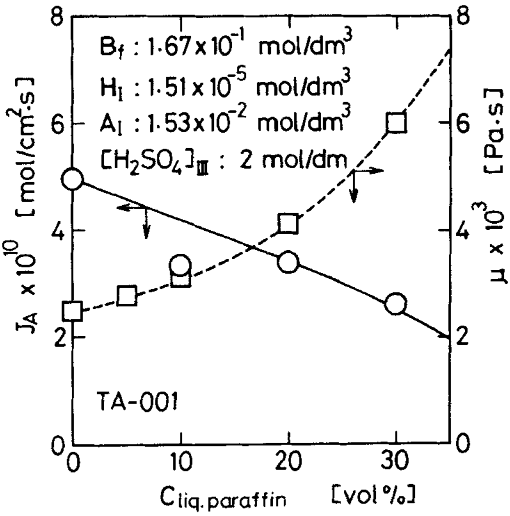

FIG. 6. Effect of membrane viscosity on the permeation rate of copper.

shown in the same figure. It should be noted that the membrane resistance becomes negligibly small compared to the external mass transfer resistance depending on the experimental condition. If it is assumed that the forward reaction at the external surface is rate-determining, the relation of $J_A \propto A_I$ also holds. However, the computed values of J_A based on this assumption were much higher than the experimental data. The value of $k_{A,I}$ was obtained from the data in this region using Eq. (19).

When A_I is higher than 1.0×10^{-3} mol/dm^3, J_A does not vary with A_I, suggesting that most of the carrier is converted to the complex at the external surface. In this region the rate-determining step is the diffusion of the carrier or the complex in the membrane. It is seen that the experimental data can be simulated by the proposed model.

(4) Effect of Membrane Viscosity

The effect of the viscosity of the organic phase on J_A was examined under the condition that the diffusion in the membrane is rate-determining. The viscosity of the membrane phase was varied by adding liquid paraffin to the organic phase. As shown in Fig. 6, J_A decreased with an increasing concentration of liquid paraffin. It is seen that the experimental data can be approximately simulated by the solid line computed on the assumption that the mass transfer coefficients of the carrier and the complex are inversely proportional to the viscosity of the membrane.

$$k_C \propto \mu^{-n}, \qquad n = 1 \tag{25}$$

(5) Effect of the Carrier Concentration

Figure 7 shows the effect of the concentration of SME529 on J_A. J_A increases with increasing B_f, the carrier concentration. However, J_A reaches maximum values when B_f is about 0.8 mol/dm^3, and a further increase in B_f lowers J_A. This behavior can be explained by the relation between the viscosity of the organic phase and B_f shown in Fig. 8 where the data for LIX65N is also shown. As B_f increases, the viscosity increases, and in turn the mass transfer coefficient decreases. Especially when B_f is high, the viscosity increases markedly with B_f, resulting in a decrease in J_A. It was found that the data can be simulated by assuming that k_B or k_C is proportional to $\mu^{-0.7}$ as shown by the solid lines in Fig. 7.

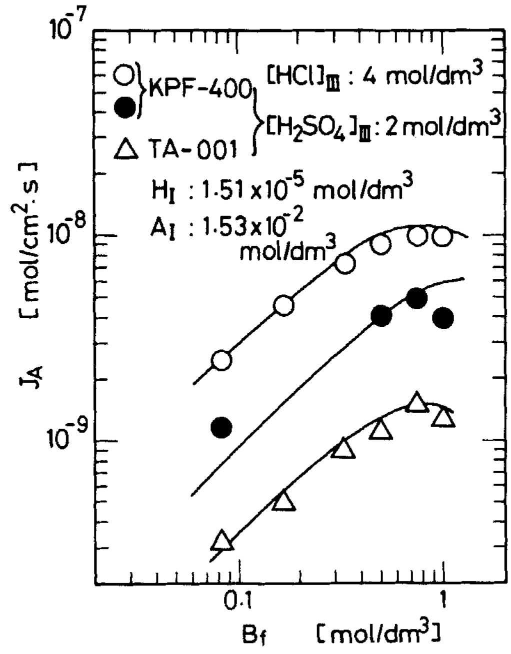

FIG. 7. Effect of carrier concentration on the permeation rate of copper.

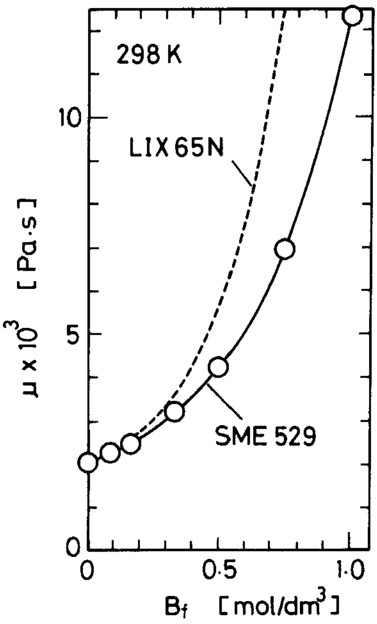

FIG. 8. Viscosities of the organic solutions as a function of carrier concentration.

$$k_C \propto \mu^{-n}, \qquad n = 0.7 \tag{26}$$

This value of n is lower than that in Eq. (25). It is known that the carrier molecules exist in aggregated forms in Dispersol, and the aggregation number increases with the carrier concentration (*8*). Thus, the apparent diffusivity of the carrier may change with the carrier concentration. Although it is difficult to discuss quantitatively the effect of the aggregation on J_A, this may be the cause of the difference in the value of n in Eqs. (25) and (26).

(6) Effect of the Acid Concentration in the Stripping Solution

As shown in Fig. 9, J_A increases with the increase in the activity of hydrogen ion in the stripping solution, and approaches an asymptotic constant value corresponding to the condition of membrane diffusion controlling and negligible resistance of the stripping reaction at the internal surface. The computed results are shown by the solid lines. When sulfuric acid is used, the computed results are in rough agreement with the data. However, when hydrochloric acid was used, the former is considerably

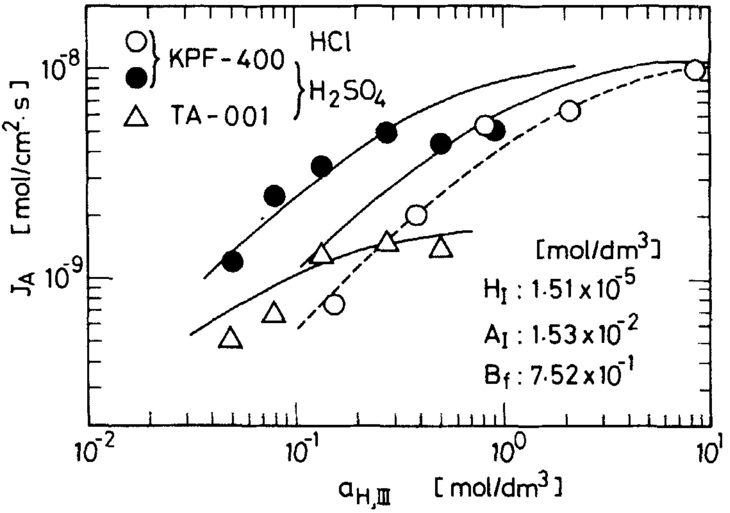

FIG. 9. Effect of acid concentration in the stripping solution on the permeation rate of copper.

higher than the latter. This may be due to the uneven wetting of the internal surface of the membrane with the organic phase. This point needs to be examined further. The experimental data agree well with the computed result, shown by the dotted line, on the assumption that only the part of the pore on the internal surface, i.e., 50% of the surface, is wetted with the organic phase.

(7) Effect of the Copper Concentration in the Stripping Solution

The effect of the copper concentration in the stripping solution on J_A is shown in Fig. 10. The abscissa is the mean concentration of copper at the inlet and the outlet of the stripping solution. The copper concentration in the feed was 0.016 mol/dm^3 and is shown by a vertical broken line in Fig. 10. The data on the right side of this line corresponds to those obtained under the condition that copper was pumped up against its concentration gradient. J_A was not influenced by $A_{III,av}$, suggesting that the stripping reaction was sufficiently fast even when $A_{III,av}$ was considerably high.

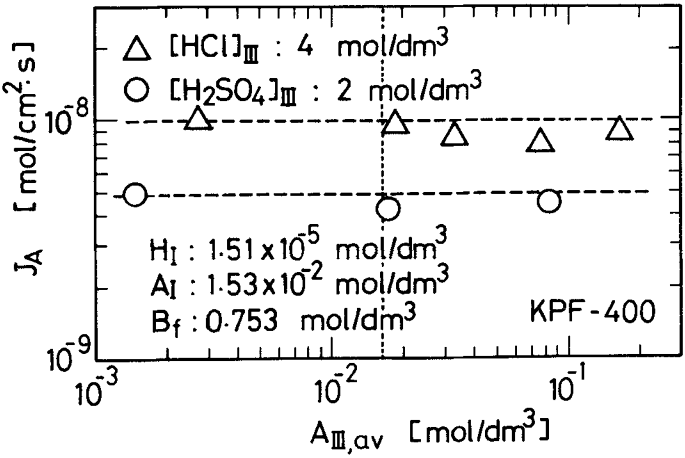

FIG. 10. Effect of copper concentration in the stripping solution on the permeation rate of copper.

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

Figure 11 shows the effect of the linear velocity of the feed solution on J_A. Under the condition that both copper and hydrogen ion concentrations are low, copper diffusion in the external aqueous film is rate-determining. Thus,

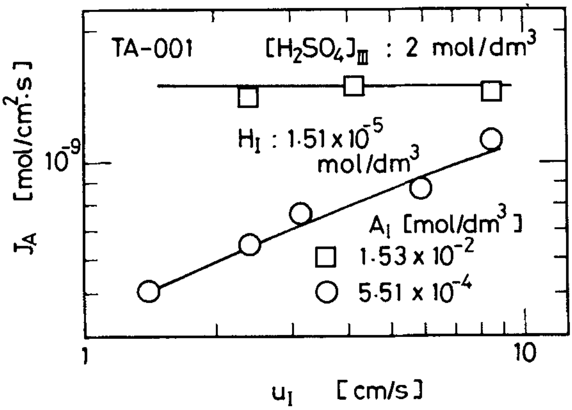

FIG. 11. Effect of the flow rate of the feed solution on the permeation rate of copper.

a considerable increase in J_A with increasing u_I is observed. The value of $k_{A,I}$ was correlated with u_I by

$$k_{A,I} = 6.45 \times 10^{-4} u_I^{0.44} \tag{27}$$

On the other hand, when the copper concentration is high and the hydrogen ion concentration is low, the diffusion in the liquid membrane limits the permeation rate. Therefore, no effect of u_I was observed.

The effect of the linear velocity of the stripping solution was also examined. However, no variation in J_A was observed in the range of u_{III} from 0.54 to 4.14 cm/s.

(9) Effect of Temperature

The effect of temperature was investigated under two extreme conditions corresponding to forward reaction rate controlling and membrane diffusion controlling. As shown in Fig. 12, the apparent activation energy was 58.9 kJ/mol for the former condition and 28.1 kJ/mol for the latter condition. It was found that the temperature dependence of J_A for the latter condition was approximately simulated by the temperature dependence of the viscosity of the organic phase and Eq. (25).

(10) Comparison of Copper Fluxes Obtained with SME529, LIX64N, and LIX65N

A series of experiments was carried out using LIX64N and LIX65N as the carrier. The relation between J_A and B_f obtained with three chelating agents under the condition of membrane diffusion controlling are shown in Fig. 13. As in the case of SME529, an optimal concentration at which J_A shows its maximum value exists for each LIX agent. However, the optimal concentration is lower than that in the case of SME 529, and the maximum value of J_A is also lower. When a LIX agent of high concentration was used, the external surface of the membrane was covered by viscous substances which might be the aggregates of the complex and the carrier, and lower the copper flux. Such a phenomenon was not observed in the case of SME529. Thus, it can be said that the selection of carriers which can be used in higher concentrations without forming aggregates of high molecular weight is necessary to obtain high permeation rates.

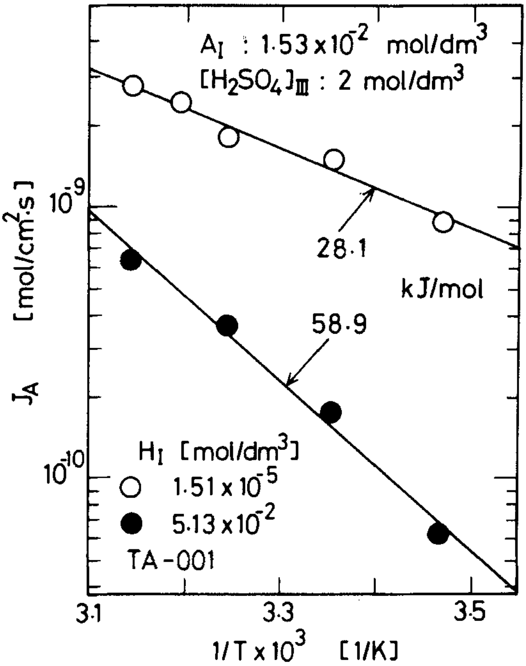

FIG. 12. Effect of temperature on the permeation rate of copper. $B_f = 0.75$ mol/dm^3.

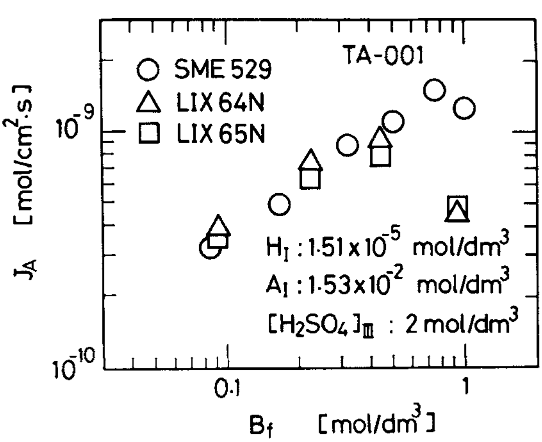

FIG. 13. Comparison of the permeation rates of copper observed with SME529, LIX64N, and LIX65N as the carriers.

(11) Comparison of Copper Fluxes Obtained with Four Microporous Solid Supports

Comparison of the copper fluxes obtained with four hollow fiber membranes under the condition that the diffusion in the membrane is rate-controlling is shown in Table 1 where mass transfer coefficients and effective diffusivities of the complex and the tortuosity factors are also known. Tortuosity factors were calculated by

$$k_C = D_{e,C}/\delta = \varepsilon D_c/(\delta\tau) \qquad (28)$$

The bulk diffusivity of the chelate, D_C, was estimated by the Wilke-Chang equation (*11*). Membrane 4 made of polyacrylonitrile is less hydrophobic compared to the other membranes, and it was observed that the organic solution came out of the pores and adhered to the external surface of the membrane as hemispherical drops during the experiment. Therefore, this membrane is not adequate for the support of liquid membranes. The extremely high value of τ obtained with this membrane may be due to insufficient filling of the organic solution in the pore, and the true value of τ may be much smaller.

(12) Contribution of the Resistance of Each Elementary Step

The straight lines in Figs. 4 and 5 show the permeation rates if one of the Steps 1, 3, 4 (or 5), and 6 is assumed to be rate-determining. It can be seen that under the condition shown in Fig. 5, both the forward reaction rate and the stripping rate are sufficiently fast, and the mass transfer resistance in the external aqueous film or that in the membrane is important depending on the copper concentration. Figure 4 shows that the contribution of the membrane resistance differs considerably depending on the thickness of the membrane. It is also seen that the stripping rate, which varies remarkably with the species and the concentration of acid, has an important influence on J_A if the KPF-400 membrane is used.

(13) Degradation and Regeneration of Liquid Membrane

Figure 14 shows the time dependence of the copper flux. When a thick membrane (TA-002) was used, the initial flux was maintained for about 30 h, and thereafter started declining (Fig. 14a). On the other hand, when a thin

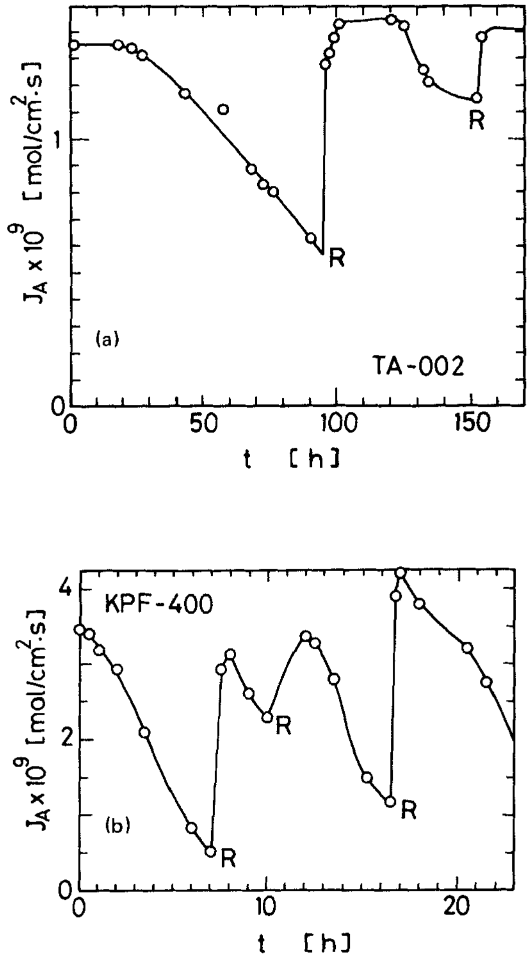

FIG. 14. Time dependencies of the permeation rate of copper and the regeneration of membranes. $A_I = 0.0153$ mol/dm^3, $H_I = 1.5 \times 10^{-5}$ mol/dm^3, $B_f = 0.75$ mol/dm^3, $[H_2SO_4]_{III} = 2$ mol/dm^3, R: Regeneration. TA-002 membrane is the same as TA-001 except that the inner diameter of TA-002 is 0.2 cm. $\delta = 0.04$ cm. (a) TA-002 membrane. (b) KPF-400 membrane.

membrane (KPF-400) was used, J_A began to decrease soon after the start of the experiment (Fig. 14b). The cause of the decrease in J_A may be the dissolution of the organic solution in the aqueous phases, and this effect is more remarkable in the case of thin membranes.

To regenerate the degraded liquid membranes, the same organic solution that was used to impregnate the hollow fiber was made to flow in the internal side of the membrane for a few minutes instead of the aqueous acid solution. As shown in the figures, the copper flux rapidly recovered to the initial value. It should be noted that the permeation of copper continues during this regeneration procedure. In this case a settler which separates the organic phase from the stripping solution is necessary. However, its scale may be very small because a very small amount of the organic solution is used in this procedure.

An alternative method for preventing the decrease in the copper flux is to add a small amount of the organic solution to the stripping solution. In this case, the organic solution flows through the inside of the fiber membrane intermittently and the pores of the polymer membrane are always filled with the organic solution. It is also noted that the copper concentration in the organic phase is kept very low in the acid solution.

CONCLUSION

Experiments on the permeation of copper through hollow fiber liquid membranes were carried out using SME529 as a carrier, and the effects of various experimental conditions on the permeation rate of copper were extensively examined. The experimental data could be interpreted by the proposed permeation model in which the diffusion processes both in the aqueous stagnant film and the liquid membrane, and the forward and stripping reaction rates were taken into account. Furthermore, the behavior of the degradation of the liquid membrane and a simple method for regenerating the membranes were proposed.

The present model may be easily extended to other permeation systems, and this work gives basic information for designing modules of hollow fiber liquid membranes.

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SYMBOLS

A	concentration of copper (mol/dm^3 or mol/cm^3)
a	activity (mol/dm^3 or mol/cm^3)
B	concentration of chelating agent (mol/dm^3 or mol/cm^3)
B_f	initial concentration of chelating agent (mol/dm^3 or mol/cm^3)
C	concentration of complex (mol/dm^3 or mol/cm^3)
D	diffusivity (cm^2/s)
D_e	effective diffusivity (cm^2/s)
D_i	inner diameter of hollow fiber (cm)
D_μ	average pore diameter (cm)
J_A	copper flux based on logarithmic mean of external and internal membrane areas (mol/cm$^2 \cdot$ s)
K_{ex}	extraction constant
k_A, k_H	mass transfer coefficients of copper and hydrogen ion through aqueous stagnant film, respectively (cm/s)
k_B, k_C	mass transfer coefficients of chelating agent and complex through liquid membrane, respectively (cm/s)
k_f	forward reaction rate constant (cm/s)
k_r	stripping rate constant (cm^4/mol $\cdot$ s)
L	flow rate of feed or stripping solution (cm^3/s)
N	mass transfer rate or reaction rate (mol/s)
p	$R_o^2/(R_o^2 - R_i^2) - 1/\{2 \ln (R_o/R_i)\}$
q	k_C/k_B
R_i, R_o	inner and outer radii of hollow fiber, respectively (cm)
S_{av}	logarithmic mean of S_i and S_o (cm^2)
S_i, S_o	areas of inner surface and outer surface of hollow fiber, respectively (cm^2)
t	time (s)
u	linear velocity of feed or stripping solution (cm/s)

Subscripts

A	copper
B	chelating agent (carrier)
C	complex

H	hydrogen ion
i	inner surface of membrane
in	inlet
o	outer surface of membrane
out	outlet
I	feed solution (external aqueous phase)
II	membrane phase
III	stripping solution (internal aqueous phase)

Greeks

δ	membrane thickness (cm)
ε	porosity of membrane
μ	viscosity of organic phase (Pa·s)
τ	tortuosity factor

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