TRANSPORT OF COPPER THROUGH A SUPPORTED LIQUID MEMBRANE

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An experimental study was carried out to elucidate the mechanism of ion transport through supported liquid membranes (SLM) and to approach liquid membrane separation in industrial uses. Two channels of 1 mm depth were prepared on both sides of a porous polymer sheet supporting extractant solution. Copper was permeated from the feed solution of copper sulfate into a strip solution of sulfuric acid through an SLM impregnated with kerosene solution of LIX65N as membrane solution. To stabilize the SLM the membrane solution was forced to flow with the strip solution. Such an operation mode allows enhancement of the rate of copper permeation, which is interpreted by a reduction in resistance for strip reaction due to sweeping the strip surface of the SLM with the membrane solution stream. The diffusion resistance of boundary film in the feed solution was significant for ion transport through the SLM in the present study.

Introduction

The use of liquid membranes is a developing technique for the separation and concentration of metal ions from aqueous solutions. In modern terminology, liquid membranes are of two kinds: liquid surfactant membranes and polymer-supported liquid membranes (SLM). The former have the advantages of large interfacial area and ultra-thin liquid membrane. The use of surfactant, however, causes unfavorable phenomena such as reduction of reaction rate,[8,11] dissolution of surfactant into aqueous phases or demulsification.

On the other hand, there are some problems to be solved for the practical applications of SLMs: the specific surface area of the SLM is comparatively small, diffusion resistance across the SLM is large and so on. Considerable efforts to obtain a large specific surface area have been made by use of hollow-fiber tubes.[1,2,4,6,12,14] It is anticipated, however, that fiber tubes tend to come in contact with each other and then a liquid meniscus around the contact point between the tubes is formed by membrane solution. Uniform flows on both sides of the SLM are desirable to avoid the pressure distribution or the maldistribution flow which causes a decrease in SLM stability or permeation efficiency. A flat sheet-supported membrane having flow channels on both sides, e.g., a spiral module membrane or a multilayer membrane, is considered to be appreciable. Lee *et al.*[3] have reported that the copper flux per unit volume in a flat-sheet SLM is comparative to that in surfactant liquid membranes.

In the present study, a SLM device has been used in which an organic membrane solution (oil phase) was forced to flow with an aqueous strip solution on one side of the membrane: a hybrid liquid membrane of bound and supported type. Copper was permeated from an aqueous feed of copper sulfate into a strip solution of dilute sulfuric acid through a liquid membrane impregnated with kerosene containing LIX65N. The experimental results were compared with calculations based on a model in terms of the aqueous film diffusion, the membrane diffusion, and the reactions both sides of the membrane.

1. Experimental

A schematic drawing of the SLM device is shown in **Fig. 1**. Nuclepore film was used as a supporter of membrane solution. The film is 10 μm in thickness and has 10^8 pores per sq cm; each pore is straight in geometry and has a circular cross section 0.4 μm in diameter. Its simple pore structure is favorable for studying the transport mechanism across the SLM. The SLM was sandwiched with two spacers on which a channel of 5 mm width, 96 cm effective length and 1 mm depth was prepared as shown in Fig. 1.

The membrane solution used for copper permeation was LIX65N-kerosene solution ($[RH]_0 = 0.049$ kmol/m^3). Commercial LIX65N was refined in the same way as described in the previous paper.[9] Copper was extracted from the feed solution of copper sulfate ($C_{W,in} = 0.001$ kmol/m^3 and $pH_{in} = 5.5$) at a surface on the feed side of the SLM, and it was

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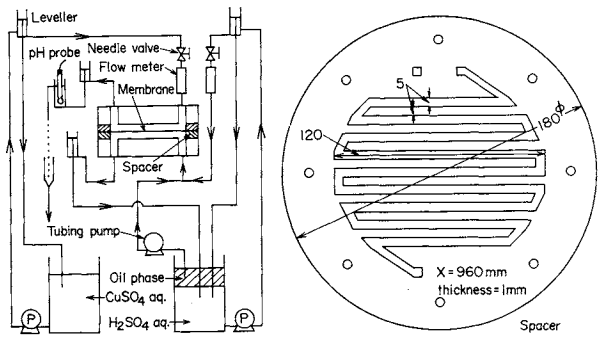


Fig. 1. Schematic diagram of experimental apparatus and details of spacer for liquid flow channel.

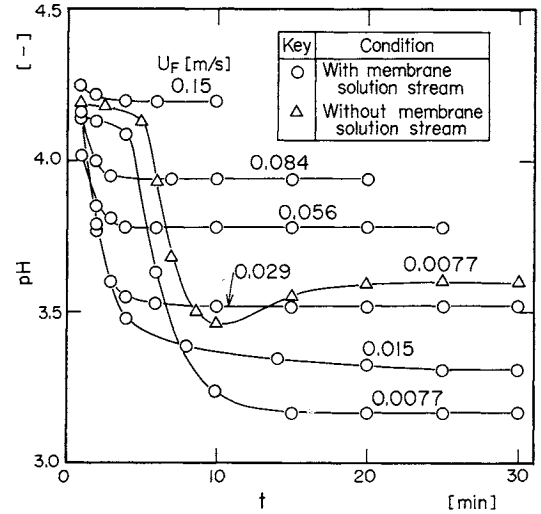


Fig. 2. Time course of pH in effluent of feed solution.

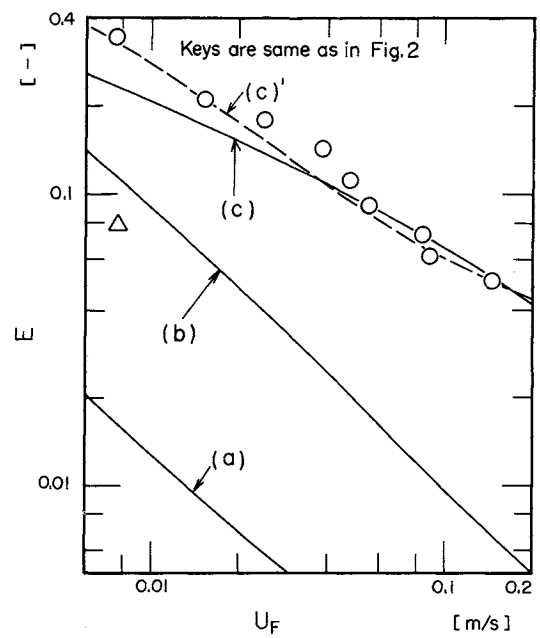


Fig. 3. Comparison between experimental and calculated values of copper permeation fraction.

stripped at a surface on the strip side of the SLM from the membrane solution into the strip solution of dilute sulfuric acid (0.93 kmol/m^3). Feed and strip solution were allowed to enter the SLM device separately, two spacers being arranged to give counter-current flow through the respective straight channels (in the lateral direction on the spacer in Fig. 1). Then both the solutions flowed stepwise from the bottom channel upward one after another. The velocity of feed solution was varied from 0.0077 m/s to 0.15 m/s, while that of strip solution was kept at 0.04 m/s.

The membrane solution was forced to flow with the strip solution to stabilize the SLM, as shown in Fig. 1. Pressure in the feed channel was kept about 15 cm H_2O higher than that in the strip channel to avoid leakage of membrane solution into the feed solution in the present experiments. The superficial velocity of membrane solution was 0.005 m/s.

A steady state was confirmed from pH of the effluent of feed solution. Copper concentrations for both the influent and effluent of feed solution at steady state were determined by an atomic absorption spectrophotometer. In some runs the strip solution was preloaded with copper sulfate to examine the feasibility of uphill transport.

Mass transfer coefficients were measured for the transport of iodine from aqueous solution of iodine-potassium iodate into kerosene across the membrane. The aqueous solution was circulated through one channel and kerosene through another in this case. All experiments were carried out at 25°C.

2. Results and Discussion

2.1 Copper permeation through the SLM

The value of pH in the feed solution decreases with the proceeding of copper permeation, owing to the ion exchange reaction between copper and hydrogen ions. pH change in the effluent of feed solution is shown in **Fig. 2**. pH at steady state was lower for a smaller velocity, U_F, of the feed solution because more copper fraction in the feed solution was permeated. A somewhat different course in the variation of pH was observed when the membrane solution stream in the strip channel was stopped at $t=0$. pH in this case became constant after going through a minimum value. This suggests that the copper permeation rates decrease with time for $t<20$ min. At steady state, pH was much higher than that with the membrane solution stream.

The permeation fraction, $E(=(C_{W,in}-C_{W,out})/C_{W,in})$, of copper at steady state is plotted against U_F in **Fig. 3**. Lines in the figure are the calculated ones mentioned below; the value of E is small, especially at large U_F. To obtain an effective permeation, therefore, a large SLM length, a small channel depth (i.e., a large specific surface area) or a small U_F is required.

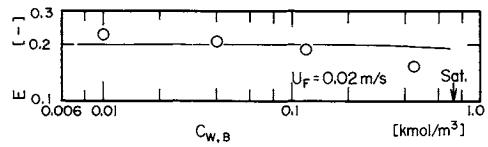


Fig. 4. Effect on permeation of copper preloaded in strip solution.

Teramoto *et al.*[12] have reported that the reproduction of hollow-fiber SLM is achieved by flowing the membrane solution through the fiber inside, and suggested that the decrease in permeation rate would be prevented by adding a small amount of organic solution to the strip solution. In this work, it was found that a difference of about four fold in E is found between the runs with and without the forced flow of membrane solution. Forcing the membrane solution to flow is also useful for the SLM to enhance the permeation rate of copper.

Results of E for the copper-loaded strip solution with the membrane solution stream are shown in **Fig. 4** together with the calculated line mentioned below. Copper was permeated from the feed solution to the strip solution even at high concentration, $C_{W,B}$, of copper in the strip solution. These results suggest that metal ions can be highly concentrated from dilute aqueous solutions by use of a SLM with the forced flow of extractant solution through the strip channel.

2.2 Mass transfer coefficient

The permeation rate of copper can be calculated when the mass transfer coefficients in the channels and the SLM are given as well as the rates of extraction and strip reactions at the surfaces of the SLM. Mass transfer coefficients k_W in aqueous phase and k_O in oil phase were determined separately from the extraction data of iodine at different concentrations of iodine in the same way as in the previous work.[7] The values of k_W and k_O were 3.5×10^{-5} and 6.4×10^{-6} m/s, respectively, for the superficial velocities $U_W=0.3$ m/s in aqueous phase and $U_O=0.06$ m/s in oil phase.

The distribution ratio, m, of iodine for the water-kerosene system greatly decreases with iodine concentration.[9] Therefore, the dependence of k_W on U_W was examined at low concentrations of iodine ($C_{W,I_2}=10^{-3}$–2×10^{-3} kmol/m³, i.e., $m\simeq7$) for $U_O=0.06$ m/s (with k_O mentioned above). k_W increases with U_W as shown in **Fig. 5** and the slope of the solid line is about 0.5. The data points, however, are best fitted by the broken curve in the figure.

On the other hand, **Fig. 6** shows k_O obtained for $U_W=0.3$ m/s and a high concentration of iodine ($C_{W,I_2}=3\times10^{-2}$ kmol/m³, i.e., $m\simeq1$). The transport process of iodine in the oil phase involves diffusions across the liquid membrane and through the boundary film in the oil channel. Thus k_O was divided into

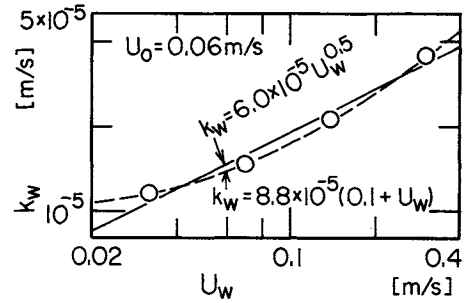


Fig. 5. Effect of flow velocity on aqueous-phase mass transfer coefficient.

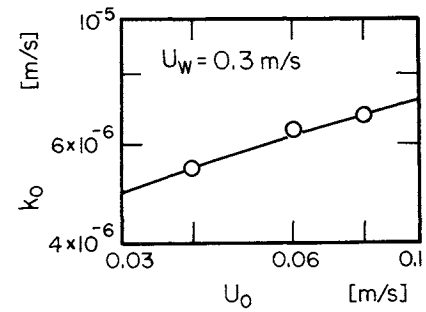


Fig. 6. Effect of flow velocity on oil-phase mass transfer coefficient.

the mass transfer coefficients $k_{O,U}$ for the boundary film and k_m for the liquid membrane by using the rule for the addition of resistances:

$$1/k_O=(1/k_{O,U})+(1/k_m) \tag{1}$$

and an assumption that $k_{O,U}$ is proportional to $U_O^{0.5}$. $k_{O,U}$ was obtained as $k_{O,U}=4.1\times10^{-5}U_O^{0.5}$. The ratio $k_{O,U}/k_W$ for the same velocities of U_W and U_O is found to be 0.68, which agrees with the value of $k_O/k_W=0.63$ in a stirred vessel with a plane interface.[7]

On the other hand, the value of k_m was found to be 1.6×10^{-5} m/s from Eq. (1). However, since the mass transfer resistance in the membrane is small as compared with the total resistance in the oil phase in the present case, the determination is sensitive to small experimental error. k_m can be also calculated from the pore geometry of supported film as follows.

$$k_m=D\pi r^2 n/\delta \tag{2}$$

where D is the diffusion coefficient, r the pore radius, n the number of pores per unit membrane area and δ the effective thickness of film. The pores of Nuclepore film are independent of each other and are straight across the film. Then tortuosity was assumed to be unity and the film thickness was taken as δ. The diffusion coefficient, D_{I_2}, of iodine in kerosene was estimated as 1.6×10^{-9} m²/s by the Wilke-Chang equation with the diffusion coefficient of CO_2 in kerosene.[5] The calculated value of k_m was 2.0×10^{-5} m/s, in comparison to the experimental value

mentioned above. Hereafter, k_m is calculated from Eq. (2).

2.3 Calculation of copper permeation

Copper ion in the feed solution is transfered from the bulk liquid to the surface of the SLM through the aqueous boundary film, and reacts at the surface with LIX65N:

$$Cu^{2+} + 2RH \longrightarrow CuR_2 + 2H^+ \qquad (3)$$

Copper complex, CuR_2, diffuses across the SLM and releases copper ion at the other surface of the SLM into the strip solution due to the reverse reaction of Eq. (3). Hydrogen ion is permeated oppositely from the strip solution to the feed solution.

Copper permeation of one mole brings about an increase of two moles of hydrogen ion in the feed solution. Such behavior is represented as a relation between pH_{out} and E in terms of the broken line in **Fig. 7**. The solid line in the figure is obtained by estimating the production of HSO_4^- in the feed solution. The experimental results with the membrane solution stream in the strip channel are in reasonable agreement with the calculated values, as shown in Fig. 7. This indicates high stability of the SLM, while for the run without the membrane solution stream a remarkable decrease in pH was observed.

Since the membrane solution was added periodically to the strip solution in comparatively large drops, it flowed as a lump filling up the strip channel. The lump of membrane solution was broken up into smaller ones as it flowed through the channel. The surface on the strip side of the SLM was swept by the membrane solution stream. By considering this situation, the calculation of copper permeation was carried out for three cases illustrated schematically in **Fig. 8**. Case (a): The membrane solution exists only in the pores of film; the shape of the interface reflects the pressure difference across the SLM. Case (b): The surface on the strip side of the SLM is covered with the membrane solution; the strip reaction occurs all over the surface. Mass transfer resistance in the covering membrane solution was neglected in the present study. Case (c): The membrane solution is interchangeable between the SLM and the stream in the strip channel. The membrane solution at the interface was assumed as copper-free, i.e., $[CuR_2]_{B,i}=0$.

The permeation rate of copper can be calculated for copper concentration, C_W, in the feed solution. The calculation is repeated by a step of ΔC_W from an inlet concentration, $C_{W,in}$, to an outlet concentration, $C_{W,out}$. C_W was regarded as an average value for the step. The permeation rate depends on both the diffusion resistance and the reaction rate. The interfacial concentrations of reactants change with permeation rate for a given diffusion resistance. Therefore, a trial-and-error method has been used to determine the permeation rate; i.e., the permeation rate was chosen to agree with the reaction rate.

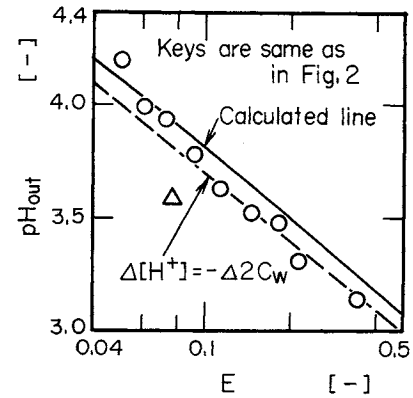


Fig. 7. Relationship between pH for effluent of feed solution and copper permeation fraction.

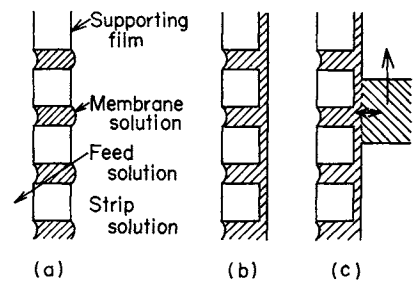


Fig. 8. Schematic situation of SLM assumed to calculate copper permeation.

Bulk concentration of each ion in the feed solution can be determined from mass balances with the dissociation constants of copper sulfate and sulfuric acid ($[CuSO_4]/[Cu^{2+}][SO_4^{2-}]=500$ and $[HSO_4^-]/[H^+][SO_4^{2-}]=130$[16]) in the same way as described in the previous paper.[9] The mass balances for H^+, SO_4^{2-} and Cu^{2+} are given by

$$[H^+]_F + [HSO_4^-]_F = [H^+]_{in} + 2(C_{W,in} - C_W) \qquad (4)$$

$$[CuSO_4]_F + [HSO_4^-]_F + [SO_4^{2-}]_F = C_{W,in} \qquad (5)$$

$$[Cu^{2+}]_F + [CuSO_4]_F = C_W \qquad (6)$$

where $[H^+]_{in}$ is the hydrogen ion concentration of inlet feed solution determined from pH_{in}.

When the value of the permeation rate, N, of copper ion is assumed, one can obtain each interfacial concentration, $[Cu^{2+}]_{F,i}$ and $[H^+]_{F,i}$, from mass transfer equations through the aqueous boundary film:

$$N = k_{Cu}([Cu^{2+}]_F - [Cu^{2+}]_{F,i}) \qquad (7)$$

$$2N = k_H([H^+]_{F,i} - [H^+]_F) \qquad (8)$$

where k_{Cu} and k_H are mass transfer coefficients for Cu^{2+} and H^+, respectively. These values are estimated from k_W, discussed in the previous section, by correcting with the diffusion coefficient evaluated

from the Vinograd-McBain equation[15] under an assumption of $k_W \propto D^{2/3}$ as for fluid inside pipes.[13]

The assumed value of N should be equal to the strip rate of copper at the surface on the strip side for steady state. The strip reaction rate, r_B, was given for $[RH]_0 < 5 \times 10^{-2}$ kmol/m^3 and $[H^+] > 0.3$ kmol/m^3 by[10]

$$r_B = 2.5 \times 10^{-8} [CuR_2]_{B,i}^{0.85} [H^+]_{B,i}^{0.7} \quad (9)$$

where $[RH]_0$ is the total concentration of LIX65N, which is given as the sum of free LIX65N and copper complex as follows.

$$[RH]_0 = [RH] + 2[CuR_2] \quad (10)$$

Since the hydrogen ion concentration is high in the strip solution, the diffusion resistance of H^+ in the strip channel is negligible, i.e., $[H^+]_{B,i} \simeq [H^+]_B$. $[CuR_2]_{B,i}$ for case (a) in Fig. 8 can be determined from Eq. (9) by use of the relation $N = \pi r^2 n r_B$; $[RH]_{B,i}$ is obtained from Eq. (10). The relations $N = r_B$ and $[CuR_2]_{B,i} = 0$ are used for cases (b) and (c) in Fig. 8, respectively. The concentration, $[RH]_{F,i}$, of free LIX65N at the surface on the feed side of the SLM is calculated from the transport equation of RH across the SLM:

$$2N = k_{m,RH}([RH]_{B,i} - [RH]_{F,i}) \quad (11)$$

where $k_{m,RH}$ is the membrane mass transfer coefficient for RH, which is obtained from Eq. (2) with $D_{RH} = 5.4 \times 10^{-10}$ m^2/s estimated by the Wilke-Chang equation.[5]

The reaction rate, r_F, for the extraction at the surface on the feed side can be evaluated from the equation[9]

$$r_F = 6.9 \times 10^{-8} [Cu^{2+}]_{F,i}^{0.85} \times ([RH]_{F,i}/[H^+]_{F,i})^{1.4} \quad (12)$$

with the interfacial concentrations obtained above. The permeation rate of copper is determined by the Newton method to satisfy $N = \pi r^2 n r_F$.

The differencial length, ΔX, of the SLM permitting ΔC_W is given by

$$\Delta X = \Delta C_W U_F z_F / N \quad (13)$$

where z_F is the depth in the channel of feed solution. Repeating the calculation above, we can obtain the SLM length permitting a desired $C_{W,out}$ or the value of $C_{W,out}$ for a given length of SLM.

The results calculated for the present experimental conditions are shown in Fig. 3 with lines (a), (b) and (c) for cases (a), (b) and (c) in Fig. 8, respectively. The line (c)′ is the calculated result for case (c) by use of k_W shown by the broken line in Fig. 5. The value of E calculated for case (a) is less than one-tenth that for case (c); the ratio of E value for (b) to (a) is nearly

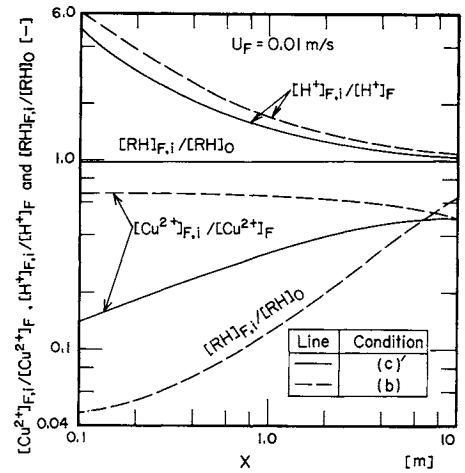


Fig. 9. Ratios of interfacial to bulk concentrations of Cu^{2+} and H^+; and $[RH]_{F,i}/[RH]_0$.

equal to $1/\pi r^2 n$ ($\simeq 8$ in the present study), which is the ratio between the interfacial areas on the strip side for the two cases. These suggest that the permeation rate of copper for case (a) is controlled by the strip reaction.

When the membrane solution was forced to flow through the strip channel, the experimental values of E agreed with results calculated for case (c), and good agreement was also obtained at low U_F by use of k_W extrapolated from the broken line in Fig. 5 (line (c)′ in Fig. 3). This indicates that copper concentration at the surface on the strip side of the SLM is kept very low due to the sweeping of the surface by the membrane solution stream. The observed value of E without the membrane solution stream was somewhat lower than the calculated line (b). In this case some part of the surface on the strip side of the SLM may change from case (b) to (a) with a decrease in the permeation rate of copper, since pH without membrane solution stream somewhat increases after having a minimum value, as shown in Fig. 2. Thus a low value of E in the case of no membrane solution stream may be due to an increase in the resistance of strip reaction. The line in Fig. 4 was calculated on the assumption that $[CuR_2]_{B,i}$ is in equilibrium with $C_{W,B}$. Very little influence of $C_{W,B}$ on E is expected from the calculation result.

Figure 9 shows the ratios of interfacial to bulk concentrations of Cu^{2+} and H^+ in the feed solution together with the ratio of $[RH]_{F,i}$ to $[RH]_0$, which were calculated under the same conditions as for line (b) or (c)′ in Fig. 3 except for the membrane length X. The value of $[H^+]_{F,i}/[H^+]_F$ decreases rapidly with X, since $[H^+]_F$ increases with X from the ion exchange reaction between Cu^{2+} and H^+; it is also followed by a reduction in N which reduces the difference between $[H^+]_{F,i}$ and $[H^+]_F$. The reduction in N is responsible for a rise in $[Cu^{2+}]_{F,i}/[Cu^{2+}]_F$ in case (c)′. A small

value of the copper ratio indicates that the diffusion resistance of copper in the feed channel is significant, especially at high value of pH in the present system. The ratio for (b) is much larger than that for (c)′, because the resistance of the strip reaction becomes significant as mentioned above. On the other hand, $[RH]_{F,i}/[RH]_0$ for (c)′ is almost unity, i.e., the diffusion resistance within the SLM is very small. The ratio of LIX65N for (b) becomes very small because of the accumulation of copper in the SLM (i.e., decrease in free LIX65N) due to the low strip rate.

Further calculations were carried out for other conditions of the feed solution to obtain the membrane length, X, required to attain a given E. Little effect of pH on X is found for pH > 3.5 due to the large resistance of diffusion through the aqueous boundary film mentioned above. However, X increases rapidly with decrease in pH for pH < 3.0 where the extraction rate r_F given by Eq. (12) becomes small. High concentration of copper in the feed solution also requires a large X, for pH in the feed solution decreases with the amount of copper permeation. Therefore, in the case of copper recovery from a leaching liquor of copper ores a very great length of SLM is required to achieve high efficiency. This may be improved by use of an extractant with a high reaction rate of extraction, e.g., LIX64N.

Conclusion

Copper permeation was carried out from copper sulfate solution into dilute sulfuric acid solution through a supported liquid membrane with LIX65N-kerosene solution. The feed and strip solutions flowed through channels of small depth located on both sides of the SLM. Forcing the membrane solution to flow with the strip solution is useful for enhancing the permeation rate of copper as well as for stabilizing the liquid membrane. The rates of copper permeation can be reasonably interpreted by supposing that the surface on the strip side of the SLM is swept with the membrane solution stream, being largely influenced by the resistance of copper diffusion through the aqueous boundary film in the feed solution. It is likely to concentrate copper highly in the liquid membrane system used in the present study, though it requires a very long contact time in practical applications to copper recovery from leaching liquor.

Acknowledgment

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Nomenclature

$[CuR_2]$	=	concentration of copper-LIX65N complex in oil phase	[kmol/m³]
C_W	=	copper concentration in aqueous phase	[kmol/m³]
C_{W,I_2}	=	iodine concentration in aqueous phase	[kmol/m³]
D	=	diffusion coefficient	[m²/s]
D_{I_2}	=	diffusion coefficient of iodine in kerosene	[m²/s]
D_{RH}	=	diffusion coefficient of LIX65N in kerosene	[m²/s]
E	=	permeation fraction of copper, $(C_{W,in}-C_{W,out})/C_{W,in}$	[—]
k_{Cu}	=	mass transfer coefficient of copper ion for aqueous boundary film	[m/s]
k_H	=	mass transfer coefficient of hydrogen ion for aqueous boundary film	[m/s]
k_m	=	mass transfer coefficient for liquid membrane	[m/s]
$k_{m,RH}$	=	mass transfer coefficient of free LIX65N for liquid membrane	[m/s]
k_O	=	mass transfer coefficient in oil	[m/s]
$k_{O,U}$	=	mass transfer coefficient for oil phase boundary film	[m/s]
k_W	=	mass transfer coefficient for aqueous boundary film	[m/s]
m	=	distribution ratio of iodine between kerosene and water	[—]
N	=	permeation rate of copper	[kmol/(m²·s)]
n	=	number of pores per unit area	[l/m²]
r	=	radius of pore	[m]
r_B	=	rate of strip reaction	[kmol/(m²·s)]
r_F	=	rate of extraction reaction	[kmol/(m²·s)]
$[RH]$	=	concentration of free LIX65N	[kmol/m³]
$[RH]_0$	=	total concentration of LIX65N	[kmol/m³]
t	=	time	[s]
U_F	=	velocity of feed solution	[m/s]
U_w	=	velocity of aqueous phase	[m/s]
U_O	=	velocity of oil phase	[m/s]
X	=	length of liquid membrane	[m]
z_F	=	depth of feed channel	[m]
δ	=	effective thickness of liquid membrane	[m]

〈Suffix〉

B	=	strip solution or strip side
F	=	feed solution or feed side
i	=	interface
in	=	inlet
out	=	outlet

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STATISTICAL REGRESSION AND CROSS-PREDICTION OF MULTICOMPONENT FLUID PHASE EQUILIBRIA

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The generalized maximum likelihood principle and other statistical regression techniques were applied to 21 sets of ternary LLE, VLE and VLLE data for estimating the pair parameters of three local-composition models (NRTL, UNIQUAC and a modified Wilson equation) and the corresponding fitting accuracies were compared. Results show that the correlation of multicomponent fluid-phase equilibria may be greatly improved by applying the maximum likelihood principle. Unique identifiability of the pair parameters for the constituent partially miscible system was observed in ternary data reduction.

Furthermore, the reliability and limitation of cross-prediction among LLE, VLE and VLLE were investigated. The gap and interdependence between LLE and VLE are also discussed.

Introduction

Multicomponent fluid-phase equilibria are basic data for separation processes such as extraction and distillation. In particular, VLLE data essential for three-phase distillation are very scarce and much more difficult to measure.

Although much effort has been exerted in the previous investigation into the satisfactory prediction of multicomponent vapor-liquid equilibria, relatively less is known about successful correlation and prediction of multicomponent liquid-liquid equilibria. No definite conclusion has been drawn concerning the reliability of cross-prediction between VLE and LLE.

As many investigators have stated, the prediction accuracies of ternary liquid-liquid equilibria based on data of constituent binaries are much poorer than those of ternary vapor-liquid equilibria. The standard deviations between predicted and experimental values are 2 to 10 times larger than those of direct correlation from ternary liquid-liquid equilibrium data.

However, the determination of six pair parameters from ternary tie-line data is essentially a curve-fitting problem. The major problem encountered is that the parameters cannot be uniquely identified. Several sets of parameters including some unrealistic ones may be obtained which fit the ternary LLE data equally well.[8,12,18]

To overcome this defect, appropriate constraint must be imposed on the model parameters. Three alternative techniques have been proposed:

1) de Fré and Verhoeye[8] used the pair parameters obtained from mutual solubility data as initial values to estimate the six pair parameters from ternary LLE data. However, the problem of unique identifiability still remains to be solved.

2) Simonetty *et al.*[25] prefixed the pair parameters obtained from the binary mutual solubility data and

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