Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Facilitated Transport of Copper in Bulk Liquid Membranes Containing LIX 984N

Xiao-Jin Yang[a]; Anthony G. Fane[a]
[a] UNESCO CENTRE FOR MEMBRANE SCIENCE AND TECHNOLOGY, THE UNIVERSITY OF NEW SOUTH WALES, SYDNEY, AUSTRALIA

To cite this Article Yang, Xiao-Jin and Fane, Anthony G.(1999) 'Facilitated Transport of Copper in Bulk Liquid Membranes Containing LIX 984N', Separation Science and Technology, 34: 9, 1873 — 1890
To link to this Article: DOI: 10.1081/SS-100100744
URL: http://dx.doi.org/10.1081/SS-100100744

SEPARATION SCIENCE AND TECHNOLOGY, **34**(9), pp. 1873–1890, 1999

Facilitated Transport of Copper in Bulk Liquid Membranes Containing LIX 984N

XIAO-JIN YANG and ANTHONY G. FANE*
UNESCO CENTRE FOR MEMBRANE SCIENCE AND TECHNOLOGY
THE UNIVERSITY OF NEW SOUTH WALES
SYDNEY 2052, AUSTRALIA

ABSTRACT

The liquid–liquid extraction of copper (II) using a novel extractant LIX 984N (a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime) was carried out. Following the liquid–liquid extraction, coupled uphill transport of copper(II) across a bulk liquid membrane containing LIX 984N as carrier was performed. The effects of aqueous stirring speed, carrier concentration, and inventory of membrane liquid were investigated. The rate-limiting step for the coupled transport of copper across a bulk liquid membrane was identified.

Key Words. Bulk liquid membrane; Copper; Facilitated transport

INTRODUCTION

Solvent extraction (SX) is a proven unit operation for recovery of a number of nonferrous metals like copper, nickel, cobalt, zinc, uranium, and various rare earths. However, as the world's need for metals increases and the grades of ores decrease, there is an incentive to find more effective and efficient purification methods. This includes synthesizing more specific and effective extraction reagents and developing new separation processes for treating the ores available to us and recycling previously used metals. In the field of extractant synthesis, Henkel Corporation (formerly General Mills Chemicals, Inc.) has successfully developed a range of liquid ion-exchange reagents such

---

[*] To whom correspondence should be addressed.

as LIX and Alamine for the recovery of copper, nickel, uranium, vanadium, molybdenum, etc. (1). They have recently introduced a new product LIX 984N, which is a 1:1 volume blend of LIX 860N and LIX 84N in a high flash point kerosene. LIX 984N is a stronger extractant than LIX 84 and will extract copper from a lower pH solution. The maximum loading capacity under standard tests for a 10% v/v solution in kerosene has been claimed to be 4.3 g/L Cu for LIX 84 and 5.1–5.4 g/L Cu for the new LIX 984N, compared to 3.15 g/L Cu for LIX 64N (2).

In terms of new separation process development, liquid membranes have great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently. The transport of metals across liquid membranes is generally considered as a combination of extraction and stripping processes. The extraction chemistry is basically the same as that found in liquid–liquid extraction, but the transport process is governed by kinetic rather than equilibrium parameters, that is, under nonequilibrium mass transfer. Generally there are three basic types of liquid membrane, the bulk liquid membrane (BLM), the emulsion liquid membrane (ELM), and the supported liquid membrane (SLM). The latter two types of liquid membrane have been studied extensively from both fundamental and technological points of view. Several investigations on the transport and recovery of copper by ELMs (3–6) and SLMs (7–11) have been published, and there are some reports on pilot-scale uses of ELM for the recovery of copper from dilute mine solutions (12, 13). The main drawback of these two liquid membrane processes is the limited membrane stability. Bulk liquid membranes appear to be the most easily operated because their configuration is simple, and they provide reproducible experimental data without difficulty and instability. They are often used to study the transport properties of novel carriers (14). Although the BLM configurations employed by various workers (15–28) are not completely the same, the principle is similar. Szpakowska et al. (16, 17) investigated the rate-limiting step and membrane material effect for copper transport by a bulk liquid membrane containing Acorga 5100 (5-nonylsalicylaldoxime, corresponding to LIX 860N), and Lazarova et al. (21) studied the kinetics and mechanism of copper transfer by a bulk liquid membrane containing LIX 860. No data have been reported on the application of the new extractant LIX 984N as a carrier for metal transport in the liquid membrane process. In this study a novel but simple transport cell for bulk liquid membrane operation was used, as shown in Fig. 1. The data obtained provide fundamental information on the kinetics of coupled transport of Cu(II) by LIX 984N and for the design of other liquid membrane transport processes.

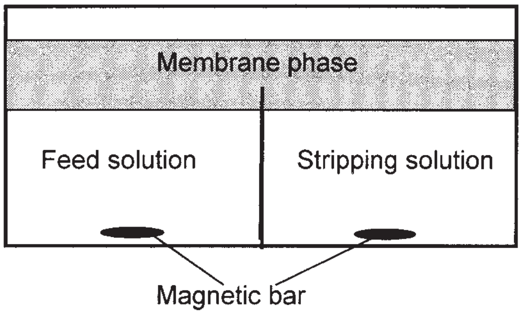

FIG. 1 Schematic of experimental setup. The inner dimensions of the transport cell: 150 mm long × 60 mm wide × 95 mm deep with an impermeable barrier of 60 mm height.

THEORETICAL

Solvent Extraction Equilibrium

LIX 984N reagent, a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime, can form water-insoluble complexes with Cu^{2+} cations, which are assumed to occur according to

$$Cu^{2+} + \frac{2+n}{2}(\overline{HR})_2 \Leftrightarrow \overline{CuR_2\,(HR)_n} + 2H^+ \tag{1}$$

where n is the number of additionally solvated molecules of extractant acid, $(HR)_2$ is the dimer of the acidic extractant molecule, and an overbar refers to the organic phase. The equilibrium constant for the extraction reaction is given by

$$K_{ex} = \frac{[\overline{CuR_2\,(HR)_n}][H^+]^2}{[Cu^{2+}][\overline{(HR)_2}]^{(2+n)/2}} \tag{2}$$

The distribution ratio of Cu^{2+}, D, is commonly written as

$$D = [\overline{Cu}]_T/[Cu]_T \tag{3}$$

where the subscript T denotes total value (all forms) at equilibrium. If the aqueous complexations of Cu^{2+} and SO_4^{2-} are assumed to be negligible and only a single complex of the type $\overline{CuR_2\,(HR)_n}$ is formed in the organic phase, the distribution ratio (D) can be expressed by

$$D = \frac{[\overline{CuR_2\,(HR)_n}]}{[Cu^{2+}]} \tag{4}$$

From Eqs. (2) and (4) we have

$$\log(D[H^+]^2) = \log K_{ex} + \log[\overline{(HR)_2}]^{(2+n)/2} \tag{5a}$$

or

$$\log D = 2\text{pH} + \log K_{\text{ex}} + \log[\overline{(\text{HR})_2}]^{(2+n)/2} \qquad (5\text{b})$$

The above equation provides a relationship between the number of solvated extractant molecules (n) and the extraction equilibrium constant (K_{ex}). As indicated in Eq. (5a), a log-log plot of $D[\text{H}^+]^2$ vs $[(\text{HR})_2]$ would give a straight line with a slope of $(2 + n)/2$ and an intercept of $\log K_{\text{ex}}$. The composition of the extracted species and the equilibrium constant can thus be determined.

Transport Model for a Bulk Liquid Membrane

The mechanism of Cu^{2+} transport across a bulk liquid membrane (BLM) is illustrated in Fig. 2. The concentration profiles of the species across the liquid membrane are shown in Fig. 3. It is generally accepted that the following elementary steps are involved in the transport process (cf. Fig. 3).

(1) Diffusion of copper ions from the bulk of the aqueous feed phase (F) to the aqueous stagnant layer of the feed phase. The flux in this step is given by

$$J_{\text{fi}} = k_{\text{fi}}([\text{Cu}^{2+}]_{\text{f}} - [\text{Cu}^{2+}]_{\text{fi}}) = k_{\text{fi}}(x_{\text{f}} - x_{\text{fi}}) \qquad (6)$$

(2) Diffusion of the carrier HR from the bulk of the organic phase (membrane phase) to the feed/membrane (f/m) interface.

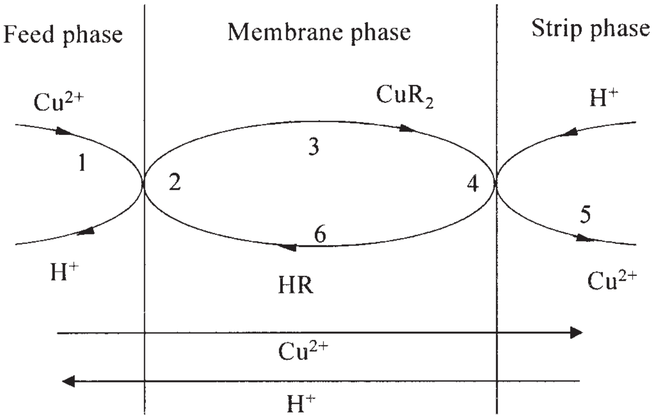

FIG. 2 Mechanism of Cu^{2+} transport across liquid membrane. 1: Diffusion of Cu^{2+} from the bulk feed solution to the feed/membrane phase interface; 2: extraction; 3: diffusion of Cu^{2+}–LIX 984N complex in the membrane phase; 4: stripping; 5: diffusion of Cu^{2+} from the membrane/stripping interface to the bulk stripping phase; 6: backdiffusion of the free carrier.

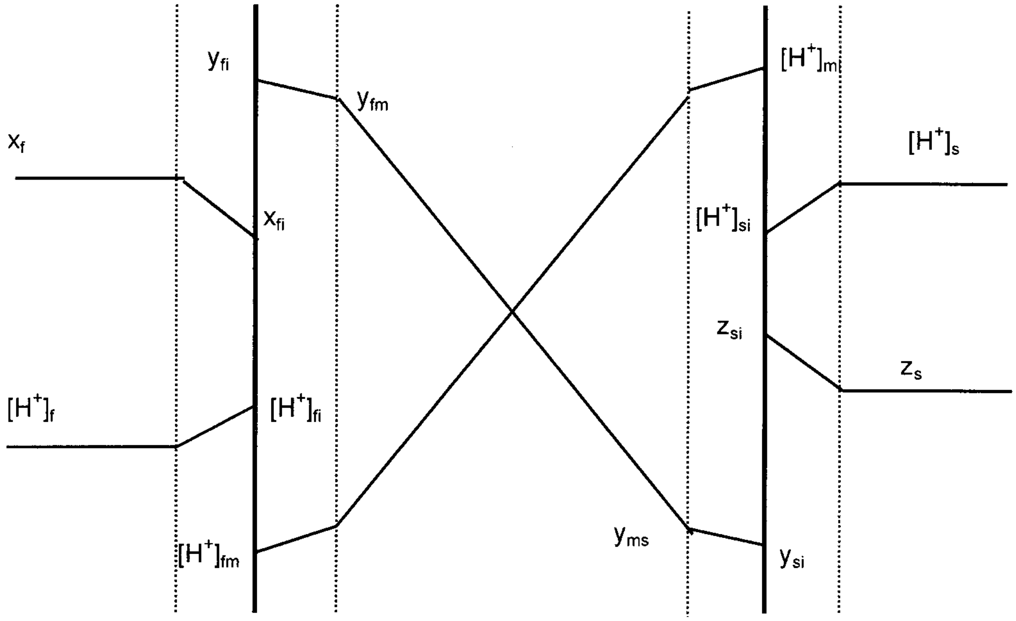

FIG. 3 Concentration profiles of the species across the liquid membrane containing LIX 984N as a mobile carrier depicting the transport model.

(3) Complexation of Cu^{2+} ion with the carrier at the f/m interface is given by

$$J_e = K_e([Cu^{2+}]_{fi} - [\overline{CuR_2\,(HR)_m}]_{fi} = K_e(y_{fi} - x_{fi}) \tag{7}$$

(4) Diffusion of the Cu–carrier complex from the f/m interface into the bulk organic phase across the organic film, given by

$$J_{fm} = k_{fm}(y_{fi} - y_{fm}) \tag{8}$$

(5) Diffusion of the Cu^{2+}–carrier complex through the bulk organic phase, given by

$$J_m = k_m([\overline{CuR_2\,(HR)_n}]_{fm} - [\overline{CuR_2\,(HR)_n}]_{ms}) = k_m(y_{fm} - y_{ms}) \tag{9}$$

(6) Diffusion of complexes from the bulk of the organic phase to the membrane/stripping phase (m/s) interface:

$$J_{ms} = k_{ms}\,(y_{ms} - y_{si}) \tag{10}$$

(7) Diffusion of H^+ from the bulk of the stripping phase toward the m/s interface.

(8) Decomplexation of Cu^{2+} ions at the m/s interface:

$$J_s = K_s(z_{si} - y_{si}) \tag{11}$$

(9) Diffusion of Cu^{2+} ions from the m/s interface to the bulk of the stripping phase across the stripping interface film:

$$J_{\mathrm{si}} = k_{\mathrm{si}}(z_{\mathrm{si}} - z_{\mathrm{s}}) \tag{12}$$

(10) Backdiffusion of the regenerated carrier molecules across the organic phase.

With the recycling of the above steps, Cu^{2+} ions can be transferred against their concentration gradient between the feed and stripping phases and concentrated in the stripping phase. It is obvious that the bulk of the organic phase located over both aqueous phases (see Fig. 1) acts as a liquid membrane. Therefore, this transfer process could be called a bulk liquid membrane (BLM) process.

At steady state the following equality holds:

$$J_{\mathrm{fi}} = J_{\mathrm{e}} = J_{\mathrm{fm}} = J_{\mathrm{m}} = J_{\mathrm{ms}} = J_{\mathrm{s}} = J_{\mathrm{si}} \tag{13}$$

In the description of the transport process, the following assumptions are made.

(1) The chemical reaction between the copper ions and the oxime molecules occurs at the interface or in the aqueous layers adjacent to both sides of the intermediate membrane phase,
(2) The resistance of the diffusion of H^+ ions in both aqueous mass transfer boundary layers is negligible.
(3) Hydrogen ion diffusion in both aqueous phases is much faster than copper ion diffusion from the reaction zones (interface) into the aqueous layers. The same holds for carrier diffusion in the membrane phase with respect to copper-complex diffusion in the same phase.
(4) The diffusion processes are described by Fick's diffusion processes equations.

Based on these assumptions, the Diffusion Steps (2), (4), (7), and (9) will have no influence on the transport kinetics. Among the other steps, one or more of them will play an important role in the transport rate. Among the diffusion steps taking place in the membrane phase, the slowest one probably involves the diffusion of the metal–carrier complex. This is because the membrane phase in our system is not stirred and also because of the greater size of the diffusing metal–carrier complex. Therefore, identification of the rate-determining step has focused on whether the formation/decomposition (Steps 3 and 8) of the complex or its diffusion (Steps 5 and 6) is the slowest step in the transport process.

EXPERIMENTAL

Reagents and Materials

The reagents used were copper(II) sulfate pentahydrate (AJAX Chemicals, Australia, analytical grade) and LIX 984N (kindly supplied by Henkel, Australia) which is a 1:1 volume blend of LIX 860N (5-nonylsalicylaldoxime) and LIX 84N (2-hydroxy-5-nonyl-acetophenome oxime) in a high flash point kerosene. The product is approximately 50% oxime and 50% kerosene. Kerosene (Aldrich, *d* 0.800, *n* 1.4420, bp 175–325°C for laboratory use only) and sulfuric acid (AJAX Chemicals, Australia), 98% 1.84 g/mL 25°C. All reagents were used without further purification. Murexide was used as the indicator in the titration method for copper measurement. Aqueous solutions were made up using Millipore water of 18 MΩ·cm purity. Dynamic viscosity of the organic phase was measured with a Brookfield viscometer (LVTDV-II model, Brookfield Engineering Laboratories, Stoughton, MA, USA) at 24.5°C.

Methods

Solvent Extraction Equilibrium Distribution Measurements

An aqueous copper solution (25 mL) was shaken with an equal volume of the organic solution of LIX 984N for 30 minutes on a shaking machine at constant temperature (25 $\pm$ 1°C). The effect of contact time, equilibrium pH, and carrier concentration on the equilibrium copper distribution between the organic and aqueous phases was examined. Samples of the loaded organic phase (5 mL) were stripped with an equal volume of 2 M H_2SO_4 by a Maxi-Mix Vortex (Barnstead/Thermolyne Corporation, USA) in a glass tube for 2 minutes.

Coupled Transport Processes

Coupled transport processes were conducted in the apparatus depicted in Fig. 1 at room temperature (20°C). The inner dimension of the transport cell was 150 mm long $\times$ 60 mm wide $\times$ 95 mm deep. A barrier of 60 mm height divided the cell into two compartments. Both feed and stripping solutions were 220 mL, and they were stirred by magnetic stirrers at the bottom of the cell (the stirring speed was usually 110 rpm). The dimension of the magnetic bar with a Telflon coat was Ø7 mm o.d. $\times$ 35 mm long. The feed phase was an aqueous $CuSO_4$ solution with an initial copper concentration of ca. 2 g/L and a pH of 2.50. The stripping phase was 2 M H_2SO_4 solution. The membrane liquid phase was LIX 984N in kerosene at a given volume percentage concentration. The volume of the membrane phase ranged from 80 to 360 mL.

Both interfaces (feed/membrane and membrane/stripping) were at the same level and were separated by a barrier above the interface of 8 mm.

The experiments were run for 30–40 hours. Samples (0.5 mL) were taken from the aqueous phases at regular time intervals, and the copper concentrations in the samples were determined by EDTA titration using murexide as an indicator or by atomic absorption spectrometry. Each experimental result reported is the arithmetic mean of two or three independent analyses (error $<$ 6%). The copper concentration in the organic phase was determined by the method mentioned above after stripping. The mass balances were between 98 and 102% when all solutions (feed, strip, and organic) were analyzed. Therefore, in most cases the copper concentration in the organic phase was calculated from the mass balance of copper in the system. The water content of the membrane liquid phase was determined by the Karl-Fischer method.

Measurement of Mass Transfer Flux across the Interfaces

The effect of process parameters is usually evaluated by the change in the fluxes $J_{\mathrm{f/m}}$, $J_{\mathrm{m/s}}$, and J_{m}, calculated by

$$J_{\mathrm{f/m}} = -\frac{V_{\mathrm{f}}}{A_{\mathrm{f/m}}}\frac{dC_{\mathrm{f}}}{dt} \tag{14}$$

$$J_{\mathrm{m/s}} = \frac{V_{\mathrm{s}}}{A_{\mathrm{m/s}}}\frac{dC_{\mathrm{s}}}{dt} \tag{15}$$

$$J_{\mathrm{m}} = \frac{V_{\mathrm{s}}}{A_{\mathrm{o}}}\frac{dC_{\mathrm{s}}}{dt} \tag{16}$$

where $J_{\mathrm{f/m}}$, $J_{\mathrm{m/s}}$, and J_{m} are the fluxes across the feed/membrane interface, the membrane/stripping interface, and the bulk liquid membrane cross section, respectively.

RESULTS AND DISCUSSION

Solvent Extraction Equilibrium

Figure 4 shows the effect of contact time on the extraction at copper concentrations of 1 and 10 g/L using 10% v/v LIX 984N as the organic phase under conditions of vigorous shaking. The extraction can reach equilibrium within a contact time of 30–50 seconds.

The measured equilibrium distribution (D) of copper between the organic and aqueous phases versus the equilibrium pH of the aqueous phase is shown in Fig. 5. As was expected from the analysis of the extraction processes, a line of slope ca. 2 was obtained for the range of concentrations and pH studied. Therefore, the exchange reaction of Cu^{2+} with H^{+} proceeds at the ratio of 1:2 according to Eq. (1).

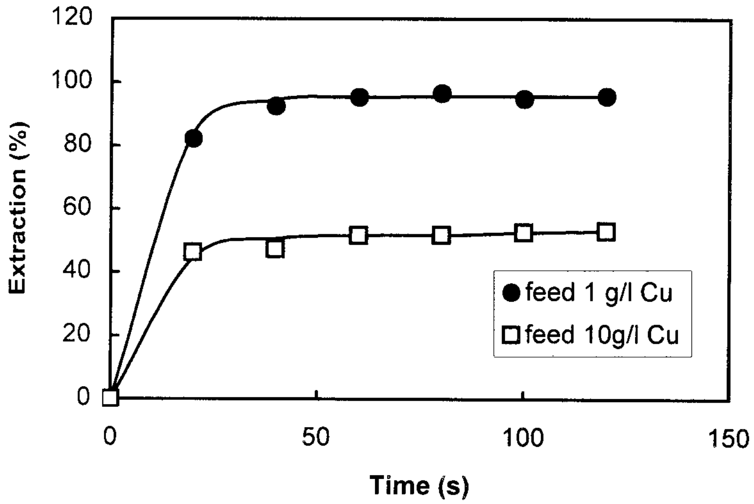

FIG. 4 Effect of contact time on the extraction.

Figure 6 shows the effect of extractant LIX 984N concentration on the percent extraction, distribution ratio, and equilibrium pH value. Because LIX 984N is a mixture of LIX 860N and LIX 84N (approximately 50% oxime and 50% kerosene), it is difficult to determine the accurate mole concentrations of the LIX 984N mixture, and therefore n and K_{ex} cannot be determined by Eq. (5a) from the data given in Fig. 6. In the copper(II) extraction by LIX 860 (21), n and K_{ex} were measured as 0 and 5.4×10^4, respectively. Therefore, it can be assumed that the present system should have a similar or higher extraction constant and that the process of copper extraction (forward reaction in Eq. 1) is much faster than the stripping

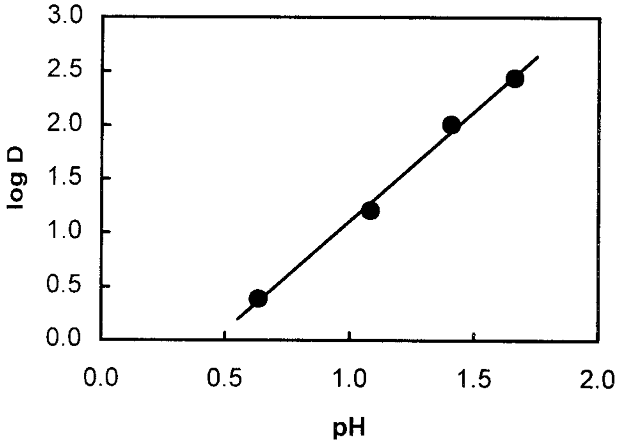

FIG. 5 The dependence of distribution coefficient on the aqueous equilibrium pH.

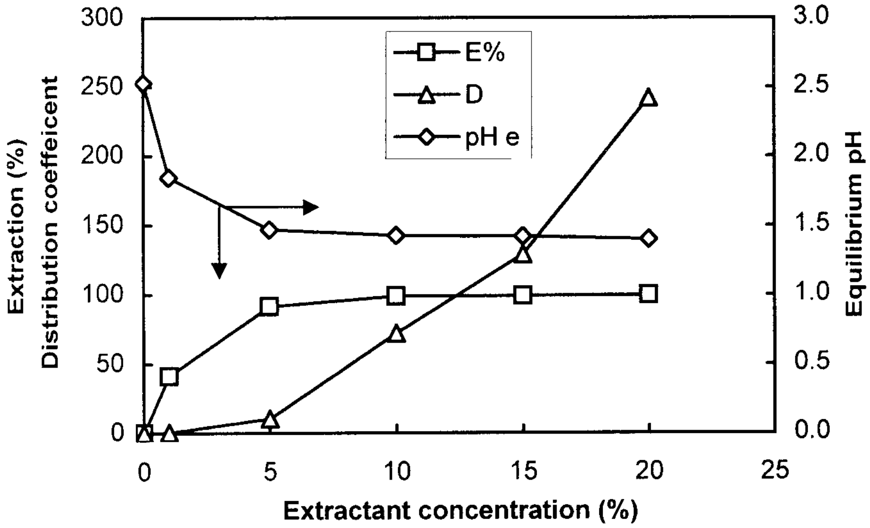

FIG. 6 Effect of LIX 984N concentration on the copper extraction and the equilibrium pH value.

process (the reverse reaction) at pH 2.5 before equilibrium is reached. The effect of contact time on the stripping rate is shown in Fig. 7. With vigorous shaking the backextraction can reach equilibrium within 50 seconds (compared with ca. 30 seconds for extraction, see Fig. 4). Therefore, the extraction and stripping reactions of Cu^{2+} with LIX 984N can be regarded as fast reactions under the conditions studied.

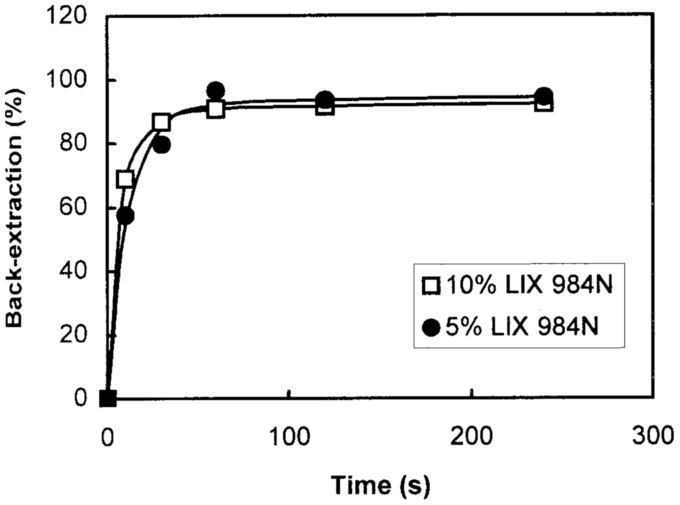

FIG. 7 Effect of contact time on the stripping rate of loaded organic phase.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

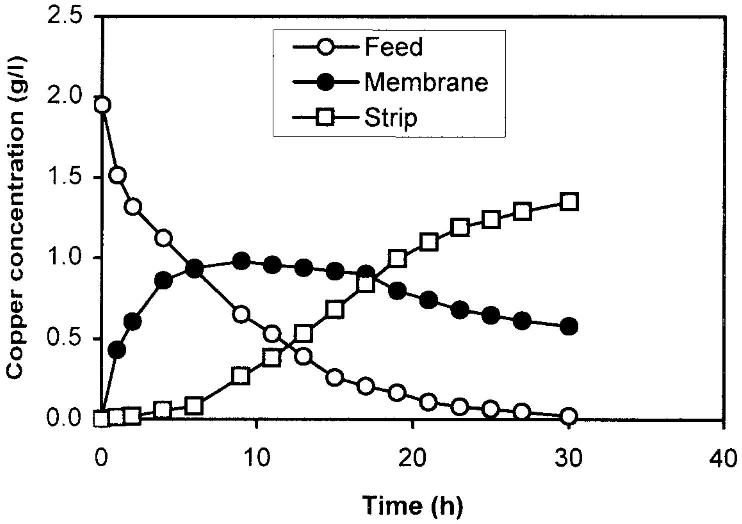

FIG. 8 Copper concentration changes as a function of time in the bulk liquid membrane process.

Copper Transport across Bulk Liquid Membranes

Figure 8 depicts the typical changes in copper concentration in the three liquid phases (feed, membrane, and stripping) as a function of time. It can be seen that copper concentration in the feed phase decreased quickly in the initial stage (about 2 hours) and then decreased gradually. In the initial stage the copper concentration of the membrane phase increased rapidly, while there was no apparent change in copper concentration in the stripping phase. From 5 to 17 hours the slopes of the transport curves for the feed and stripping phases were almost constant, indicating that during this period the copper transport reached steady, or at least quasi-steady state, that is, $J_{f/m} = J_m = J_{m/s}$. Thus, at the beginning of operation there was no loading for the membrane liquid phase, so the copper could be transferred quickly from the feed into the membrane phase. Subsequently, the increase in loading of the membrane phase and decrease in copper concentration in the feed solution caused a decrease in the copper transfer rate. However, the simultaneous stripping process removed copper from the membrane phase and, as a result, the overall transfer rate did not continue to decrease significantly. This is the advantage of liquid membrane processes, which circumvents the usual equilibrium limitation of solvent extraction. In other words, the extraction equilibrium limitation between the feed phase and the organic phase is eliminated because of the backdiffusion of regenerated carrier. This characteristic is called nonequilibrium mass transfer, the most important feature of liquid membrane processes. This coupled liquid membrane process for metal extraction involves concurrent extraction and stripping in a single stage rather than the two separate stages required by conventional solvent extraction. By concurrent extraction and stripping, the system drives the extraction equilibrium, as shown by Eq. (1), to the right by removal of the complexed ions as they are formed. This removes the equilibrium limitation inherent in the conventional extraction methods, resulting in the use of a much lower concentration of complexing agent in the membrane phase than in a solvent extraction process for the same separation.

It is well known that hydrodynamic conditions play an important role in mass transfer from one phase to another phase through the interface in liquid–liquid extraction, especially in the case where diffusion is the controlling step. In order to examine the effect of hydrodynamics on copper ion transfer, experiments were carried out over the 60–145 rpm range. The results are illustrated in Fig. 9, which plots initial flux versus stirring speed. The transfer rate at the feed/membrane interface shows a reasonably linear dependence in the 60–145 rpm range, whereas at the membrane/stripping interface the transfer rate is lower and not affected by the stirring speed until 110 rpm. It should be noted that when the stirring speed was higher than 150 rpm, the hydrodynamic stability of the two interfaces was affected significantly and drops of emulsion were observed in both aqueous phases. In this case the initial permeation rate (mol/s) was used rather than flux to describe the transfer rate and is plotted versus the stirring speed in Fig. 10. It can be seen that under higher stirring speed the transfer rate increased very rapidly. At a stirring speed of 300 rpm, the copper transport from the feed to the strip can be completed within 5 hours, whereas it needs about 40 hours at 110 rpm. This is mainly attributed to the changed hydrodynamic conditions and the increase in contact area between the aqueous and membrane phases. It should be noted that the

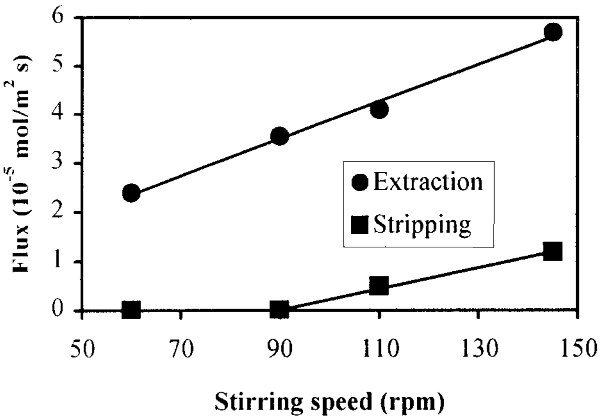

FIG. 9 Effect of stirring speed on the copper transfer rate.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

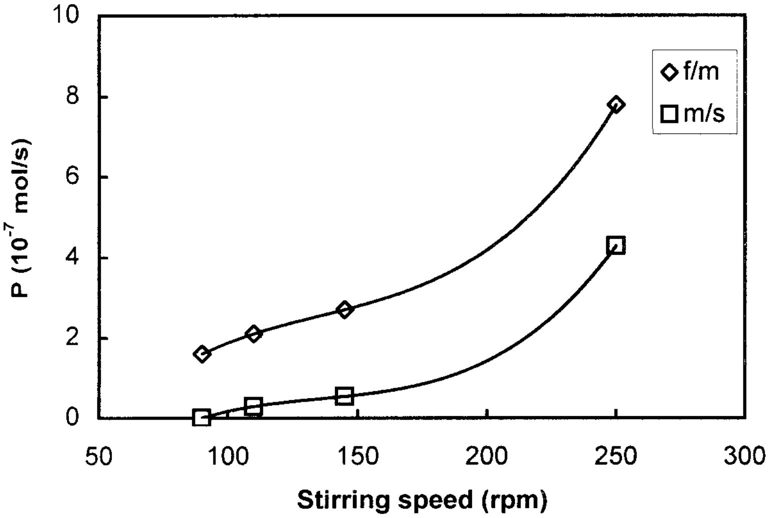

FIG. 10 Dependence of permeation rate on the stirring speed.

stirring speed could not exceed 330 or the aqueous drops of the feed and stripping solutions would communicate with each other.

The effect of the extractant LIX 984N concentration on the mass flux is presented in Fig. 11. On increasing the carrier concentration, fluxes through the two interfaces increased. The fluxes increased linearly with carrier concentration between 0 and 10%, but at a slower rate for higher than 10%. This might be attributed to the viscosity increase at higher carrier concentration. The dynamic viscosity of LIX 984N is typically 60.1 cP (error 12%), and that of kerosene is 2.15 cP (error 4.2%). Consequently the viscosity of the mixture

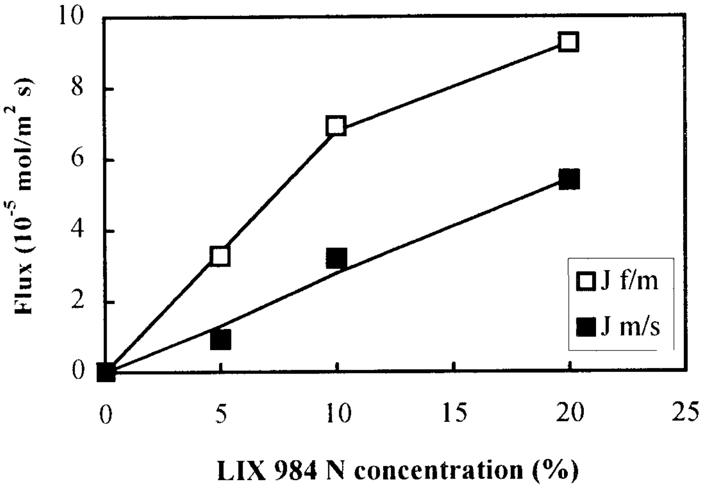

FIG. 11 Effect of the carrier concentration on the mass transfer fluxes across the interfaces.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

would be expected to be increased with an increase in LIX concentration. A similar phenomenon has been found for supported liquid membranes and emulsion liquid membranes (9–12). However, the slower rate at higher carrier concentration could signify a shift toward less membrane transport control.

Copper concentrations in the membrane phase both above the feed cell and stripping cell were determined, and it was found that the concentration difference was only about 0.02 g/L at the quasi-steady state (5–17 hours). Therefore, it can be concluded that diffusion in the membrane is not the controlling step, so it is not necessary to stir the membrane phase. In all the BLM configurations reported in the literature (15–28), the membrane phase was stirred. This could have caused unspecified hydrodynamic instability of the membrane/aqueous phase interfaces. In the SLM and ELM processes, there is no moving part for the membrane phase, which is one of the reasons that capital, operating, and energy consumption costs are low in liquid membrane processes. In our system, no water content was detected in the membrane phase after copper transport (about 40 hours). This agrees with Szpakowska's bulk liquid membrane (Acorga P 50 in *n*-octane) system for copper transport (17), where water did not penetrate the membrane phase beyond the limits of its solubility.

Figure 12 shows the effect of inventory of membrane liquid phase on the mass transfer flux. The inventory of the membrane liquid had no pronounced influence on the flux through the first interface $J_{f/m}$, while it did affect the second interface $J_{m/s}$ more significantly. It can be seen that the inventory of the membrane liquid plays an important role in the overall transport rate of copper. In previous studies on copper transport by bulk liquid membranes

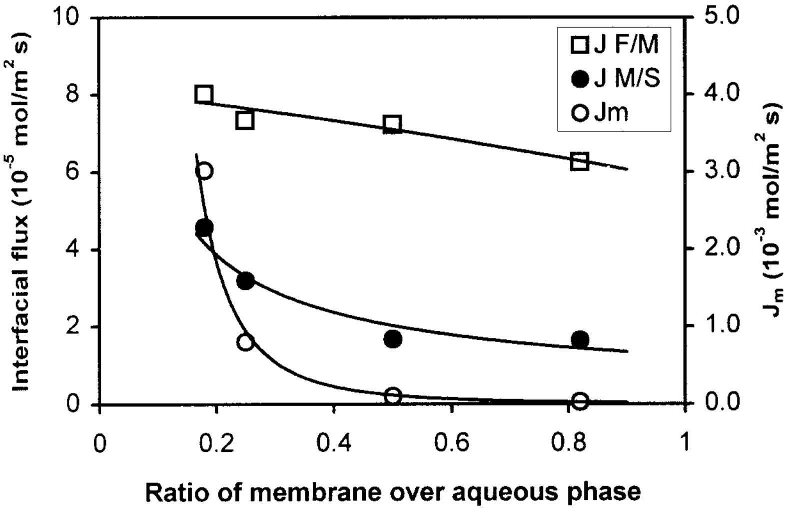

FIG. 12 Effect of inventory of membrane liquid on the mass transfer rate.

(16–22), there was no investigation of this aspect. The explanation is that the lower the inventory of the membrane liquid, the more quickly the copper concentration in the membrane phase increased, which led to an increase in the copper–carrier complex concentration in the narrow layers (refer to Fig. 3), and the stripping rate in turn increased. On the other hand, low organic inventory leading to higher efficiency is one of the features of the liquid membrane process. It can be deduced that the transfer rate would continue to increase if the organic inventory is decreased further. However, due to the limitation of the BLM configuration, it is not feasible to assess this (in the case of a ratio of 0.18, i.e., 80 mL of the membrane phase and 220 mL of the feed and stripping phases, respectively, the distance between the top of the barrier plate and the interface of the membrane phase is less than 1 mm). Supported liquid membranes using porous hydrophobic polymer membranes as support have an advantage in that the organic inventory can be minimized as far as possible, but with a disadvantage of the limited membrane lifetime, as was mentioned earlier. The transport performance and stability of supported liquid membranes using porous hydrophobic polymer membranes containing LIX 984N for copper transport has been investigated and the results have been published elsewhere (29, 30).

CONCLUSIONS

The uphill transport of copper has been successfully performed using a very simple transport cell through a bulk liquid membrane containing LIX 984N as carrier. In the present bulk liquid membrane system, the diffusion of copper ions from the bulk feed phase to the aqueous/oil interfacial layer is the rate-limiting step for copper transfer into the membrane. At the interface between the membrane phase and the stripping phase, the diffusion of Cu–LIX 984N complexes from the bulk membrane phase to the interfacial layer is the rate-controlling step. Membrane–stripping interfacial film diffusion is the rate-limiting step among the three diffusion steps (feed–membrane interfacial film diffusion, membrane phase diffusion, and membrane–stripping interfacial film diffusion) for the overall coupled transport. Therefore, it may be concluded that among the factors affecting the diffusion of copper, the water film is predominant in the feed side and the oil film is predominant in the stripping side. The higher transport efficiency for reduced organic inventory demonstrates a key feature of liquid membrane processes.

SYMBOL

$(HR)_2$	dimeric form of LIX 984N
A	interface area of phases (m^2)

C	concentration (mol/L)
D	distribution coefficient (—)
J	copper flux ($\mathrm{mol/m^2 \cdot s}$)
$J_{\mathrm{f/m}}$	flux from the feed to the membrane phases ($\mathrm{mol/m^2 \cdot s}$)
$J_{\mathrm{m/s}}$	flux from the membrane to the stripping phases ($\mathrm{mol/m^2 \cdot s}$)
k	mass transfer coefficient (m/s)
K_{e}	extraction rate constant (—)
K_{ex}	equilibrium constant (—)
K_{s}	backextraction rate constant (—)
P	permeation rate (mol/s)
t	time (s)
V	volume (L)
x	$\mathrm{Cu^{2+}}$ concentration in the feed phase (mol/L)
y	$\mathrm{Cu^{2+}}$ concentration in the organic membrane phase (mol/L)
z	$\mathrm{Cu^{2+}}$ concentration in the stripping phase (mol/L)

Subscripts

e	extraction
f	feed phase
fi	feed/membrane phase interface
fm	surface between the feed and membrane phases
I	interface
m	membrane phase
ms	surface between the membrane and stripping phase
o	organic membrane phase cross section
s	stripping phase
si	membrane/stripping interface

ACKNOWLEDGMENTS

Support for this research from the Australian Research Council and the Australian Government OPRS scheme is gratefully acknowledged.

REFERENCES

1. G. A. Kordosky, *The Chemistry of Metals Recovery Using LIX Reagents*, Henkel Corp., Minerals Industry Division Red Book, 1988–1990 ed.
2. *Standard Henkel Quality Control Test for the Oxime LIX Copper Solvent Extraction Reagents*, Technical Bulletin, Henkel/MID, Minerals Industry Division Red Line, 1993.
3. T. P. Martin and G. A. Davies, "The Extraction of Copper from Dilute Aqueous Solutions Using a Liquid Membrane Process," *Hydrometallurgy, 2,* 315–334 (1976/1977).
4. W. Volkel, W. Halwachs, and K. Schugerl, "Copper Extraction by Means of a Liquid Surfactant Membranes Process," *J. Membr. Sci., 6*, 19–31 (1980).

5. N. N. Li, R. P. Cahn, D. Naden, and R. W. M. Lai, “Liquid Membrane Process for Copper Extraction,” *Hydrometallurgy*, *9*, 277–305 (1983).
6. O. Tutkun and R. A. Kumbasar, “Selective Transport of Copper through Liquid Membranes Using LIX 860 as Mobile Carrier,” *Sep. Sci. Technol.*, *29*(16), 2197–2201 (1994).
7. P. A. O’Hara and M. P. Bohrer, “Supported Liquid Membranes for Copper Transport,” *J. Membr. Sci.*, *44*, 273–287 (1989).
8. R. W. Baker, M. E. Tuttle, D. J. Kelly, and H. K. Lonsdale, “Coupled Transport Membranes. I. Copper Separations,” *Ibid.*, *2*, 213 (1977).
9. K. H. Lee and E. L. Cussler, “Selective Copper Recovery with Two Types of Liquid Membranes,” *AlChE J.*, *24*(5), 860–868 (1978).
10. J. Marchese, M. Campderros, and A. Acosta, “Transport and Separation of Coblt, Nickel and Copper Ions with Alamine Liquid Membranes,” *J. Chem. Tech. Biotechnol.*, *64*, 293–297 (1995).
11. P. A. O’Hara and M. P. Bohrer, “Application of a Liquid Membrane for Copper Recycling,” in C. J. King and J. D. Navratil (Eds.), *Chemical Separations, Vol. II, Applications*, Litarvan Literature, Denver, CO, 1986.
12. R. P. Cahn, J. W. Frankenfeld, N. N. Ki, D. Naden, and K. N. Subramanian, “Extraction of Copper by Liquid Membranes,” in *Recent Developments in Separation Science, Vol. VI*, CRC Press, Cleveland, OH, 1981.
13. J. B. Wright, D. N. Nilsen, G. Hundley, and G. J. Galvan, “Field Test of Liquid Emulsion Membrane Technique for Copper Recovery from Mine Solutions,” *Miner. Eng.*, *8*(4/5), 549–556 (1995).
14. M. Hiraoka (Ed.), *Crown Ethers and Analogous Compounds* (Studies in Organic Chemistry, Vol. 45), Elsevier, Amsterdam, 1992, p. 146.
15. J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Beolke, M. S. Astin, and R. M., Izatt, “Effects of Salt Concentration and Anion on the Rate of Carrier-Facilitated Transport of Metal Cations through Bulk Liquid Membranes Containing Crown Ethers,” *J. Am. Chem. Soc.*, *102*, 3399 (1980).
16. M. Szpakowska and O. B. Nagy, “Membrane Material Effect on Copper Coupled Transport through Liquid Membranes,” *J. Membr. Sci.*, *64*, 129–143 (1991).
17. M. Szpakowska, “Investigation of the Rate-Limiting Step of Coupled Copper Ion Transport through Membranes by Means of Variable Speed Experiments,” *Ibid.*, *90*, 101–108 (1994).
18. M. Szpakowska and O. B. Nagy, “Application of the Competitive Preferential Solvation Theory to Facilitated ion Transport through Binary Liquid Membranes,” *J. Phys. Chem.*, *93*, 3851 (1989).
19. M. Szpakowska and O. B. Nagy, “Effect of Physical-Chemical Properties of Binary Liquid Membranes on Steady-State Transport of Copper(II) Ions,” *Polyhedron*, *12*, 1277 (1993).
20. P. Scrimin, U. Tonellato, and N. Zanta, “Cu(II) Mediated Selective Transport of Amino Acids across a Bulk Liquid Membrane Using a Chiral Lipophilic Ligand as a Carrier,” *Tetrahedron Lett.*, *29*(39), 4967–4970 (1988).
21. Z. Lazarova and L. Boyadzhiev, “Kinetic Aspects of Copper(II) Transport across Liquid Membrane Containing LIX-860 as a Carrier,” *J. Membr. Sci.*, *78*, 239–245 (1993).
22. Z. Lazarova, T. Sapundzhiev, and L. Boyadzhiev, “Kinetics and Mechanism of Copper Transfer by Hydroxy-oximes in Three-Phase Liquid Systems,” *Sep. Sci. Technol.*, 27(4), 493–505 (1992).
23. S. Yoshida and S. Hayano, “Kinetics of Partition between Aqueous Solutions of Salts and Bulk Liquid Membranes Containing Neutral Carriers,” *J. Membr. Sci.*, *11*, 157 (1982).
24. E. Kokufuta and M. Nobusawa, “Uphill Transport of Phosphate Ion through an Oxo-

molybdenum(V)–Tetraphenylporphyrin-Complex-Containing Bulk Liquid Membrane: Effect of Halogen Ions on Phosphate Ion Flux, *Ibid.*, *48*, 141 (1990).

25. G. C. Sahoo, A. C. Ghosh, N. N. Dutta, and R. K. Mathur, "Facilitated Transport of 7-Aminocephalosporanic Acid in a Bulk Liquid Membranes," *Ibid.*, *112* 147 (1996).
26. M. Kobya, N. Topcu, and N. Demircioglu, "Kinetic Analysis of Coupled Transport of Thiocyanate Ions through Liquid Membranes at Different Temperatures," *Ibid.*, *130*, 7–15 (1997).
27. I. M. Coelhoso, J. P. S. G. Crespo, and M. J. T. Carrondo, "Kinetics of Liquid Membrane Extraction in Systems with Variable Distribution Coefficient," *Ibid.*, *127*, 141–152 (1997).
28. K. Hiratani, T. Takahashi, H. Sugihara, K. Kasuga, K. Fujiwara, T. Hayashita, and R. A. Bartsch, "Selective Liquid Membrane Transport of Lead(II) by an Acyclic Polyether Dicarboxylic Acid Ionophore," *Anal. Chem.*, *69*(15), 3002–3007 (1997).
29. X. J. Yang and A. G. Fane, "Effect of Membrane Preparation on the Lifetime of Supported Liquid Membranes," *J. Membr. Sci.*, *133*, 269–273 (1997).
30. X. J. Yang and A. G. Fane, "Performance and Stability of Supported Liquid Membranes Using LIX 984N for Copper Transport, *Ibid.*, In Press.

Received by editor April 7, 1998
Revision received October 1998

Downloaded At: 11:09 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100100744