Kinetic modelling of the active transport of copper(II) across liquid membranes using thiourea derivatives immobilized on microporous hydrophobic supports

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The facilitated transport of Cu^{II} from chloride media through a flat-sheet supported liquid membrane (FSSLM) is investigated, using thiourea derivatives as ionophores, as a function of hydrodynamic conditions, concentration of copper ($1–3 \times 10^{-7}$ mol cm^{-3}) and H^+ (pH 0.1–2.5) in the feed solution, structure of carrier, carrier concentration ($0.7–3 \times 10^{-5}$ mol cm^{-3}) in the membrane, strippant in receiving phase and support characteristics. A model is presented that describes the transport mechanism, consisting of diffusion through a feed aqueous diffusion layer, a fast interfacial chemical reaction, and diffusion of carrier and its metal complex through the organic membrane. The organic membrane diffusional resistance (Δ_o) and aqueous diffusional resistance (Δ_a) were calculated from the proposed model, and their values were 107×10^2 s cm^{-1} and 625 s cm^{-1}, respectively. It was observed that the Cu^{II} flux across the membrane tends to reach a plateau at a high concentration of Cu^{II} or a low concentration of H^+ owing to carrier saturation within the membrane, leading to a diffusion-controlled process. The values of the apparent diffusion coefficient (D_o^a) and limiting metal flux J_{lim} were calculated from the limiting conditions and found to be 2.9×10^{-6} cm^2 s^{-1} and 1.4×10^{-9} mol cm^{-2} s^{-1}, respectively. The values of the bulk diffusion coefficient ($D_{o,b}$) and diffusion coefficient (D_o) calculated from the model were 2.6×10^{-6} cm^2 s^{-1} and 1.2×10^{-6} cm^2 s^{-1}. The polymeric microporous solid support, Durapure, was selected throughout the study as it gave the best performance.

Membrane science has taken a place among the most important topics of research in the world today, with sales of membrane systems topping $1 billion annually.[1] Among the processes being developed, liquid membranes (LMs) have been showing tremendous potential and different configurations of LMs are being investigated for various applications.[2] The importance of LMs is unquestioned, particularly in instances where solute concentrations are extremely low and large volumes of solutions must be processed without generating secondary wastes. These techniques have been extensively deployed in separation science, for example in metal recovery from leaching and waste waters, winning of precious and strategic metals from neutral waters, and treatment of large volumes of effluents including toxic and hazardous wastes generated by industries.[3]

The supported liquid membrane (SLM) techniques in flat sheet (FSSLM),[4–5] hollow fibre (HFSLM)[6–8] and spiral wound[9,10] configurations are gaining considerable importance owing to their application in the recovery and separation of metal species from aqueous solutions. These potential techniques may offer a number of advantages over other traditional separation processes.[11–12] Furthermore, analytical applications of SLM and HFSLM for analytical preconcentration[13,14] and determining ultratrace level concentrations[15,16] of metal ions have been reported. It is very important to elucidate the mechanisms of both the permeation of the metal with a carrier and the stripping of the metal with a stripping agent on both sides of the porous membrane. In 1971, Cussler highlighted the potential of liquid membranes by giving them the title "membranes which pump" and presented them with a theoretical model.[17] Further, Danesi and coworkers have focused the liquid membrane modelling and developed models for the flat sheet and hollow fibre supported liquid membranes.[18–20] Marr and Kopp,[21] as well as Noble and coworkers,[22] have also made attemps to model liquid membranes for various chemical systems in the early eighties. Since then, more attention has been paid to mass transfer and the modelling of membrane processes in order to understand the permeation mechanisms before introducing SLM or HFSLM into either a metal separation process or analytical scheme. It is of prime importance to focus on interfacial phenomenon subjected to metal-carrier chemical reactions between the feed interface and membrane when metal ion permeation takes place against a concentration gradient of complexing species.[23–26]

Extensive research has been conducted into the types of compounds that can be used as complexing agents for Cu^{II} and also into their applications as carriers. The organic carriers used for membrane permeation of Cu^{II} were derivatives of hydroxyoxime (LIX 65N),[27] 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A),[28] *N*-8-quinolyl-*p*-dodecylbenzenesulfonamide (C_{12}phSAQ), *N*-8-inolyloctanesulphonamide (nC_8SAQ),[29] and a tertiary amine, Alamine 336.[30] Recently, derivatives of thiourea have gained prominence in the field of solvent extraction and liquid membranes for palladium[31] and gold.[32] Their performance in liquid–liquid extraction studies of Cu^{II} were quite promising as compared to other conventional extractants[33] but little work has been done to evaluate their performance as carriers for copper from chloride media in liquid membrane studies.

Before scaling up the FSSLM, either in the form of hollow fibre or spiral wound membrane extraction, a theoretical model of the liquid membrane system is needed in order to design an efficient recovery process in terms of better stability.

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Table 1 List of symbols and their definitions

$\Delta_a = d_a/D_a$	transport resistance due to diffusion by the aqueous feed boundary layer (s cm^{-1})
$\Delta_o = d_o/D_o$	transport resistance due to diffusion through the membrane (s cm^{-1})
$[\mathrm{Cu^{II}}]_b$	bulk copper concentration
$[\mathrm{Cu^{II}}]_{tot}$	total copper concentration in the feed phase
$[\mathrm{Cu^{II}}]_{i,\,tot}$	total copper concentration at the feed solution–membrane interface where i is the interface
$[\mathrm{CuL_2}]_{i,\,f}$	$\mathrm{CuL_2}$ organic concentration at the feed solution–membrane interface
$[\mathrm{CuL_2}]_{i,\,s}$	$\mathrm{CuL_2}$ organic concentration at the membrane–stripping phase interface
d_a	thickness of the aqueous feed boundary layer (cm)
D_a	average aqueous diffusion coefficient of the copper-containing species (cm^2 s^{-1})
d_o	thickness of the membrane (cm)
D_o	membrane diffusion coefficient of the copper-containing species (cm^2 s^{-1})
D_o^a	apparent diffusion coefficient of the copper-carrier species (cm^2 s^{-1})
$D_{o,\,b}$	diffusion coefficient of the copper-containing species in the bulk phase (cm^2 s^{-1})
τ	tortuosity of the membrane
$\tau' = \tau^2/\varepsilon$	membrane constant where ε represents porosity
J	permeability flux (mol cm^{-2} s^{-1})
P	permeability coefficient (cm s^{-1})
f,i and s,i	feed interface and strip interface, respectively, shown in Fig. 2
x	membrane path length (cm)

This paper presents the kinetic modelling of active transport of $\mathrm{Cu^{II}}$ using thiourea derivatives immobilized on microporous hydrophobic supports. The organic membrane diffusional resistance (Δ_o) and the aqueous diffusional resistance (Δ_a) were calculated from the proposed model. The influence of hydrodynamic conditions and chemical parameters were examined in order to obtain efficient and stable FSSLMs. A list of the symbols used in this work is given in Table 1.

Experimental

All the chemicals used were of AR or GR grade unless stated otherwise. Analytical grade diluents, namely cumene (Fluka), kerosene (Fluka) and toluene (Merck), were used as received. $\mathrm{CuCl_2(s)}$ and NaSCN(s) were procured from Merck.

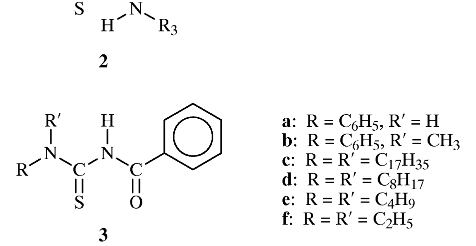
The extractants, *N*-(thiocarbamoyl)benzamidine derivatives (**2a**–**c**) and *N*-benzoylthiourea derivatives (**3a**–**f**), were kindly donated by Prof. L. Beyer (Department of Inorganic Chemistry, University of Leipzig, Germany). The structures of **2a**–**c** and **3a**–**f** are shown in Fig. 1 and some of their properties are presented in Table 2.

FSSLM preparation and measurements

Single-stage FSSLM measurements were carried out with a simple two-compartment permeation cell that consisted of a source (or feed) phase (generally 200 cm^3) separated from a receiving (or stripping) phase chamber (200 cm^3) by a liquid membrane having an effective membrane area of 11.33 cm^2. The source and receiving phases were mechanically stirred at about 1200 rpm at room temperature (24 ± 1 °C) to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. Using 1200 rpm, $\mathrm{Cu^{II}}$ concentrations in the various phases such as centre, corner or near membrane in the FSSLM cell were found to be reproducible within ±10%. Membrane permeabilities were determined by monitoring the $\mathrm{Cu^{II}}$ concentration in the source phase as a function of time by atomic absorption spectrometry using a 2380 Perkin Elmer absorption spectrometer. The permeation coefficient (P_{Cu}) was computed from the following equation:

$$\ln(C/C_0) = -(A/V)P_{\mathrm{Cu}}t \qquad (1)$$

where V is the volume of the source phase solution (cm^3), A the effective membrane area (cm^2), C_o and C are concentrations of metal ion in the source phase at time zero and at a given time, t, respectively (mol cm^{-3}), where t is the elapsed time (s).



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a: $R_1 = R_2 = C_2H_5$, $R_3 = C_6H_5$
b: R_1—R_2 = —$C_2H_4OC_2H_4$—, $R_3 = C_6H_5$
c: $R_1 = R_2 = C_2H_5$, R_3 = H

3

a: $R = C_6H_5$, R' = H
b: $R = C_6H_5$, $R' = CH_3$
c: $R = R' = C_{17}H_{35}$
d: $R = R' = C_8H_{17}$
e: $R = R' = C_4H_9$
f: $R = R' = C_2H_5$

Fig. 1 The chemical structures of the derivatives of benzoylthiourea and *N*-(thiocarbamoyl)benzamidine used in this study.

Table 2 Some properties of the extractants used

Extractant	M/g mol^{-1}	Diluent	Solubility^a/mol L^{-1}
3a	256.33	Benzene	10^{-2}
		Kerosene	Insoluble
		Cumene	10^{-2}
3b	270.36	Benzene	10^{-2}
		Cumene	7×10^{-3}
3c	657.14	Cumene	3×10^{-2}
3d	404.66	Cumene	3×10^{-2}
3e	292.44	Cumene	3×10^{-2}
3f	236.33	Cumene	3×10^{-2}
2a	311.45	Benzene, kerosene	1×10^{-2}
		Methylene chloride	3×10^{-2}
		Cumene	2×10^{-2}
2b	325.45	Benzene, kerosene	$10^{-3}-10^{-2}$
		Methylene chloride	$10^{-3}-10^{-2}$
		Cumene	10^{-2}
2c	235.38	—	

^{a} Values taken from ref. 25.

Membrane support

The organic membrane phase was prepared by dissolving a weighed quantity of **2a**–**c** and **3a**–**f** in organic diluents to obtain carrier solutions of various concentrations. The polymeric supports were impregnated with the carrier solutions containing the extractant in kerosene, cumene or toluene by immersion for 24 h, then left to drip for a few seconds before being placed in the FSSLM cell. The physical characteristics of the supports are summarized in Table 3.

Permeation model of $\mathrm{Cu^{II}}$ across FSSLMs

The flux of $\mathrm{Cu^{II}}$ across the membrane may be described by applying Fick's first diffusion law to the diffusion layer at the feed side, to the membrane and finally to the receiving phase. Fig. 2 shows a possible transport scheme for $\mathrm{Cu^{II}}$ with **3c** dissolved in cumene across a SLM.

Extraction equilibrium

The extraction of $\mathrm{Cu^{II}}$ by the organic extractants (**2a**–**c** or **3a**–**f**) dissolved in cumene has been studied and described elsewhere.[33] The extraction equilibrium can be described by the following reaction:

$$\mathrm{Cu^{II}} + 2\,\mathrm{HL_{org}} \rightleftharpoons \mathrm{CuL_{2org}} + 2\,\mathrm{H^+} \qquad (2)$$

Table 3 Influence of the characteristics of supports impregnated with **3c** carrier on the permeability of Cu^{II} in cumene[a]

Support	Thickness $d_o/\mu m$	Porosity $\varepsilon/\%$	Tortuosity τ	$J/10^{-11}$ mol cm^{-2} s^{-1}
Durapore (polyvinylidene difluoride)	125	75	1.67	19
Fluoropore (polytetrafluoroethylene)	175	85	1.86	6.7
Celgard 2500 (polypropylene)	25	45	4.26	5.6
Celgard 2400 (polypropylene)	25	38	4.26	3.1
Celgard 2402 (polypropylene)	50	38	3.44	4.7

[a] Feed composition, Cu^{II}: 1×10^{-7} mol cm^{-3} at pH 2.5 in 1×10^{-3} mol cm^{-3} NaCl. Receiving phase composition: 0.5×10^{-3} mol cm^{-3} NaSCN in 0.5×10^{-3} mol cm^{-3} NaCl at pH 2.5. Carrier concentration (**3c**): 3×10^{-5} mol cm^{-3} in cumene.

and the equilibrium constant, K_{ex} by

$$K_{ex} = \frac{[CuL_2]_{org}[H^+]^2}{[Cu^{2+}][HL]^2_{org}} \quad (3)$$

where HL is the organic extractant.

Model

The mass transfer of Cu^{II} across the membrane is described considering only diffusional parameters. The interfacial flux due to the chemical reaction has been neglected, as the chemical reactions taking place at aqueous feed solution–membrane and membrane–stripping aqueous solution interfaces are sufficiently fast, and previous studies suggest that rapid chemical reactions can be considered to occur instantaneously relative to the diffusion processes.[34] Therefore, the Cu^{II} transport rate is determined by the rate of diffusion of copper-containing species through the feed diffusion layer and the rate of diffusion of the CuL_2 species through the membrane. Then, the flux of Cu^{II} crossing the membrane may be derived by applying Fick's first diffusion law to the diffusion layer at the feed side and to the membrane.

The diffusional fluxes in the feed aqueous boundary layer, J_a, and in the membrane phase, J_o, can be expressed by the following equations, where Δ_a and Δ_o are diffusional resistances caused by the aqueous feed boundary layer and due to diffusion through the membrane, respectvely.

$$J_a = \Delta_a^{-1}([Cu^{II}]_{tot} - [Cu^{II}]_{i,\,tot}) \quad (4)$$

$$J_o = \Delta_o^{-1}([CuL_2]_{i,\,f} - [CuL_2]_{i,\,s}) \quad (5)$$

As the distribution coefficient of Cu^{II} between the membrane and the stripping phase is much lower than that between the feed phase and the membrane, the concentration of the metal-extracted complexes in the membrane phase at the stripping solution side may be negligible compared with that at the feed solution side. Then, eqn. (5) can be written as:

$$J_o = \Delta_o^{-1}[CuL_2]_{i,\,f} \quad (6)$$

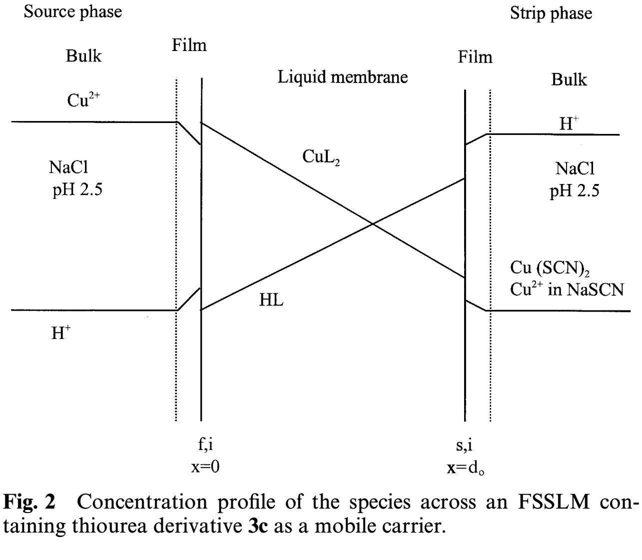

Fig. 2 Concentration profile of the species across an FSSLM containing thiourea derivative **3c** as a mobile carrier.

Furthermore, the following equilibrium occurs in the aqueous phase:

$$Cu^{II} + Cl^- \rightleftharpoons CuCl^+$$

with

$$\beta_1 = \frac{[CuCl^+]}{[Cu^{II}][Cl^-]} \quad (7)$$

Log $\beta_1 = 0.93$.[35]

The distribution coefficient of copper (D) is defined as

$$D = \frac{[CuL_2]_{org}}{[Cu^{II}]_{tot}} = \frac{K_{ex}}{1 + \beta_1[Cl^-]}\frac{[HL]^2_{org}}{[H^+]^2} = K'_{ex}\frac{[HL]^2_{org}}{[H^+]^2} \quad (8)$$

where $K_{ex} = 4.0 \pm 0.1$ and the conditional equilibrium constant $K'_{ex} = K_{ex}(1 + \beta_1[Cl^-])$.

If the chemical reaction expressed by eqn. (2) is assumed to be fast in the forward direction compared to the diffusion rate, local equilibrium at the interface is reached and concentrations at the interface are related through eqns. (3) and (7). Thus, at steady state, $J_a = J_o = J$ and combining eqns. (3), (4), (6) and (8), the following expression can be obtained:

$$J = \frac{[Cu^{II}]_{tot}K'_{ex}[HL]^2_{org}[H^+]^{-2}}{\Delta_o + \Delta_a K'_{ex}[HL]^2_{org}[H^+]^{-2}} \quad (9)$$

The permeability coefficient, $P = J/[Cu^{II}]_{tot}$, is given by:

$$P = \frac{K'_{ex}[HL]^2_{org}[H^+]^{-2}}{\Delta_o + \Delta_a K'_{ex}[HL]^2_{org}[H^+]^{-2}} \quad (10)$$

This expression combines in one equation the equilibrium and diffusion parameters involved in the Cu^{II} transport process from aqueous chloride media through supported liquid membranes using thiourea derivatives as carriers.

Eqn. (10) indicates that permeability is a function of the H^+ concentration in the feed phase and the extractant (HL) concentration in the membrane.

Results and discussion

The following parameters were studied to elucidate the kinetics and mechanism of the permeation of Cu^{II} using a thiourea derivative across an FSSLM: (*a*) structure of the carrier, (*b*) characteristics of the support material (*c*) pH of the source phase, (*d*) carrier concentration in the membrane, (*e*) copper concentration in the feed phase, and (*f*) nature and type of stripping agent in the receiving phase. It was observed that the logarithm of the concentration of Cu^{II} in either the feed or strip solutions varies linearly with time over a period of at least 3 h. The slope of the resultant straight line gave the permeability coefficient [eqn. (1)] from which the flux (J) was calculated according to the following relationship:

$$J = P_{Cu} \cdot [Cu^{II}]_{tot} \tag{11}$$

Effect of carrier structure on Cu^{II} permeability

The solvent extraction behaviour of **3a**–**f** in cumene with Cu^{II} indicates that their performance should be satisfactory in liquid membrane experiments as their distribution ratio (D) in solvent extraction studies ranged between 1–100 except for **3a**. However, D values ranged between 0.01 and 0.1 for the **2a**–**c** series, which also gave poor performance as carrier in LM.[33] The permeability behaviour of these compounds for Cu^{II} were in the following order:

$$\mathbf{3e} > \mathbf{3c} \approx \mathbf{3d} \gg \mathbf{3f} \approx \mathbf{3b} \approx \mathbf{3a} \approx \mathbf{2c} \approx \mathbf{2a} \approx \mathbf{2b}$$

Of the carriers used, **2a**–**c** have shown poor permeability of the metal ion, as their metal recovery never exceeded 10% in the receiving phase. The permeability coefficients of **2a**–**c** and **3a**–**f** with Cu^{II} are presented in Table 4. It is evident from Fig. 3 that *N*-(thiocarbamoyl)benzamide derivatives are comparatively poorer carriers than *N*-benzoylthiourea derivatives. This may be explained in terms of the structure of the compounds, that is, the possible formation of a six-membered ring for series **2a**–**c** with an intramolecular hydrogen bond which may constitute a drawback for the reaction with copper. On the other hand, compounds **3c**–**f** have alkyl chains of varying lengths (Table 2). In this way, the solubility of the organic reagent in cumene was increased as compared to **2a**–**c**. The permeation behaviour of Cu^{II} was found to improve with **3c**–**e**. The results obtained show that the solubility is directly related to the lipophilicity of the alkyl chain, which systematically increases from **3f** to **3c**. Similar behaviour was observed by Antico *et al.*[31] while studying liquid membrane transport of Pd^{II} with thiourea derivatives dissolved in cumene across an SLM. Bearing this in mind, the entire study was carried out using **3c** as a carrier and taking into account the complete stripping of Cu^{II} into the receiving phase.

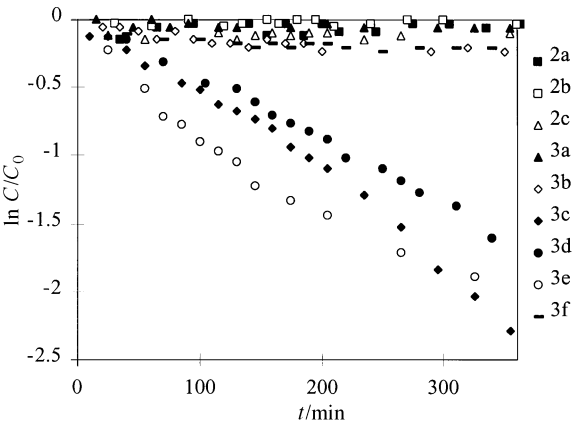

Fig. 3 The permeability behaviour of copper ion with carriers **2a**–**c** and **3a**–**f** dissolved in cumene as a function of time. Cu^{II}: 1.0×10^{-7} mol cm^{-3} in 1×10^{-3} mol cm^{-3} Cl^-, pH 2.5. Extractant concentration: 3.0×10^{-5} mol cm^{-3}. Stripping solution: 0.5×10^{-3} mol cm^{-3} NaSCN in 0.5×10^{-3} mol cm^{-3} Cl^- at pH 2.5. Stirring rate: 1200 rpm. Support: Durapore.

Table 4 Permeability coefficients of Cu^{II} with thiourea derivatives as ionophores[a]

Carrier	$P_{Cu}/10^{-5}$ cm s^{-1}
2a	2.9
2b	0.02
2c	2.6
3a	2.9
3b	1.2
3c	186
3d	150
3e	230
3f	15

[a] Source phase composition, Cu^{II}: 1×10^{-7} mol cm^{-3} at pH 2.5 in 1×10^{-3} mol cm^{-3} NaCl. Receiving phase composition: 0.5×10^{-3} mol cm^{-3} NaSCN in 0.5×10^{-3} mol cm^{-3} NaCl at pH 2.5. Carrier concentration (**3c**): 7×10^{-6} mol cm^{-3} in cumene.

Influence of support material on the permeability of Cu^{II}

The characteristics of the polymeric support play an important role in the effectiveness of the transport of metal species.[3] Membranes supported on the polymers listed in Table 3 were tested under identical experimental conditions. The flux values obtained are presented in Table 3. Celgard 2400 showed a reduction in transport flux in comparison with Celgard 2500, owing to a decrease in porosity (from 45% for Celgard 2500 to 38% for Celgard 2400 at constant thickness), which resulted in a decrease in the area of liquid membrane available for complexation of the metal ion. The polymeric microporous solid support, Durapure, was selected throughout the study as it gave the best performance.

Influence of stirring speed

In order to achieve effective permeation of Cu^{II} in an FSSLM system, it is necessary to explore the effect of stirring speed on the permeability coefficient. Diffusional resistances encountered during the transport of a metal ion across a supported liquid membrane are of two types: (*a*) the resistance due to the liquid boundary layer and (*b*) that due to the membrane. Indeed, in many cases the magnitude of the boundary layer resistance is comparable to or even greater than the membrane resistance.[36] In the present investigations, stirring of the source and receiving phases was carried out from 200 to 2000 rpm (Fig. 4). The permeability coefficient increased from 200 to 1100 rpm, and beyond that no appreciable increase in Cu^{II} permeability was observed. This indicates that the aqueous boundary layer thickness diminishes continuously with increasing stirring speed and that the boundary layer is a minimum above 1000 rpm for the difference ($[Cu^{II}]_b - [Cu^{II}]_{i,\,tot}$), and the permeability coefficient remains constant in the range 1000 to 1200 rpm. At high concentrations of $[Cu^{II}]$ this difference is indistinguishable with respect to $[Cu^{II}]_b$, as the carrier concentration reaches saturation. Therefore, the appearance of a plateau region does not neces-

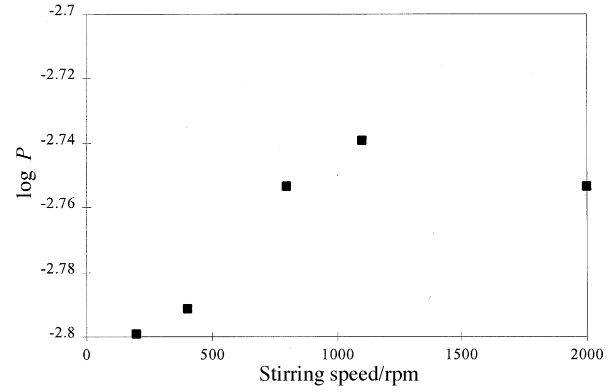

Fig. 4 Influence of stirring speed on permeability of Cu^{II} as a function of log P_{Cu}. See Fig. 3 for conditions.

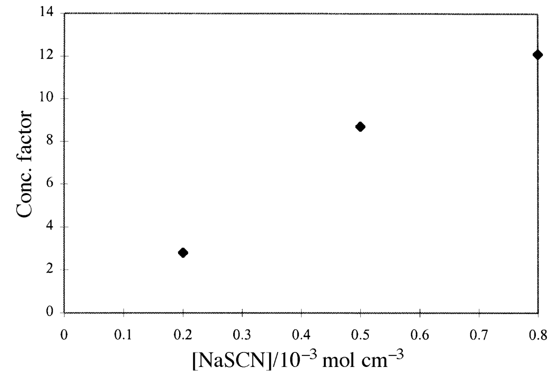

Fig. 5 Effect of thiocyanate concentration on permeability of Cu^{II} as a function of concentration factor. See Fig. 3 for conditions.

sarily mean the elimination of the aqueous diffusion layer, although the resistance due to it is minimized.[37] Further, a slight decrease in permeability at 2000 rpm could be due to the high turbulence caused by stirring, resulting in displacement of carrier from the membrane pore. Thus, a stirring speed of 1200 rpm was maintained throughout the subsequent FSSLM investigations.

Effect of different strippants

Since the extraction and stripping processes in FSSLM systems are carried out simultaneously for continuous transport of metal ion, it is important to examine the effect of different strippants in the receiving phase in order to enhance effective ion transport by making the stripping process efficient at the interface of the membrane and receiving solutions. Of several strippants tested, such as thiourea (0.5×10^{-3} mol cm^{-3}), sodium thiocyanate (0.5×10^{-3} mol cm^{-3}) and HCl (1×10^{-3} mol cm^{-3}), sodium thiosulfate (0.5×10^{-3} mol cm^{-3} in 0.5×10^{-3} mol cm^{-3} NaCl) proved to be the most efficient.

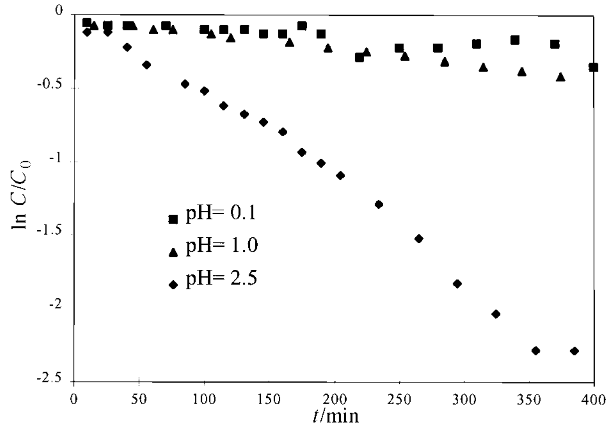

Fig. 6 Influence of initial pH on permeability of Cu^{II} as a function of ln C/C_0. See Fig. 3 for conditions.

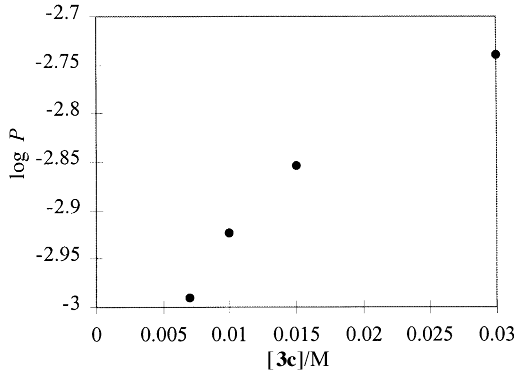

Fig. 7 The influence of carrier (**3c**) concentration on copper permeability. See Fig. 3 for conditions.

Effect of NaSCN concentration in the receiving phase

The effect of NaSCN concentration has been studied in the range 0.2–0.8 $\times 10^{-3}$ mol cm^{-3} NaSCN in 0.5×10^{-3} mol cm^{-3} NaCl using **3c** as carrier. There was no copper transport without thiocyanate. The permeability coefficient increased with the increase in thiocyanate concentration. The maximum flux of copper, 5.5×10^{-10} mol cm^{-2} s^{-1}, was obtained when the receiving phase contained 0.8×10^{-3} mol cm^{-3} thiocyanate. The plot of the concentration factor $[\mathrm{Cu^{II}}]_{\mathrm{p,\,4h}}/[\mathrm{Cu^{II}}]_{\mathrm{f,\,4h}}$ [ratio of the concentration of copper in product (p) and feed (f) after 4 h] *versus* thiocyanate concentration is depicted in Fig. 5. The reason for selecting 0.5×10^{-3} mol cm^{-3} SCN$^-$ concentration in the receiving phase was the reproducibility of the results, because a 0.8×10^{-3} mol cm^{-3} thiocyanate concentration resulted in poor reproducibility.

Effect of source phase pH

In an FSSLM system, the pH gradient between source and stripping phases is one of the important driving forces for the permeation of the metal ion. In order to assess the role of source phase pH, pH variation studies in the range of 0.1 to 2.5 were carried out in the presence of 10^{-3} mol cm^{-3} NaCl in the source phase. The receiving phase consisted of 0.5×10^{-3} mol cm^{-3} NaSCN in 0.5×10^{-3} mol cm^{-3} NaCl at pH 2.5. Equal ionic strength was maintained in the source and receiving phases to provide better membrane stability conditions. The concentration of membrane carrier **3c** was 7.0×10^{-6} mol cm^{-3}. It is evident from Fig. 6 that the permeability of copper increases with an increase in pH from 0.1 to 2.5, although at higher pH it remained unaffected (not shown in figure). Moreover, at low H$^+$ concentration the diffusion of carrier through the membrane becomes rate determining. From the permeability equation [eqn. (10)], two limiting cases can be derived:

(*a*) at low pH and high carrier concentration, the equation reduces to:

$$P_{\mathrm{Cu}} = \frac{K'_{\mathrm{ex}}[\mathrm{HL}]^2[\mathrm{H^+}]^{-2}}{\Delta_{\mathrm{o}}} \tag{12}$$

$$\log P_{\mathrm{Cu}} = \log K'_{\mathrm{ex}} + 2\log[\mathrm{HL}] - \log \Delta_{\mathrm{o}} + 2\mathrm{pH} \tag{13}$$

and the flux can be defined as:

$$\log J = \log K'_{\mathrm{ex}} + 2\log[\mathrm{HL}] - \log \Delta_{\mathrm{o}} + 2\mathrm{pH} + \log[\mathrm{Cu^{II}}] \tag{14}$$

(*b*) at high pH and high carrier concentration, the equation reduces to:

$$P_{\mathrm{Cu}} = \frac{1}{\Delta_{\mathrm{a}}} \tag{15}$$

and permeability is independent of pH.

Effect of extractant concentration on the permeability of Cu^{II}

The carrier plays a significant role in making the FSSLM system efficient and economically viable. Therefore, it is essential to evaluate the effect of carrier concentration on the permeability of Cu^{II}. A supported liquid membrane having no carrier immobilized on the support results in no transport of copper cations. The effect of **3c** concentrations on P_{cu} was studied from 7×10^{-6} to 3.0×10^{-5} mol cm^{-3}. As can be seen from Fig. 7, the permeability of Cu^{II} increases with carrier concentration and the permeability coefficient has a maxima at a **3c** concentration of 3.0×10^{-5} mol cm^{-3} ($P_{Cu} = 1.86 \times 10^{-3}$ cm s^{-1}). However, beyond a certain limiting concentration, the permeability coefficient approaches a maximum, P_{lim}, and levels off. The value of P_{lim} is equal to $1/\Delta_a = 1.6 \times 10^{-3}$ cm s^{-1}. This is due to the fact that at low **3c** concentrations, diffusion of the complex across the liquid membrane is the rate-determining step, while at higher **3c** concentrations, diffusion of the cation across the aqueous phase boundary layers is the rate-determining step. A similar behaviour of permeability with ligand concentration has been observed by Danesi *et al.*[38] The recovery of copper in the stripping phase exceeds 95% at a **3c** concentration of 3×10^{-5} mol cm^{-3} in the membrane phase; thus, this **3c** concentration was selected throughout the study. Assuming that the carrier concentration in the membrane phase is constant, the following equation can be written to determine the apparent diffusion coefficient of copper:[39]

$$D_o^a = Jd_o/[\mathrm{HL}] \tag{16}$$

The value of D_o^a was calculated to be 2.9×10^{-6} cm^2 s^{-1}, taking a Durapore support of thickness 125×10^{-4} cm and using a carrier concentration of 7×10^{-6} mol cm^{-3}. A similar value (2.0×10^{-6} cm^2 s^{-1}) for the apparent diffusion coefficient was obtained by Bromberg *et al.* while performing liquid membrane studies of silver using di(2-ethylhexl) dithiophosphoric acid as carrier.[40]

Effect of membrane solvent on the permeability of Cu^{II}

The LM solvent is equally an important parameter to obtain stable FSSLMs, as the characteristics of the diluents are mainly responsible for the stable liquid membrane phase. Permeation of Cu^{II} in the receiving phase was more than 95% with the diluents cumene and kerosene. This may be owing to the low volatility and low aqueous solubility of cumene and kerosene. The results of Cu^{II} permeability using various diluents are presented in Fig. 8. In solvent extraction studies, the performance of kerosene and cumene as diluents was satisfactory, and further improved in LM as expected. However, toluene as a membrane solvent showed poor results in spite of its satisfactory performance in solvent extraction.[33] The reason for this behaviour of toluene is under investigation.

Effect of metal concentration on the permeability of Cu^{II}

Figure 9 shows a plot of the initial copper ion flux (J) *versus* the concentration of copper ranging from $1–3 \times 10^{-7}$ mol cm^{-3} in the source phase. At low copper ion concentrations, the average initial flux is a strong function of the initial concentration in the source phase. Hence, the permeation process is controlled by diffusion of metal species in the lower range of copper concentrations. However, beyond a certain limiting concentration, J approaches a maximum and levels off. The most probable reason for this may be the rate-determining step for the permeation process. Under the limiting condition the total concentration of **3c** [HL] becomes equivalent to $[\mathrm{CuL_2}]_{org}$, and on the basis of the following equation:[37]

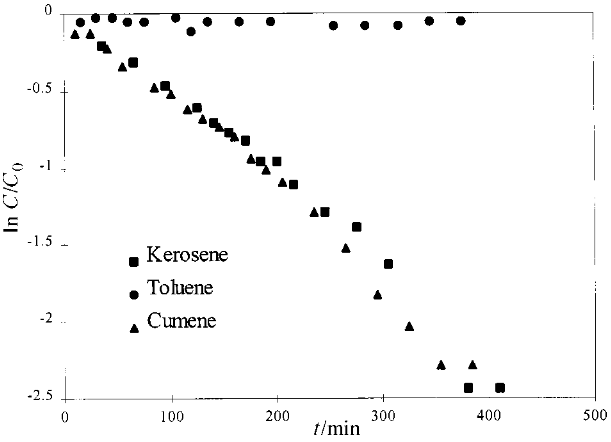

Fig. 8 Effect of different diluents on the permeability of Cu^{II} with carrier **3c** as a function of ln C/C_o. See Fig. 3 for conditions.

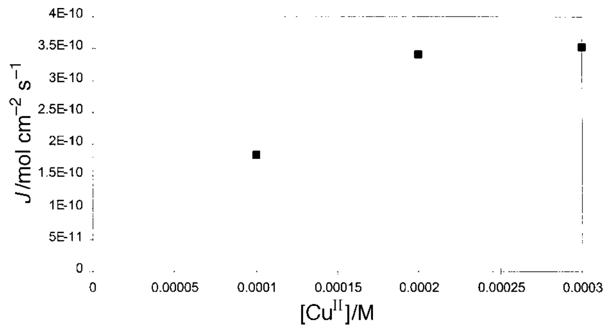

Fig. 9 The influence of initial concentration of Cu^{II} on the permeability flux (J) of Cu^{II} with carrier **3c**. See Fig. 3 for conditions.

$$J_{lim} = \frac{D_o}{d_o} \frac{[\mathrm{CuL_2}]_{org}}{n} \tag{17}$$

where n is the stoichiometric coefficient of the reaction. The value of J_{lim} is determined to be 1.4×10^{-9} mol cm^{-2} s^{-1}.

Evaluation of diffusional parameters

As can be seen from Fig. 10, plotting $1/P$ as a function of $1/AB$ (where $A = K'_{ex}\,[\mathrm{HL}]^2_{org}$ and $B = [\mathrm{H}^+]^{-2}$) for different extractant concentrations of **3c** in 1 mol cm^{-3} Cl$^-$ at pH 2.5, should give a straight line with slope Δ_o and ordinate Δ_a. The calculated value of the diffusion coefficient ($\Delta_o = d_o/D_o$, $d_o = 0.0125$ cm) was $D_o = 1.17 \times 10^{-6}$ cm^2 s^{-1}. The mass transfer coefficient (Δ_a^{-1}) was calculated to be 1.6×10^{-3} cm s^{-1}. In addition, assuming $D_a \approx 10^{-5}$ cm^2 s^{-1},[41] the thickness of the aqueous boundary layer was calculated to be approximately 1.0×10^{-3} cm, which is almost of the same order of magnitude as reported by other researchers in earlier studies.[40] The diffusion coefficient of the copper complexes in the bulk organic phase, $D_{o,\,b}$, can be evaluated from the diffusivity (D_o) in the membrane with micropores from the relation[42] $D_{o,\,b} = D_o\tau'$, where $\tau' = \tau^2/\varepsilon$. The value of $D_{o,\,b}$ was calculated to be 2.60×10^{-6} cm^2 s^{-1}. Theoretically, apparent and bulk diffusion coefficients are the same but their method of evalution is different as explained earlier. It is interesting to note that in the present liquid membrane system, the bulk diffusion coefficient ($D_{o,\,b}$) and apparent diffusion coefficient (D_o^a) are almost

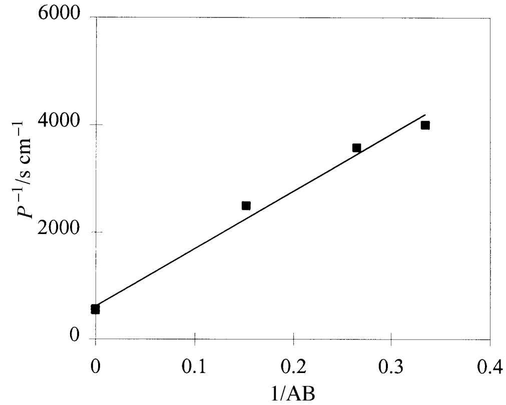

Fig. 10 Plot of $1/AB$ *vs.* $1/P$ for carrier **3c** (for more details see text).

of the same order of magnitude whereas D_o is roughly half of $D_{o,\,b}$ and D_o^a, which is due to diffusional resistance caused by a microporous thin membrane placed between the feed and receiving phases.

Conclusions

Of the thiourea derivatives used as membrane carriers, **3c** is highly efficient for copper transport across an FSSLM. Based on the present kinetic model for copper permeation, it can be inferred that the permeation process is controlled by diffusion of metal ions across the feed aqueous layer and the metal carrier complex across the liquid membrane phase. Furthermore, the role of membrane diffusion becomes dominant under the conditions of high $[Cu^{II}]_{tot}$, high pH and low carrier concentrations in the membrane phase.

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