

# Modelling of mass transfer in facilitated supported liquid membrane transport of copper(II) using MOC-55 TD in Iberfluid

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## Abstract

The transport of copper(II) through a supported liquid membrane using MOC-55 TD (oxime derivative), dissolved in Iberfluid, as a carrier has been studied. A physico-chemical model is derived to describe the transport mechanism which consists of: diffusion process through the feed aqueous diffusion layer, fast interfacial chemical reaction and diffusion through the membrane. The experimental data can be explained by mathematical equations describing the rate of transport. The mass transfer coefficient was calculated from the described model as  $2.8 \times 10^{-3} \text{ cm s}^{-1}$ , the thickness of the aqueous boundary layer as  $2.6 \times 10^{-3} \text{ cm}^{-1}$  and the membrane diffusion coefficient of the copper-containing species as  $1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Copper(II) permeability; MOC-55 TD; Supported liquid membrane

## 1. Introduction

Liquid–liquid extraction is widely used in the processing of a number of non-ferrous metals; this is particularly sound in the case of copper in which the application of this technology, based in the right choice of suitable extractants: oximes, produces the most economical copper in the world.

However, a great majority of natural mining waters or leach residual solutions contain less than  $1.0 \text{ g dm}^{-3}$  copper, thus, they are considered as very dilute streams unsuited to be treated by conventional liquid–liquid extraction processing [1].

The use of liquid membranes containing a carrier has been proposed as an alternative to liquid–liquid extraction technology for the selective separation and concentration of copper (and other metals) from dilute aqueous solutions. Two configurations of liquid membranes are currently being used: supported liquid membranes (SLMs) and liquid surfactant membranes (LSMs); in both cases, the extraction, stripping and regeneration stages are combined in a single one [2].

Several studies deal about the use of liquid membranes on copper extraction from various aqueous media and using different extractants [1,3–16].

MOC-55 TD, an oxime based extractant, has been proved to be a suitable and selective reagent for Cu(II) when used in liquid–liquid extraction [17]; however, no data is available about its uses in liquid membrane technology.

In the present work, the transport of Cu(II) from sulphate solutions through a supported liquid membrane

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### Nomenclature

$\Delta_{aq} = d_a/D_a$	transport resistance due to diffusion by the aqueous feed boundary layer ( $\text{s cm}^{-1}$ )
$\Delta_{org} = d_{org}/D_{org}$	transport resistance due to diffusion through the membrane ( $\text{s cm}^{-1}$ )
$d_a$	thickness of the aqueous feed boundary layer (cm)
$d_{org}$	thickness of the membrane (cm)
$D_a$	average aqueous diffusion coefficient of the copper-containing species ( $\text{cm}^2 \text{s}^{-1}$ )
$D_{b,org}$	diffusion coefficient of the copper-containing species in the bulk phase
$D_{org}$	membrane diffusion coefficient of the copper-containing species ( $\text{cm}^2 \text{s}^{-1}$ )
$J$	copper flux ( $\text{mol cm}^{-2} \text{s}^{-1}$ )
$M$	molecular weight of the diluent ( $\text{g mol}^{-1}$ )
$T$	absolute temperature (K)
$V$	molar volume of the extractant ( $\text{cm}^3 \text{mol}^{-1}$ )
$X$	association parameter of the diluent

### Greek letters

$\tau$	Tortuosity of the membrane
$\tau' = \tau^2/\varepsilon$	Membrane constant
$\mu$	Dynamic viscosity of the diluent (cP)

impregnated with MOC-55 TD dissolved in Iberfluid is studied and a permeation model describing the transport mechanism is reported.

## 2. Experimental

### 2.1. Reagents and solutions

MOC-55 TD (actually a product from Cognis (ex-Henkel Corp.)) was obtained from its former manufacturer Allco Chem. (Inspec Mining Co.); and was used without further purification. Its characteristics

were given elsewhere, being the active component of the reagent 5-dodecylsalicylaldoxime [17].

Iberfluid (CS, Spain) was employed as organic diluent for MOC-55 TD and has the following specifications: density  $782 \text{ kg m}^{-3}$ , boiling range  $210\text{--}284^\circ\text{C}$ , flash point  $96^\circ\text{C}$ , aromatic components  $<2\%$ .

Stock metal solutions were prepared by dissolving the required amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Panreac) in distilled water. All the other chemicals used in this work were of reagent grade.

### 2.2. Membrane

The flat-sheet supported liquid membrane was impregnated with a carrier solution containing MOC-55 TD dissolved in Iberfluid by immersion for 24 h and then leaving it to drip for a few seconds before being placed in the transport cell. Previous experiments had shown that prolonged immersion times (e.g. 36 and 48 h) of the membrane in the carrier solution had not influence respect to the permeation coefficient values obtained using 24 h.

The flat-sheet membrane used was Millipore Durapore GVHP 4700 of  $12.5 \times 10^{-3} \text{ cm}$  thick microporous polyvinylidenedifluoride (PVDF) film with nominal porosity of 75%, effective pore size of  $2.2 \times 10^{-5} \text{ cm}$  and tortuosity 1.67 [18].

### 2.3. Transport experiments

The batch transport experiments were carried out in a permeation cell consisting of two cubic compartments made of methacrylate and separated by the microporous membrane. The membrane geometrical area was  $11.33 \text{ cm}^2$  and the volume of the source and receiving solutions 200 ml.

The experiments were performed at  $20^\circ\text{C}$  at a mechanical stirring speed of 1600 rpm in the receiving phase and 1600 rpm in the source phase, except in the experiments where the stirring speed was varied. Agitation was performed in both compartments by using cylindrical Teflon impellers having a diameter of 2.4 cm.

In preliminary studies, various sulphuric acid concentrations were tested as receiving phases. Solutions which contained  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$  gave the best performance for copper stripping and were employed as receiving phase in all the experimental runs.

Membrane permeability was determined by monitoring copper concentration by atomic absorption spectrophotometry (Perkin-Elmer 1100B) in the source phase as a function of time. The copper concentration in the various phases was found to be reproducible within  $\pm 2.5\%$ . The permeation coefficient ( $P_{\text{Cu}}$ ) was computed by the following equation:

$$P_{\text{Cu}} = \frac{-d[\text{Cu}]_{\text{feed}}}{dt} \frac{V}{Q [\text{Cu}]_{\text{feed}}} \quad (1)$$

where  $Q$  and  $V$  are the effective membrane area and the volume of feed solution. Additional experiments were performed to study the membrane stability, results obtained at this speed range (600–2000 rpm) show that the permeability values are constant and reproducible within  $\pm 3\%$ .

### 3. Results and discussion

#### 3.1. Influence of stirring speed of the source phase

The influence of the stirring speed of the source phase was studied in order to optimise uniform mixing of both aqueous phases and to minimise thickness of aqueous boundary layer with feed and strip conditions being maintained as:  $7.9 \times 10^{-5}$  M of Cu(II) at pH 2.5 and  $180 \text{ g dm}^{-3}$   $\text{H}_2\text{SO}_4$ , respectively. The extractant concentration was 0.36 M in Iberfluid immobilised on a Durapore microporous support. Fig. 1 shows the results obtained, the permeability coefficient ( $P_{\text{Cu}}$ ) becomes virtually independent of the stirring speed above 1200 rpm, indicating a decrease in the aqueous boundary layer thickness, and then a minimum value of thickness is reached at this range.

The stirring speed of the source phase was kept constant at 1600 rpm throughout the experiments conducted and keeping constant the agitation of the receiving phase also at 1600 rpm (previous experiments had shown that the variation of the stirring speed of this phase had not great influence on copper permeation, though data are not reported here).

#### 3.2. Effect of the pH of the source phase solution

In order to assess the significance of the role of the pH of the source phase solution during the permeation

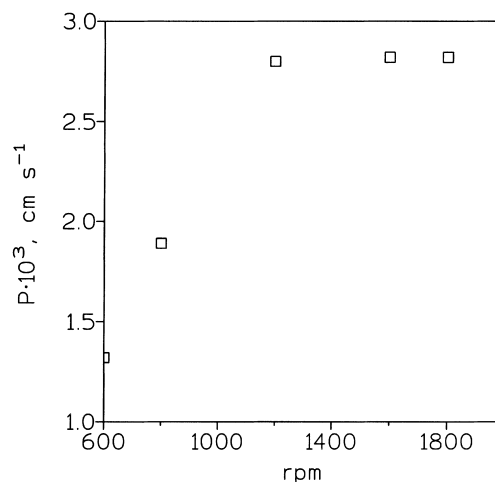


Fig. 1. Variation of copper permeability coefficient with the stirring speed of the source phase.

of copper, pH variation studies in the range 1.0–3.0 were carried out using a receiving phase of  $180 \text{ g dm}^{-3}$   $\text{H}_2\text{SO}_4$  and being the concentration of the membrane carrier of 0.36 M.

As seen from Fig. 2, permeability of copper increased with increases in the pH value up to 2.5. Similar results were obtained varying MOC-55 TD concentrations (0.09–0.36 M) in Iberfluid.

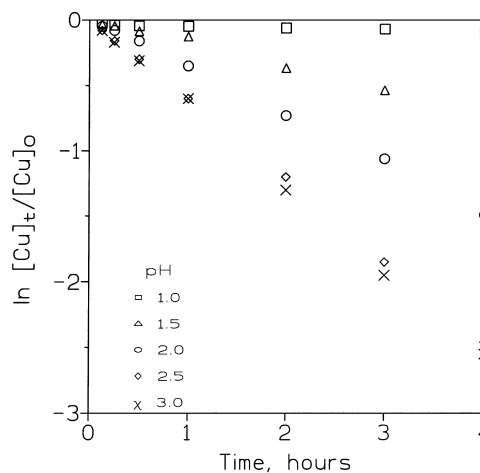


Fig. 2. Influence of pH (source phase) on copper permeation. Source phase:  $7.9 \times 10^{-5}$  M Cu(II).

Table 1  
Copper permeability at various MOC-55 TD concentrations<sup>a</sup>

[MOC-55 TD] (M)	$P_{\text{Cu}} \times 10^3 \text{ (cm s}^{-1}\text{)}$
0.09	2.70
0.14	2.73
0.18	2.76
0.27	2.79
0.36	2.82

<sup>a</sup> Permeation coefficients reproducible  $\pm 3\%$ .

### 3.3. Effect of MOC-55 TD concentration on permeability of copper

The results concerning transport of copper from the source phase containing  $7.9 \times 10^{-5} \text{ M Cu(II)}$  at pH 2.5 and the receiving phase  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ , and varying concentration of the carrier in the range 0.09–0.36 M dissolved in Iberfluid revealed no significant change in  $P_{\text{Cu}}$  with carrier concentration (Table 1).

This constant permeability value  $P_{\text{lim}}$ , known as limiting permeability, could be explained by assuming that diffusion in the organic membrane is negligible compared with the term accounting for aqueous diffusion in Eq. (5) and the permeation process is controlled by the diffusion in the stagnant film of the aqueous feed phase ( $P_{\text{lim}} = 1/\Delta_{\text{aq}} = 2.8 \times 10^{-3} \text{ cm s}^{-1}$ ).

### 3.4. Effect of ionic strength on the permeation of copper

Experiments conducted to study the influence of the variation of the ionic strength of the source phase ( $7.9 \times 10^{-5} \text{ M Cu(II)}$  at pH 2.5) when the receiving phase was of  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$  and the carrier solution of 0.36 M MOC-55 TD in Iberfluid, shows that there is only a very slight decrease in the copper permeation coefficient when the aqueous ionic strength is increased (e.g.  $2.8 \times 10^{-3}$  and  $2.7 \times 10^{-3} \text{ cm s}^{-1}$  at 0 and 1 M  $\text{Na}_2\text{SO}_4$ , respectively).

### 3.5. Effect of metal concentration on permeability of copper

Studying the effect of the initial concentration of copper ( $3.9 \times 10^{-5}$ – $3.9 \times 10^{-4} \text{ M}$ ) in the source

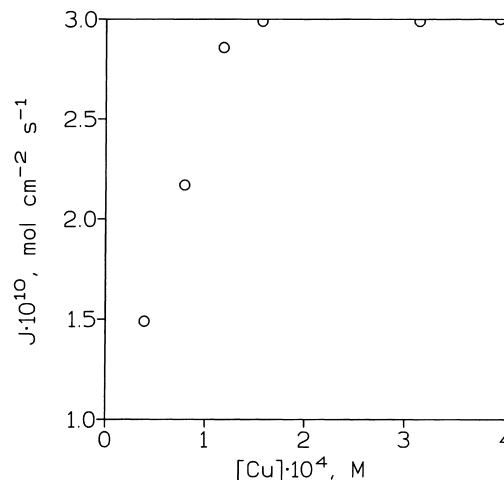


Fig. 3. Influence of initial concentration of Cu(II) on permeability flux ( $J$ ) of the metal. Source phase: Cu(II) at pH 2.5. Extractant concentration: 0.18 M MOC-55 TD in Iberfluid. Receiving phase:  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ .

phase of pH 2.5, when the receiving phase contained a negligible concentration of copper, it was shown that the cation flux initially increased sharply from  $3.9 \times 10^{-5}$ – $1.2 \times 10^{-4} \text{ M}$  and beyond this became independent of the initial concentration, ranging from  $1.6 \times 10^{-4}$ – $3.9 \times 10^{-4} \text{ M}$ .

The results of copper permeability flux through the membrane as a function of copper concentration are shown in Fig. 3. The initial increase in copper permeability is partly in accordance with the expected trend, since the flux of a cation varies with metal concentration accordingly with the ratio

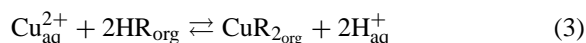
$$J \propto [\text{Cu}]_{\text{feed}} \quad (2)$$

and hence, there should be an increase in flux with an increase in metal concentration. Evidently, this is true up to  $1.6 \times 10^{-4} \text{ M}$  concentration of copper, beyond which  $J$  became constant, probably due to membrane saturation and lower effective membrane area in the supported liquid membrane and secondly due to maximisation as a result of saturation of membrane pores with metal carrier species and build-up of the carrier layer on the membrane interface, enhancing the retention of the separating constituent on the entry side and thus causing the permeability flux to be constant.

### 3.6. Permeation model of Cu(II) across the supported liquid membrane

In the membrane permeation using the supported liquid membrane, the solute diffuses through the aqueous feed boundary layer and reacts with the carrier at the interface, resulting in the formation of the complex species. Then, the complex species diffuses through the membrane to the receiving phase because of the concentration gradient of the metal species. Finally, the metal carrier complexes release metal ions into the aqueous strip solution at the interface.

The extraction of Cu(II) by the organic extractant MOC-55 TD dissolved in Iberfluid has been studied and described elsewhere [17]. The extraction equilibrium can be described by the following reaction and extraction constant:



$$K_{\text{ext}} = \frac{[\text{CuR}_2]_{\text{org}}[\text{H}^+]_{\text{aq}}^2}{[\text{Cu}^{2+}]_{\text{aq}}[\text{HR}]_{\text{org}}^2} \quad (4)$$

where HR is the extractant and  $\text{CuR}_2$  the copper-oxime species formed in the organic phase. The value of  $K_{\text{ext}}$  was found to be 89.13. The mass transfer of the metal crossing the membrane is described considering only diffusional parameters. The interfacial flux due to the chemical reaction has been neglected, as the chemical reactions seem to take place at the aqueous feed solution/membrane and membrane/stripping aqueous solution interfaces, and previous studies suggest that chemical reactions can be considered to occur instantaneously relative to the diffusion processes. Therefore, the metal transport is determined by the rate of diffusion of the metal-containing species through the feed diffusion layer and the rate of diffusion of metal-carrier species through the membrane. Then, the flux of the metal crossing the membrane may be derived by applying Fick's first diffusion law to the diffusion layer on the feed side and to the membrane [18].

Accordingly, the permeability coefficient  $P_{\text{Cu}} = J/[\text{Cu}]_{\text{tot}}$  can be written as

$$P = \frac{K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}}{\Delta_{\text{org}} + \Delta_{\text{aq}}(K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2})} \quad (5)$$

This expression combines in one equation, the equilibrium and diffusion parameters involved in the Cu(II)

transport process through a supported liquid membrane using MOC-55 TD dissolved in Iberfluid as a carrier.

### 3.7. Evaluation of diffusional parameters

From Eq. (5), the next expression can be obtained

$$\frac{1}{P} = \Delta_{\text{aq}} + \frac{\Delta_{\text{org}}}{K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}} \quad (6)$$

By plotting  $1/P$  as a function of  $1/K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}$ , for different extractant concentrations and aqueous pH of 2.5, one should obtain a straight line with slope  $\Delta_{\text{org}}$  and ordinate to calculate  $\Delta_{\text{aq}}$ . The values of  $\Delta_{\text{org}}$  and  $\Delta_{\text{aq}}$  obtained from the proposed model are 1043714 and 357 s cm<sup>-1</sup>, respectively. The calculated value of the diffusion coefficient was  $D_{\text{org}} = 1.2 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, being of the same magnitude order than that obtained using the Wilkie and Chang equation [19]

$$D_{\text{org}} = \frac{7.4 \times 10^{-8} X^{0.5} T M^{0.5} \times 3600}{\mu V^{0.6}} \quad (7)$$

The mass transfer coefficient was calculated as  $\Delta_{\text{aq}}^{-1} = 2.8 \times 10^{-3}$  cm s<sup>-1</sup>. In addition, assuming  $D_{\text{aq}} = 7.2 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> [18], the thickness of the aqueous boundary layer was calculated to be  $2.6 \times 10^{-3}$  cm.

The diffusion coefficient of the copper complex in the bulk organic phase  $D_{\text{b,org}}$  can be evaluated from the diffusivity in the membrane with micropores,  $D_{\text{org}}$ , from the next ratio [20]

$$D_{\text{org}} = \frac{\varepsilon}{\tau^2} D_{\text{b,org}} = \frac{D_{\text{b,org}}}{\tau'} \quad (8)$$

The value of  $D_{\text{b,org}}$  was calculated to be  $4.5 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>.

## 4. Conclusions

MOC-55 TD dissolved in Iberfluid can be used successfully as a carrier for the facilitated membrane transport of copper using a supported liquid membrane. From the permeation model of Cu(II) derived, the permeability of the metal seems to be governed by the diffusion of copper species at the feed/membrane

interface. From the model presented, the mass transfer coefficient of  $2.8 \times 10^{-3} \text{ cm s}^{-1}$ , the thickness of the aqueous boundary layer of  $2.6 \times 10^{-3} \text{ cm}$  and the membrane diffusion coefficient of the copper-containing species of  $1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  were calculated. The results obtained in the present investigation being comparable to those obtained using other oxime derivatives as carriers in supported liquid membranes. The method developed can be used for the recovery of copper from sulphate media at a pH near 2.5.

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### References

- [1] F. Valenzuela, C. Basualto, C. Tapia, J. Sapag, Application of hollow-fiber supported liquid membrane technique to the selective recovery of a low content of copper from a Chilean mine water, *J. Membr. Sci.* 155 (1999) 163–168.
- [2] A.M. Sastre, A. Kumar, J.P. Shukla, R.K. Singh, Improved techniques in liquid membrane separations: an overview, *Sep. Purif. Methods* 27 (1998) 213–298.
- [3] P.R. Danesi, Separation of metal species by supported liquid membranes, *Sep. Sci. Technol.* 19 (1984) 857–894.
- [4] A. Alderman, M. Cox, R.F. Dalton, Hollow fibre supported liquid extraction of copper from chloride media using Acorga CLX50, in: D.H. Logsdail, M.J. Slater (Eds.), *Solvent Extraction in the Process Industries*, Vol. 2, Elsevier, London, UK, 1993, pp. 883–888.
- [5] J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, USA, 1993, pp. 345–366.
- [6] Z. Lazarova, L. Boyadzhiev, Kinetic aspects of copper(II) transport across liquid membrane containing LIX 860 as a carrier, *J. Membr. Sci.* 78 (1993) 239–245.
- [7] M. Campderrós, J. Marchese, Membrane transport of cobalt copper and nickel with triethylamine, *Indian J. Chem. Technol.* 1 (1994) 35–40.
- [8] A. Safavi, S. Rastegarzadeh, Selective and efficient uphill transport of Cu(II) through liquid membrane, *Talanta* 42 (1995) 2039–2042.
- [9] I. Alexandrova, G. Iordanov, Nickel transfer and selective transport through weak acid ion-exchange membrane based on poly (vinylchloride)/poly (methylmethacrylate-co-divinylbenzene) system, *J. Appl. Polym. Sci.* 60 (1996) 721–725.
- [10] D. Kralj, G.R. Breembroek, L. Brecevic, Selective dissolution of copper oxalate using supported liquid membranes, *Solvent Extr. Ion Exch.* 14 (1996) 705–712.
- [11] M. Szpakowska, Coupled transport of copper through different types of liquid membranes containing Acorga P-50 as carrier, *J. Membr. Sci.* 109 (1996) 77–86.
- [12] F.R. Valenzuela, C. Basualto, J. Sapag, C. Tapia, Membrane transport of copper with LIX 860 from acid leach waste solutions, *Min. Eng.* 10 (1997) 1421–1427.
- [13] K. Scott, *Handbook of Industrial Membranes*, Elsevier, Kidlington, UK, 1997, pp. 643–651.
- [14] M. Szpakowska, O.B. Nagy, Stability of supported liquid membranes containing Acorga P-50 as carrier, *J. Membr. Sci.* 129 (1997) 251–261.
- [15] R.F. De Ketelaere, J. van del Linden, Selective recuperation of copper by supported liquid membrane (SLM) extraction, Abstracts of the International Solvent Extraction Conference 1999 (ISEC'99), Barcelona, Spain, 1999, p. 171.
- [16] L. Wang, R. Paimin, R.W. Cattrall, S.D. Kolev, The use of a PVC-based Aliquat 336 membrane to extract Cd(II) and Cu(II) from chloride solutions, Abstracts of the International Solvent Extraction Conference 1999 (ISEC'99), p. 184.
- [17] N. Ocaña, F.J. Alguacil, Solvent extraction of iron(III) by MOC-55TD: experimental equilibrium study and demonstration of lack of influence on copper(II) extraction from sulphate solutions, *Hydrometallurgy* 48 (1998) 239–249.
- [18] A. Sastre, A. Madi, J.L. Cortina, N. Miralles, Modelling of mass transfer in facilitated supported liquid-membrane transport of gold(III) using phospholene derivatives as carriers, *J. Membr. Sci.* 139 (1998) 57–65.
- [19] J.F. Dozol, J. Casas, A.M. Sastre, Transport of cesium from reprocessing concentrate solutions through flat-sheet supported liquid membranes: influence of the extractant, *Sep. Sci. Technol.* 30 (1995) 435–448.
- [20] T.C. Huang, R.S. Juang, Rate and mechanism of divalent metal transport through supported liquid membrane containing di(2-ethylhexyl)phosphoric acid as mobile carrier, *J. Chem. Technol. Biotechnol.* 42 (1988) 1–17.