

Copper separation from nitrate/nitric acid media using Acorga M5640 extractant Part II. Supported liquid membrane study

F.J. Alguacil^{a,*}, M. Alonso^a, A.M. Sastre^b

^a Centro Nacional de Investigaciones Metalúrgicas (C.S.I.C.), Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, Spain

^b Department of Chemical Engineering, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, E-08028 Barcelona, Spain

Received 23 October 2000; received in revised form 19 March 2001; accepted 28 March 2001

Abstract

The facilitated transport of copper(II) from nitrate/nitric acid media through a flat-sheet supported liquid membrane (FSSLM) is investigated, using the commercially available oxime Acorga M5640 as ionophore, as a function of hydrodynamic conditions, concentration of copper (7.9×10^{-5} to 1.3×10^{-3} M) and H^+ (pH 1.0–2.0) and ionic strength in the feed solution, carrier concentration (5–40% v/v) in the membrane and support characteristics. The performance of the system is also compared using various diluents for the organic phase and against other available oxime extractants (MOC-55TD, LIX 860 and LIX 622). A model is presented that describes the transport mechanism, consisting of diffusion through a feed side 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 7.6×10^6 and 273 s/cm, respectively. It was observed that the copper flux across the membrane tends to reach a plateau at high concentration of copper or a low concentration of H^+ owing to carrier saturation within the membrane, and leads 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 2.0×10^{-8} cm²/s and 2.3×10^{-11} mol/cm² s, respectively. The values of the bulk diffusion coefficient ($D_{o,b}$) and diffusion coefficient (D_o) calculated from the model were 5.9×10^{-9} and 1.6×10^{-9} cm²/s, respectively. The polymeric microporous solid support, Durapore GVHP 04700, was selected throughout the study as it gave the best performance. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Nitrate/nitric acid; Acorga M5640; Membrane transport

1. Introduction

In 1986, it was questioned about considering supported liquid membranes (SLMs) as a new technology or a scientific curiosity [1]. After one and a half decade the supported liquid membranes techniques in flat-sheet (FSSLM), hollow-fibre (HFSLM) and spiral wound configurations are taking an unquestionable position due to their application in the recovery and separation of metal species from aqueous solutions [2,3]. It is also well worth notice here that expected membrane sales for 2002 will reached US\$ billionaire amounts [4].

The supported liquid membrane consists of an organic solution containing an extractant or carrier dissolved in a suitable diluent which impregnates the pores of a porous polymeric solid support by capillary action. The mem-

brane formed is clamped between two cells which are filled with an aqueous source and receiving phase and also constantly stirred, either mechanically or magnetically, in order to homogenize the corresponding solution and to reduce the thickness of the stagnant aqueous layers. One claimed advantage of the above configuration is that the extraction, stripping and regeneration operations are combined in a single stage [5], whereas it was also stated that from the engineering and practical standpoint, SLMs are of particular interest because of its stability and simplicity [6].

Research has been conducted into the types of compounds that can be used as complexing agents for copper(II) and also into their applications as carriers. It is often found that the organic carriers used for membrane permeation of copper(II) were derivatives of hydroxyoximes, which are widely used in solvent extraction processing of acidic copper-bearing solutions [7–21], though that other compounds were also used [22–29]. In the case of oxime derivatives, little work

* Corresponding author.

E-mail addresses: fjalgu@cenim.csic.es (F.J. Alguacil), sastre@eq.upc.es (A.M. Sastre).

Nomenclature

| | |
|-----------------|--|
| $[Cu]_b$ | bulk copper concentration |
| $[Cu]_{i,TOT}$ | total copper concentration at the feed phase–membrane interface |
| $[Cu]_{TOT}$ | total copper concentration in the feed phase |
| $[CuR_2]_{i,r}$ | CuR_2 organic concentration at the membrane–receiving phase interface |
| $[CuR_2]_{i,s}$ | CuR_2 organic concentration at the feed phase–membrane interface |
| d | membrane pore size |
| d_a | thickness of the aqueous feed boundary layer |
| d_0 | thickness of the membrane |
| D_a | average aqueous diffusion coefficient of the copper-containing species |
| D_o | membrane diffusion coefficient of the copper-containing species |
| D_o^a | Apparent diffusion coefficient of the copper-carrier species |
| $D_{o,b}$ | diffusion coefficient of the copper-containing species in the bulk organic phase |
| J | permeability flux |
| J_N | normalized flux |
| P | permeability coefficient |

Greek letters

| | |
|---------------|--|
| Δ_a | transport resistance due to diffusion by the aqueous feed boundary layer |
| Δ_o | transport resistance due to diffusion through the membrane |
| ε | membrane porosity |
| τ | tortuosity of the membrane |

has been done to evaluate their performance as carriers for copper from nitrate/nitric acid media in liquid membrane studies.

Before scaling-up the flat-sheet solid supported liquid membrane, 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 and efficient recovery process in terms of better stability.

This second part of the investigation presents the kinetic modeling of active transport of copper(II) using Acorga M5640 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 investigated in order to obtain efficient and stable FSSLMs.

2. Experimental

Copper stock solution was prepared by dissolving 5 g of electrolytic (grade A) copper in nitric acid and diluting to one liter with distilled water. All the other chemicals used were of AR grade unless stated otherwise. The extractants Acorga M5640, MOC-55TD, LIX 860 and LIX 622 were obtained from their respective manufacturers and were used as received. Some of their characteristics are presented in Table 1. Diluents used in the present study were Iberfluid (CS, Spain), Escaid 100, Solvesso 100 and Exxsol D100 (ExxonMobil Chem. Iberia, Spain) and Cumene (Fluka), their characteristics are given in Table 2.

2.1. FSSLM preparation and measurements

Batch FSSLM measurements were carried out with a two-compartment permeation cell that consisted of a source phase (200 ml) separating from a receiving chamber (200 ml) by a liquid membrane having an effective membrane area of 11.33 cm². As it was described elsewhere [30], solutions of 180 g/l sulphuric acid are suitable for copper stripping from loaded Acorga M5640-Iberfluid solutions and thus were employed as receiving phase in all the experimental runs. The source and receiving phases were mechanically stirred at 1350 min⁻¹ at 20 °C to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. Using 1350 min⁻¹, copper concentrations in the different phases such as center, corner or near membrane in the FSSLM cell were found to be reproducible within ±8%. Membrane permeabilities were determined by monitoring the copper concentration in the feed phase as a function of time by AAS using a Perkin-Elmer 1100B spectrophotometer. The permeation coefficient (P) was computed from the following equation:

$$\ln \frac{C_t}{C_0} = -\frac{A}{V}Pt \quad (1)$$

where V is the volume of the feed phase solution (cm³), A the effective membrane area (cm²), C_t and C_0 the concentrations of copper in the feed phase at a given time and time zero, respectively, and t is the elapsed time (s).

2.2. Membrane support

The organic membrane phase was prepared by dissolving the extractant in the diluent to obtain carrier solutions of various concentrations. The polymeric supports were impregnated with the carrier solutions containing the extractant 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 microporous supports are summarized in Table 3.

Table 1
The extractants used in the FSSLM transport of copper(II) from nitrate/nitric acid media

| Trade name | Active substance | Modifier | Manufacturer (former) |
|--------------|---------------------------|---------------|-----------------------|
| Acorga M5640 | 5-Nonylsalicyl-aldoxime | Unknown ester | AVECIA (Astra Zeneca) |
| MOC-55TD | 5-Dodecylsalicyl-aldoxime | Tridecanol | COGNIS (Henkel) |
| LIX 860 | 5-Dodecylsalicyl-aldoxime | No | COGNIS (Henkel) |
| LIX 622 | As LIX 860 | Tridecanol | COGNIS (Henkel) |

Table 2
Characteristics of the diluents used in the FSSLM transport of copper(II) by Acorga M5640

| Trade name | Aromatics (%) | Boiling range (°C) | Flash point (°C) | Density (kg/m ³) |
|---------------------|---------------|--------------------|------------------|------------------------------|
| Iberfluid | <2 | 210–284 | 96 | 785 |
| Escaid 100 | 20 | 200–250 | 78 | 805 |
| Solvesso 100 | >99 | 162–178 | 48 | 901 |
| Exxsol D100 | 0.9 | 234–264 | 99 | 816 |
| Cumene ^a | 100 | 153 | NA | 862 |

^a Data from Handbook of Chemistry and Physics, CRC Press, Boca Rattan.

Table 3
Characteristics and influence of the support used in the FSSLM transport of copper(II) by Acorga M5640

| Support | Thickness (μm) | Porosity (%) | Tortuosity ^a | Pore size (μm) | J (10 ⁻¹⁰ mol/cm ² s) ^b | J_N (10 ⁻¹⁰ mol/cm ² s) |
|----------------------|----------------|--------------|-------------------------|----------------|--|---|
| Durapore GVHP04700 | 125 | 75 | 1.67 | 0.22 | 5.8 | 5.8 |
| Durapore HVHP04700 | 125 | 75 | 1.67 | 0.45 | 3.6 | 3.6 |
| Fluoropore FGLP04700 | 175 | 70 | 1.86 | 0.22 | 3.1 | 5.2 |

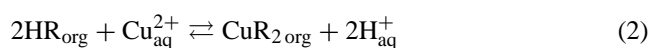
^a The value was evaluated according to the equation $\tau = (1 + V_p)/(1 - V_p)$, where $V_p (=1 - \varepsilon)$ is the volume fraction of the polymeric framework [31].

^b Source phase: 1.6×10^{-4} M Cu at pH 2.0 ± 0.02 ; membrane phase: 20% v/v Acorga M5640 in Iberfluid; receiving phase: 180 g/l sulphuric acid.

3. Results and discussion

3.1. Permeation model of copper(II) across FSSLMs

The extraction of copper by Acorga M5640 dissolved in Iberfluid has been studied and described before [30]. The extraction equilibrium can be described by



and the equilibrium constant, K_{ext} , is given by

$$K_{\text{ext}} = \frac{[\text{CuR}_2]_{\text{org}}[\text{H}^+]_{\text{aq}}^2}{[\text{HR}]_{\text{org}}^2[\text{Cu}^{2+}]_{\text{aq}}} \quad (3)$$

where HR represents the active substance of the extractant.

The mass transfer of copper across the membrane is described considering diffusional parameters. The interfacial flux due to the chemical reaction has not been considered, as the chemical reactions taking place at the aqueous feed phase–membrane and membrane–receiving solution interfaces are fast, and previous investigations suggest that rapid chemical reactions can be considered to occur instantaneously relative to the diffusion processes [32]. Therefore, the copper transport rate is determined by the rate of diffusion of copper-containing species through the feed phase diffusion layer and the rate of diffusion of the CuR_2 species

through the membrane. Then, the flux of copper crossing the membrane may be derived by applying Fick's first diffusion law to the diffusion layer at the feed phase side and to the membrane.

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

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

$$J_o = \Delta_o^{-1}([\text{CuR}_2]_{\text{i,s}} - [\text{CuR}_2]_{\text{i,r}}) \quad (5)$$

As the distribution coefficient of copper between the membrane and the receiving 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 receiving solution side may be negligible compared with that at the feed solution side. Then Eq. (5) can be written as

$$J_o = \Delta_o^{-1}[\text{CuR}_2]_{\text{i,s}} \quad (6)$$

If the chemical reaction expressed by Eq. (2) is assumed to be fast compared to the diffusion rate, local equilibrium at the interface is reached and concentrations at the interface are related through Eq. (3). At steady state, $J_a = J_o = J$

and by combination of Eqs. (3), (4) and (6), the following expression can be obtained:

$$J = \frac{K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}[\text{Cu}]_{\text{TOT}}}{\Delta_o + \Delta_a K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}} \quad (7)$$

The permeability coefficient ($P = J/[\text{Cu}]_{\text{TOT}}$) is given by

$$P = \frac{K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}}{\Delta_o + \Delta_a K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}} \quad (8)$$

This expression combines in one equation the equilibrium and diffusion parameters involved in the copper transport process from aqueous nitrate/nitric acid media through a supported liquid membrane using Acorga M5640 as carrier. Eq. (8) indicates that permeability is a function of the carrier concentration in the membrane and the pH of the source phase.

The following parameters were studied to elucidate the kinetics and mechanism of the permeation of copper using Acorga M5640 across a FSSLM: (i) stirring speed of the source phase, (ii) characteristics of the support material, (iii) pH of the feed phase, (iv) carrier concentration in the membrane, (v) copper concentration in the source phase, (vi) ionic strength of the source phase, (vii) diluent of the organic phase. Furthermore, the performance of the Acorga M5640-Ibfluid phase as a carrier has been compared against other commercially available salicylaldoximes. It was observed that the logarithm of the concentration of copper in the source solution vary linearly with time, the slope of the resultant straight line gave the permeability coefficient (Eq. (1)) from which the flux (J) was calculated according to the following relationship:

$$J = [\text{Cu}]_{\text{TOT}} P \quad (9)$$

3.2. Influence of stirring speed of the source phase

In order to achieve effective permeation of copper in a 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: (i) the resistance due to the liquid boundary layer and (ii) that due to the membrane. Indeed, sometimes the magnitude of the boundary layer resistance is comparable to or even greater than the membrane resistance [33]. In the present work, stirring of the feed phase was carried out from 600 to 1600 min^{-1} (Fig. 1). The permeability coefficient increased from 600 to 1200 min^{-1} , and beyond that no appreciable increase in copper permeability is observed. This indicates that the aqueous boundary layer thickness diminished continuously with increasing stirring speed and that the boundary layer is a minimum above 1200 min^{-1} for the difference $[\text{Cu}]_{\text{b}} - [\text{Cu}]_{\text{i,TOT}}$, and the permeability coefficient remains constant in the range 1200–1400 min^{-1} . At high concentrations of copper this difference is indistinguishable with respect to $[\text{Cu}]_{\text{b}}$,

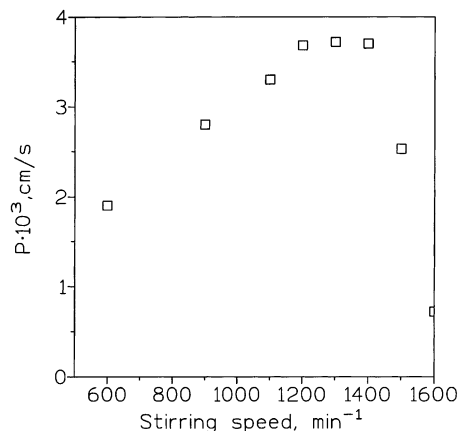


Fig. 1. Influence of stirring speed on permeability of copper(II) as a function of P -values. Feed phase: 1.6×10^{-4} M Cu at $\text{pH } 2.0 \pm 0.02$; membrane phase: 20% v/v Acorga M5640 in Iberfluid, Durapore GVHP 04700 support; receiving phase: 180 g/l sulphuric acid.

as the carrier reaches saturation. Therefore, the appearance of a plateau region does not necessary mean the elimination of the aqueous diffusion layer, but the resistance due to it is minimized [34]. Further, a decrease in permeability from 1400 min^{-1} could be due to the high turbulence caused by stirring, resulting in displacement of carrier from the membrane pore. Thus, a stirring speed of 1350 min^{-1} in the source phase was maintained throughout the subsequent investigation; in the case of the receiving phase, a stirring speed of 1300 min^{-1} was maintained in the experimentation.

3.3. Influence of the support characteristics on the flux

Three membranes (Table 3) with different characteristics were experimented in the same experimental conditions of aqueous source and receiving solutions and carrier concentrations. In Table 3, the obtained flux values are given, it can be seen that the best value is obtained when Durapore GVHP 04700 was used as support and, thus, was selected throughout the study. However, to correct the fact that the diffusion path is greater than the distance perpendicular to the interface, values of the flux were normalized (J_{N}) to the thickness ($d_{0,\text{GVHP}}$), porosity ($\varepsilon_{\text{GVHP}}$) and tortuosity (τ_{GVHP}) of the Durapore GVHP 04700 membrane using the following equation [31,35]:

$$J_{\text{N}} = \frac{d_0 \tau}{\varepsilon} \frac{\varepsilon_{\text{GVHP}}}{d_{0,\text{GVHP}} \tau_{\text{GVHP}}} \quad (10)$$

About the same flux values were obtained for the Durapore GVHP 04700 and Fluoropore FGLP 04700 supports (Table 3). In the case of the Durapore HVHP 04700, the difference found should be attributable to its higher pore size which makes the carrier more unstable in the membrane and thus having a lower permeability coefficient than that obtained with the GVHP 04700 support, despite their same characteristics (Table 3).

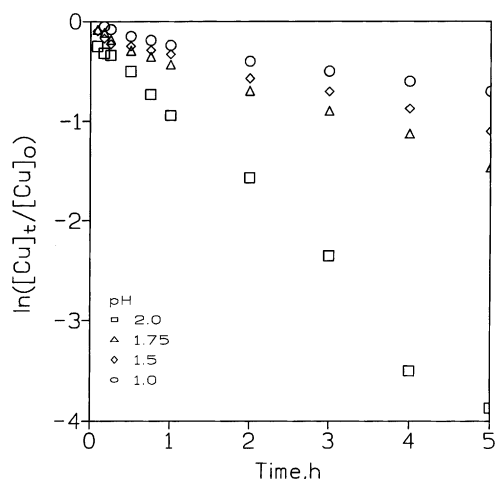


Fig. 2. Influence of initial pH on permeability of copper(II) as a function of $\ln([Cu]_t/[Cu]_0)$. Experimental conditions as in Fig. 1.

3.4. Influence of source phase pH

In the present FSSLM system, the pH gradient between feed and receiving phases is one of the important driving forces for the permeation of copper. In order to assess the role of feed phase pH, pH variation studies in the range 1.0–2.0 were carried out. The receiving phase consisted of 180 g/l sulphuric acid, whereas the concentration of the membrane carrier was 20% v/v in Iberfluid. It is evident from Fig. 2 that the permeability of copper increases with an increase in pH from 1.0 to 2.0, 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 Eq. (8), the following two limiting cases can be derived:

1. at low pH and high carrier concentration, the equation reduces to

$$P = \frac{K_{\text{ext}}[\text{HR}]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^{-2}}{\Delta_o} \quad (11)$$

2. at high pH and high carrier concentration, the equation reduces to

$$P = \frac{1}{\Delta_a} \quad (12)$$

and permeability is independent of pH.

3.5. Influence of carrier concentration on the permeability of copper

The carrier plays a decisive 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 copper. A supported liquid membrane having no carrier immobilized on the support results in no transport of copper. The effect of Acorga M5640 concentration on P

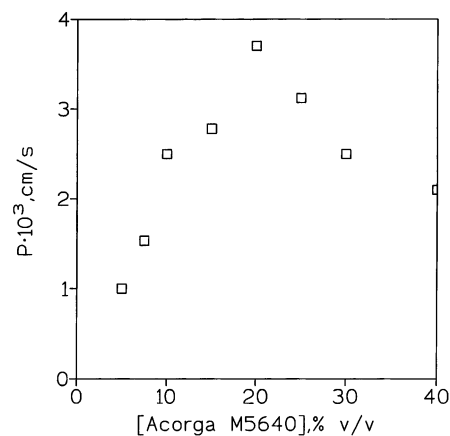


Fig. 3. The influence of Acorga M5640 concentration on copper permeability. Experimental conditions as in Fig. 1.

was studied from 5–40% v/v (0.09–0.72 M) in Iberfluid. As can be seen from Fig. 3, the permeability of copper increases with carrier concentrations up to 20% v/v and then decreases. The maximum limiting permeability (P_{lim}) could be explained by assuming that diffusion in the organic membrane is negligible compared with the term accounting for aqueous diffusion in Eq. (4) and the permeation process is controlled by diffusion in the stagnant film of the source phase ($P_{\text{lim}} = 1/\Delta_a = 3.7 \times 10^{-3}$ cm/s). The recovery of copper exceeds 97% at 20% v/v Acorga M5640 concentration in the membrane phase, thus, this concentration was selected throughout the study. Assuming that the carrier concentration in the membrane phase is constant, the next equation can be used to determine the apparent diffusion coefficient of copper [36]

$$D_o^a = \frac{Jd_0}{[\text{HR}]} \quad (13)$$

The value of D_o^a was calculated to be 2.0×10^{-8} cm²/s taking the Durapore GHVP 04700 support of thickness 125 μm and using a carrier concentration of 20% v/v. At higher carrier concentrations (Fig. 3), the decrease of permeability can be explained in terms of the increase in solution viscosity that increases membrane resistance [37].

3.6. Influence of metal concentration on the permeability of copper

Fig. 4 shows a plot of the initial copper ion flux (J) versus the concentration of copper ranging from 7.9×10^{-5} to 1.3×10^{-3} M in the source phase. At low copper concentrations, the average initial flux is a strong function of the initial concentration in the feed phase. Hence, the permeation process is controlled by diffusion of copper species in the lower range of metal concentrations. However, beyond a certain limiting concentration, J tends to be independent of the metal concentration, the most probable reason for this may be the rate-determining step for the permeation

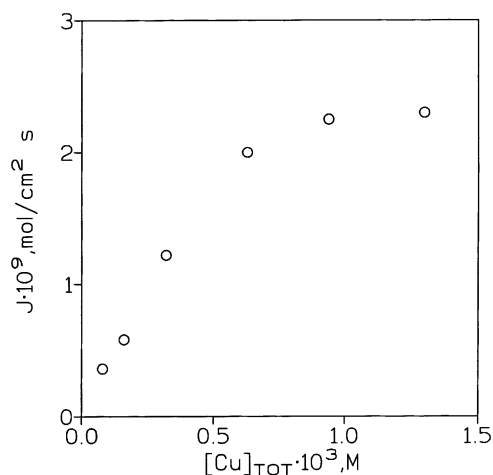


Fig. 4. The influence of initial concentration of copper(II) on permeability flux (J) of the metal. Experimental conditions as in Fig. 1.

process. Under the limiting condition the total concentration of Acorga M5640 ([HR]) becomes equivalent to $[\text{CuR}_2]_{\text{org}}$, and on the basis of the next equation [34]

$$J_{\text{lim}} = \frac{D_o[\text{CuR}_2]_{\text{org}}}{d_0 n} \quad (14)$$

where n is the stoichiometric coefficient of the reaction. The value of J_{lim} is determined to be 2.3×10^{-11} mol/cm² s.

3.7. Influence of source phase ionic strength on copper permeation

This study was carried out using an aqueous feed phase of 1.6×10^{-4} M Cu and pH 2.0 ± 0.02 which also contained 0.5 M lithium nitrate or no salt, the membrane phase was of 20% v/v Acorga M5640 in Iberfluid, whereas the receiving solution was of 180 g/l sulphuric acid. The results obtained shown that there is not apparent influence of the presence of the nitrate salt on copper permeation coefficient respect to when no salt is present in the feed phase.

3.8. Evaluation of diffusional parameters

As can be seen from Fig. 5, plotting $1/P$ as function of $1/AB$ (where $A = K_{\text{ext}}[\text{HR}]_{\text{org}}^2$ and $B = [\text{H}^+]_{\text{aq}}^{-2}$) for different extractant concentrations at pH 2.0 ± 0.02 , gives a straight line with slope Δ_o and ordinate Δ_a . The calculate value of the diffusion coefficient ($\Delta_o = d_0/D_o$, $d_0 = 125 \mu\text{m}$) was 1.6×10^{-9} cm²/s. The mass transfer coefficient (Δ_a^{-1}) was calculated to be 3.7×10^{-3} cm/s. In addition, assuming $D_a = 10^{-5}$ cm²/s [38], the thickness of the aqueous boundary layer was calculated to be 2.7×10^{-3} cm, which is of the same order of magnitude as reported in [39]. The diffusion coefficient of the copper complex in the bulk organic phase ($D_{o,b}$) can be evaluated from the diffusivity

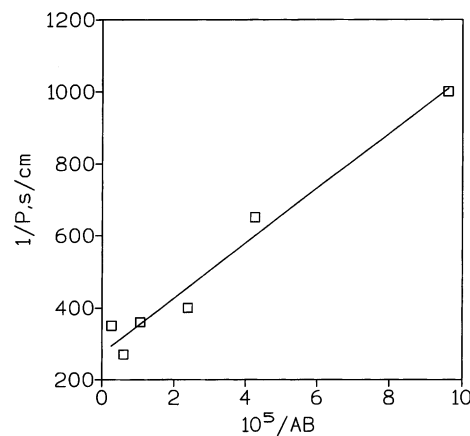


Fig. 5. Plot of $1/P$ vs. $1/AB$ (see text for details).

(D_o) in the membrane with micropores from the relation [23]

$$D_{o,b} = D_o \tau' \quad (15)$$

where $\tau' = \tau^2/\varepsilon$. The value of $D_{o,b}$ was calculated to be 5.9×10^{-9} cm²/s. It should be noted that in the present system, D_o presents a lower value than that of the bulk diffusion coefficient or to that of the apparent diffusion coefficient, this is attributable to diffusional resistance caused by microporous thin membrane placed between the feed and receiving phases.

3.9. Influence of membrane diluent on the permeation of copper

The liquid membrane diluent is equally an important parameter to obtain a stable FSSLM, as the characteristics of the diluent are mainly responsible for the stable liquid membrane phase. The results of copper permeation using various diluents are presented in Fig. 6. It can be seen that best copper permeation is obtained when Iberfluid (mainly aliphatic) is used as diluent of the organic phase. However, it seems that there is not a direct relation between the character of the diluent (aliphatic versus aromatic) and copper permeation. The behavior should be better explained taking into account the various properties of the diluent (i.e. viscosity) as occurs in many solvent extraction systems [40].

3.10. Copper permeation using salicylaldoximes as carriers

The performance of the system Acorga M5640-Iberfluid on copper permeation has been compared against other commercially available salicylaldoximes using the same experimental conditions. Fig. 7 shows the results of this study, it can be seen that Acorga M5640 gives the best copper permeation, whereas with LIX 860 the lowest permeation is obtained, this should be due to the stronger chelating character of LIX 860 (with no modifier) against copper and

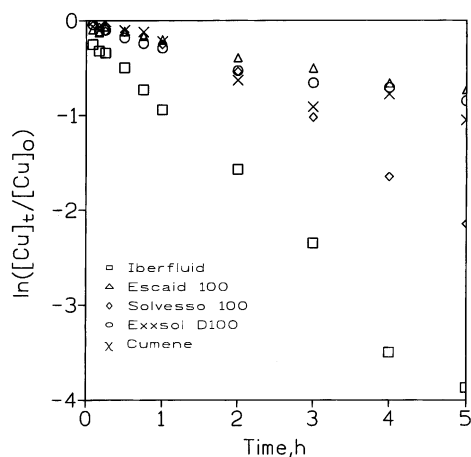


Fig. 6. Effect of various diluents on the permeability of copper(II) with Acorga M5640 as a function of $\ln([Cu]_t/[Cu]_0)$. Experimental conditions as in Fig. 1.

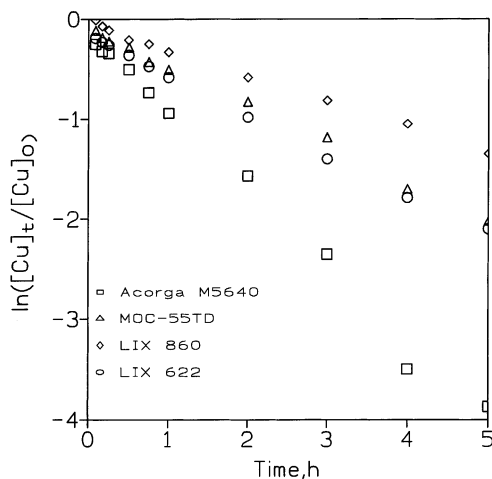


Fig. 7. Permeation of copper(II) using different salicylaldoximes (20% v/v in Iberfluid) as carriers. Experimental conditions as in Fig. 1.

respect to that of Acorga M5640, MOC-55TD and LIX 622 (which present a modifier in their composition), resulting in a more difficult copper strippability. Although the overall performance also should be related to other properties of the carrier solution (i.e. viscosity, which changes membrane resistance).

4. Conclusions

Of the salicylaldoximes derivatives used as membrane carriers, Acorga M5640 is the most efficient for copper transport across a FSSLM under the present experimental conditions. The transport of copper(II) using Acorga M5640 in Iberfluid under various experimental conditions has been studied and a mechanism of copper transport considering the aqueous film diffusion of metal ions, fast chemical reaction

at the interface and diffusion of CuR_2 through the membrane is proposed. A limiting value of 3.7×10^{-3} cm/s for permeability is obtained and the transport process is controlled by the diffusion in the aqueous stagnant film. Mass transfer coefficients in the membrane and in the aqueous phase are found to be 1.3×10^{-7} and 3.7×10^{-3} cm/s, respectively. The membrane stability was evaluated, under the conditions shown in Fig. 3 (20% v/v Acorga M5640), and good performance ($P = 3.7 \pm 0.2 \times 10^{-3}$ cm/s) in the metal transport was observed after 3 cycles of continuous use of the same membrane.

Acknowledgements

This work was supported by CAM (Spain) Project 07/M0053/1998. Also technical assistance of Mr. J.L. Bascones and Mr. M. López is appreciate.

References

- [1] P.R. Danesi, In: Proceedings of the ISEC 1986 International Conference on Solvent Extraction, Preprints Vol. I, Dechema, Munich, 1986, p. I-527.
- [2] K. Scott, Handbook of Industrial Membranes, Elsevier Advanced Technology, Kidlington, 1997, p. 643.
- [3] A.M. Sastre, A. Kumar, J.P. Shukla, R.K. Singh, Sep. Purification Meth. 27 (1998) 213.
- [4] M.R. Wiesner, S. Chellam, Environ. Sci. Technol. 33 (1999) 360A.
- [5] P.R. Danesi, Sep. Sci. Technol. 19 (1984) 857.
- [6] M. Rovira, A.M. Sastre, J. Membr. Sci. 149 (1998) 241.
- [7] M. Cox, D. Mead, J. Melling, in: Proceedings of the ISEC 1986 International Conference on Solvent Extraction, Preprints Vol. I, Dechema, Munich, 1986, p. I-537.
- [8] H.J. Bart, R. Watcher, R. Marr, in: Proceedings of the ISEC 1986 International Conference on Solvent Extraction, Preprints Vol. I, Dechema, Munich, 1986, p. I-567.
- [9] Z. Fan, X. Zhan, X. Su, in: Proceedings of the ISEC 1988, Conference Papers, Vol. III, USSR Academy of Sciences and International Committee for Solvent Extraction Chemistry and Technology, Moscow, 1988, p. 82.
- [10] M. Szpakowska, O.B. Nagy, J. Membr. Sci. 64 (1991) 129.
- [11] Z. Lazarova, T. Sapundzhiev, L. Boyadzhiev, Sep. Sci. Technol. 27 (1992) 493.
- [12] Z. Lazarova, L. Boyadzhiev, J. Membr. Sci. 78 (1993) 239.
- [13] J. Szymanowski, Hydroxyoximes and Copper Hydrometallurgy, CRC Press, Boca Raton, 1993, p. 345.
- [14] A. Alderman, M. Cox, R.F. Dalton, in: D.H. Logsdail, M.J. Slater (Eds.), Solvent Extraction in the Process Industries, Vol. 2, Elsevier, London, 1993, p. 883.
- [15] M. Szpakowska, O.B. Nagy, Polyhedron 12 (1993) 1277.
- [16] M. Szpakowska, J. Membr. Sci. 90 (1994) 101.
- [17] M. Szpakowska, J. Membr. Sci. 109 (1996) 77.
- [18] F.R. Valenzuela, C. Basualto, J. Sapag, C. Tapia, Min. Eng. 10 (1997) 1421.
- [19] F.R. Valenzuela, C. Basualto, C. Tapia, J. Sapag, J. Membr. Sci. 155 (1999) 163.
- [20] R.F. de Ketelaere, J. van del Linden, Abstract of ISEC 1999, Barcelona, 1999, p. 121.
- [21] J.S. Gill, H. Singh, C.K. Gupta, Hydrometallurgy 55 (2000) 113.
- [22] K. Yoshizuka, K. Kondo, F. Nakashio, J. Chem. Eng. Jpn. 19 (1986) 312.

- [23] T.-C. Huang, R.-S. Juang, *J. Chem. Tech. Biotechnol.* 42 (1988) 3.
- [24] Y. Sato, K. Kondo, F. Nakashio, *J. Chem. Eng. Jpn.* 23 (1990) 23.
- [25] F. Nakashio, *J. Chem. Eng. Jpn.* 26 (1993) 123.
- [26] J. Marchese, M.E. Campderros, A. Acosta, *J. Chem. Tech. Biotechnol.* 64 (1995) 293.
- [27] I. Alexandrova, G. Iordanov, *J. Appl. Pol. Sci.* 60 (1996) 721.
- [28] N. Parthasarathy, M. Pelletier, J. Buffle, *Anal. Chim. Acta* 350 (1997) 183.
- [29] F.Z. El Aamrani, A. Kumar, A.M. Sastre, *New J. Chem.* 23 (1999) 517.
- [30] F.J. Alguacil, A. Cobo, M. Alonso, *Hydrometallurgy*, 85 (2002), in press.
- [31] T.B. Stolwijk, E.J.R. Sudhölter, D.N. Reinhoudt, *J. Am. Chem. Soc.* 109 (1987) 7042.
- [32] G. Zuo, S. Orecchio, M. Muhammed, *Sep. Sci. Technol.* 31 (1996) 1597.
- [33] M.P. Bohrer, *Ind. Eng. Chem. Fundam.* 22 (1983) 72.
- [34] R. Mahapatra, S.B. Kanungo, P.V.R.B. Sarma, *Sep. Sci. Technol.* 27 (1992) 765.
- [35] W.C. Babcock, R.W. Baker, E.D. Lapochelle, K.L. Smith, *J. Membr. Sci.* 7 (1980) 71.
- [36] L. Bromberg, G. Levin, J. Libman, A. Shanzer, *J. Membr. Sci.* 69 (1992) 143.
- [37] C. Fontàs, V. Salvadó, M. Hidalgo, *Solvent Extr. Ion Exch.* 17 (1999) 149.
- [38] J.F. Dozol, J. Casas, A.M. Sastre, *Sep. Sci. Technol.* 28 (1993) 2007.
- [39] L. Bromberg, I. Lewin, A. Warshawsky, *J. Membr. Sci.* 70 (1992) 31.
- [40] G.M. Ritcey, A.W. Ashbrook, *Solvent Extraction, Part I*, Elsevier, Amsterdam, 1984, p. 172.