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FACILITATED TRANSPORT OF COPPER FROM SOLUTIONS OBTAINED BY ELUTION OF CUPROCYANIDE COMPLEXES BY MEANS OF ACIDIC THIOUREA

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ABSTRACT

Facilitated transport of copper from copper–thiourea solutions is not recommended because of the formamidine disulfide presence, which constitutes an obstacle for the complexation of metal ions at the feed phase/membrane interface. The transport flux of copper ion decreases when the concentration of thiourea increases. In this work, the facilitated transport of copper in acidic thiourea medium has been shown that becomes possible when the solutions are pretreated by means of elution of cuprocyanides, fixed initially to

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an anion-exchange resin, by using thiourea. On the other hand, the use of thiourea solutions in different acids (nitric, chlorydric, sulfuric, and phosphoric) affects the transport of copper ions. The following order of flux was obtained: $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-}$ depending on the type of anion taking part in the complex.

Key Words: Facilitated transport; Copper; Dibenzo-18-crown-6; Elution; Thiourea

INTRODUCTION

In previous work (1), it was shown that facilitated transport of copper from acidic thiourea solutions, using dibenzo-18-crown-6 as a carrier, was hampered by the formation of formamidine disulfide, product of thiourea oxidation in the presence of copper(II). Formamidine disulfide ($[(NH_2)_2CSSC(NH_2)_2]^{2+}$) is a low-mobility cation, which is strongly retained by the carrier in the supported liquid membrane (SLM) competing with other cations. Then it prevents the metal ions transfer to the strip phase.

According to reviewed literature, no study related to a facilitated transport of copper in thiourea medium, through an SLM, has been reported to date. The difficulties arisen in the treatment of this medium were the nature and the concentration of the species. They are linked to both redox potentials and to the metal and thiourea concentration in the solution.

Cyanide ion is used in major leaching processes of precious metals, such as copper, present in polymetallic ores but it has been demonstrated that thiourea $[SC(NH_2)_2]$ gives rise to more stable complexes with these metal ions (see Table 1 in the case of copper) (2–5). Despite this advantage, thiourea in the presence of copper(II) forms formamidine disulfide as a by-product that hampers the use of an SLM process for copper recovery. To overcome this problem, the cyanide ion can be used as a leaching agent and then the cuprocyanide complexes can be fixed to an anion-exchange resin. Next, the elution with the thiourea gives a solution

Table 1. Global Formation Constants of Copper(I) Complexes in Cyanide and Thiourea Mediums

Metal	Log β_1	Log β_2	Log β_3	Log β_4
CN^-	—	24.0 [Ref. (4)]	28.6 [Ref. (4)]	30.3 [Ref. (4)]
Tu	11.00 [Ref. (5)]	12.80 [Ref. (5)]	14.00 [Ref. (5)]	15.40 [Ref. (5)]

containing metal–thiourea complexes without the presence of formamidine disulfide (6).

The variety of complex species, which can be formed between metal ions and cyanide ions has greatly attracted the interest of many authors, especially the characterization of the nature of these species (7–11). But, the results obtained by each author are often contradictory and the mechanisms are not well elucidated yet.

Burstall et al. (7), Kunin (8), and Stamboliades et al. (9), in their different studies related to the fixation of copper–cyanide complexes on an anion-exchange resin, found that $Cu(CN)_4^{3-}$ species is fixed preferentially to the resin. Riveros (11) and Tataru et al. (12) have put the evidence that $Cu(CN)_3^{2-}$ species is principally formed. Friedman et al. (13), for their part, have emitted the hypothesis of the formation of a $Cu(CN)_3^{2-}$ and $Cu(CN)_2^{-}$ mixture.

In the first part of this work, the distribution of copper–cyanide species, as a function of the initial concentrations of cyanide ion and thiourea, will be discussed. In the next part, some experimental results concerning the transport through the SLM will be described and the uses of thiourea solutions in different acids will be brought into focus.

THEORY

Synthetic solutions (or leaching solutions) containing anionic copper–cyanide complexes were passed through an anion-exchange resin. The exchange equilibrium between copper–cyanide species and cyanide ions previously fixed on the resin can be represented by the following general equation:

$$[\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{S} + n\mathrm{CN}_\mathrm{R}^- \Leftrightarrow [\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{R} + n\mathrm{CN}_\mathrm{S}^- \tag{1}$$

where the indices S and R refer to the solution and the resin, respectively, and $n = 2$–4.

For this equilibrium can be defined an exchange constant as:

$$K_{\mathrm{CN}/[\mathrm{Cu(CN)}_n^{1-n}]} = \frac{[\mathrm{CN}^-]_\mathrm{S}^n[\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{R}}{[\mathrm{CN}^-]_\mathrm{R}^n[\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{S}} \tag{2}$$

and a partition coefficient P as:

$$P = \frac{[\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{R}}{[\mathrm{Cu(CN)}_n^{1-n}]_\mathrm{S}}. \tag{3}$$

The equilibrium (2) can then be written as:

$$K_{\mathrm{CN}/[\mathrm{Cu(CN)}_n^{1-n}]} = P\frac{[\mathrm{CN}^-]_\mathrm{S}^n}{[\mathrm{CN}^-]_\mathrm{R}^n}. \tag{4}$$

Since several complex species can exist in solution, which can be exchanged with cyanide ions initially present in the resin, the equilibrium (1) can be decomposed to several partial equilibriums with numbers equal to that of the species present in the solution. The dominating equilibrium will depend on the partition of the species in solution before fixation, but other factors can also take part in the exchange mechanism since the species are interdependent. For this reason the global partition coefficient represented by the following equation is considered:

$$P = \frac{[\mathrm{Cu(I)_R}]}{[\mathrm{Cu(I)}]_\mathrm{S}}. \tag{5}$$

The concentrations of all the species are known by experiments (analyses of free cyanide and total concentration of copper(I)) and also by calculation from the global formation constants of the cyanide–copper complexes. In fact, the mass balance permits the following equations to be written:

$$[\mathrm{Cu}]_\mathrm{T} = [\mathrm{Cu^+}] + [\mathrm{Cu(CN)_2^-}] + [\mathrm{Cu(CN)_3^{2-}}] + [\mathrm{Cu(CN)_4^{3-}}] \tag{6}$$

$$\begin{aligned}[\mathrm{CN^-}]_\mathrm{T} = {} & [\mathrm{CN^-}] + [\mathrm{HCN}] + 2[\mathrm{Cu(CN)_2^-}] + 3[\mathrm{Cu(CN)_3^{2-}}] \\ & + 4[\mathrm{Cu(CN)_4^{3-}}].\end{aligned} \tag{7}$$

By introducing the global constants of complex formation, β_n ($n = 2$–4) defined as

$$\beta_n = \frac{[\mathrm{Cu(CN)}_n^{1-n}]}{[\mathrm{Cu^+}][\mathrm{CN^-}]^n},$$

in Eq. (6), we can write:

$$[\mathrm{Cu}]_\mathrm{T} = [\mathrm{Cu^+}](1 + \beta_2[\mathrm{CN^-}]^2 + \beta_3[\mathrm{CN^-}]^3 + \beta_4[\mathrm{CN^-}]^4). \tag{8}$$

Putting:

$$X = 1 + \beta_2[\mathrm{CN^-}]^2 + \beta_3[\mathrm{CN^-}]^3 + \beta_4[\mathrm{CN^-}]^4 \tag{9}$$

and subtracting the expression of $[\mathrm{Cu^+}]$ from Eqs. (8) and (9), we can express the total concentration of cyanide by the following equation:

$$[\mathrm{CN^-}]_\mathrm{T} = [\mathrm{CN^-}]\left(1 + \frac{[\mathrm{H^+}]}{K_\mathrm{a}} + 2\frac{\beta_2[\mathrm{Cu}]_\mathrm{T}[\mathrm{CN^-}]}{X} + 3\frac{\beta_3[\mathrm{Cu}]_\mathrm{T}[\mathrm{CN^-}]^2}{X} + 4\frac{\beta_4[\mathrm{Cu}]_\mathrm{T}[\mathrm{CN^-}]^3}{X}\right) \tag{10}$$

where K_a is related to HCN formed in the eluted solution after the exchange. $[\mathrm{CN^-}]_\mathrm{T}$ and $[\mathrm{Cu}]_\mathrm{T}$ were fixed before experience so that $[\mathrm{CN^-}]$ at equilibrium is computed by using a GW-BASIC program. The concentrations of all the copper–cyanide complexes in solution are determined from the relation:

$$[\mathrm{Cu(CN)}_n^{1-n}] = \frac{[\mathrm{Cu}]_\mathrm{T}\beta_n[\mathrm{CN}^-]^n}{X} \quad (11)$$

The elution of the cuprocyanide species, fixed on the resin, is realized by means of acidic thiourea at pH = 1. The evolved reaction is represented by the following equilibrium:

$$(\mathrm{Cu(CN)}_n^{1-n})_\mathrm{R} + m(\mathrm{Tu})_\mathrm{S} \Leftrightarrow (\mathrm{Cu(Tu)}_m^+)_\mathrm{S} + n(\mathrm{CN}^-)_\mathrm{R} \quad (12)$$

The complexes $\mathrm{Cu(Tu)}_m^+$ will be present in the eluate with $m = 1-4$.

In Table 1, the global formation constants (stability constants) of copper complexes in cyanide and thiourea medium are collected. The concentrations of the different complexes, by means of a conditional calculus, vs. thiourea concentration, were reported in a previous paper (1).

SUPPORTED LIQUID MEMBRANE SYSTEM

The basic principles describing how an SLM works are widely known (1).

In the case of transport of copper ions in acidic-thiourea medium using a crown ether as a carrier, a facilitated co-transport is obtained; the transport mechanism is represented in Fig. 1. The positively charged metal–thiourea complex is further complexed at the interface feed-phase/membrane and the neutral complex formed diffuses through the membrane phase to the interface membrane/strip-phase where the decomplexation of the metal-complex is realized.

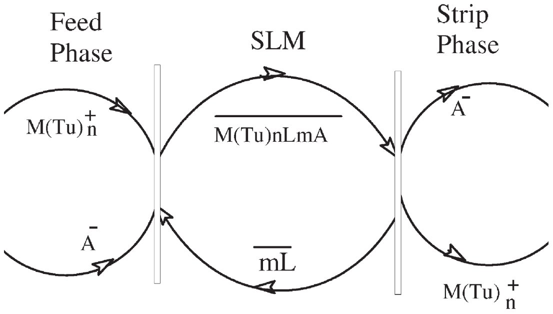

Figure 1. Scheme of the co-transport of $\mathrm{Cu(Tu)}_n^+$ complexes in acidic thiourea medium by using DB18C6 as carrier.

The equilibrium reaction can be represented as:

$$\mathrm{M(Tu)}_n^+ + \overline{m\mathrm{L}} + \mathrm{A}^- \Leftrightarrow \overline{\mathrm{M(Tu)}_n\mathrm{L}_m\mathrm{A}} \tag{13}$$

where $\mathrm{M(Tu)}_n^+$ (M = Cu) is the metal–thiourea complex, L the ligand (crown ether), and A^- the co-ion (NO_3^- or Cl^-, SO_4^{2-}, PO_4^{3-} in this work). The bars indicate that the species are in the organic phase. The mass flux J ($\mathrm{mol\,cm^{-2}\,sec^{-1}}$) of the metal ions through the membrane from the feed side to the strip side can be determined by applying its definition:

$$J = \frac{\Delta n V}{A \Delta t} \tag{14}$$

where Δn represents the variation of the number of moles of the metal ions in the strip solution during the reference time Δt, A the membrane area ($8.04\,\mathrm{cm}^2$), and V the volume of the strip phase (the volumes of both the feed and strip phases are equal to 43 mL). The mass transfer of copper across the membrane has been described by considering only diffusional parameters because the boundary layers were minimized by stirring the feed and strip solutions at 800 rpm. The interfacial resistance of the chemical reaction on mass transport has been neglected since the chemical reactions of complexation and decomplexation at interfaces are very fast compared to the diffusion time inside the membrane.

EXPERIMENTAL

Reagents and Membranes

Copper(I) cyanide, sodium hydroxide, potassium cyanide, thiourea, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, and chloroform were obtained from Fluka (PA, Buchs, Switzerland). Dibenzo-18-crown-6 (DB18C6) was obtained from Aldrich (ACS, Steinheim, Germany). Double distilled water was used for all experiments.

Celgard 2500 (from Hoechst Celanese Corporation, North Carolina), a macroporous film of 25 μm thickness, was used as a solid support for the liquid membranes. The nominal porosity of the film was 45% and the effective pore size was 0.04 μm.

The pretreatment was carried out by using an anion-exchange resin, Amberlite IRA 9000C (OH) (STyrene-DVB), of analytical grade quality (Alfa products) with characteristics (not mentioned by the producer) determined as follows using the different methods mentioned elsewhere (4).

Pretreatment of the Anion-Exchange Resin

Before utilization, the resin was pretreated with ethanol with some repeated washing cycles (according to instructions of manufacturer) to eliminate the organic residue entrapped in the resin grains. Then, a further washing with hydrochloric acid 0.1 *M* was carried out to eliminate the iron fixed on the resin in the course of its manufacture.

After washing with double distilled water, rapid exchange cycles were carried out with HCl 1 *M* and NaOH 1 *M*, respectively. Each cycle was followed by a washing with double distilled water. The resin was then left at ambient temperature during 24 hr, and next dried in an oven at 60°C until it took a constant weight.

Characteristics of the Anion-Exchange Resin

Granulometric Classification

Sieves of different mesh sizes were used to measure the size of the resin grains. It was comprised between 3.5 and 5 mm.

Exchange Capacity

For determining the exchange capacity of the resin, the OH^- ions initially present in the resin were replaced by ions which had a bigger affinity with Cu(I). A 100 mL solution of CN^- ion at a concentration of 0.1 *M* was used to conditionate 10 g of the resin. The exchange reaction that occurred is:

$$[(-\overset{+}{N}R_3)OH^-] + CN^- \longrightarrow [(-\overset{+}{N}R_3)]CN^- + OH^-. \qquad (15)$$

The free cyanides concentration in the time was determined till reaching breakthrough conditions using a Carlo Erba reagent kit using a Uv–visible spectrophotometer (Shimadzu Uv-160A). The exchange capacity was found to be 0.979 meq g^{-1} of resin.

Swelling Index

The swelling index I_G of the resin in potassium cyanide 0.1 *M*, was determined putting a quantity of 10 g of the resin in a graduated column of 15 cm height and 1.5 cm diameter. The initial resin height was H_1, then, after equilibrium with the solution, the height reached a value H_2. The swelling index was calculated from the equation:

$$I_{\mathrm{G}} = \frac{H_2 - H_1}{H_1} \times 100 \tag{16}$$

obtaining a value equal to 157%.

Quantity of Humidity

The hygroscopic character of the resin shows that it retains a certain quantity of humidity. This quantity was determined by drying a quantity M_1 of the resin from the bottle at 110°C until the weight reached a constant value M_2. The amount of bounded water was defined by the following relation:

$$\tau_H = \frac{M_1 - M_2}{M_1} \times 100. \tag{17}$$

The obtained value was 203.4% of humidity, which is relatively high.

Determination of the Partition Coefficient and the Rate of Fixation of Cu(I)

The partition coefficient and the rate of fixation of Cu(I) was determined by means of a static method. The steps of the method were:

Resin of quantity 10 g was equilibrated with a solution of KCN 0.1 *M* during 24 hr.

The resin was filtered, rinsed with the filtrate and with double distilled water, and then dried at ambient temperature during 3 or 4 hr.

The resin was put in contact with the solution containing the ions to be exchanged (a solution 0.01 *M* of copper cyanide in 0.1 *M* potassium cyanide). The resin was submerged in the solution and shaken sufficiently for reaching the exchange equilibrium.

At the end, the mixture resin-solution was filtered and the filtrate was analyzed for evaluating the partition coefficients and the rates of fixation. Then, the resin was rinsed with double distilled water.

The last two steps were realized at a constant temperature of 25 ± 0.1°C.

The rate of fixation of Cu(I) was found by analyzing the concentration of copper in the solution; it was 98.7% and the partition coefficient *P*, defined by Eq. (5), was 76.04.

Supported Liquid Membrane Apparatus

Transport experiments were carried out by using a membrane cell, made by Teflon, containing two separate compartments of 45 mL, each one (for the aqueous feed and the stripping solutions) divided by a window, where the impregnated membrane was placed. Each compartment, the feed containing the metal–thiourea solution (after elution or without elution) and the strip containing distilled water, was provided with a mechanical stirrer at 800 rpm. At different intervals of time, aliquots of 0.5 mL each were withdrawn from the feed and strip solutions and analyzed with an atomic absorption spectrophotometer (Model Perkin Elmer 2280). All the experiments were performed in a thermostated bath at 25 ± 0.1°C. The fluxes were calculated after 5 hr of transport, taking into account the right volume in the cell after each measurement. The volume of each half cell was still enough to cover all the membrane surface during all the experimental runs with a collection of 5 samples.

Procedure

Before mass transfer tests using the SLM, the support was soaked in a 0.01 M carrier (DB18C6) solution in chloroform for 1 hr, then it was put between the two half cells. The value of concentration was chosen according to the results (high transport flux) obtained in a previous work (1). The experiments began by starting the stirring motors in the two compartments of the cell.

A quantity of 5 g of the resin, pretreated as described before, was saturated initially with a solution of CuCN 0.01 M in KCN 0.1 M at $\mathrm{pH} = 11$ to promote the formation of the most stable metal–cyanide complex, which is $\mathrm{Cu(CN)}_4^{3-}$. Then the elution was realized by feeding an acidic thiourea solution at $\mathrm{pH} = 1$ at different concentrations in the range 2×10^{-5}–$2 \times 10^{-3}\,M$ to obtain Cu(I)–thiourea complexes, according to Eq. (12), avoiding formamidine disulfide formation. The eluate was collected continuously and fractioned into four solutions of different copper concentrations (50 mL each one) and put in the transport cell. The initial concentration of each solution before transport was determined by using the atomic absorption spectrophotometer. In order to compare the effect of elution on the transport of copper(I), solutions of thiourea (at $\mathrm{pH} = 1$) and copper(II), at same concentrations used before were prepared without elution and used for performing other transport experiments.

RESULTS AND DISCUSSION

Partition of the Different Species

Figure 2 shows the partition of the different species formed between copper(I) ions and cyanide ions calculated from Eq (11). It can be seen that at high cyanide concentration (at pH = 11), the $Cu(CN)_4^{3-}$ species predominates in the solution. Cu(I) ions did not predominate in all the range of cyanide ions concentration. Figure 3shows that in thiourea medium, with the same concentration of metal ion ([Cu(II)] = 0.01 *M*), $Cu(Tu)_4^+$ species are preferentially formed at high thiourea concentrations (1). However, the concentration of formamidine disulfide increases when the initial concentration of thiourea increases (Figure 4). So, by using an initial metal ion concentration [Cu(I) or Cu(II)] of 0.01 *M*, $Cu(CN)_4^{3-}$ and $Cu(Tu)_4^+$ will be preferentially formed in solutions at concentrations of CN^- and thiourea about 0.1 *M*.

Effect of Thiourea Concentration

Table 2 shows that fluxes of copper(I) transported to the strip phase decrease when the concentration of thiourea in the feed phase increases. This could be due to the formation of formamidine disulfide produced by thiourea oxidation in the presence of copper that competes with copper(II) in the formation of a complex with DB18C6 or to the presence of $Cu(Tu)_n^+$ ($n = 1-4$)

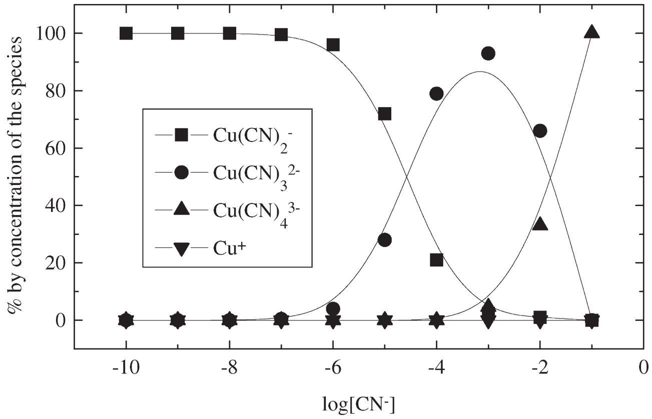

Figure 2. Partition of copper species in cyanide medium. $[Cu^+] = 0.01\,M$ at pH = 11.

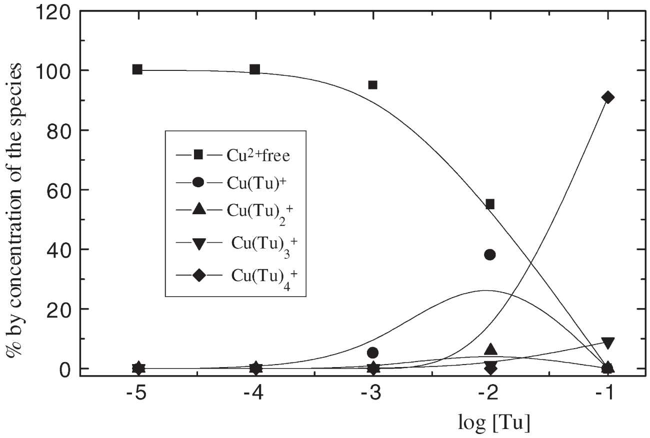

Figure 3. Partition of copper species in acidic-thiourea medium. $[Cu^{2+}] = 0.01\,M$ at $pH = 1$.

complexes of Cu(I) with thiourea. Indeed, in the absence of thiourea, a greater flux of Cu(II) is obtained.

Figure 5 shows the scanning electron micrographs (SEM) of the Celgard 2500 support before and after transport of copper(I) from acidic-thiourea solutions. The major part of the pores is blocked with the oxidation product (formamidine disulfide) (Fig. 5b); on the contrary, no deposit was observed on

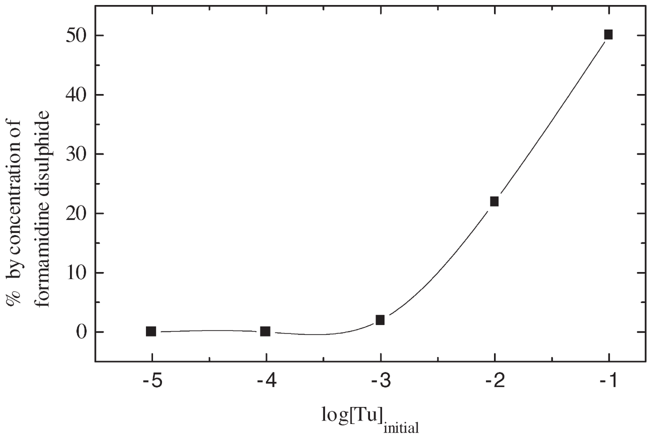

Figure 4. Percentage of formamidine disulfide formed vs. initial thiourea concentration. $[Cu^{2+}] = 0.01\,M$.

Table 2. Mass Flux of Copper(I) and Copper(II) ([Tu] $= 0\,M$) Ions by Changing Thiourea Concentration (at Initial pH $= 1$) in the Feed Phase. [DB18C6] $=$ $0.001\,M$; $[Cu^{2+}] = 0.01\,M$; Support: Celgard 2500

[Tu]	Flux 10^{10} (mol cm^{-2} sec^{-1})
10^{-1}	0.68
10^{-3}	1.11
10^{-4}	2.13
0	3.27

the support surface when using the eluate solutions because a picture similar to Fig. 5a was obtained. By using eluate solutions, the strip concentration increased when thiourea concentration increased as it is shown in Fig. 6; the comparison between mass fluxes of copper ion, e.g., for [Tu] $= 10^{-3}\,M$, showed values of 1.11×10^{-10} mol cm^{-2} sec^{-1} (without elution, as reported in Table 2) and 3.08×10^{-10} mol cm^{-2} sec^{-1} (with elution, as calculated from Figure 6), so the effect of the absence of formamidine disulfide is evident.

Figure 7 also shows that transport is more efficient for the eluted solutions than that for solutions prepared from copper nitrate using the same concentration of thiourea in nitric acid ($0.1\,M$ at pH $= 1$). The observed behavior, other than to the absence of formamidine disulfide in the eluted solutions, could be also attributed to the higher affinity of CN^- ion with respect to NO_3^- ion when forming the complex with DB18C6. However, the main advantage of the elution process is to avoid the formation of formamidine disulfide.

Effect of the Nature of the Acid for Adjusting pH of Thiourea

In Table 3 the mass fluxes of copper in the presence and absence of thiourea are reported.

The transport fluxes of both ions [Cu(II) and Cu(I)] from aqueous solutions, containing different kinds of anions of the acids at same pH, followed the order: $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-}$. In the absence of thiourea, for both metal ions, the flux was higher than in the presence of thiourea because of the formation of the oxidation product formamidine disulfide that competes with the carrier. The nature of the acid had a low influence on mass flux in the absence of thiourea and a significant influence in the presence of thiourea. This last behavior can be attributed to the difference in the ability of the co-ions to bind to the copper–

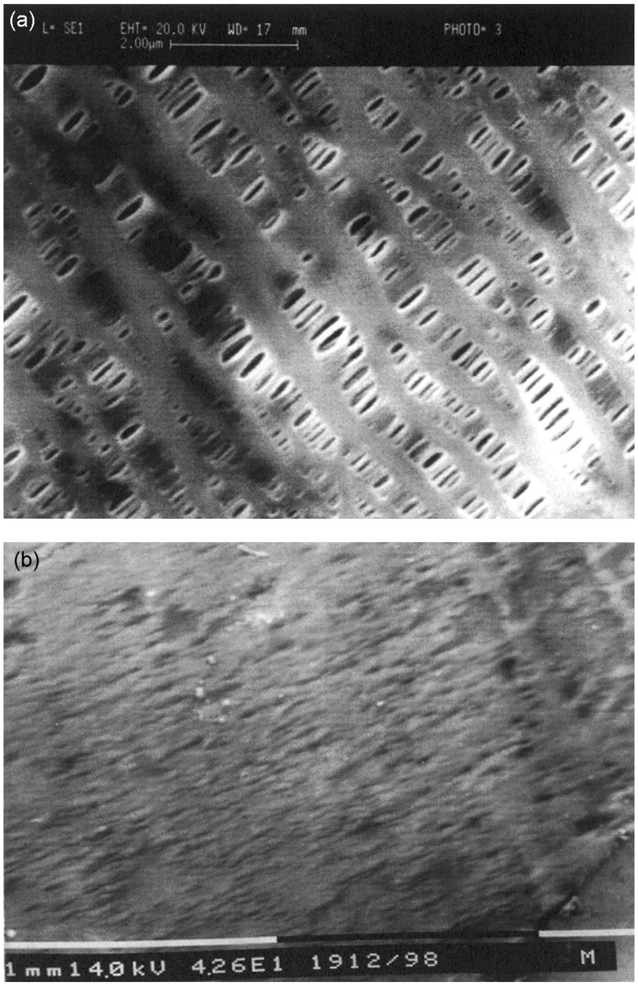

Figure 5. SEM micrographs of Celgard 2500 films. (a) Before transport of copper; (b) after transport of copper; ([DB18C6] = 0.001 *M*; [Metal] = 0.01 *M*; [Tu] = 0.1 *M* at pH = 1).).

thiourea charged complex and also to the nature of the metal species because in the absence of thiourea, Cu(II) ions are transported but in the presence of thiourea Cu(II) ions are reduced to Cu(I) species which are then complexed by thiourea molecules.

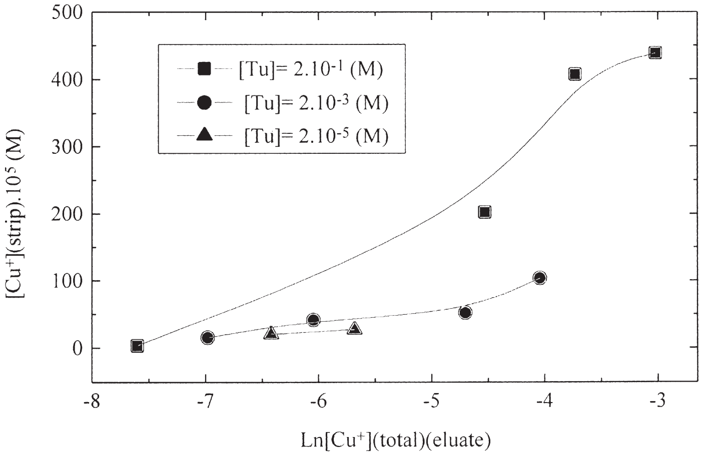

Figure 6. Concentration of copper(I) in the strip phase vs. the initial concentration of copper(I) in the eluted solutions obtained at various thiourea concentrations at pH = 1.

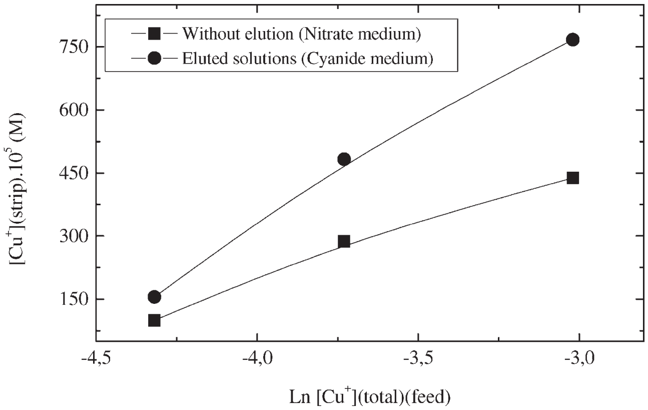

Figure 7. Concentration of copper(I) in the strip phase vs. the initial concentration of copper(I) in the feed obtained by eluted and prepared solutions containing [Tu] = 0.1 *M* at pH = 1.

Study of the Supported Liquid Membrane Stability

Continuous operation has been simulated by using the Celgard 2500 support, impregnated in a 0.001 *M* DB18C6 solution, by changing the feed and strip solutions every 24 hr. Two types of feed were used: (i) solutions of

Table 3. Mass Flux of Copper Ions by Changing the Nature of the Acid. [DB18C6] = 0.001 *M*; Support: Celgard 2500; $[Cu^{2+}] = 0.01\,M$

	$J \times 10^{10}$ (mol cm^{-2} sec^{-1})	
Acid	In Absence of Thiourea	In Presence of Thiourea [Tu] = 0.1 *M* at pH = 1
HNO_3	3.27	0.68
HCl	3.05	0.55
H_2SO_4	2.90	0.33
H_3PO_4	2.79	0.17

cuprocyanide complexes obtained by elution with 0.1 *M* thiourea at pH = 1 as described in the experimental part ($[Cu^{+}] = 0.01\,M$); (ii) solutions of 0.01 *M* copper nitrate in 0.1 *M* thiourea at initial pH = 1 in nitric acid.

Figure 8 shows that the membrane works for a long time (more than 15 days), by using eluted solutions containing cuprocyanide complexes. In the case of solutions prepared without elution, the support was completely covered by a film of formamidine disulfide and the flux reached a value of almost zero

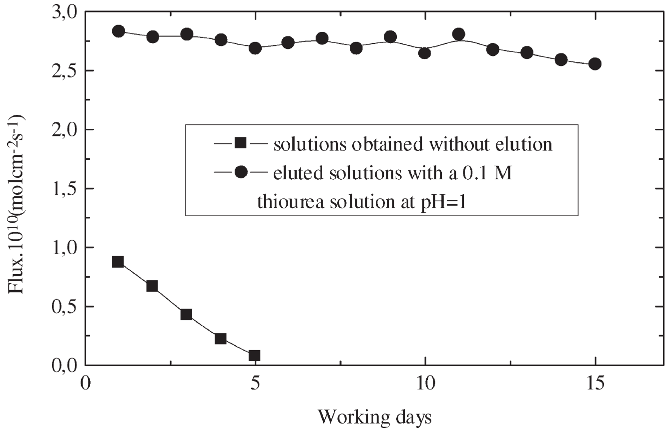

Figure 8. Evolution of the mass flux of copper ions through the SLM vs. the working time. (i) solution containing the cuprocyanide complex from elution with 0.1 M solution of thiourea at pH = 1; (ii) 0.01 *M* copper nitrate solution in 0.1 *M* thiourea at pH = 1. [DB18C6] = 0.001 *M*; Support: Celgard 2500.

after 5 days of transport. It must be noted that, despite the different starting feed solutions (copper nitrate and CuCN in the presence of $0.1\,M$ thiourea concentration), the only species quantitatively present in solution was $\mathrm{Cu(Tu)}_n^+$ (see Fig. 3). This means absence of Cu(II) species in solution can create a competition in the transport mechanism of the metal–thiourea complexes.

CONCLUSION

In this work it was shown that facilitated transport of copper (Cu(I)–thiourea complexes) from copper–thiourea solutions was not possible because of the formamidine disulfide presence, which constitutes an obstacle for the complexation of the metal ions at the feed phase/membrane interface. However, the transport became possible when the solutions were obtained by means of elution of cuprocyanide complexes by thiourea. The mechanisms of exchange on resins and transport in membrane were elucidated by comparing the fluxes of transport of copper ions by using cyanide and nitrate ions as co-ions. The use of thiourea solutions in different acids (nitric, chlorydric, sulfuric, and phosphoric) also affected the transport mass flux of both copper ions. The following order of flux was obtained: $\mathrm{NO_3^-} > \mathrm{Cl^-} > \mathrm{SO_4^{2-}} > \mathrm{PO_4^{3-}}$ depending on the anion of the acid taking part in the complex. This was related to the difference in the anion affinity to form neutral complexes with the positively charged copper–thiourea complexes.

The elution of cuprocyanides using a pretreatment on an anion-exchange resin may give a new perspective for the use of the SLM process for recovering copper from an acidic-thiourea leaching medium.

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