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Utilization of Mono and Bicyclic Polyethers as Mobile Carriers of Silver, Copper, and Zinc Through a Supported Liquid Membrane

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ABSTRACT

The behavior of a monocyclic polyether (crown ether) and a bicyclic polyether (cryptand) towards liquid–liquid extraction and facilitated cotransport of silver, copper, and zinc was investigated. It was shown that, with regard to their structure, the relative size of their macrocycle cavities, and the nature of the inserted ion, considerably influences the efficiency of the extraction and the cotransport. On the other hand, this study also revealed the formation of emulsions in the monocyclic polyether organic phase that constitute a barrier for the carrier–metal complex formation in the membrane support. An impregnation time of 1 hr of the support in the organic phase is necessary to achieve good efficiency for the supported liquid membrane (SLM). The optimum of the other

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fundamental parameters (polyether concentration, metal concentration, and support characteristics) were determined.

Key Words: Facilitated transport; Silver; Copper; Zinc; Macrocyclic polyethers.

INTRODUCTION

Most of the conventional processes of separation and concentration used in hydrometallurgy, as precipitation, ion exchange on resins, or liquid–liquid extraction,[1–3] are today reconsidered in view of their possible substitution with new processes using synthetic membranes. During the last decades, among involved processes, membrane-supported liquid membranes (SLM)[4–8] appear especially interesting for the treatment of hydrometallurgical diluted solutions, because they permit the combination of the advantages of liquid–liquid extraction and those of other membrane processes (Donnan dialysis, ultrafiltration, electrodialysis, etc). They also permit selective transport of a metal ion from a source to a receiving liquid phase by means of a selective carrier present in the membrane. This process also allows reaching high permeability factors, and operating a separation and a concentration at the same time with a low consumption of energy and low costs. An SLM usually consists of an organic solution immobilized in the pores of a hydrophobic microporous membrane, containing a complexing agent (carrier), which binds one of the components very selectively in the feed solution. The SLM separates, by means of two interfaces, the aqueous solution containing the species that reach the membrane interface by diffusion (feed) and the solution into which the species will be released (strip). The species are accumulated in the strip at a concentration generally greater than that in the feed. The permeation of the species is due to a chemical potential gradient (the driving force of the process) existing between the two opposite sides of the SLM.

However, in spite of their advantages, SLMs are not yet used for industrial applications owing to the low stability of the organic supported liquid phase or short life time of the membrane support due to its deterioration under the action of the solvent, which provokes a reduction of its porosity, release of the organic phase, and mixing with aqueous phases, leading to the formation of emulsions also participates in their poor stability. Concerning the specificity of the transport, a current trend of research in hydrometallurgy, is the use of very selective and specific extractants of metallic ions. Macrocyclic polyethers have held researchers interest since their synthesis[9–16] owing to their structure: the dimension of their cavity and the size of the ion inserted are the two fundamental parameters that confer a high selectivity to the extraction process. However, few works have been dedicated to precious metal extraction by this type of extractants.

In the present work, we compared the behavior of a monocyclic polyether, (the 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane noted 2.2) and a bicyclic polyether, [the 4,7,13,16,21,24-hexacosa-1,10-diaza, bicyclo (8.8.8) hexacosane noted 2.2.2] towards liquid–liquid extraction and facilitated cotransport of silver, copper, and zinc through a SLM.

EXPERIMENTAL

Materials and Methods

Solutions of each metal ion were prepared from silver, copper, and zinc nitrates (Fluka) at variable concentrations. The carriers were organic solutions of different concentrations of 2.2 and 2.2.2 (Fig. 1) (Aldrich) dissolved in chloroform (Fluka). Double distilled water was used as a stripping solution.

The permeation cell consisted of two compartments separated by the SLM. Each compartment, feed and strip, had a maximum volume of 45 mL and was provided with a mechanical stirrer. Polypropylene microporous membranes of different characteristics: Celgard 2500 (porosity $\varepsilon = 45\%$, pore size $\Phi = 0.04\,\mu m$, thickness $d_0 = 25\,\mu m$), Celgard 2400 (porosity $\varepsilon = 38\%$, pore size $\Phi = 0.02\,\mu m$, thickness $d_0 = 25\,\mu m$), Celgard 2402 (porosity $\varepsilon = 38\%$, pore size $\Phi = 0.02\,\mu m$, thickness $d_0 = 50\,\mu m$) (Hoechst Celanese Corporation, North Carolina), and Accurel PP (pore size $\Phi = 0.10\,\mu m$, thickness $d_0 = 75–110\,\mu m$) (Akzo Noble) were used as supports. The useful area of the membrane supports in the cell was $8.04\,cm^2$.

The immobilized liquid membrane was prepared by soaking the porous polymer in the carrier solution. Then, the SLM was placed between the two

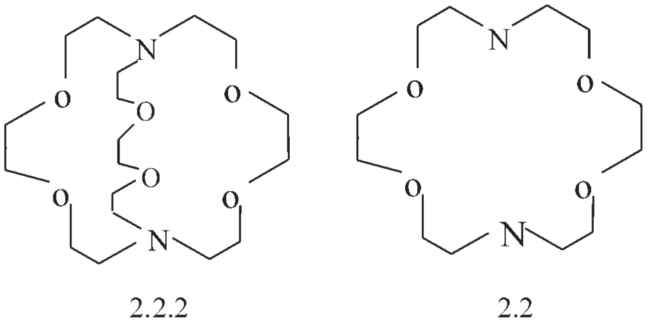

Figure 1. The macrocyclic polyethers used.

half cells. The two compartments were filled with the feed and strip solutions (43 mL each).

The experiments began when the cell was filled with both aqueous phases under stirring. The concentrations of silver, copper, and zinc ions and that of the carriers were fixed at 0.01 M except when the concentration was studied as a transport parameter. At different intervals of time, aliquots of solutions of 0.5 mL each were withdrawn from the feed and strip compartments and analyzed by atomic absorption spectroscopy (Perkin Elmer spectrophotometer model 2380). All the experiments were performed in a thermostated bath at 25 ± 0.1°C.

Equilibrium investigations were carried out by liquid–liquid (L–L) extractions: equal volumes (3/3 mL) of the aqueous phase containing the investigated metal, and the organic phase 2.2/chloroform or 2.2.2/chloroform at the chosen concentrations, respectively, were contacted for 5 min. It is sufficient time for an exchange area wide enough to reach equilibrium in 24 hr, by means of an agitator of variable speeds (Heidolph, type Top-Mix 94323). The temperature of the liquid–liquid extraction experiments was 25°C. The metal ion concentration in the aqueous phase was determined and the distribution ratio D ($D = \bar{C}/C_a$ with C the overall concentration of all forms of the metal where the bar indicates the organic phase and "a" the aqueous phase) was calculated from a mass balance of the ion between organic and aqueous phases.

Theory

The equilibrium reaction can be schematized as:

$$M^{n+} + m\bar{L} + nA^- \Longleftrightarrow \overline{ML_mA_n} \qquad (1)$$

where M^{n+} is the metal ion, L the ligand, and A^- the co-ion (NO_3^- in this work).

The extraction constant K_e is defined by:

$$K_e = \frac{[\overline{ML_mA_n}]}{[M^{n+}][A^-]^n[\bar{L}]^m} \qquad (2)$$

This constant is bound to the coefficient of distribution, D, of the metallic ions in the organic phase by:

$$K_e = \frac{D}{[A^-]^n[\bar{L}]^m} \qquad (3)$$

Eq. (3) can be written as: $\log D = [n\log(A^-) + \log K_e] + m\log(\bar{L})$.

In this hypothesis, the variation of log D vs. the log ($\bar{L}$) maintaining (M^{n+}) as the constant, permits the calculation the value of m (which corresponds to the stoichiometry of the complex formed in the organic phase).

Transport of silver, copper, and zinc ions using polyethers, obeys as a facilitated cotransport. The metal ion is complexed at the interface feed-phase/membrane, and the complex formed diffuses through the membrane phase to the interface membrane/strip-phase where the decomplexation of the metal ion is realized.

The mass flux can be calculated by the equation $J = \Delta n/S\Delta t$ where Δn is the variation of the number of moles in the feed phase during the interval time Δt (sec) and S is the membrane area (cm^2).

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

Figures 2 and 3 represent the evolution of the logarithm of the distribution coefficient, D, vs. the concentration variation of extractant from 10^{-8} to 10^{-2} M. Concentration of metal was fixed at 0.01 M.

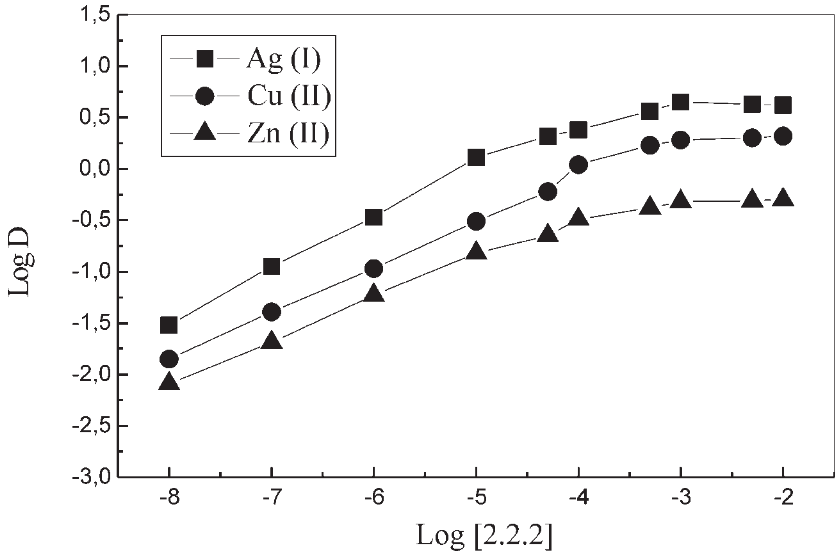

Figure 2. Logarithm of the distribution coefficient D vs. logarithm of extractant concentration. Organic phase 2.2.2/chloroform; [Metal] = 0.01 M.

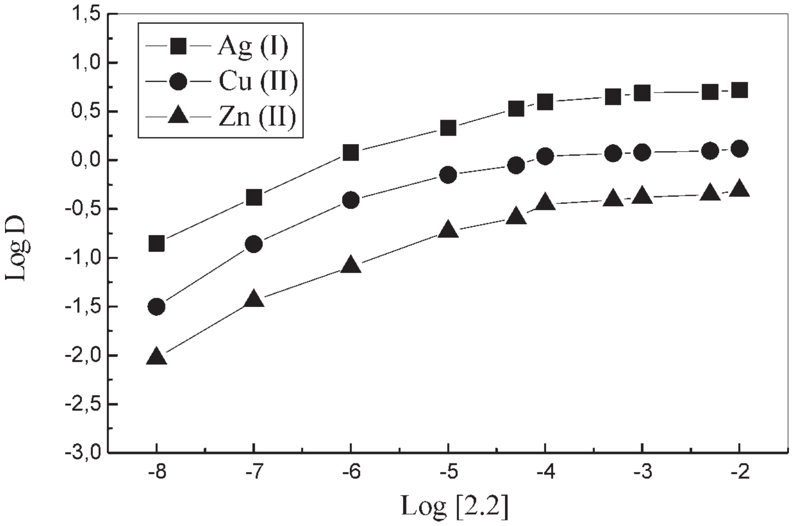

Figure 3. Logarithm of the distribution coefficient *D* vs. logarithm of extractant concentration. Organic phase 2.2/chloroform; [Metal] = 0.01 M.

The results obtained show that the distribution coefficient increases when the initial extractant concentration increases in the range 10^{-8}–10^{-4} M. Beyond a concentration of 10^{-4} M, the extractant concentration has a limited effect on Ag(I), Cu(II), and Zn(II) ion extraction. This could be due to the increasing organic phase viscosity when increasing the extractant concentration as shown on Fig. 4.

The extractant 2.2 solution is more viscous than the 2.2.2 solution. The two extractants showed a better efficiency towards silver and 2.2.2 behaves as the best extractant for the three studied metal ions. The efficiency of the interface is much higher when the metal cation is inserted deeper in the polyether cavity;[14] silver(I) ions are more adaptable to the cavities of [2.2.2] and [2.2] than are copper(I) and zinc(II) ions. This is due to the silver(I) ion size (252 pm) which is nearest the size of the cavities of [2.2.2] (280 pm) and [2.2] (180 pm) than are copper (II) ion size (138 pm) and zinc ion size (144 pm). On the other hand, it appears that both carriers have a good affinity vs. monovalent ions. This can be related to the nature of the heteroatoms forming the carrier.

Table 1 presents the extraction constants of the three metallic ions with 2.2.2 and 2.2. The coordinate of the complexes formed is of the 1 : 1 type.

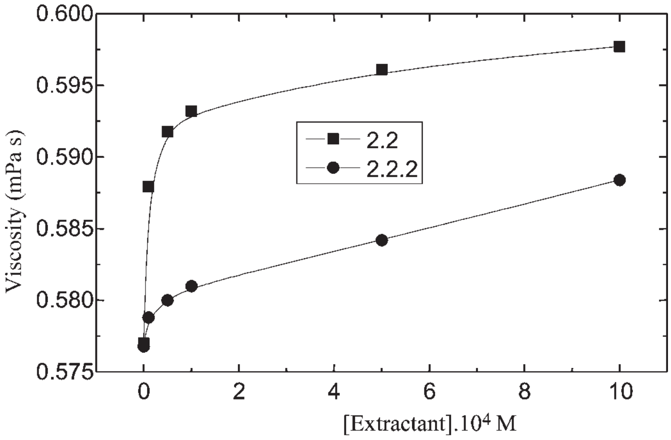

Figure 4. Evolution of the organic phase of viscosity vs. the extractant concentration.

Influence of the Carrier Concentration

Membrane supports were soaked for 1 hr in organic solutions of 2.2.2 and 2.2 of different concentrations and were used for transport of Ag(I), Cu(II), and Zn(II) ions whose initial concentrations were fixed at 0.01 M. The variation of the fluxes of the three ions across the SLM vs. the concentration of the two carriers are reported in Figs. 5 and 6, respectively, and in Table 2. An increase of the fluxes with the concentration of the carrier was observed. Above 5 mM the carrier does not affect the transfer rate of the metal ions. This behavior is in agreement with the results found by some authors with other systems.[17,18] Furthermore, fluxes obtained with 2.2 are slightly lower than those of 2.2.2. This can also be related to the difference in viscosity between the two organic phases of 2.2.2 and 2.2, and probably, to the formation of emulsions in the organic phase of 2.2 that would block the pores of the support and prevent the metallic ions to react with 2.2 molecules present in the membrane.

Table 1. Coordination and extraction constant of silver, copper, and zinc with 2.2.2 and 2.2.

	Ag(I)		Cu(II)		Zn(II)	
Ligand	*m*	log *Ke*	*m*	log *Ke*	*m*	log *Ke*
2.2.2	0.85	7.08	0.76	6.78	0.89	6.65
2.2	0.71	6.96	0.75	6.65	0.82	6.26

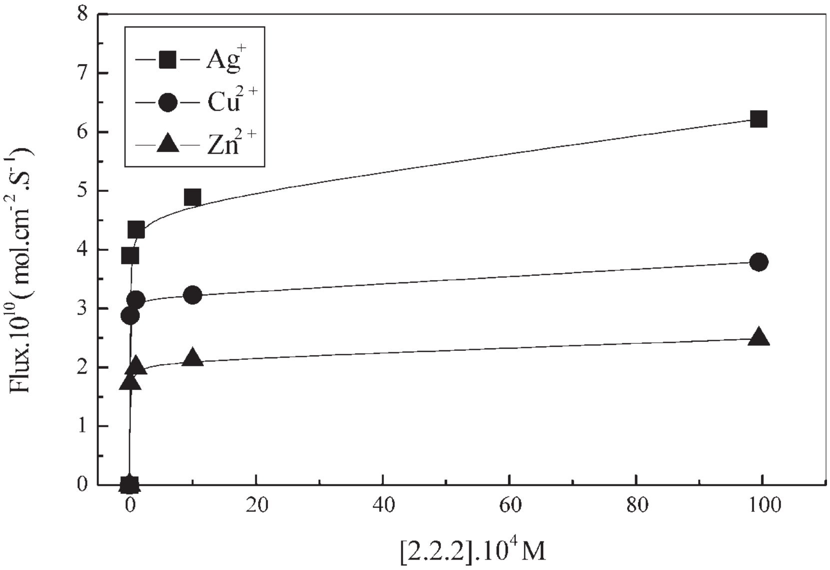

Figure 5. Evolution of the mass flux of silver, copper, and zinc vs. 2.2.2 concentration. [Metal] = 0.01 M; support: Celgard 2500 impregnated during 1 hr.

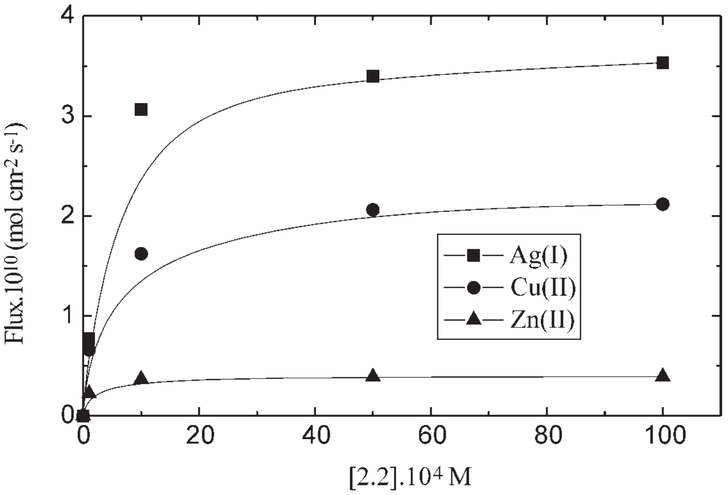

Figure 6. Evolution of the mass flux of silver, copper, and zinc vs. 2.2 concentration. [Metal] = 0.01 M; support: Celgard 2500 impregnated during 1 hr.

Table 2. Fluxes and permeabilities of silver(I), copper(II), and zinc(II) ions through the supported liquid membrane.

	$\text{Flux} \cdot 10^{10}$ (mol cm^{-2} sec^{-1})			$P \cdot 10^{5}$ (cm sec^{-1})		
[Carrier] M	Ag(I)	Cu(II)	Zn(II)	Ag(I)	Cu(II)	Zn(II)
2.2.2	6.22	3.51	2.27	7.81	4.49	2.82
2.2	3.53	2.11	0.37	3.98	2.83	0.49

Note: SLM: organic phase 2.2.2/$CHCl_3$ and 2.2/$CHCl_3$ 10 mM [metal] = 10 mM; support: Celgard 2500 impregnated during 1 hr.

The two extractants showed the same order of efficiency as well as in the case of liquid–liquid extraction. However, the same explanations remain valid. This shows, in fact, not only that the size of the polyether cavities represents a fundamental key factor for the transport and the metallic ion extraction, but also that the shape of the carrier molecule (monocyclic or bicyclic) can also have an influence. Thus, we have used the most selective carrier (2.2.2) for the following part of this work.

Influence of the Metal Concentration

Figure 7 represents the variation of Ag(I), Cu(II), and Zn(II) ions mass flux vs. the initial concentration of these ions. This figure shows that in the case of weak metal concentrations (10^{-5}–10^{-3} M), the flux is a function of the feed initial concentration. However, beyond a concentration of 10^{-3} M, the flux tends to a maximal value and becomes independent of the metallic ion concentration. This is due to the saturation of the membrane by the metal–carrier complex molecules as the decomplexation at the strip interface is presumably the rate-limiting step.

Influence of the Support Characteristics

Thickness and porosity of the membrane support are also some fundamental operative parameters that can influence the stability of the SLM and, therefore, the value of the metallic ion transfer flux. The influence of these parameters was studied using four supports of different physical characteristics. The results obtained (Table 3) show that for the three ions, the flux:

- Increases when the porosity of the support increases.
- Decreases when the thickness of the support increases.

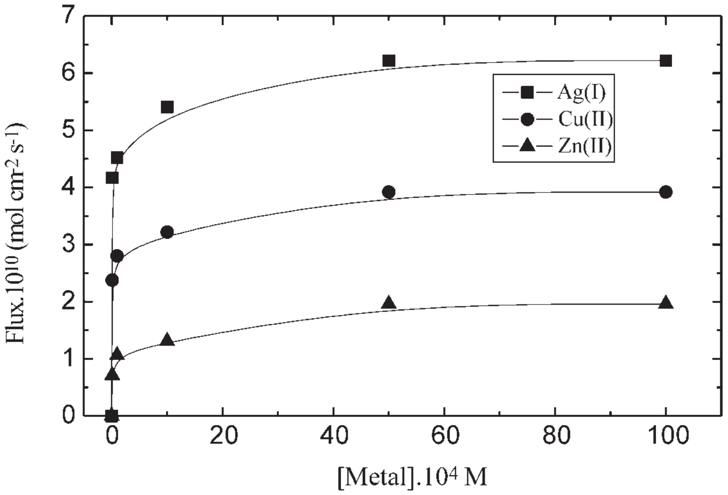

Figure 7. Evolution of Ag(I), Cu(II), and Zn(II) mass flux vs. the metal initial concentration. [2.2.2] = 0.01 M; Support: Celgard 2500 impregnated during 1 hr.

This is in conformity with the results obtained by some authors.[19,20]

The membrane Celgard 2500, more porous and less thick, is the one giving better mass fluxes of the three metallic ions.

Separation of Silver, Copper, and Zinc

The optimal parameters determined previously (a carrier concentration of 0.01 M; support Celgard 2500 impregnated during 1 hr; concentration of the three metals of 0.01 M) have been used to achieve the separation of silver, copper, and zinc from a synthetic equimolar solution.

Table 3. Transfer flux of silver, copper, and zinc changing the support characteristics. MLS: 2.2.2/chloroform 0.01 M, support impregnated during 1 hr, [metal] = 0.01 M.

Support	$J_{Ag(I)} \cdot 10^{10}$ (mol cm^{-2} sec^{-1})	$J_{Cu(II)} \cdot 10^{10}$ (mol cm^{-2} sec^{-1})	$J_{Zn(II)} \cdot 10^{10}$ (mol cm^{-2} sec^{-1})
Celgard 2500	6.22	3.51	2.27
Celgard 2400	2.81	1.52	1.29
Celgard 2402	2.50	1.13	0.92
Accurel	0.034	0.019	0.01

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To appreciate the possibility of separation of two metals M_1 and M_2, we have defined a separation factor by: $F_{M_2}^{M_1} = ([M_1]_t/[M_1]_t)/([M_1]_i/[M_2]_i)$ The subscripts *t* and *i* represent the concentrations of the metal at time *t* and initial in solution, respectively. This factor permits evaluating the efficiency of a separation. Indeed, the separation is better when $F_{M_2}^{M_1}$ moves away the unit. Figure 8 gives the evolution of the three metal concentrations in the strip compartment vs. transport time. The obtained results show that silver is well separated from copper and zinc using 2.2.2 as the carrier. Hence, by multiplying the number of compartments, we will be able to completely separate silver from copper and zinc.

Table 4 collects the separation factors of the three metals calculated by considering two to two the three metals.

CONCLUSION

This work shows that, liquid–liquid extraction and facilitated cotransport of silver, copper, and zinc with macrocyclic polyethers depends on the size of the carrier cavities and the inserted metallic ion size. The carrier 2.2.2, with cavities size closer than that of Ag(I), Cu(II), and Zn(II), is the one which

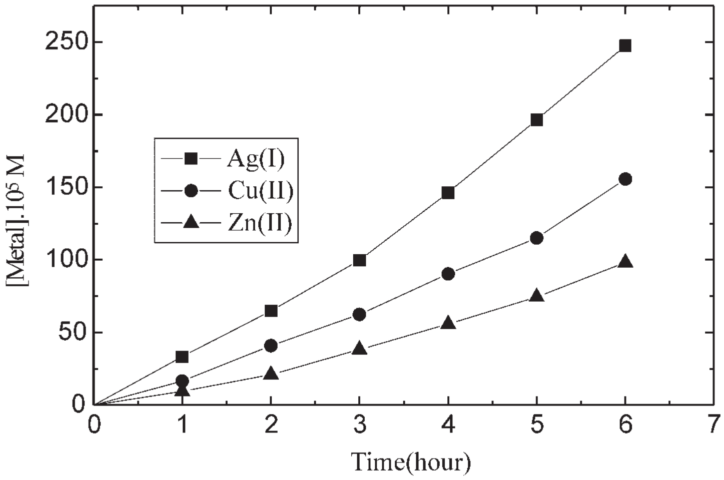

Figure 8. Evolution of silver, copper, and zinc concentrations in the strip compartment vs. time. SLM: 2.2.2/Chloroform 0.01 M; Support: Celgard 2500 impregnated during 1 hr; [metal] = 0.01 M.

Table 4. Separation factors of Ag(I), Cu(II), and Zn(II) ions. SLM: 2.2.2/Chloroform 0.01 M, support Celgard 2500 impregnated during 1 hr; [metal] = 10 mM.

F_{Ag}^{Cu}	F_{Zn}^{Cu}	F_{Zn}^{Ag}
1.64	1.42	2.5

gives the best distribution factors and transfer fluxes. However, other physicochemical factors also influence the efficiency of extraction and transport: organic phase viscosity, carrier concentration, metal concentration, and membrane support characteristics. Carrier and metal concentrations of 0.01 M; impregnation time of 1 hr for 2.2.2 and 2.2; and Celgard 2500 support were shown to be the best conditions for maximum efficiency of the studied systems.

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