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### FACILITATED COTRANSPORT OF Ag(I), Cu(II), AND Zn(II) IONS BY DB18C6 AND DA18C6 CROWN ETHERS AS CARRIERS: INTERFACE BEHAVIOR ON ION TRANSPORT

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## **FACILITATED COTRANSPORT OF Ag(I), Cu(II), AND Zn(II) IONS BY DB18C6 AND DA18C6 CROWN ETHERS AS CARRIERS: INTERFACE BEHAVIOR ON ION TRANSPORT**

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### **ABSTRACT**

The interface behavior in the facilitated cotransport of Ag(I), Cu(II), and Zn(II) ions through supported liquid membranes (SLMs) made of a flat polypropylene membrane sheet containing dibenzo-18-crown-6 (DB18C6) or 4,13-diaza-18-crown-6 (DA18C6) as carriers was studied. The liquid-liquid extraction tests showed a maximum distribution coefficient when the carrier con-

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centration was greater than 0.01 mmol/L. In transport experiments the transmembrane flux increased with increasing carrier concentrations that reached a limiting value over 5 mmol/L. The calculation of the diffusion coefficients in membranes showed a lower diffusivity of DA18C6-metal complexes than did DB18C6-metal complexes for all 3 ions:  $(\text{Ag}^+) > (\text{Cu}^{2+}) > (\text{Zn}^{2+})$ . The diffusivity was significantly higher using a Celgard 2500 support than with Celgard 2400 or 2402. The immobilized interfaces were soaked for various times. The membranes with the highest capability to retain ions were immersed for 30 days. Phase fluxes of almost zero, at less than  $10^{-2}$  mol/L concentration, were obtained. In the transient state of the transport through the SLM, different molar flow rates at the feed-membrane and membrane-strip interfaces were observed. The selectivity of the interfaces containing DB18C6 in the separation binary mixtures of ions showed the following separation factors:  $SF_{\text{Ag-Zn}} = 2.9$ ;  $SF_{\text{Ag-Cu}} = 2.5$ ;  $SF_{\text{Cu-Zn}} = 1.2$ .

**Key Words:** Supported liquid membranes; Crown ethers; Separation and concentration of silver, copper, and zinc; Selective interfaces

## INTRODUCTION

Many of the conventional separation and concentration processes used in hydrometallurgy, like precipitation, ion exchange with resins or liquid-liquid extraction (1,2), are today reconsidered with processes based on synthetic membranes viewed as possible substitutes. Membrane processes, in particular of the pressure-driven type, are used in many industrial fields for the recovery and recycling of substances and by-products. New types of membranes, such as supported liquid membranes (SLMs), are particularly interesting and are being considered for the treatment of diluted solutions containing metal ions (3–7) because their use combines the advantages of solvent extraction and those of the other membrane processes (ultrafiltration, reverse osmosis, dialysis, etc). This technique is also simpler than that using a combination of micelles and ultrafiltration for metal ions removal (8). A SLM is expected to be one of the most efficient membranes for separation processes because the interface can selectively recognize one ion, and furthermore, facilitated transport is more effective than passive transport. Other advantages of SLM separation are high permeability, possibility to separate and to concentrate species at the same time, and the great potential for low cost and energy savings. This type of transport has been experimentally successful in the hydrometallurgical field for the recovery and separation of various metal ions



(9–11). Despite their advantages, SLMs have not been used on a large scale in industry because membrane lifetime is relatively low. The instability of the interface, such as the loss of carrier and/or membrane solvent from the membrane phase and degradation of the support under the action of solvents, which leads to the loss of porosity and emulsion formation in the aqueous or organic phases (12), contributes to the low life expectancy of SLMs. The use of SLMs in processes that are selective toward metal ions is a current trend in hydrometallurgy research. Because of their structures, macrocyclic polyethers have been widely identified in the literature as selective extractants of metals (13–16). The sizes of the polyether cavities and of the inserted ions are fundamental parameters that make polyethers effective at selective extraction.

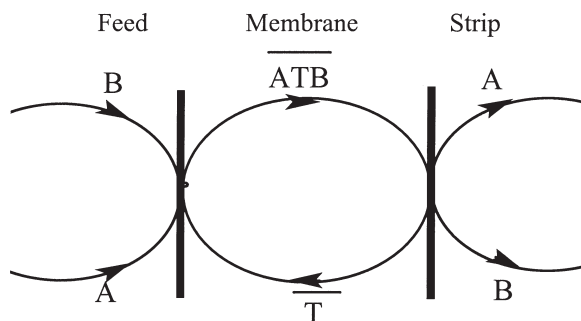
In the present work, the behavior of the immobilized interface was studied through the use of dibenzo-18-crown-6 (DB18C6) and diaza-18-crown-6 (DA18C6) as specific extractants of silver, copper, and zinc ions, which are usually found together in leaching solutions of polymetallic ores. The distribution coefficients of each metal ion, between organic and aqueous phases, were determined; then the mass transport was studied as a function of 1) carrier concentration, viscosity of the organic phase, and type of membrane support; 2) preparation time of the immobilized interface; and 3) metal ion concentration in the feed phase. The accumulation of the metal ions in the 2 interfaces of the SLM, as well as the effectiveness of the SLM process as a concentration and separation technique, was studied. Furthermore, the diffusion coefficients of the 3 ions in the SLMs were determined.

## THEORY

A SLM usually consists of an organic solution immobilized in the pores of a hydrophobic macroporous membrane that contains a complexing agent (carrier) that selectively binds one of the components from the feed solution. The SLM separates, by means of 2 interfaces, the aqueous solution containing the species that diffuse (feed) and the solution into which the species will diffuse (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) that exists between the opposite sides of the SLM.

Transport of silver, copper, and zinc ions by crown ethers can be facilitated by cotransport. The transport mechanism is represented in Fig. 1. The metal ion is complexed at the feed-phase/membrane interface, and the complex formed diffuses through the membrane phase to the membrane/strip-phase interface where the metal ion is removed from the complex. The equilibrium reaction can be represented as





**Figure 1.** Scheme of the facilitated cotransport. *A* and *B* represent the ion and co-ion to be transported;  $\bar{T}$  is the carrier; and  $\overline{ATB}$  refers to the complex.

where  $M^{n+}$  is the metal ion,  $L$  the ligand, and  $A^-$  is the co-ion ( $\text{NO}_3^-$ ). The over-bars show that the reaction takes place in the organic phase.

The permeability  $P$  (cm/s) of an ion through the interface is defined as  $J/[\text{Metal}]_{f,0}$ , where the initial molar flux is denoted by  $J$  (mol/cm<sup>2</sup>·s) and the initial metal concentration is measured in mol/dm<sup>3</sup>.  $J$  can be calculated by using the expression of flux defined by Danesi (17)  $J = -\Delta n/(A\Delta t)$ , where  $\Delta n$  is the variation of the number of moles in the feed phase during the variation of time ( $\Delta t$ ) in seconds, and  $A$  is the membrane area (cm<sup>2</sup>).  $P$  can be obtained from the equation:

$$\ln \frac{[\text{Metal}]_{f,t}}{[\text{Metal}]_{f,0}} = -P \frac{A}{V} t \quad (2)$$

where  $V$  (cm<sup>3</sup>) represents the volume of the aqueous feed solution. A linear dependence of the feed solution, denoted by  $\ln [\text{Metal}]_{f,t}/[\text{Metal}]_{f,0}$ , with time is obtained, and the permeability can be calculated from the slope of the straight line that fits the experimental data.

The diffusion coefficient  $D_o$  (cm<sup>2</sup>/s) of the metal complex through the organic phase can be determined when diffusion resistances in the aqueous, feed-solution/membrane layer is absent by the following expression (17):

$$C = C_0 - \frac{[\bar{L}]At}{n\Delta_o V} \quad (3)$$

where  $\Delta_o = d_o/D_o$  (s/cm) is the transport resistance to diffusion through the membrane;  $d_o$  (cm) is the thickness of the SLM;  $n$  is the number of moles of the carrier in the complex ( $n = 1$  in this work because the polyether cavity hosts one ion);  $[\bar{L}]$  is the initial concentration of the extractant in the organic phase;  $C$  and  $C_0$  are the concentrations of the metal in the feed phase at time  $t$  and 0 respectively.

The curves  $C_0 - C = f(t)$  allowed us to calculate the diffusion coefficients  $D_o$  of the metal complex species in the immobilized organic phase. The diffusion



coefficient is dependent on the chemical-physical characteristics of the diffusing species and that of the medium as reported in the Stokes-Einstein equation  $D = kT/(6\eta\pi r)$ . The viscosity,  $\eta$ , depends on the absolute temperature  $T$  according to the Guzman-Andrade equation  $\eta = A \exp(B/T)$ .  $A$  and  $B$  are constants that can only be evaluated when knowledge of 2 or more values of  $\eta$  are known, and  $r$  is the radius of the diffusing complex.

The molar flow rate  $F$  (mol/h) of an ion in the aqueous solution is defined by the number of moles  $n$  transferred per unit time from the feed phase to the feed-membrane interface or from the strip-membrane interface to the strip phase through the membrane.  $F$  can be determined by the following expressions:

$$F_f = \frac{\Delta n(f)}{\Delta t}; \quad F_s = \frac{\Delta n(s)}{\Delta t} \quad (4)$$

where  $\Delta n(f)$  and  $\Delta n(s)$  represent the variation of the number of moles in the feed (f) and strip (s) phases respectively.

The separation (or selectivity) factor  $SF$  in the separation of a metal ion  $M_2$  from a metal ion  $M_1$ , both contained in the same feed solution, can be defined as follows:

$$SF = \frac{[M_1]_t/[M_2]_t}{[M_1]_i/[M_2]_i} \quad (5)$$

where the subscripts  $t$  and  $i$  represent the concentrations of the metals in the feed solution at times  $t$  and  $i$  (initial), respectively. This selectivity factor permits immediate evaluation of separation efficiency using parameters of the solution, which is an alternative to the definition based on permeabilities of metals ( $SF = P_{Me1}/P_{Me2}$ ). The separation of the metals is better when  $SF$  is greater than unity.

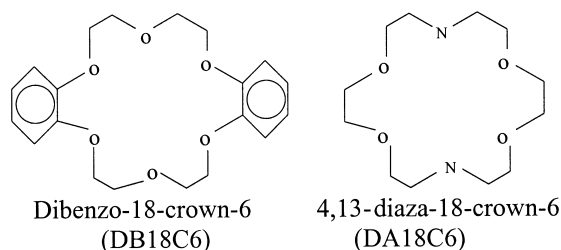
## EXPERIMENTAL

### Materials and Methods

The solutions of each metal ion were prepared from silver, copper, and zinc nitrates (from Fluka, Switzerland) at variable concentrations. The carriers (Fig. 2) were organic solutions of different concentrations of dibenzo-18-crown-6 and di-aza-18-crown-6 (from Aldrich, Steinheim) dissolved in chloroform (from Fluka). Many researchers have used chloroform as a crown ether solvent in extraction (18–20) or SLM experiments (21,22). Chloroform is a preferred solvent, despite its volatility, because crown ethers have low solubility in the other solvents. Double-distilled water was used as a stripping solution.

The permeation cell consisted of 2 compartments separated by the SLM as described elsewhere (23). Each compartment, feed and strip, had a maximum vol-





**Figure 2.** Structural formula of the 2 macrocyclic polyethers.

ume of 45 mL. The agitation of the solutions was realized by 2 synchronized motors that relied on generators of variable tension with a stirring rate of 800 rpm. The rate was measured with a phototachometer by Cole Parmer Instruments Co. The stirring rate was high enough to minimize boundary layer resistances. Polypropylene microporous membranes (from Hoechst Celanese Corp, North Carolina, USA) of different characteristics were used as supports: Celgard 2500 (porosity  $\varepsilon = 45\%$ ; pore size  $\Phi = 0.04 \mu\text{m}$ ; thickness  $d_0 = 25 \mu\text{m}$ ), Celgard 2400 (porosity  $\varepsilon = 38\%$ ; pore size  $\Phi = 0.02 \mu\text{m}$ ; thickness  $d_0 = 25 \mu\text{m}$ ), and Celgard 2402 (porosity  $\varepsilon = 38\%$ ; pore size  $\Phi = 0.02 \mu\text{m}$ ; thickness  $d_0 = 50 \mu\text{m}$ ). The useful area of the supports in the cell was  $8.04 \text{ cm}^2$ .

Equilibrium investigations were carried out by liquid-liquid (L-L) extractions: Equal volumes of the aqueous phases, containing the investigated metal, and of the organic phases DB18C6/ Chloroform or DA18C6/Chloroform at the chosen concentrations were contacted for 1 h. Then the 2 phases were completely separated by centrifugation. The metal ion concentration in the aqueous phase was determined and the distribution ratio ( $D$ ) was calculated from a mass balance of the ion between organic and aqueous phases and from  $D = \bar{C}/C_a$  with  $C$  the overall concentration of all forms of the metal. The overbar indicates that the metal is in the organic phase, and "a" indicates that it is in the aqueous phase.

In all cases, the concentrations of silver, copper, and zinc were determined in the aqueous phase using an atomic absorption spectrophotometer (AAS) from Perkin Elmer 2380.

The immobilized interface was prepared by soaking the support in the carrier solution for 14 days. This soak time was chosen for most of the experiments because good fluxes were previously obtained by Gherrou et al. (23). In some experiments the support was soaked with variable times; then the SLM was placed between the 2 half-cells. The 2 compartments were filled with the feed and the strip solutions (43 mL each). The concentrations of silver, copper, and zinc ions and those of the carriers were fixed at 0.01 M except when the concentration was studied as a transport parameter. The experiments were begun by starting the stir-



ring motors in the 2 compartments. At different intervals of time, aliquots of 1 mL were withdrawn from the feed and strip compartments and analyzed by AAS. All the experiments were performed in a thermostated bath at 25°C.

The viscosities of the organic phases were measured by using a Hubbelohde viscosimeter containing 20 mL of DB18C6/Chloroform or DA18C6/Chloroform solutions at variable concentrations. The viscosity of the solution is linked to its flow time  $t$  by the following expression (24):

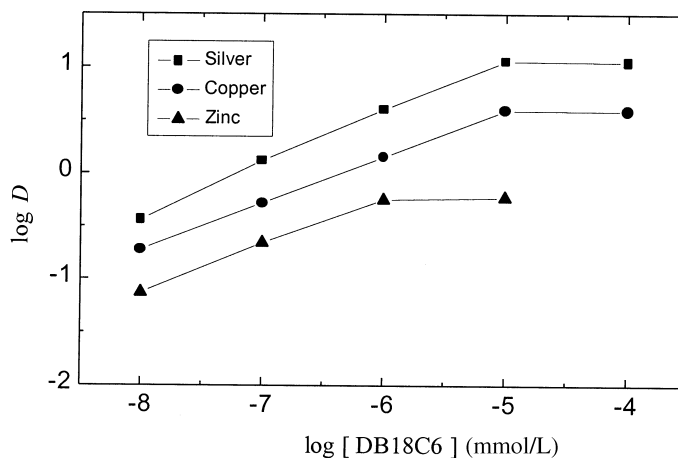
$$\eta = \rho_s K t$$

where  $\rho_s$  is the density of the solution and  $K$  ( $= 0.00498$ ) is the specific constant of the viscosimeter.

## RESULTS AND DISCUSSION

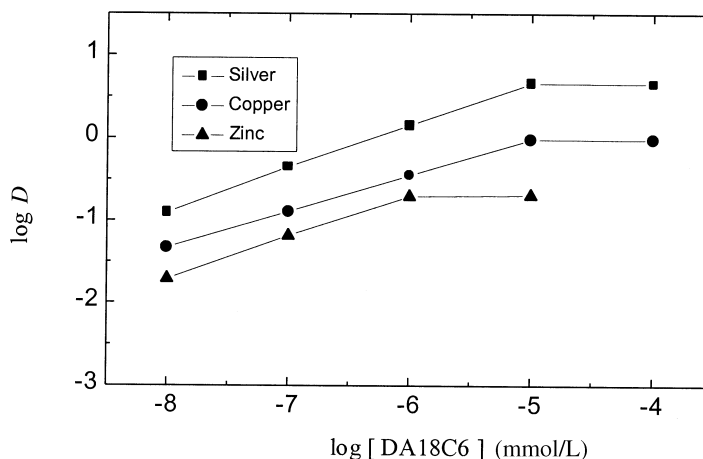
### Liquid-Liquid Extraction

The equilibrium behavior of the interfaces was studied by means of L-L extraction tests. The distribution ratios obtained for Ag(I), Cu(II), Zn(II), and the 2 crown ethers are plotted in Figs. 3 and 4 as a function of the initial extractant concentration. The obtained results show that the distribution coefficients reached a maximum value when the concentration of the extractant was greater than 0.01



**Figure 3.** Distribution coefficients of silver, copper, and zinc ions vs. the initial concentration of the extractant. Organic phase DB18C6/Chloroform ranged from  $10^{-8}$  to  $10^{-4}$  mmol/L; aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  were made with distilled water;  $[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = [\text{Ag}^+] = 10 \text{ mmol/L}$ .





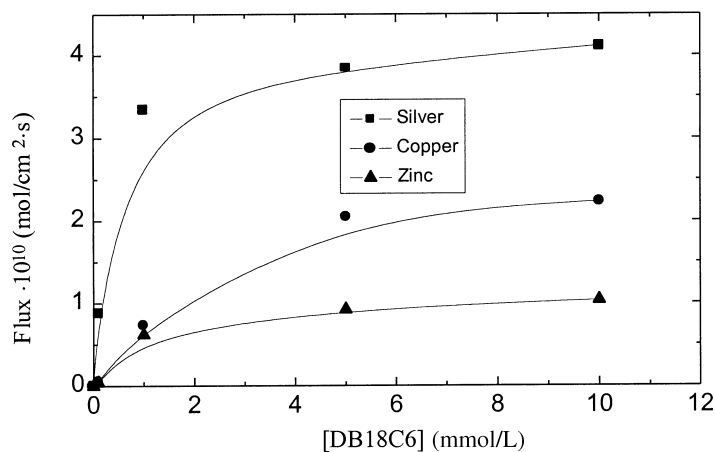
**Figure 4.** Distribution coefficients of silver, copper, and zinc ions vs. the initial concentration of the extractant. Organic phase DA18C6/Chloroform ranged from  $10^{-8}$  to  $10^{-4}$  mmol/L; aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  were made with distilled water;  $[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = [\text{Ag}^+] = 10$  mmol/L.

mmol/L. The selectivity of the interface is much higher when the metal cation is inserted deeper in the polyether cavity (14); silver (I) species are more adaptable to the cavities of DB18C6 and DA18C6 than are copper (II) and zinc (II). This is due to the silver (I) ion size (radius 126 pm), which is more similar to that of the cavities of DB18C6 (diameter 260–320 pm) and DA18C6 (180 pm). Copper (II) has a radius of 69 pm and the zinc ion has a radius of 72 pm. Both carriers have a good affinity for the monovalent ions, but DB18C6 is more selective for silver than for copper or zinc. This affinity can be related to the nature of the heteroatoms forming the carrier. In fact, oxygen atoms have more affinity with charged species than do the nitrogen atoms of DA18C6.

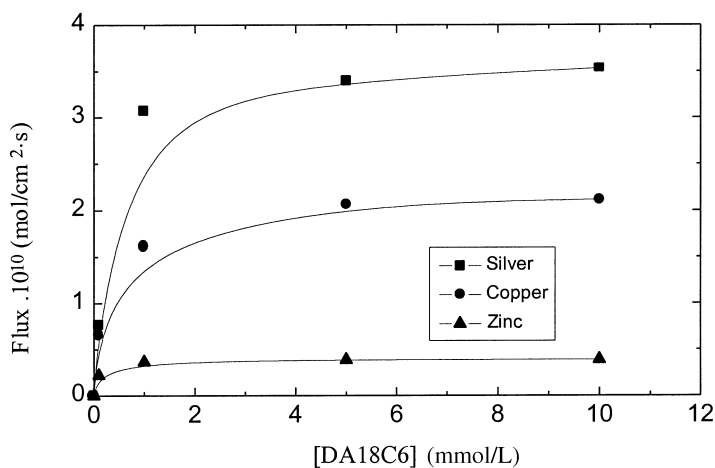
#### Influence of the Carrier Concentration, Viscosity, and Type of Membrane Support

The variation of the fluxes of the 3 ions across the SLM vs. the concentration of the 2 carriers are reported in Figs. 5 and 6. At a concentration greater than 5 mmol/L, the carrier does not affect significantly the transfer rate of the metal ions. This behavior agrees with the results found by some authors who studied other systems (25–29). Furthermore, the fluxes obtained with DA18C6 were slightly lower than those of DB18C6 for all 3 ions.



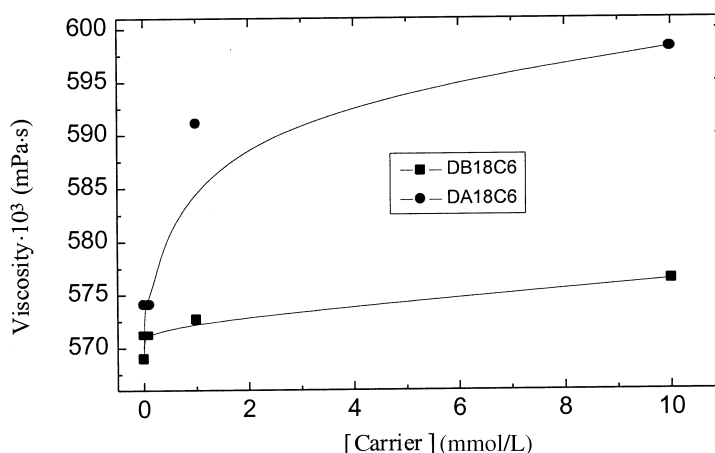


**Figure 5.** Fluxes of silver (I), copper (II), and zinc (II) vs. the initial concentration of the carrier DB18C6. SLM was in organic phase of DB18C6/Chloroform; support was Celgard 2500 impregnated for 14 days; feed solution consisted of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  in water with  $[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = [\text{Ag}^+] = 10 \text{ mmol/L}$ ; the strip solution consisted of distilled water.



**Figure 6.** Fluxes of silver (I), copper (II), and zinc (II) vs. the initial concentration of the carrier DA18C6. SLM was in organic phase of  $10^{-5}$ – $10^{-2}$  mmol/L DA18C6/Chloroform; support was Celgard 2500 impregnated for 14 days; feed solution consisted of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  in water with  $[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = [\text{Ag}^+] = 10 \text{ mmol/L}$ ; strip feed consisted of distilled water.





**Figure 7.** Viscosities of the organic phases vs. the concentration of the carriers. Organic phases consisted of DB18C6 and DA18C6 in chloroform.

The low increase of flux at high carrier concentration is generally due to an increase of the viscosity of the organic phase, which affects the diffusion coefficient. Figure 7 shows the increase of the viscosity with the increased concentration of the carrier in the organic phase. Higher viscosity of the DA18C6 solutions is consistent with the lower flux values for metal ions with the DA18C6 carrier. The higher fluxes depicted in Figs. 5 and 6 were obtained for a 10 mmol/L carrier concentration, so this concentration value was fixed in the subsequent part of the work.

In Table 1 the fluxes and the permeabilities, obtained from Eq. (2) of silver (I), copper (II), and zinc (II) through the SLM containing 10 mmol/L of DB18C6 or DA18C6, are reported. Both the flux and the permeabilities of silver (I) were higher than those of copper (II) and zinc (II). Because the only difference in the 3

**Table 1.** Fluxes and Permeabilities of Silver (I), Copper (II), and Zinc (II)

Carrier	$J \cdot 10^{10} \text{ (mol/cm}^2 \cdot \text{s}^{-1}\text{)}$			$P \cdot 10^3 \text{ (cm/s}^{-1}\text{)}$		
	$\text{Ag}^+$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Ag}^+$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$
DB18C6	4.42	2.53	1.03	5.02	3.57	2.94
DA18C6	3.53	2.11	0.37	3.98	2.83	0.493

SLM: Organic phase of 10 mmol/L DB18C6/Chloroform and DA18C6/Chloroform 10 mmol/L. Support: Celgard 2500 impregnated during 14 days. Feed: 10 mmol/L aqueous solutions of  $\text{Cu(NO}_3)_2$ ,  $\text{Zn(NO}_3)_2$ , and  $\text{AgNO}_3$ . Strip: distilled water.



**Table 2.** Diffusion Coefficients of Silver (I), Copper (II), and Zinc (II) Through the Supported Liquid Membrane

Carrier Concentration (mol/L)	$D_o \cdot 10^9$ (cm <sup>2</sup> /s)					
	Ag <sup>+</sup>		Cu <sup>2+</sup>		Zn <sup>2+</sup>	
	DB18C6	DA18C6	DB18C6	DA18C6	DB18C6	DA18C6
10 <sup>-2</sup>	188.45	160.25	126.63	105.8	42.3	32.17
5 · 10 <sup>-3</sup>	191.55	167.81	129.67	112.8	42.08	35.17
10 <sup>-3</sup>	—	170.11	175.46	140.11	100.79	35.17

SLM: Organic phase DA18C6/Chloroform and DB18C6/Chloroform. Support: Celgard 2500 impregnated for 14 days. Feed: 10 mmol/L Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, and AgNO<sub>3</sub>. Strip: distilled water.

—Data not available.

SLM systems is the type of transported ion, the findings are in accordance with the higher distribution ratio seen in L-L liquid-liquid extraction.

Table 2 reports the diffusion coefficients, obtained by applying Eq. (3), for the 2 crown ethers and the 3 ions. DA18C6-metal complexes have lower diffusivity than DB18C6-metal complexes for all 3 ions. A sequence of diffusivity was found, (Ag<sup>+</sup>) > (Cu<sup>2+</sup>) > (Zn<sup>2+</sup>), which is related to the interactions of crown-metal ions with the organic solvent in the SLM.

In Table 3, the diffusion coefficients for 3 different Celgard supports are reported. The diffusivity was significantly higher when the Celgard 2500 support was used: This can be related to the smaller pore sizes of the other 2 supports, which affects the ability of the organic phase to penetrate through the pores (23) and to the higher friction for the transport of complexes inside the pores. In the subsequent work, only the Celgard 2500 support was used.

**Table 3.** Diffusion Coefficients of Silver (I), Copper (II), and Zinc (II) Through the Supported Liquid Membrane

Support	$D_o \cdot 10^9$ (cm <sup>2</sup> /s)		
	Ag <sup>+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
Celgard 2500	188.45	126.63	42.30
Celgard 2400	17.79	10.206	6.43
Celgard 2402	26.76	18.89	7.45

SLM: Organic phase DB18C6/Chloroform. Support: Celgard 2500 impregnated for 14 days. Feed: 10 mmol/L of Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, and AgNO<sub>3</sub>. Strip: distilled water.

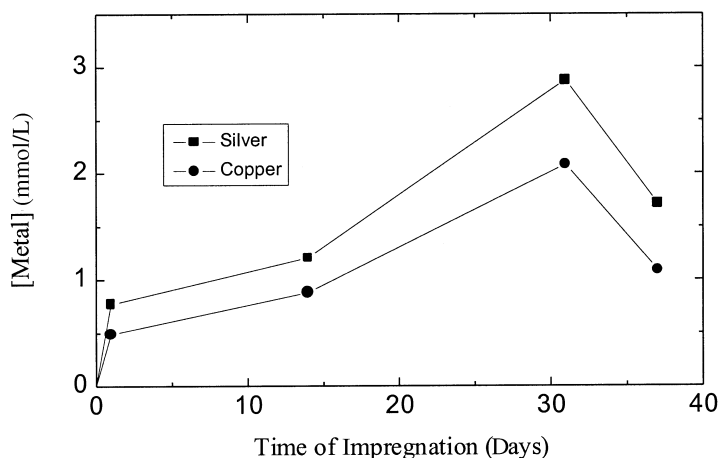


### Impregnation Time of the Immobilized Interfaces

To act as a transporting phase, a SLM requires that some amount of the metal be present as a complex inside it. The concentration of metal accumulated in the immobilized organic phase was determined from a mass balance by measuring its concentration at regular intervals in the strip and feed phases. The evolution of the concentrations of silver and copper ions retained in the organic phase is reported in Fig. 8; each value was obtained after 420 minutes of a transport test carried out with membranes prepared by immersion of the support in the organic phase for various times. The values of the fluxes during the 420 minutes of tests were almost constant except in the first 3 hours of transport, which corresponded to the saturation of the interface. Fluxes shown in Fig. 8 decreased after 30 days of support immersion in the organic phase as the metal concentration in the membrane phase decreased. As was shown in a previous work (23), this decreased flux is due to the degradation of the support under the action of the solvent after relatively long durations of impregnation.

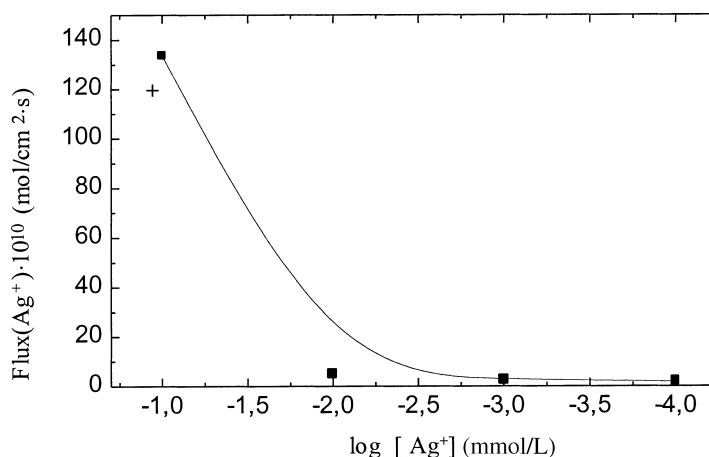
### Influence of the Metal Concentration

Flux through the interfaces depends also on the initial metal ion concentration. Figure 9 shows that the flux of silver increases when the concentration of sil-



**Figure 8.** Concentrations of the carrier-silver (I) complex and of the carrier-copper (II) complex in the SLM phase vs. the impregnation time of the support. SLM was in organic phase of 10 mmol/L DB18C6/Chloroform; support was Celgard 2500; feed solution consisted of  $\text{AgNO}_3$  and  $\text{Cu}(\text{NO}_3)_2$  in water with  $[\text{Cu}^{2+}] = [\text{Ag}^+] = 10 \text{ mmol/L}$ ; strip solution consisted of distilled water.





**Figure 9.** Fluxes of silver (I) vs. the logarithm of the initial concentration of silver in the feed phase. SLM was in organic phase of 10 mmol/L DB18C6/Chloroform; support was Celgard 2500 impregnated for 14 days; feed solution consisted of  $10^{-4}$  to  $10^{-1}$  mol/L of  $\text{AgNO}_3$  in water; strip solution consisted of distilled water.

ver in the feed phase is in the range of  $10^{-2}$ – $10^{-1}$  mol/L. Below  $10^{-2}$  mol/L, the flux decreases to nearly zero; this is due to diffusion resistances that are directly linked to the metal ion concentration in the feed phase (30,31).

#### Accumulation of the Metal Ions at the Interfaces

In the transient state of a SLM, metal ions are complexed at the feed-membrane interface where they accumulate; consequently the molar flow rate at this interface can be different than the molar flow rate from the membrane-strip interface solution. Table 4 reports the evolution of the molar flow rates of silver, copper, and zinc ions to the feed-membrane interface and from the membrane-strip interface. The 2 flow rates differ significantly at the beginning of the transport. This can be attributed to the low diffusivity of the complexes inside the SLM or to a lower decomplexation rate at the strip side than the complexation rate at the feed side. The fluxes become equal (reach a steady state) after more than 3 h of transport. So, the use of fluxes, feed or strip side, as a parameters to compare the performances of different SLMs must be done with caution.

#### Application of the SLM as a Separation Technique

The selectivity of a SLM is a parameter that allows for the evaluation of the degree of purification of a species with respect to others. Figure 10 shows the evo-

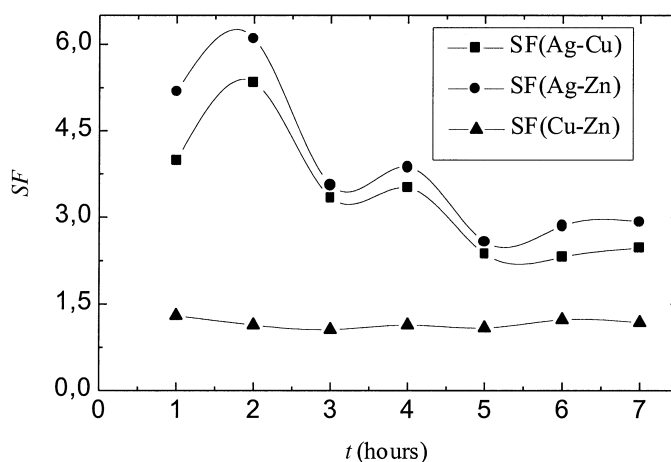


**Table 4.** Molar Flow Rate of Ag(I), Cu(II), and Zn(II) from the Feed Phase to the Organic Phase and from the Organic Phase to the Strip Phase vs. Time

Time (h)	Molar flow rate $\cdot 10^5$ (mol/h)					
	Feed			Strip		
	Ag <sup>+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Ag <sup>+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
1	116.00	92.54	64.88	26.00	13.88	5.33
3	28.28	25.95	10.25	31.82	22.17	10.00
5	29.00	23.54	10.78	33.35	18.55	9.33
6	27.00	19.99	10.21	30.21	20.77	10.02
7	32.34	20.98	9.21	34.8	19.19	9.65

SLM: Organic phase of 10 mmol/L DB18C6/Chloroform. Support: Celgard 2500 impregnated for 14 days. Feed: 10 mmol/L Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, and AgNO<sub>3</sub>. Strip: distilled water.

lution of the separation factor, obtained from Eq. (5), of silver, copper, and zinc ions from binary solutions though the analysis of each ion concentration in the strip phase vs. time. The obtained results at pseudo steady state showed that silver ions had higher mobility than zinc and copper ions ( $SF_{Ag-Zn} = 2.9$ ;  $SF_{Ag-Cu} = 2.5$ ;  $SF_{Cu-Zn} = 1.2$ ); furthermore, if the separation is stopped after 2 h, a higher  $SF$  is obtained with respect to the steady state. In an industrial separation, in which



**Figure 10.** Separation factors of silver, copper, and zinc from their mixtures. SLM was in organic phase of 10 mmol/L DB18C6/Chloroform; the support was Celgard 2500 impregnated for 14 days; the feed solution consisted of Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, and AgNO<sub>3</sub> in water with [Cu<sup>2+</sup>] = [Zn<sup>2+</sup>] = [Ag<sup>+</sup>] = 10 mmol/L; strip solution consisted of distilled water.



the number of strip stages is multiplied, silver ions can be completely separated from copper and zinc ions.

## CONCLUSION

The optimum values and the behaviors of the main parameters influencing the transport of silver, copper, and zinc ions through SLM that contained DB18C6 or DA18C6 as carriers were determined. L-L extraction tests showed a maximum distribution coefficient using a carrier concentration greater than 0.01 mmol/L. In transport experiments, the transmembrane flux increased with increased carrier concentration and reached a limiting value when the concentration was greater than 5 mmol/L. The fluxes obtained with DA18C6 were slightly lower than those obtained with DB18C6; these results agreed with the viscosity measurements. The calculation of the diffusion coefficients in membranes showed a lower diffusivity of DA18C6-metal complexes with respect to DB18C6-metal complexes for all 3 ions and a sequence of diffusivity ( $\text{Ag}^+$ ) > ( $\text{Cu}^{2+}$ ) > ( $\text{Zn}^{2+}$ ). The diffusivity was significantly higher using the Celgard 2500 support than it was when Celgard 2400 or 2402 were used. For preparing the immobilized interface, 30 days was the optimum membrane-support immersion time in organic solution. Fluxes close to zero were obtained when the ion concentration in the feed phase was less than  $10^{-2}$  mol/L. In the transient state of the transport through the SLM, different molar flow rates at the feed-membrane and membrane-strip interfaces were measured. The selectivity of the interfaces for SLMs containing DB18C6 in the separation binary mixtures of ions showed the following results:  $SF_{\text{Ag-Zn}} = 2.9$ ;  $SF_{\text{Ag-Cu}} = 2.5$ ;  $SF_{\text{Cu-Zn}} = 1.2$ . DB18C6 was more selective for silver than for copper and zinc ions.

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