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Preconcentration and analytical separation of silver (Ag^{+1}), copper (Cu^{+2}) and zinc (Zn^{+2}) ions using supported liquid membrane technology

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ABSTRACT

Analytical separation and transport behavior of silver, copper and zinc across supported liquid membrane using crown ethers dithio-18-crown-6 (DT18C6) and dicyclohexano-18-crown-6 (DC18C6) in chloroform, has been investigated. Phase distribution studies show that selectivity of the interface is much higher when the metal cation is inserted deeper in the polyether cavity. Silver ions specie are more adaptable to the cavities of DT18C6 and DC18C6 than are copper and zinc. Transport studies showed that fluxes obtained with DT18C6 were slightly lower than those of DC18C6 for all three ions studied. Use of different solid supports revealed that fluxes increase with increasing porosity of the support but decrease with increasing thickness. Differences in molar flow rates (F) at feed and strip membrane interfaces were observed, due to the reason that decomplexation rate at the strip side is slower than complexation rate at the feed side. The magnititude of separation factor (SF=2.51) showed that Ag^+ could very well be separated from Cu^{++} and Zn^{++} using DC18C6/chloroform membrane. The feasibility of preconcentration of Ag^+ was also studied by using the hollow fiber module system. Highest enrichment factor (EF) was obtained for 40 mg/L whereby all the metal ions were transported to the stripping phase and resulting Ag+ concentration was 490 mg/L (EF=12.3). © 2012 Trade Science Inc. - INDIA

INTRODUCTION

Heavy metals often appear in high concentrations in all kinds of industrial effluents giving rise to hazards of pollution because of their high toxicities and wide environmental spreading. The removal of heavy metal ions from waste waters is of great significance due to environmental and economical aspects. The toxic metals have been recovered with separation methods based on solvent extraction, which consume large amounts of organic extractants and solvents. Membrane processes are a reality in many industrial fields for the recovery and recycling of substances and by-products. Supported Liquid Membranes (SLM) appear particularly interesting for the treatment of dilute solutions containing metals because they allow the combination of the advantages of solvent extraction and those of other membrane processes like ultrafilteration, RO, dialysis, etc. SLMs have the added advantage of high transport rates, selectivity and minimization of the required organic components[26]. In a SLM the interface can selectively recognize one ion, and furthermore, facilitated transport is more effective than passive transport. Other advantages are the high permeability, possibility of separating and concentrating 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 fields for the recovery and separation of various metal ions[2, 27]. Many researchers have used commercially available extractants as membrane liquids for the individual separations of silver, copper and zinc ions. Oxime reagents are well known for Cu(II) extraction. Molinari et al[13] have used D2EHPA (diethylhexyl phosphoric acid) for the selective removal of Cu(II) versus Ni(II), Zn(II) and Mn(II). Osman et al[15] have used the same extractant for the transport of Zn(II) from aqueous solution containing Fe(II), Ca(II) and Mg(II). Canet et al[6] have reported comparative transport data for Pb(II), Cd(II) and Ag(I) through a lasalocid supported liquid membrane. They explained the higher transport flux for Ag(I) on the basis of smaller hydration shell of silver (0.212nm).

Supported liquid membrane systems containing macrocycles of the cyclic crown ethers have been used for selective transport of cations from mixtures of two or more metal ions[24]. Factors affecting crown ether mediated transport of cations in bulk liquid membranes have been studied extensively, but the data related to SLM needs to be substantiated[16]. Improvement of selectivity of the trans-membrane transport has been the subject of much discussion. Classical routes concern synthesis of porous inorganic or hybrid membranes of well-defined pore size. More specific approaches based upon involvement of molecular recognition process, and accelerated by breakthroughs in supramolecular chemistry have provided very sophisticated chemical structures such as highly specific ion complexing agents like crown ethers. Crown ether is a molecule containing hydrogen, carbon and heteroatom. Each heteroatom is bound between two of the carbon atoms and arranged in a ring. The previous studies outlined several features of macrocycle design needed for selective extraction of specific metal cations[3, 19, 25]. However, these studies do not allow one to make reliable predictions about cation selectivities and transport rates in SLM systems. The size of the polyether cavity and the size of the inserted ion are two of the fundamental parameters that give a selective extraction[4, 11].

Transport of silver, copper, and zinc ions by crown ethers can be facilitated by co-transport phenomenon[8, 10]. 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 complexing ability of ordinary crown ethers towards soft heavy metal ions is quite low. This weakness has been improved by substitution of some oxygen atoms of crown ethers by sulfur or nitrogen atoms which result in considerable increase in the stability of cations such as Ag(I), Au(I), Hg(II) etc. in solution. Thus, in recent years some sulfur containing crown ethers have been used as neutral carriers in solvent extraction and PVC membrane electrode studies of some heavy metal ions[19]. In the present work, the behavior of SLM was studied through the use of dicyclohexano-18-crown-6 (DC18C6) and dithio-18-crown-6 (DT18C6) as specific carriers for Ag(I), Cu(II) and Zn(II). These ions are usually present together in metallic ore leaching solutions. The extraction percentages of each ion were determined with both extractants, along with nature of the porous solid supports, effect of feed concentration, molar flow rates, separation factors and enrichment factors.

EXPERIMENTAL

Materials and methods

The solutions of each metal ion were prepared from silver, copper, and zinc nitrate (Fluka) at variable concentrations. The carriers were organic solutions of different concentrations of dicyclohexano-18-crown-6 and dithio-18-crown-6 (Fluka) dissolved in chloroform. Despite of its volatility, chloroform was used as diluent because crown ethers have low solubility in the other solvents. It has a higher dielectric constant (5.5) as compared to toluene (2.3) and xylene (2.2). Moreover, it is miscible with other organic solvents, so an environment friendly mixture of diluents can be prepared for specific applications. Many researchers have used chloroform as crown ether solvent in SLM extraction experiments[1, 4, 5, 10, 14]. Double-distilled water was used as a stripping solution.

The permeation cell used for SLM experiments consisted of 2 compartments separated by the membrane. Each compartment, feed and strip, had a maximum volume of 140 mL. A membrane of effective surface area 14.2cm^2 could be fixed amid the two chambers. The agitation of the solutions was carried out by 2 synchronized motors that relied on variable power supply with a stirring rate of 1000 rpm. The stirring rate was high enough to minimize boundary layer resistances. Figure 1 shows the experimental set up.

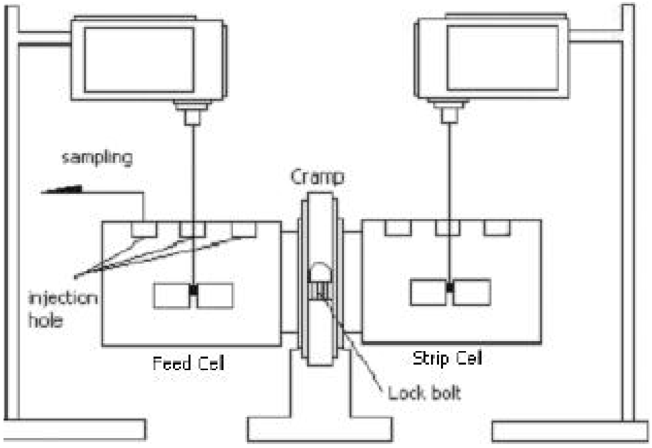

Figure 1 : Schematic diagram of the permeation cell

Phase distribution studies were carried out by liquid-liquid extractions. Equal volumes (20.0mL) of the aqueous phases, containing the investigated metal (10mM of Cu^{++}, Ag^{+} or Zn^{++} each), and of the organic phases DC18C6/Chloroform or DT18C6/Chloroform at the chosen concentrations were contacted for 3 hours on a mechanical shaker (120rpm). Then the 2 phases were completely separated by centrifugation. The metal ion concentration in the aqueous phase was determined and the extraction percent (E%) was calculated from mass balance of the ion between organic and aqueous phases (Equation 1).

$$\%E = \frac{[Me]_{org}}{[Me]_{org} + [Me]_{aq}} X100 \qquad (1)$$

Where, Me = [Cu(II),Ag(I) or Zn(II)]

In all cases, the concentrations of silver, copper, and zinc were determined in the aqueous phase using an atomic absorption spectrophotometer (Solaar Thermo Elemental).

The immobilized interface was prepared by soaking the support in the carrier solution for 24 hours. Then the SLM was placed between the 2 half-cells. The 2 compartments were filled with the feed and the strip solutions. The concentrations of silver, copper, and zinc ions were fixed at 0.01 M except when the concentration was studied as a transport parameter. The experiments began by starting the stirring motors in the two compartments of the experimental set up as shown in Figure 1. 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 thermostat bath at 25°C.

The relationship which correlates the membrane flux (J) to concentration (C), to the aqueous feed volume V, and to membrane area Q is given in Equation 2 below.

$$J = -\frac{dC}{dt}\frac{V}{Q} \qquad (2)$$

The integrated form of flux equation is Equation 3,

$$\ln\frac{C}{C_0} = -\frac{Q}{V}Pt \qquad (3)$$

Where C_o is value of C at time zero and P is permeability. A linear dependence of the feed solution with time is obtained, and the permeability can be calculated from the slope of the straight line that fits the experimental data[8].

Experiments for the simultaneous transport and enrichment of Ag(I) were conducted by using an hollow fiber module. Hydrophobic polypropylene hollow fibers from Celgard were used as solid supports for the liquid membrane, with the following characteristics; inner diameter = 240 μm, outer diameter =300 μm, pore size = 0.04 μm, porosity = 40%, length = 5.5 inches.

The HF SLM was prepared by impregnation of the tubular microporous fiber, passing a 5% solution of DT18C6 in chloroform. Experimental set up is shown in Figure 2. The flow rate of both solutions was fixed at 0.5mL/minute. Each experiment was conducted over a period of 16 hours.

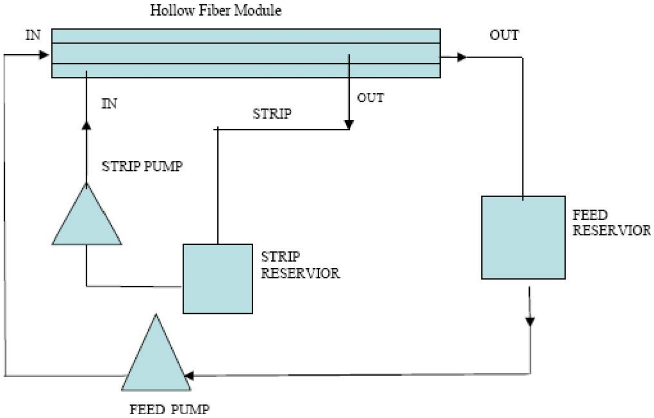

Figure 2 : Single hollow-fiber module used in a recycling mode

RESULTS AND DISCUSSION

Liquid-liquid extraction

The distribution behavior of the metal ions was studied by means of L-L extractions. The distribution ratios obtained for Ag(I), Cu(II), Zn(II), and the 2 crown ethers are plotted in Figures 3 & 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 0.05 mol/L. The selectivity of the interface is much higher when the metal cation is inserted deeper in the polyether cavity; silver (I) species are more adaptable to the cavities of DC18C6 and DT18C6 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 DC18C6 (diameter 260-320 pm) and DT18C6 (180 pm). Copper (II) has a radius of 69 pm and the zinc ion has radius of 72 pm. Both carriers have a good affinity for the monovalent ion, but DC18C6 seems to be more selective for silver than for copper or zinc. This affinity can be related to the nature of the heteroatom forming the carrier. The oxygen atoms may have more affinity with singly charged species having higher charge density, than do the sulphur atoms of DT18C6. These interactions show that ion-crown association depends on several factors related to characteristic properties of the ligand, reacting ion and the solvent[5]. Substitution of oxygen atoms by heteroatom like sulphur gives host molecules with different complexation properties[7,17].

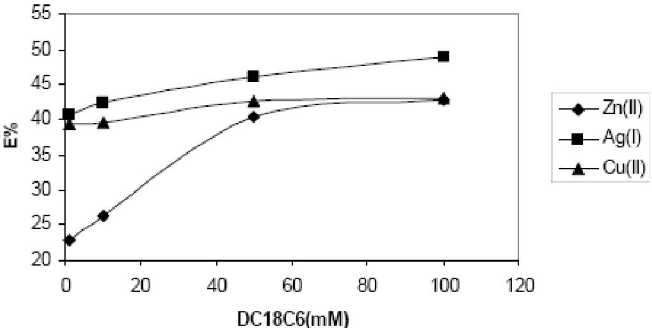

Figure 3 : Percentage of extraction of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

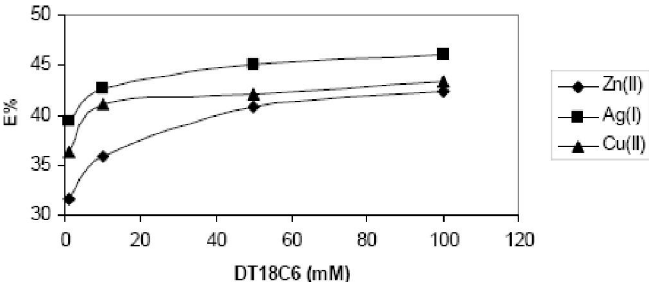

Figure 4 : Percentage of extraction of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DT18C6 in chloroform

Influence of the carrier concentration

The variations of the fluxes of the three ions across the SLM vs. the concentration of the 2 carriers are reported in Figures 5 and 6. At a concentration greater than 6 mmol/L, the carrier does not affect significantly the transfer rate of the metal ions. Furthermore, the fluxes obtained with DT18C6 were slightly lower than those of DC18C6 for all three ions. The permeabilities are shown in Figures 7 and 8.

The low increase of flux at high carrier concentration is due to an increase of the viscosity of the organic phase, which affects the diffusion[5]. Higher viscosity of the DT18C6 is consistent with the lower flux values for metal ions with the DT18C6 carrier. Other researchers have also reported similar findings. Mohapatra et al[12] have used polypropylene flat sheet membrane (pore size 0.57μm; porosity 84%; thickness 112μm) to study transport of Cs^+ ions. They have shown that extraction of Cs^+ increased linearly with crown ether concentration and then decreased. However, they have suggested the extraction of 1:1 and 1:2 M:CE species. Shamsipur et al[18] have used thio-crown ether supported PP membrane (Celgard K-256) for the separation of Ag(I) ions. They have shown that percent transport of Ag(I) increases with an increase in carrier concentration up to 0.01M. At higher macrocycle concentration, the transport efficiency remained unchanged.

Both the flux and the permeabilities of silver (I) were found to be higher than those of copper (II) and zinc (II). Because the only difference in the 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.

Effect of the solid support

Stability of the SLM is directly related to the thickness and porosity of the solid support. These two parameters also affect the fluxes of permeating ions. The influence of both parameters has been studied using supports with different characteristics. The obtained results are reported in TABLE 1. It was observed that fluxes increase with increasing porosity of the support. On the other hand, fluxes decreased with increasing

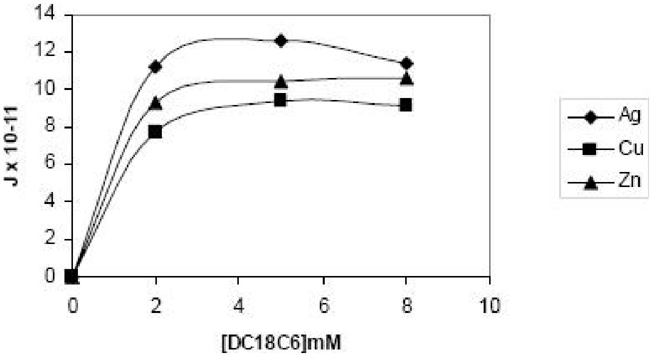

Figure 5 : Fluxes (10^{-11} mol-cm^{-2}-sec^{-1}) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

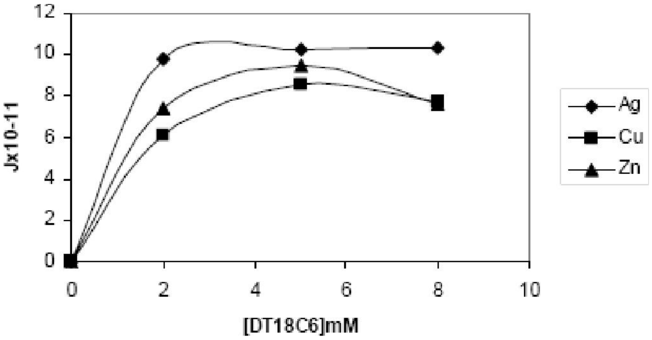

Figure 6 : Fluxes (10^{-11} mol-cm^{-2}-sec^{-1}) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

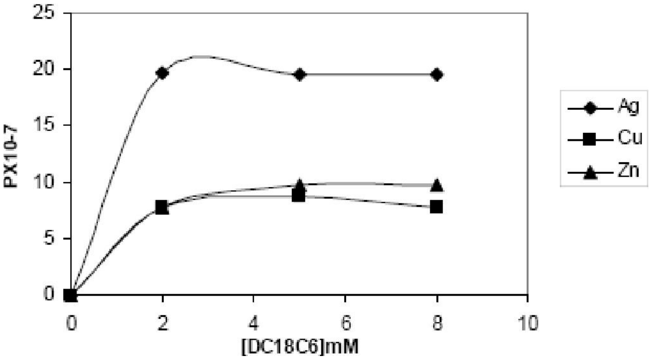

Figure 7 : Permeabilities (10^{-7} cm-sec^{-1}) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

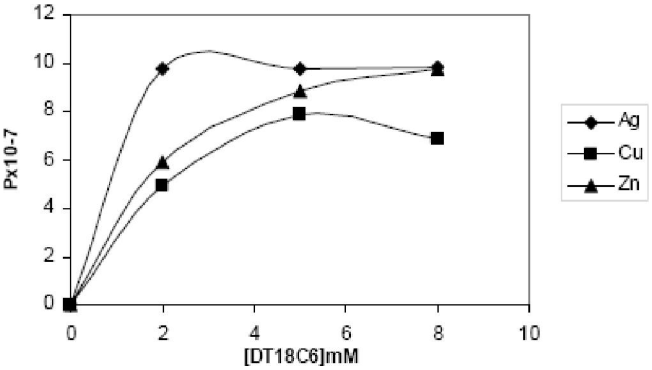

Figure 8 : Permeabilities (10^{-7} cm-sec^{-1}) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DT18C6 in chloroform.

TABLE 1 : Fluxes of Ag(I), Cu(II) and Zn(II) with different supports. M^+ = 0.05M, DC18C6 = 2.0mM

Supports *(Thickness/Porosity)µm*	**Ag(I) $Jx10^{-11}$(mol-cm^{-2}-sec^{-1})**	**Cu(II) $Jx10^{-11}$(mol-cm^{-2}-sec^{-1})**	**Zn(II) $Jx10^{-11}$(mol-cm^{-2}-sec^{-1})**
Accural PP1E *92/0.1*	8.34	6.75	8.74
Accural PP2E *150/0.2*	5.13	3.47	4.35
Celgard 2500 *25/0.075*	10.7	7.36	8.80
Celgard 2400 *25/0.05*	11.2	7.78	9.30
Durapore *125/0.2*	4.71	2.17	3.13

thickness. Therefore, it could be concluded that to get a reasonable stability and life-time, a compromise is required between thickness and porosity.

Determination of molar flow rate

The molar flow rate F (mol/h), of an ion in the aqueous solution is defined by 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. Following relationships (Equations 4 & 5) is used to determine F;

$$F_f = \frac{\Delta n(f)}{\Delta t} \tag{4}$$

$$F_s = \frac{\Delta n(s)}{\Delta t} \tag{5}$$

Where Δn(f) and Δn(s) represent the change in the number of moles in the feed (f) and strip (s) phases, respectively. During the transport process, metal ions are complexed at the feed-membrane interface where they accumulate; consequently, F_f at this interface can be different from F_s at membrane-strip interface. TABLE 2 reports the molar flow rates for Ag(I), Cu(II) and Zn(II) ions to the interface feed-membrane and from the interface membrane-strip. A different behavior of the two flow rates was observed at the beginning of the transport. This may be due to low diffusivity of the complexes inside the membrane or lower decomplexation rate at the strip side than the complexation rate at the feed side[10]. Figure 9 shows that fluxes become steady after 2 hours of transport. This shows that the complex formed, in the beginning, at the feed-membrane inter-

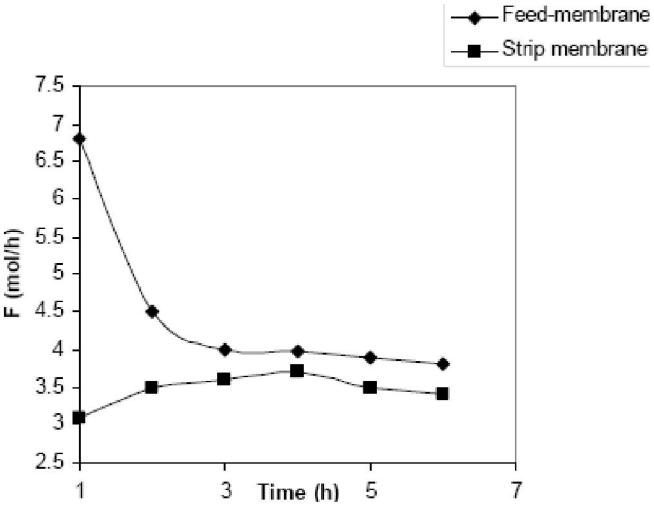

Figure 9 : Molar flow rate of Ag(I) ions from the feed phase and organic phase VS. time. SLM: DC18C6 (2.0mM); Celgard 2400; Feed: 0.05M Ag(I); Strip: Distilled Water

TABLE 2 : Molar Flow rates for metal ions

Ions	F_f x 10^6 (mol/h)	F_s x 10^6 (mol/h)
Ag(I)	3.97	3.80
Cu(II)	2.73	1.93
Zn(II)	2.18	1.97

face is accumulated there.

Determination of separation factors

The separation factor (selectivity) of a SLM is a parameter that allows for the evaluation of the degree of purification of a specie with respect to others in a mixture. TABLES 3 and 4 show separation factors for Ag(I), Cu(II) and Zn(II) with both carriers and concentrations. The relationship given in Equation 6 has been used for this purpose;

$$S.F = P_{Me1}/P_{Me2} \qquad (6)$$

Where P is permeability of metals 1 and 2 in the mixture. Higher the SF value, better will be the separation between the two metals[10]. The obtained results at pseudo steady state showed that silver ions had higher mobility than zinc and copper ions. It is clear that Ag(I) can be very well separated from Cu(II) and Zn(II) using DC18C6/chloroform membrane (SF = 2.51). The separation of copper and zinc from an aqueous sulphate media by supported liquid membrane using di-2-ethyl hexyl phosphoric acid (TOPS-99) as mobile carrier has been studied by[22]. Celgard-2500 polypropylene film was used as the solid support for the liquid membrane. They found separation factor for Cu-Zn to be 1.19 and 2.25 at pH 5 and 4, respectively.

TABLE 3 : Separation factor values for Ag(I), Cu(II) and Zn(II) ions for DB18C6/ chloroform membrane

S.F	2.0mM	5.0mM	8.0mM
Ag-Cu	2.0	2.20	2.51
Ag-Zn	1.66	2.0	2.0
Cu-Zn	1.20	1.10	1.25

TABLE 4 : Separation factor values for Ag(I), Cu(II) and Zn(II) ions for DT18C6/ chloroform membrane

S.F	2.0mM	5.0mM	8.0mM
Ag-Cu	2.0	1.25	1.42
Ag-Zn	1.66	1.11	0.99
Cu-Zn	1.20	1.12	1.43

Preconcnetration of Ag(I) with a hollow fiber system

The feasibility of preconcentration of Ag(I) by using the proposed SLM parameters, was also studied by using hollow fiber system. Enrichment factors (E.F) were calculated by using different initial concentrations in the feed solution. E.F is defined as ratio of metal concentration in the stripping phase and the initial metal concentration in the feed phase[9]. Highest E.F value was obtained for 40 mg/L whereby all the metal was transported to the stripping phase and the resulting Ag concentration was 490 mg/L (E.F = 12.3).

It was observed that while treating more diluted solutions, the enrichment factor decreases. Values of E.F equal to 7.6 and 10.2 were found for initial Ag concentration of 10 and 30 mg/L. The results can be improved by two ways; by using a hollow fiber module with more fibers, and, by increasing the length of experimental time.

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