Silver(I) ion selective transport through a bulk liquid membrane containing 5,12-di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclodo-decane-2,3-dione as carrier

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Abstract

5,12-Di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclododecane-2,3-dione is an excellent synthetic carrier for highly efficient and selective transport of Ag(I) ions through a liquid membrane. In the presence of thiosulfate as stripping agent in the receiving phase and at the optimum pH of 4, about 80% of silver was transported over a period of 5 h. The carrier can selectively and efficiently transport Ag(I) ion from aqueous solutions containing other cations such as Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, Cd^{2+}.

Keywords: 5,12-di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclododecane-2,3-dione, bulk liquid membrane, silver(I).

Introduction

Separation of a given species from a complex mixture of other species is of special importance in industrial and analytical chemistry and separation sciences. Often, various interfering compounds must be removed and/or the compounds of interest must be enriched before detection is possible. Liquid membranes (organic liquids contact with two separated aqueous phases) are well known as one of the most powerful tools for such separation and enrichment purposes [1–3]. Carrier mediated transport through liquid membranes is not only an interesting technique for concentration, separation and recovery, but is also of fundamental importance from the biological point of view [2,4–6]. The transport of metal ions across liquid membranes can generally be considered as a combination of extraction and stripping processes. The extraction chemistry is basically similar to that found in classical liquid–liquid extraction, but the transport process is governed by kinetic rather than equilibrium parameters, under nonequilibrium mass transfer [7]. Compared with solvent extraction, liquid membrane transport for the selective

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removal, concentration or purification of given metal ions from their mixtures have the advantage that the amounts of organic solvents and metal ion complexing agents are markedly reduced [2,4,8].

Thiacrown ethers are macrocyclic rings containing sulfur donor atoms, which have high bonding affinities with soft metal ions such as Cu^+, Ag^+, Tl^+ and Hg^{2+} ions [9–11]. These macrocyclic ligands are free of any protonation consideration and hardly soluble in water. Due to their similarities with biological systems of interest [12], the complexation behavior of thiacrown ethers with transition and heavy metal ions in different solvents has been particularly investigated [9–14]. In recent years, some sulfur containing crown ethers have been used as neutral carriers in solvent extraction [15–17] and PVC membrane studies of some transition and heavy metal ions [18–22].

Recently, we have reported a highly selective competitive membrane transport of silver(I) by 5, 12- di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclododecane-2,3-dione(**I**) as carrier [23]. In this investigation, we employed this new synthesized crown ether as an excellent specific ion carrier for the highly efficient and selective transport of Ag^+ ions through a bulk dichloromethane membrane. In the presence of thiosulfate as a suitable metal ion acceptor in the receiving phase, the silver ions were transported quantitatively and selectively across the liquid membrane at a time period of 5 hours.

Results and Discussion

In the preliminary experiments, it was found that ligand (**I**) has the desired ability to transport Ag(I) against its concentration gradient and the presence of a complexing agent in receiving phase for metal ion increases the efficiency of metal ion transport. The thiacrown ethers react selectively with soft Lewis acids such as Ag^+, Hg^{2+}, Au^{3+}, etc. to form a selective and stable cation complex [24-27]. The resulting positive charged complex can form an ion paired complex with an appropriate anion. The neutral ion pair thus formed can be quantitatively extracted into a suitable organic solvent [28–30]. Thus, in this work, we were interested to investigate the transport behavior of Ag^+ ion through a liquid membrane containing ligand (**I**) as a potential ion carrier. The presence of a complexing ligand in the receiving phase as a scavenger for metal ion increases the efficiency of metal ion transport. For this reason, and in order to achieve the highest efficiency in the transport of Ag(I) across the membrane system, the influences of the experimental variables such as receiving phase composition, pH of the source and receiving phase, concentration of fatty acid as surfactant in the membrane phase, concentration of thiosulfate in receiving phase and concentration of ligand in organic phase were optimized on the transport of silver ion.

Effect of type and concentration of stripping agent in the receiving phase

Preliminary experiments revealed that the nature and composition of the strippinging agent in the outer aqueous phase could have a significant effect on the efficiency of transport. As it is seen from Table 1, among the different stripping agents which were used in these experiments, the $S_2O_3^{2-}$ ion with increased complexing ability towards Ag^+ ion acts as the most suitable receiver for the release of this cation from the membrane phase into the receiving phase.

The influence of the concentration of $S_2O_3^{2-}$ in the receiving phase on the transport efficiency of Ag^+ ion was also investigated and the results are shown in Fig. 2. As is obvious, while only 20% silver ion transport occurs in the absence of the receiving agent, the transport of Ag^+ ion
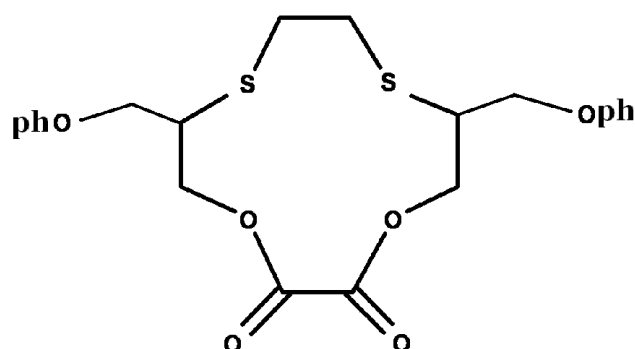
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increases sharply with increasing the concentration of $S_2O_3^{2-}$. The most transport of silver (I) ions occurs at a 5.0×10^{-3} M of this stripping agent. Thus, 5.0×10^{-3} M thiosulfate concentration was adopted for further studies.

Table 1: Effect of type of stripping agent on the silver transport

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
SCN⁻	26.41	2.20
CN⁻	23.48	58.70
$S_2O_3^{2-}$	80.86	3.68
Thiourea	32.49	10.88

Table 2: Effect of type of surfactant on the silver transport

surfactant	Percentage transported into receiving phase	Percentage remaining in source phase
Palmitic acid	80.86	3.68
Stearic acid	65.03	4.54
Oleic acid	65.23	3.35

Scheme I: Structure of 5,12-di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclodode-cane-2,3-dione
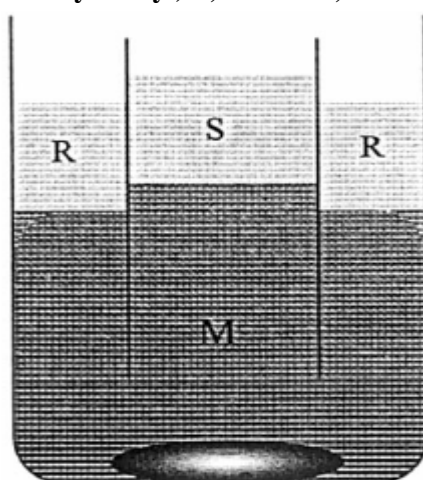

Figure 1: Liquid membrane apparatus (S: source phase; R: receiving phase; M: liquid membrane).
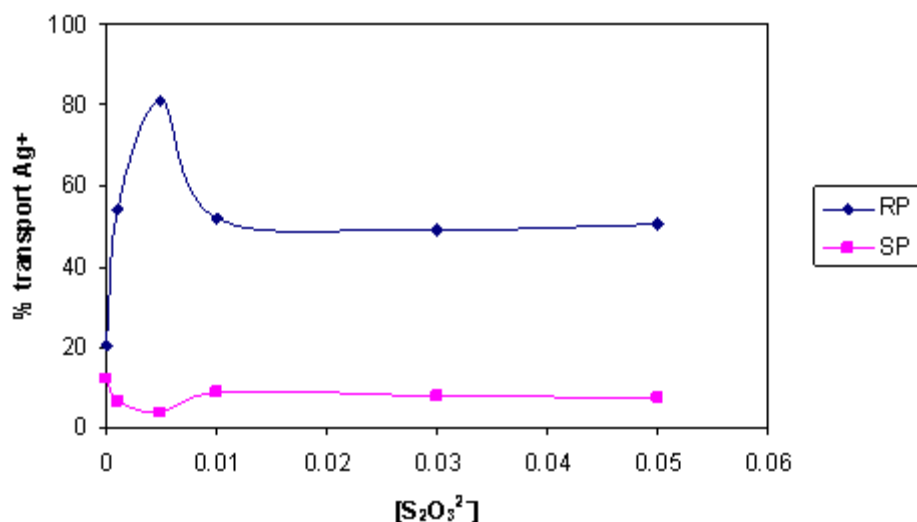
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Figure 2: Effect of $S_2O_3^{2-}$ concentration in the receiving phase on silver ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag^+; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetice acid in DCM; receiving phase, 30 ml with different concentrations of sodium thiosulfate; transport time, 5 hours
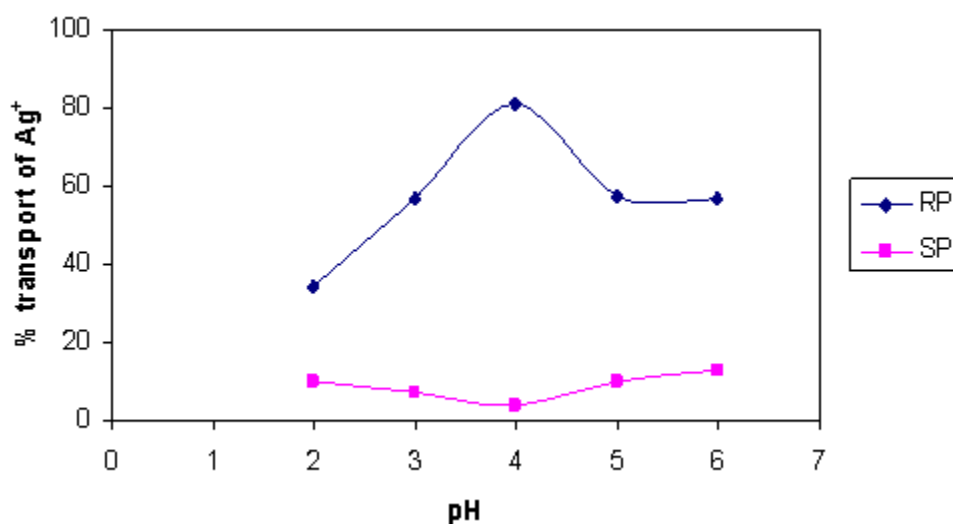

Figure 3: Effect of pH of the receiving phase on silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag^+; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetice acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate; transport time, 5 hours

Effect of the pH of receiving phase on silver ion transport

The influence of the receiving phase pH on the transport of silver ion can be seen from the results which are shown graphically in Fig. 3. It was found that maximum silver transport occurs at pH = 4.
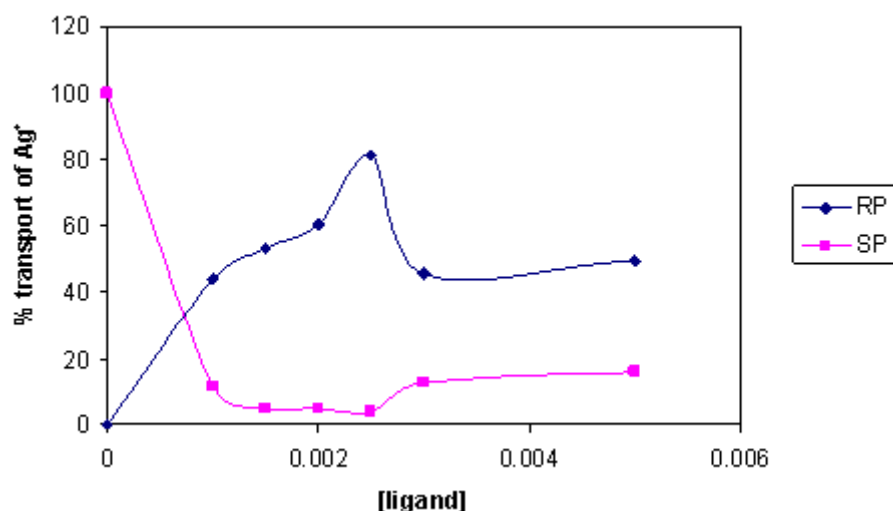
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Figure 4: Effect of carrier concentration in the membrane phase on silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag$^+$; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetic acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate; transport time, 5 hours.
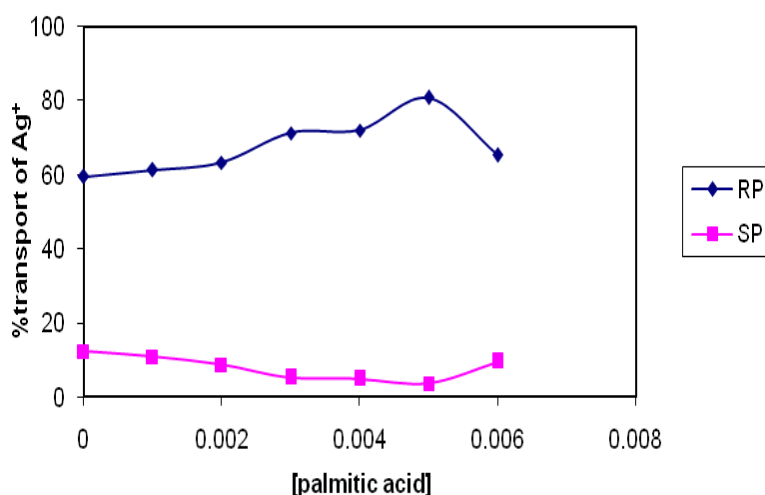

Figure 5: Effect of concentration of palmitice acid in the membrane phase on silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag$^+$; membrane phase, 50 ml of 2.5×10^{-3} M carrier and different concentrations of palmitic acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate; transport time, 5 hours

Effect of concentration of ion carrier in organic phase

The effect of the concentration of ion carrier in the membrane phase on transport efficiency of silver ion was also investigated. The percentage of silver ion transported increases with an increase in ion carrier concentration in dichloromethane (Fig. 4). Maximum transport occurs at a concentration of about 2.5×10^{-3} M ion carrier. Further increase in carrier concentration caused a slight decrease in transport efficiency.
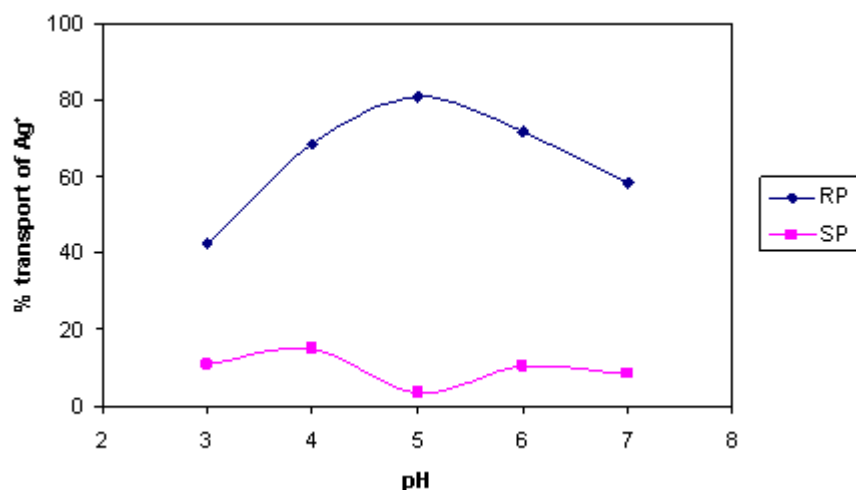
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Figure 6: Effect of pH of source phase on silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag$^+$; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetic acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate; transport time, 5 hours
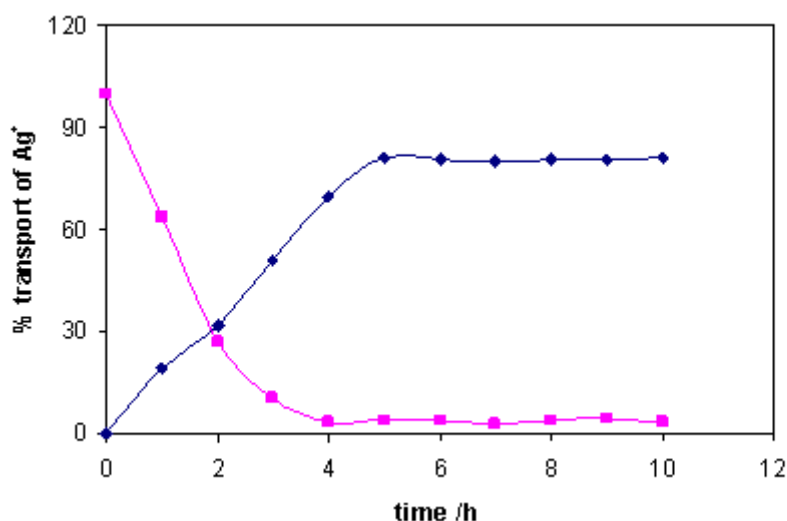

Figure 7: Time dependence of silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag$^+$; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetic acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate

Effect of type and concentration of fatty acid as surfactant in membrane phase

It has been found that a major role of the fatty acids is to aid the transport process by increasing in lipophilicity of crown-cation complex through some proton-donor and proton-acceptor interactions between surfactant (as proton donor) and oxygen atoms of ligand (as proton acceptor) which can facilitate the cation transport through liquid membrane [31] and also serve to inhibit any bleeding of partially species from the organic membrane phase into either of the aqueous phases. The results of the influence of the stearic acid, palmetic acid and oleic acid as surfactants in the membrane phase containing dichloromethane on the silver ion transport are given in Table 2. As is obvious from these data, the palmitice acid which increases the complexing ability towards silver ion, acts as the most suitable surfactant for the transport of this metal cation. The influence of the concentration of palmitice acid in the organic membrane phase on the transport efficiency of silver(I) ion was also investigated (Fig. 5). As is seen, the

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percentage transport of Ag$^+$ ion increases sharply with increasing concentration of palmitice acid in the organic phase. The most transport of silver ion occurs at a 5.0×10^{-3} M of this fatty acid.
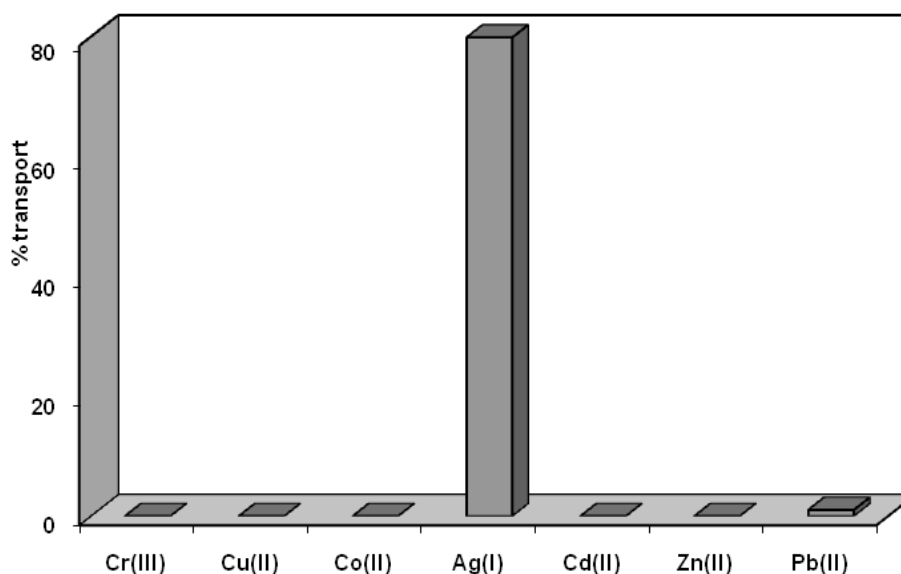

Figure 8: Selectivity of bulk membrane technique on silver(I) ion transport. Conditions: source phase, 10 ml of 5.0×10^{-4} Ag$^+$ with equimolar concentration from different cations ; membrane phase, 50 ml of 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetic acid in DCM; receiving phase, 30 ml of 0.005 M of sodium thiosulfate; transport time, 5 hours

Effect of pH of source phase

Figure 6 shows the effect of pH of the source phase on the efficiency of silver ion transport. The results revealed that the maximum Ag$^+$ ion transport occurs at pH = 5. Therfore, a pH of 5 was selected for further studies.

Time dependence of silver ion transport

Figure 7 shows the time dependence of Ag$^+$ ion transport through the liquid membrane under optimal experimental conditions. It is obvious that both the extraction of Ag$^+$ ion from the source phase into the membrane phase and its release from the membrane into the receiving phase are almost fast, so that under the optimum exprimental conditions, about 80% of Ag$^+$ ion transport occurs after 4 hours.

Competitive metal ion transport through the liquid membrane

The selectivity of the above system was investigated under optimum experimental conditions by undertaking the competitive transport experiments with equimolar concentrations of some metal ions, such as Co^{2+}, Cu^{2+}, Zn$^{2 +}$, Pb^{2+}, Cr^{3+} and Cd^{2+}, using the liquid membrane containing the ion carrier. The results obtained for the competitive metal ion transport are shown in Figure 8. As can be seen from this figure, after 5 hours, Ag$^+$ ions were highly transported through the dichloromethane membrane from the source phase into the receiving phase. Meanwhile, most of the other metal ions used, were hardly transferred through the membrane.

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Suggested mechanism

The silver ions are transported from source phase into the receiving phase through a dichloromethane membrane with simultaneous counter-transport of protons. The Ag^+ transport can be explained as follows: (i) at source phase/membrane interface, the carrier selectively complexes the silver ion from mixture, and hence, facilitates the extraction of this cation into the membrane phase (by forming uncharged complex). At this stage, the carrier splits off proton(s) into the source phase; (ii) the complex which formed diffuses across the membrane; (iii) at the membrane/receiving phase interface, the release of the Ag^+ ion into the receiving phase occurs via the formation of complex between silver ion and $S_2O_3^{2-}$ as a stripping agent. At this stage, the carrier associates with proton from the receiving phase and released Ag^+ ion is stripped by thiosulfate with complex formation; (iv) the free carrier diffuses back across the membrane to the source phase/membrane interface, where the cycle starts again. Permeability of the membrane system for Ag^+ ion depends largely on the mechanism of releasing of the cation in the receiving phase. The presence of thiosulfate as a stripping agent in the receiving phase, is believed to play an essential role in the metal ion releasing process via formation of complex. The formation of the above mentioned complex, reduces the concentration of free Ag^+ ion in the receiving phase and consequently increases the concentration gradient between two aqueous phases, which in turn results in a higher transport flux.

Materials and Methods

Experimental

5,12-di(phenoxymethyl)-1,4-dioxa-7,10-dithiacyclododecane-2,3-dione was prepared by a method similar to that in the literature [32]. Silver(I) nitrate (Merck), sodium acetate, sodium hydroxide, palmetice acid, sodium cyanide (all from Riedel), stearic acid (BDH), oleic acid, sodium thiosulfate ($Na_2S_2O_3.5H_2O$), sodium thiocyanate and thiourea (all from Merck) were used without further purification. Chloroform (BDH), 1,2-dichloroethane, dichloromethane and nitrobenzene (all from Merck) with highest purity were used as liquid membranes. Acetic acid (Merck) and formic acid (Riedel) were used as received. All aqueous solutions were prepared using deionized double distilled water.

Procedure

The transport experiments employed standardized concentric cells in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) separated by an organic phase (50 cm^3) (Fig.1). All transport experiments were carried out at ambient temperature. The organic layer was stirred by a Teflon-coated magnetic bar. Speed of stirrer was adjusted so that the phases did not mix with each other. Under these conditions, not only the mixing process is perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined.

The inner aqueous phase (source phase, SP) containing silver nitrate (5×10^{-4} M) was buffered at pH = 4.9 ± 0.1. The membrane phase (MP) contained the macrocycle ionophore (2.5×10^{-3}M) and palmetice acid (5×10^{-3}M). The outer aqueous phase (receiving phase, RP) consisted of a sodium thiosulfate solution (5×10^{-4} M) was buffered at pH = 4 ± 0.1. In the course of the transport experiment, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy (Shimadzu-670).

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Conclusion

The transport of silver(I) ion through a DCM–carrier bulk liquid membrane was investigated. The optimum conditions of transport was found as 2.5×10^{-3} M carrier and 5.0×10^{-3} M palmetice acid in the dichloromethane membrane, 5.0×10^{-3} M $S_2O_3^{2-}$ at pH 4 and 5 in the receiving phase and source phase, respectively, a transport time period of 5 hours. The simplicity, low cost, excellent efficiency, high degree of selectivity and a relatively short time period for Ag^+ ion transport obtained by the liquid membrane system demonstrate its potential applicability to selective removal, concentration or purification of silver from its mixtures.

Acknowledgments

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