ORIGINAL ARTICLE

Transport of silver ion through bulk liquid membrane using macrocyclic and acyclic ligands as carriers in organic solvents

G. H. Rounaghi · M. S. Kazemi · H. Sadeghian

Abstract The bulk liquid membrane transport of silver (I) ion was studied by dibenzopyridino-18-crown-6(DBPY18C6), 4-nitrobenzo-15-crown-5(NB15C5), 2-aminothiaphenol and a new synthesized ligand, 1,4-dioxa-7,10-dithiacyclodode-cane-2,3-dione as carriers in nitrobenzene (NB). The effects of pH on the source phase and receiving phase, the nature and concentration of stripping agents in the receiving phase and the picrate concentration as counter ion in source phase were investigated. The results show that the efficiency of transport of the Ag^+ ion through membranes, changes with the nature of the ligand. The efficiency transport increases for the ligands with donating nitrogen and sulfur atoms with respect to oxygen donor atoms. Maximum transport efficiency was observed for silver (I) ion in the presence of thiosulfate ion ($S_2O_3^{2-}$) as a suitable stripping agent. The results show that the sequence of transport efficiency for Ag^+ ion using DBPY18C6, NB15C5, 2-aminothiaphenol and 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione as carriers in organic solvents is: nitrobenzene > dichloromethane > 1,2- dichloroethane > chloroform.

Keywords Silver ion · Didibenzopyridino-18-crown-6 · 4-Nitrobenzo-15-crown-5 · 2-Aminothiophenol · 1,4-Dioxa-7,10-dithiacyclododecane-2,3-dione · Bulk liquid membrane transport · Nitrobenzene

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Introduction

The silver content of environmental samples is increased with the increasing use of silver compounds in industry and medicine [1, 2]. The separation, concentration and sensitive determination of Ag^+ ion are of increasing interest.
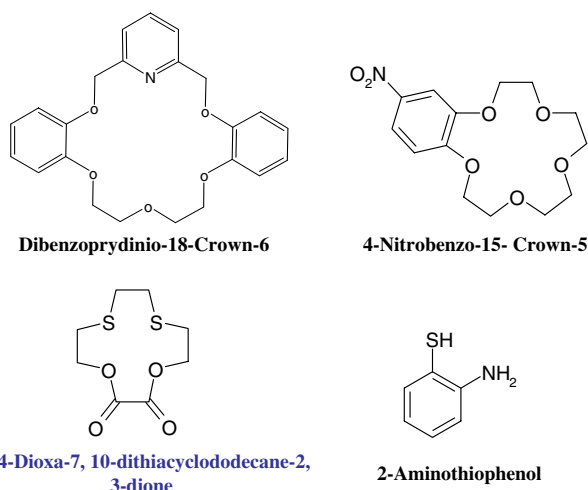
In many analytical procedures usually a separation step is needed before the final analysis can be performed. Often various interesting compounds must be removed and/or the compounds of interest must be enriched before determination is possible. Liquid membrane, i.e. organic liquid in contact with two separated aqueous phases, has many applications in the separation sciences. This technique has been widely used for carrier facilitated metal ion separations [3–5], and to a lesser degree separation of organic substances [6, 7]. In comparison with liquid-liquid extraction, liquid membrane transport in which the extraction and stripping operations are combined in a single process reduces the solvent inventory requirement and also allows the use of expensive and highly selective extractants, which otherwise would be uneconomic in solvent extractions.

The complexing ability of crown ethers toward soft heavy metal cations is quite low [8–10]. This problem has been overcome by substitution of some oxygen atoms by sulfur or nitrogen atoms which results in a considerable increase in the stability of complexes of these cations such as Ag^+, Tl^+ and Hg^{2+} ions in solution [11, 12].

In this study, we report the transport efficiency of silver (I) ion through bulk liquid membrane (BLM) with macrocyclic ligands: dibenzopyridino-18-crown-6,4-nitro-benzo-15-crown-5,2-aminothiaphenol and 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione as carriers (Scheme 1) in nitrobenzene, dichloromethane, 1,2-dichloroethane, and chloroform.

Dibenzoprydinio-18-Crown-6

4-Nitrobenzo-15- Crown-5

1, 4-Dioxa-7, 10-dithiacyclododecane-2, 3-dione

2-Aminothiophenol

Scheme 1 The structure of the ligands

Experimental

Reagents and solvents

Dibenzopyridino-18-crown-6(DBPY18C6), 4-nitrobenzo-15-crown-5(NB15C5), sodium thiosulfate ($Na_2S_2O_3 \cdot 5 H_2O$), sodium thiocyanate (NaSCN), thiourea, sodium diethyldithiocarbamate, silver (I) nitrate, picric acid, 1,8-dihyroxy-3,6-dithiaoctane, triethylamine, dichloromethane, oxalyl chloride, dichloromethane, methanol, sodium bicarbonate, brine, sodium sulfate all perchased from Merck company. Sodium cyanide (Riedel), 2-aminothiaphenol (Sigma), nitrobenzene (Analar) and silica gel $60F_{256}$ (Merck) were used as received.

Synthesis of 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione

A mixture of 1,8-dihyroxy-3,6-dithiaoctane(0.55 g, 30 mmol) and triethylamine(0.65 g, 6.4 mmol) in dried dichloromethane(10 mL) was cooled to 5–10 °C. Oxalyl chloride (0.4 g, 3.1 mmol) in dried dichloromethane (10 mL) was then added in one portion to the mixture while the mixture was allowed to warm to room temperature. After 30 min the mixture poured into cold distilled water (100 mL) and acidified with 5% HCl (20 mL). The aqueous solution was extracted with dichloromethane (2 × 30 mL). The combined organic extract was washed with 5% NaHCO₃ (2 × 30 mL), brine (2 × 30 mL), dried with Na_2SO_4 and concentrated under reduced pressure to provide the desired compound. Purity of the compound was checked on TLC (silica gel $60F_{265}$, dichloromethane-metanol 9:1). White solid (54%), Mp: 112 °C; ^{1}HNMR: δ 2.84 (s, 4H, –S

CH₂CH₂S–), 2.88 (t, $J = 8$ Hz, 4H, –SCH₂–), 4.45 (t, $J = 8$ Hz, 4H, –CH₂OCO); ^{13}CNMR: δ 30.8 (–SCH₂CH₂S–), 32.6 (–SCH₂–), 68.3 (–CH₂OCO), 158.6 (C=O); MS m/z: 238 (M+), 148 (100%) with high purity [13].

Procedure

All aqueous solutions were prepared using deionized double distilled water. The organic solvents, which were used as membrane phase (MP), were presaturated with water by shaking a two-phase mixture and then removing the aqueous phase. The transport experiments employed a "concentric cell" in which the aqueous source phase and receiving phase were separated by an organic phase. Details of the cell design have been reported elsewhere [14]. The cell was enclosed by a water jacket and thermostated at 25 °C. The inner source phase (source phase, SP) contained silver nitrate (10 mL, 5×10^{-4} M) and picric acid (1×10^{-3} M). The outer aqueous phase (receiving phase, RP) was a $Na_2S_2O_3$ solution (30 mL, 0.01 M). The MP contained 50 mL of 0.001 M DBPY18C6 in organic solvents. The organic layer was magnetically stirred by Teflon-coated magnetic bar (2.0 cm × 5 mm). Under these conditions, not only the mixing processes are perfect but also the two aqueous phases remained flat. Determination of the metal ion concentration in both aqueous phases was carried out by atomic absorption (Shimadzu-670) spectroscopy.

The pH was adjusted by addition of 0.1 M nitric acid or 0.1 M sodium hydroxide. A digital pH meter, Metrohm model 620, equipped with a combined glass electrode was used for pH adjustments.

Results and discussion

As expected, it was found that the nature of macrocylic ligand used as carrier in the organic MP has a significant effect on the efficiency and selectivity of metal ion transport [15, 16]. It can be seen from Table 1 that the DBPY18C6 carrier shows the highest transport efficiency for silver ion. The substitution of one of the donating oxygen with nitrogen atom results in (based on the hard and soft acid-base concept) a strong interaction between the Ag⁺ cation (soft acid) and the nitrogen atom of the carrier as a soft base, therefore, the Ag⁺ cation forms a strong complex with this ligand [17]. In addition, the interaction of Pi electron system present in aromatic ring with the silver ion may be effective on complexation between this metal cation and this ligand. The diminished efficiency of Ag⁺ ion transport in the presence of 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione ligand could be

Table 1 Effect of carrier structure on silver (I) transport

Carrier	Percentage transport into receiving phase	Percentage remaining into source phase
Dibenzopyridino-18-Crown-6 (DBPY18C6)	56	12
1,4-dioxa-7,10-dithiacyclo dodecane-2,3-dione	19	14
2-Aminothiophenol	0	21
4-Nitrobenzo-15Crown-5 (NB15C5)	0	39

related to the small cavity size of this carrier for Ag$^+$ ion which results in formation of a weak complex between this metal cation and the ligand [18]. The transport of Ag$^+$ ion into the receiving phase was undetectable in absence of the ligands in the organic liquid membrane.

As is seen from Table 2, the transport efficiency of silver ion by DBPY18C6 is varied in order: NB > DCM > 1,2-DCE > CHCl$_3$. The higher polarity of nitrobenzene ($\mu = 4$) [19] compared to the other organic solvents results in higher solubility of the (DBPY18C6 Ag)$^+$ complex in MP and, therefore, the transport of Ag$^+$ ion in this organic phase is bigger than the other organic solvents [20].

In preliminary experiments, it was found that the nitrate ion is not a suitable counter anion to accompany the (DBPY18C6-Ag$^+$) complex into organic phase, only 33% of Ag$^+$ ion was transported into the receiving phase. However, addition of picric acid to the source phase increased the Ag$^+$ ion transport. The influence of the concentration of picric acid in the source phase on the silver ion transport was investigated and the results are shown in Fig. 1. As seen from this Figure, the efficiency of silver ion transport increases with increasing picric acid concentration until to 0.001 M. But futher increase in the concentration of picric acid caused a pronounced decrease in the transport efficiency of silver ion. This behaviour may be due to the competition of picric acid with silver ion for transport process. Similar behaviour has been observed for selective transport of silver ion through a supported liquid membrane using hexathia-18-crown-6 [21].

Table 2 Effect of organic solvent on silver (I) transport

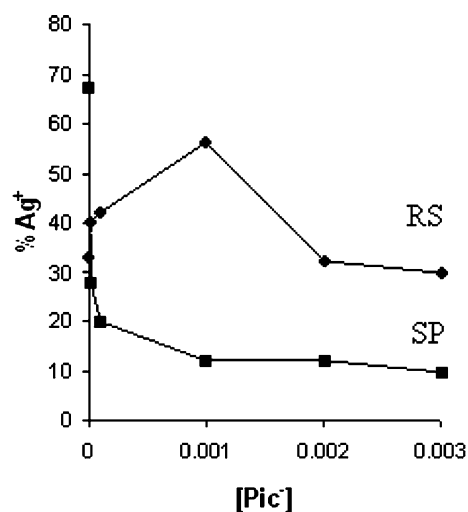| Solvent	Percentage transport into receiving phase	Percentage remaining into source phase
Nitrobenzene	56	12
Dichloromethane	40.18	17.4
Dichloroethane	29.0	21.69
Chloroform	21.96	12

Fig. 1 Effect of picric acid concentration on the silver ion transport. Conditions: source phase; 10 mL of 5×10^{-4} M Ag$^+$; membrane phase, 50 mL of 1×10^{-3} M carrier (DBPY18C6) in nitrobenzene; receiving phase, 30 mL of 0.01 M of thiosulfate; transport time, 8 h (RP = Receiving phase, SP = Source phase)

Permeability of the membrane system for Ag$^+$ ion was found to be largely dependent on the nature and concentration of stripping ligand used in the receiving phase. As is evident from Table 3, the use of thiosulfate as stripping agent in the receiving phase caused a rather large increase in the efficiency of Ag$^+$ ion transport. While the presence of other stripping agents such as SCN$^-$, CN$^-$, EDTA, thiourea, diethyldithiocabamate results in diminished transport efficiency. The optimum concentration of thiosulfate ion in the receiving phase was investigated (Fig. 2) and it was found to be 0.01 M. It is worthily to note that in the absence of the stripping agents on the receiving phase, the silver ion transports only 10% into the receiving phase.

Figure 3 shows the time dependence of Ag$^+$ ion transport through the liquid membrane under optimized experimental conditions. It is obvious that the extraction of Ag$^+$ ion from the source phase into the MP occurs faster than the release of Ag$^+$ ion from the MP into the receiving phase. Thus, it seems reasonable to assume that the release of the Ag$^+$ ion from the complex is the rate determining step

Table 3 Effect of the stripping agent on silver (I) transport

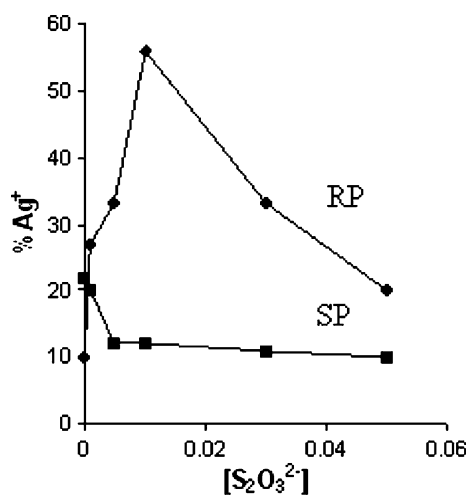| Receiving agent	Percentage transport into receiving phase	Percentage remaining into source phase
S$_2$O$_3^{2-}$	56	12
SCN$^-$	0	58
CN$^-$	23	37
EDTA	10	32
Thiourae	0	56
Diethyldithiocarbamate	30	47

Fig. 2 Effect of thiosulfate concentration on the silver ion transport. Conditions: source phase; 10 mL of 5×10^{-4} M Ag^+ and 1×10^{-3} M picric acid; membrane phase, 50 mL of 1×10^{-3} M carrier (DBPY18C6) in nitrobenzene; transport time, 8 h (RP = Receiving phase, SP = Source phase)

of the membrane transport. It was also found that the transport of Ag^+ ion from the aqueous source phase into receiving phase after 8 h is (57 ± 0.08)%.

The influence of pH of the source phase and receiving phase on the transport efficiency of silver ion is shown in Figs. 4 and 5, respectively. As is evident from Fig. 4, the maximum silver ion transport occurs at pH = 5. It seems that the thiosulfate ion decomposes in more acidic solutions [22].

The liquid membrane used in this study is shown schematically in Fig. 6. The Ag^+ ion is transported from the source phase into receiving phase via organic
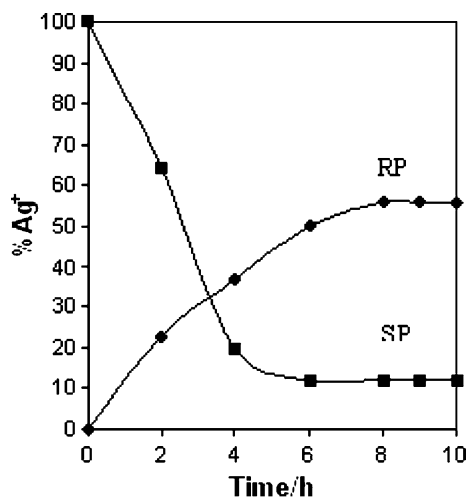

Fig. 4 Effect of pH of source phase on silver ion transport. Conditions: source phase; 10 mL of 5×10^{-4} M Ag^+ and 1×10^{-3} M picric acid; membrane phase, 50 mL of 1×10^{-3} M carrier (DBPY18C6) in nitrobenzene; receiving phase, 30 mL of 0.01 M of thiosulfate; transport time, 8 h (RP = Receiving phase, SP = Source phase)

membrane. Movement of the charge species through the hydrophobic organic membrane is accomplished by the presence of host carrier DBPY18C6, ion paired with picrate as a suitable counter anion. The picrate ion not only neutralizes the charged (DBPY18C6-Ag^+) complex, but also induces a more lipophilic character to the silver ion with carrier on the left side of the membrane, the complex diffuses down its concentration gradient. On the right side of the membrane, the metal ion is released into the

Fig. 3 Effect of time on silver ion transport. Conditions: source phase; 10 ml of 5×10^{-4} M Ag^+ and 1×10^{-3} M picric acid; membrane phase,: 50 mL of 1×10^{-3} M carrier (DBPY18C6) in nitrobenzene; receiving phase, 30 mL of 0.01 M of thiosulfate (RP = Receiving phase, SP = Source phase)
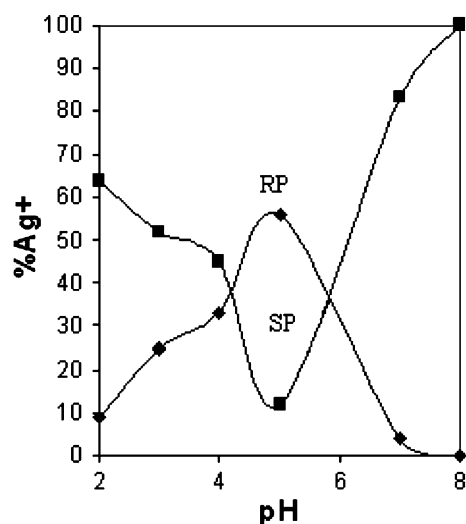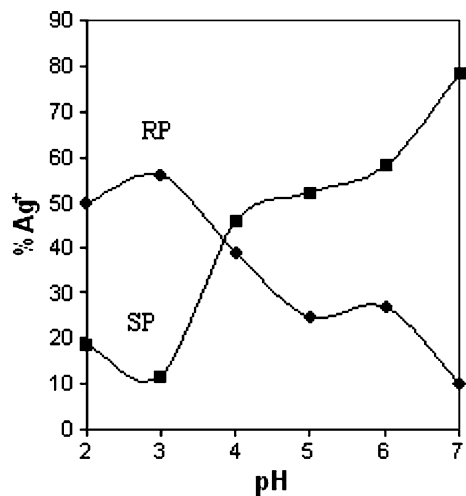

Fig. 5 Effect of pH of receiving phase on silver ion transport. Conditions: source phase; 10 mL of 5×10^{-4} M Ag^+ and 1×10^{-3} M picric acid; membrane phase, 50 mL of 1×10^{-3} M carrier (DBPY18C6) in nitrobenzene; receiving phase, 30 ml of 0.01 M of thiosulfate; transport time, 8 h (RP = Receiving phase, SP = Source phase)
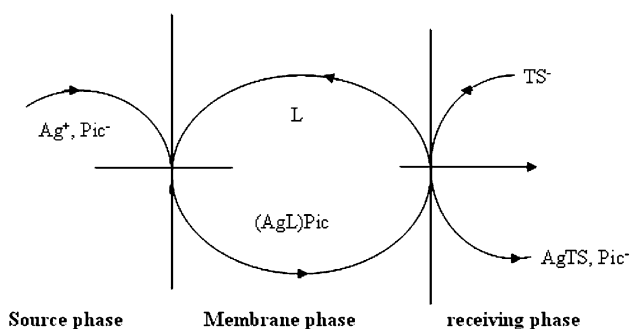
Fig. 6 Liquid membrane system for transport of Ag$^+$ ion

receiving phase via formation of a ternary complex (DBPY18C6-Ag$^+$-S$_2$O$_3^{2-}$). Then the free carrier diffuses back across the liquid membrane and cycle starts again. The net results are the transport of Ag$^+$ ion from the aqueous source phase to the receiving phase.

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