

## Highly Selective Transport of Silver(I) Cation Across a Bulk Liquid Membrane Containing an Acyclic Thioether Ligand as Carrier

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(Received: 6 April 2010;

Accepted: 6 November 2010)

AJC-9253

A 1,2-dichloroethane bulk liquid membrane system containing a new synthetic acyclic thioether ligand, *i.e.* 2,9-dihydroxy-1,10-diphenoxy-4,7-dithia decane; (C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>) and palmitic acid was used for highly selective and efficient transport of Ag<sup>+</sup> cation. The transport process was maintained by the buffering the source and receiving phases. For these systems that displayed transport behaviour, sole selectivity for Ag<sup>+</sup> cation was observed under the employed experimental conditions. In the presence of thiosulfate ion (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) as suitable metal ion acceptor in the receiving phase, the amount of Ag<sup>+</sup> cation transported across the liquid membrane after 4 h was (90.2 ± 2.0 %). The membrane solvents include: 1,2-dichloroethane (1,2-DCE), chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), nitrobenzene (NB) and nitromethane (NM). The results show that the sequence of transport efficiency for Ag<sup>+</sup> cation in organic solvents is: 1,2-DCE > CHCl<sub>3</sub> > DCM > NB > NM. The experimental variables such as the concentration of carrier in the membrane phase, the nature and concentration of fatty acids in the membrane phase, the nature and concentration of the stripping agents in the receiving phase, receive phase volume and the effect of other parameters such as pH of source and receiving phases and the time of transport were optimized in order to achieve the highest transport efficiency of a 5 × 10<sup>-4</sup> M solution of Ag<sup>+</sup> cation across the bulk liquid membrane systems. The proposed transport method is simple, rapid, selective and reproducible compared with the other methods of separation.

**Key Words:** Liquid membrane transport, Ag<sup>+</sup> cation, 1,2-Dichloroethane, Synthetic acyclic thioether ligand, 2,9-Dihydroxy-1,10-diphenoxy-4,7-dithia decane.

### INTRODUCTION

Selective separation of a given metal ion from a complex mixture of other ionic species is of increasing importance in industrial and analytical chemistry and separation sciences. In most cases, various interfering species must be removed and/or the species of interest must be enriched before detection. Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery processes. The selective transport of metal cations across a membrane is also known to play an essential role in many biological processes. There has been a growing interest in the transport of metal ions mediated by receptor molecules where the carrier operates selective across artificial or biological membranes<sup>1-4</sup>.

An important advantage for the use of this procedure is that in the liquid membrane technology, the extraction, stripping and regeneration operations are combined in one single step. Proton-driven cation transport through a liquid membrane containing an ion-selective ionophore bearing a proton dissociable moiety is one of the most effective separation techniques for a particular metal ion<sup>5-8</sup>.

There has been considerable interest in the use of proton ionizable carriers for the transport of metal cations between two aqueous solutions through an organic membrane<sup>9</sup>. These pH-regulated ligands described until now, present the fact that the transfer of the counter-anion from the aqueous phase into the organic medium is avoided. Such chelating agents do not involve concomitant transfer of one or more aqueous phase anions into the organic medium. This factor was of immense importance to potential applications in which hard aqueous phase anions such as chloride, nitrate and sulfate would be involved<sup>10,11</sup>.

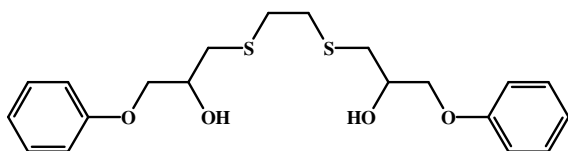
Low level exposure to silver compounds is widespread owing to the use of soluble silver compounds to disinfect water for drinking and recreation purposes. It is suggested that silver might pose a potential risk as water pollutant because of the lack of recycling of mixed silver. Silver also enters the environmental through industrial wastes because it often exists as an impurity in Zn, Cu, As and Sb ores<sup>12</sup>.

It is well known that sulfur ligands coordinate with transition metal cations as exclusive donor atoms. In this respect, macrocyclic and noneycyclic thio compounds have attracted wide

spread attention owing to the unique properties of these compounds<sup>13</sup>. In aqueous solutions, little or no reaction occurs between the sulfur-containing ligands and either alkali or alkaline earth metal ion, but the stability of the complexes with Hg<sup>2+</sup> and Ag<sup>+</sup> cations are enhanced markedly<sup>14</sup>.

Acyclic polyether (podand) chemistry has received a great deal of attention for many years and various types of compounds have been synthesized<sup>15-17</sup>. Several studies have focused on determination of the selectivity and efficiency of the podand-mediated extraction or transport of metal cations through an organic medium into an aqueous receiving phase<sup>18</sup>.

The present paper describes the use of a new synthetic acyclic thioether ligand *i.e.*, 2,9-dihydroxy-1,10-diphenoxy-4,7-dithia decane (C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>) (**Scheme-I**), as a selective neutral carrier for Ag<sup>+</sup> cation transport through a proton driven bulk liquid membrane system. It has been demonstrated that such a system is capable of transporting cations against a proton gradient, as driving force. The potential of this ligand to complex and transport Ag<sup>+</sup> cation was verified. In this work, we used such a pH difference as a driving force in the transport of Ag<sup>+</sup> cation across a 1,2-dichloroethane membrane containing the ligand. For this purpose, the influence of effective parameters was optimized.



**Scheme-I:** Structure of 2,9-dihydroxy-1,10-diphenoxy-4,7-dithia decane (C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>)

## EXPERIMENTAL

Analytical grade of silver(I) nitrate (Merck), chromium(III) nitrate (BDH), cobalt(II) nitrate (BDH), copper(II) nitrate (BDH), zinc(II) nitrate (Merck), cadmium(II) nitrate (Riedel), lead(II) nitrate (BDH), sodium acetate (Riedel), sodium hydroxide (Riedel), stearic acid (BDH), palmitic acid (Riedel), oleic acid (Merck), sodium thiosulfate (Merck), sodium sulfite (Merck), sodium thiocyanide (Merck), thiourea (Merck), sodium cyanide (Riedel), EDTA (Riedel) were used as received. 1,2-Dichloroethane (1,2-DCE), dichloromethane (DCM), chloroform (CHCl<sub>3</sub>), nitrobenzene (NB), nitromethane (NM), formic acid, acetic acid and nitric acid (all from Merck) were used with the highest purity. Doubly distilled deionized water was used through out. Synthetic route for the preparation of new synthetic acyclic thioether ligand (C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>) is described in reference<sup>19</sup>.

The determination of silver(I) content was carried out by a Shimadzu AA-670 atomic absorption spectrometer equipped with an Ag-hallow cathode lamp and was made under the recommended conditions for silver cation. A pH meter, Metrohm 692 pH/ion meter equipped with a combined glass electrode was used for pH adjustments. A bulk liquid membrane cell was used in all transport experiments.

**Procedure:** All bulk liquid membrane transport experiments were carried out at ambient temperature in a cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside

diameter 2 cm), thus separating the two aqueous phases. The inner aqueous phase (source phase, SP) contained silver nitrate (10 mL, 5 × 10<sup>-4</sup> M). The outer aqueous phase (receiving phase, RP) contained different stripping agents (20 mL, 1 × 10<sup>-2</sup> M). The membrane phase (MP) containing 50 mL of 2 × 10<sup>-3</sup> M C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub> ligand and 4 × 10<sup>-3</sup> M of various types of fatty acids in 1,2-dichloroethane, dichloromethane, chloroform, nitrobenzene and nitromethane lay below these aqueous phases which bridged these two phases. The membrane phase was magnetically stirred using a teflon-coated magnetic bar at 200 rpm. The pH of each source and receiving phases were adjusted to 6 and 5, respectively, using CH<sub>3</sub>COOH/CH<sub>3</sub>COONa buffer solution.

Under these conditions, not only is the mixing process is perfect, but also the interfaces between the organic membrane phase and two aqueous phases remained flat and were well defined. Determination of the silver(I) cation concentration in both aqueous phases was carried out by AAS. Reproducibility was confirmed as ± 2.0 % or better. A similar transport experiment was carried out in the absence of the carrier for reference. The data points reported are averages of three replicate measurements.

## RESULTS AND DISCUSSION

Complexing agents with soft coordination sites like sulfur atoms are known to generate a great affinity toward *d*<sup>10</sup> transition metal cations<sup>20</sup> such as Ag<sup>+</sup>.

The structural formulas 2,9-dihydroxy-1,10-diphenoxy-4,7-dithia decane (C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub>) is shown in **Scheme-I** was used as a new synthetic sulfur donor acyclic ligand with two ionizable protons and insoluble in water for this study.

In our early experiments, we tested the competitive transport of Cr<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ag<sup>+</sup> and Pb<sup>2+</sup> metal cations from an aqueous source phase into the receiving phase through 1,2-DCE, CHCl<sub>3</sub>, DCM, NB and NM organic solvents as liquid membranes containing the new synthetic acyclic thioether ligand at ambient temperature<sup>21</sup>. The obtained results show that this ligand is a highly selective ionophore for Ag<sup>+</sup> cation among the other metal cations and the Ag<sup>+</sup> cation gets self encapsulated into the pseudo cavity and hence shows maximum transport efficiency. The sequence of transport efficiency for Ag<sup>+</sup> cation in organic solvents was found to be: 1,2-DCE > CHCl<sub>3</sub> > DCM > NB > NM.

In order to increase the efficiency and selectivity of Ag<sup>+</sup> cation transport, we could use a particular stripping agent in the receive phase. One of the interesting possibilities for this purpose was the use of thiosulfate ion (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>). In the next step, the experimental variables were optimized in order to achieve the highest efficiency in the transport of Ag<sup>+</sup> cation across the membranes.

Surfactant systems have been recognized as very useful agents for improving surface properties and development new concepts in analytical chemistry. Surfactants, well known as wetting agents, lower the surface of a liquid, allow easier spreading and reduce the interfacial tension between organic solvents and water by adsorbed at the liquid-liquid interface. Surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophobic groups

(their "tails") and hydrophilic groups (their "heads"). Therefore, they are typically sparingly soluble in both organic solvents and water. The hydrophobic non-polar end is attached to organic solvents while the hydrophilic end attaches to water<sup>22-25</sup>. In fact, they serve as a bridge between two immiscible solvents in liquid-liquid interface through which the transport and exchange of molecules and ions takes place easily.

Although the maximum percentage of silver(I) cation that transports to the receiving phase that contains buffer solution at pH 5 after 24 h does not exceed 10 %, but it exceeds 90 % after 4 h when 0.01 M of anionic surfactant, sodium thiosulfate ( $S_2O_3^{2-}$ ) is added to the receiving phase and palmitic acid to the 1,2-DCE organic phase. It seems that the surfactants lying at the membrane/receiving phase interface catalyze the exchange process of  $Ag^+$  and  $H^+$  cations to the carrier.

In this work, we used such a pH difference as a driving force in the transport of  $Ag^+$  cations across a 1,2-DCE membrane containing ligand and palmitic acid. The pH of each source and receiving phases were adjusted to 6 and 5, respectively. Therefore, by a change in pH ( $\Delta pH$ ), complexation and decomplexation of ligand to  $Ag^+$  cations can be achieved and will have a significant effect on the rate of transport of this metal cation.

**Effect of organic solvent in the membrane phase:** The ability of solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of cations is one of the factors that can thermodynamically influence the complexation process<sup>26</sup>. The data for selective transport of  $Ag^+$  cation from an aqueous source phase through 1,2-DCE,  $CHCl_3$ , DCM, NB and NM membranes containing synthetic ligand at ambient temperature is given in Table-1. As is seen, the transport efficiency of  $Ag^+$  cation by  $C_{20}H_{26}O_4S_2$  ligand is varied in order: 1,2-DCE >  $CHCl_3$  > DCM > NB > NM.

TABLE-1  
EFFECT OF THE ORGANIC SOLVENT ON  
SILVER(I) CATION TRANSPORT<sup>a</sup>

Organic solvent	Percentage transported into receiving phase	Percentage remaining in source phase
1,2-Dichloroethane	90	5
Chloroform	52	12
Dichloromethane	48	16
Nitrobenzene	21	62
Nitromethane	11	76

<sup>a</sup>Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $Ag^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $C_{20}H_{26}O_4S_2$  carrier and  $4 \times 10^{-3}$  M palmitic acid in different organic solvent; receiving phase, 20 mL of 0.01 M  $S_2O_3^{2-}$  at pH 5; time of transport, 4 h

According to the physico-chemical properties of the solvents, this result may be attributed to the lower donor number of 1,2-dichloroethane which leads to decreasing the competition between the solvent and the ligand molecules which results in increasing the stability of the complex formed between the silver(I) cation and the ligand and, therefore, increasing the rate of cation transfer in this organic solvent compared to the other three organic solvents. According to Izatt and coworkers<sup>27,28</sup>, several parameters whose values depend on the membrane solvent can affect the transport of metal cations through bulk liquid membranes. These are the

thickness of the unstirred boundary layers in the membrane (*i.e.*, the diffusion path length), coefficients of all mobile species in these boundary layers and the  $\log k_f$  value for formation of the cation-ligand complex in the organic phase. Additional parameters are the partition coefficients of the ligand and cation-ligand complex. The thickness of the boundary layers is a function of the rate at which the solvent is stirred, as well as, its viscosity. The composition of the boundary layers is a function of the mutual water-solvent solubilities. The partitioning of metal cations into the organic phase should also be affected by the dielectric constant of the organic solvent as membrane phase. The physical and chemical properties of solvents are closely related to their structures and play important roles in solute-solvent and solute-solute interactions in solutions<sup>27,28</sup>.

#### Effect of ligand concentration in the membrane phase:

The influence of the concentration of ligand as ion carrier in the organic phase on the transport efficiency of silver(I) cation was studied and the graphical results are shown in Fig. 1. It is clear that, the percentage of transported this cation increases with increasing the concentration of carrier in organic phase. The maximum transport lies between concentration ranges  $1 \times 10^{-3}$  M to  $6 \times 10^{-3}$  M.

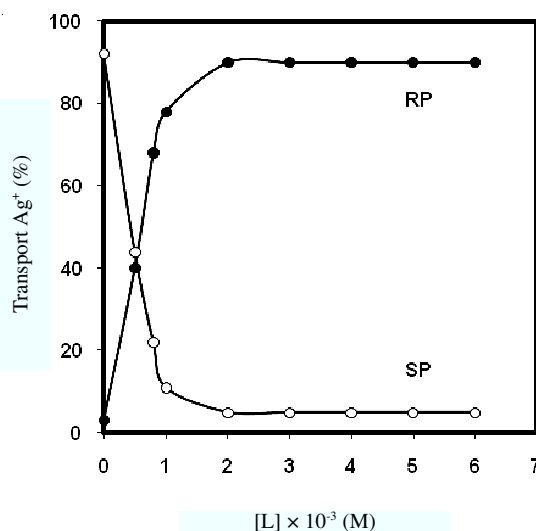


Fig. 1. Effect of carrier concentration on silver(I) cation transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $Ag^+$  at pH 6; liquid membrane phase, 50 mL of varying concentration of  $C_{20}H_{26}O_4S_2$  carrier and  $4 \times 10^{-3}$  M palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $S_2O_3^{2-}$  at pH 5; time of transport, 4 h

**Effect of fatty acid type in the membrane phase:** In another experiment, the silver(I) cation transport processes (water-1,2-DCE-water) employed an organic phase containing known concentrations of the ionophore and fatty acids, such as palmitic acid, stearic acid and oleic acid. A major role of the fatty acids is to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralization of the metal cation being transported through ion pairing or adduct formation<sup>29</sup>. In this manner the uptake of lipophilic nitrate anions into the organic phase is avoided. Normally, ion pair/adduct formation serves to inhibit any bleeding of

partially species (such as the protonated ionophore and/or its corresponding charged metal ion complex) from the organic membrane phase into either of the aqueous phases<sup>30</sup>. It was seen a considerable change in transport percentage of silver(I) cation in presence of palmitic acid rather than the other fatty acids (Table-2). The optimum concentration of palmitic acid in the membrane phase was also investigated and was found to be  $4 \times 10^{-3}$  M. The graphical results are shown in Fig. 2.

TABLE-2  
EFFECT OF THE FATTY ACIDS AS SURFACTANT IN THE MEMBRANE PHASE ON SILVER(I) CATION TRANSPORT<sup>a</sup>

Fatty acid	Percentage transported into receiving phase	Percentage remaining in source phase
Palmitic acid	90	5
Stearic acid	44	41
Oleic acid	51	32

<sup>a</sup>Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of different fatty acids in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  at pH 5; time of transport, 4 h

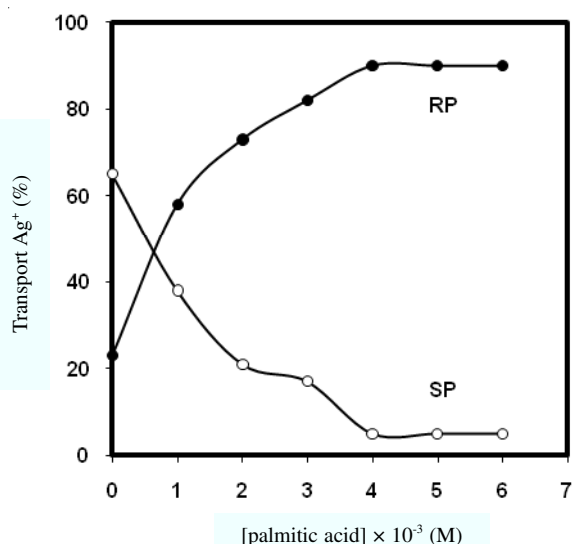


Fig. 2. Effect of palmitic acid concentration on  $\text{Ag}^+$  transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and varying concentration of palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  at pH 5; time of transport, 4 h

#### Effect of stripping agent type in the receiving phase:

Table-3 shows that the permeability of the membrane system for  $\text{Ag}^+$  cation is considerably dependent on the nature of stripping agent for this cation in receiving phase. In the presence of thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) in the receiving phase, 90.2 % of  $\text{Ag}^+$  cation transported through the membrane during 4 h, while the use of the other reagents such as  $\text{SO}_3^{2-}$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$ , EDTA and thiourea results in much lower transport efficiency of the silver(I) cation. The optimum concentration of thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) in the receiving phase was also investigated and it was found to be  $1 \times 10^{-2}$  M. The graphical results are shown in Fig. 3. Notably, the absence of a metal ion acceptor in the receiving phase resulted in no appreciable transport of silver(I) cation even in much longer periods of time.

TABLE-3  
EFFECT OF THE DIFFERENT SURFACTANT PRESENT IN THE RECEIVING PHASE AS STRIPPING AGENT ON  $\text{Ag}^+$  TRANSPORT<sup>a</sup>

Nature of stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
$\text{S}_2\text{O}_3^{2-}$	90	5
$\text{SO}_3^{2-}$	53	11
$\text{SCN}^-$	21	53
$\text{CN}^-$	38	29
EDTA	16	41
Thiourea	24	50

<sup>a</sup>Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of different fatty acids in 1,2-dichloroethane; receiving phase, 20 mL of 0.01M of different stripping agent at pH 5; time of transport, 4 h

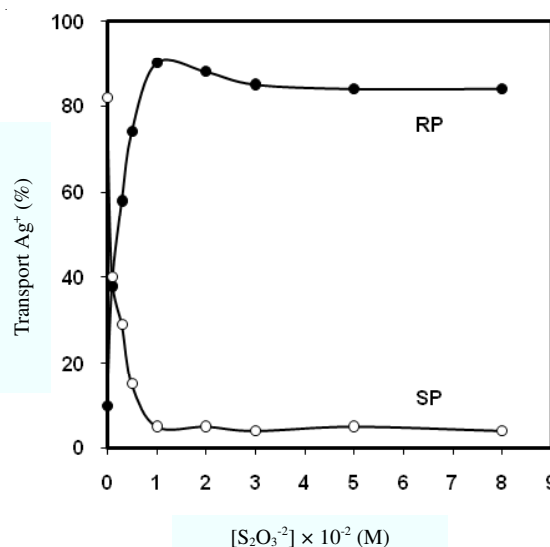


Fig. 3. Effect of  $\text{S}_2\text{O}_3^{2-}$  concentration in the receiving phase on  $\text{Ag}^+$  transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  cation at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of varying concentration of  $\text{S}_2\text{O}_3^{2-}$  at pH 5; time of transport, 4 h

**Effect of pH of source phase:** The influence of pH of the source phase on the transport efficiency of  $\text{Ag}^+$  cation was studied in pH range 3-8 and it was found that maximum transport of this cation occurs at buffer solution at pH 6 (Fig. 4). According to the couple-proton mechanism that we suggested for the  $\text{Ag}^+$  cation transport, we should adjust a less acidic media for the source phase rather than the receiving phase. The influence of the buffer solution in the source phase was studied and we adjusted the pH of the source phase with  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer solution.

**Effect of pH of receiving phase:** The effect of pH of the receiving phase was also studied and it was seen that the suitable pH is 5, because the thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) solution decomposes in more acidic solutions<sup>31</sup>. For further studies the thiosulphate was omitted and the receiving phase with different pH was used and the transport efficiency was investigated. The results show that thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ) has an important role for silver(I) cation transport and acidic receiving solution is not suitable for silver transport itself. The results are shown in Fig. 5.

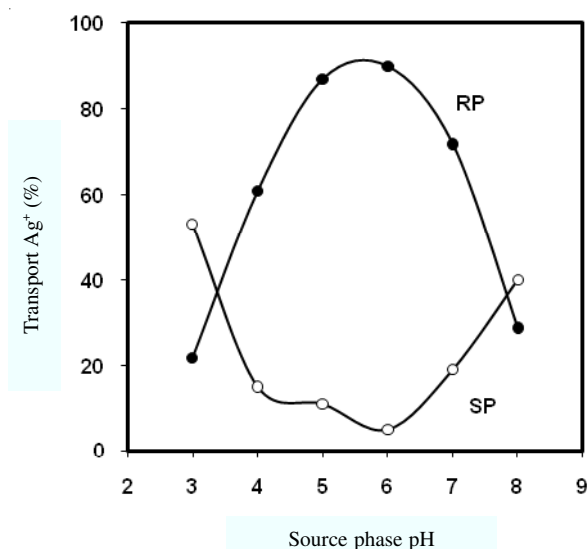


Fig. 4. Effect of pH in source phase on  $\text{Ag}^+$  transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  with various pH; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  at pH 5; time of transport, 4 h

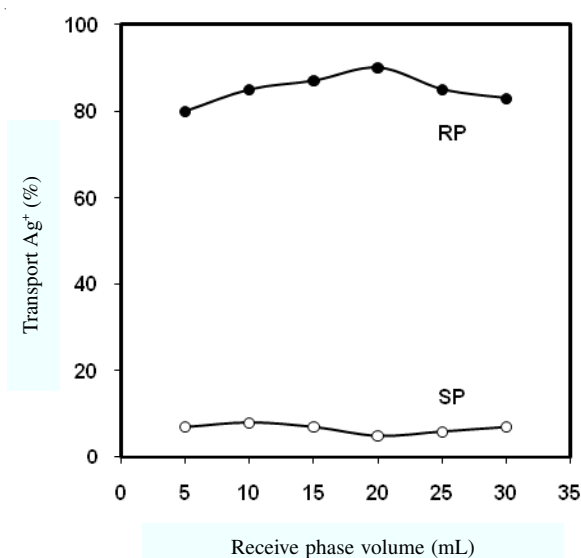


Fig. 6. Effect of the receiving phase volume on  $\text{Ag}^+$  transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-dichloroethane; receiving phase, varying volume of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  at pH 5; time of transport, 4 h

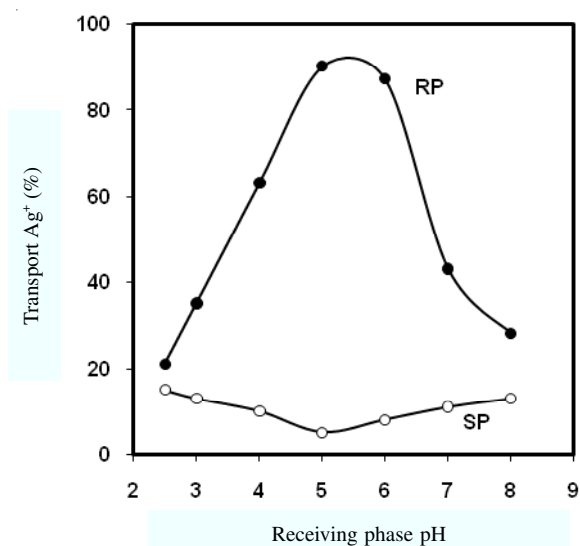


Fig. 5. Effect of pH in receiving phase on  $\text{Ag}^+$  transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  with various pH; time of transport, 4 h

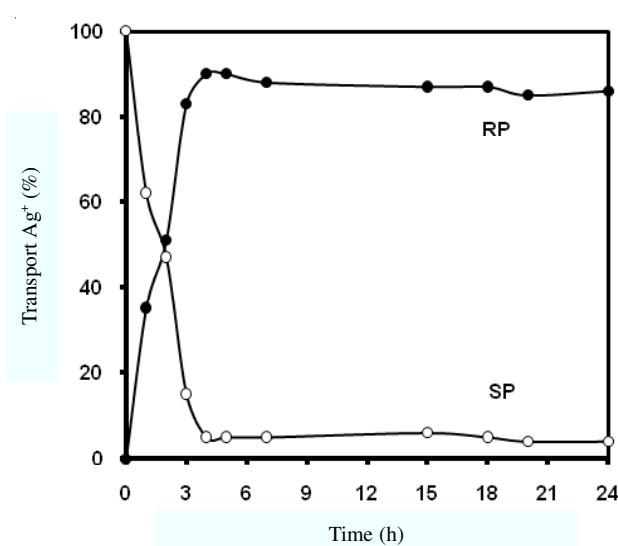


Fig. 7. Effect of time on silver transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M  $\text{Ag}^+$  at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-dichloroethane; receiving phase, 20 mL of 0.01 M  $\text{S}_2\text{O}_3^{2-}$  at pH 5

**Effect of receiving phase volume:** The influence of receiving phase volume on the transport efficiency of silver was studied and the results are shown in Fig. 6. The optimum volume of the receiving phase was investigated and it was found to be 20 mL.

**Effect of time of transport:** Fig. 7 shows the time dependence of silver(I) cation transport through the liquid membrane under the optimal experimental conditions. It is obvious that the transport of this cation into the receiving phase increases with time. According to the results obtained in this study, the extraction of  $\text{Ag}^+$  cation from the source phase into the organic membrane phase is fast and its release from the organic phase into the receiving phase is to some extent quick,

that is the silver(I) cation transport seems to be completed above 4 h.

**Reproducibility of the bulk liquid membrane technique:** The reproducibility of silver transport was investigated and the per cent of  $\text{Ag}^+$  cation transported after 4 h from eight replicate measurements was found to be  $(90.2 \pm 2.0 \%)$ .

**Transport selectivity:** The selectivity of the above liquid membrane system for transport of  $\text{Ag}^+$  cation over the other metal cations such as  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in equimolar mixtures is illustrated in Table-4 and the interference effects of these cations were investigated. All of these cations remained in the source phase. As is seen in this table and also in Fig. 8, the system is very selective for  $\text{Ag}^+$  and none of the

TABLE-4  
AMOUNT OF CATIONS TRANSPORTED FROM VARIOUS  
CATION MIXTURES THROUGH THE LIQUID MEMBRANE<sup>a</sup>

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Ag <sup>+</sup>	90	5
Pb <sup>2+</sup>	0	95
Cd <sup>2+</sup>	0	98
Mixture 2		
Ag <sup>+</sup>	90	5
Cr <sup>3+</sup>	0	97
Co <sup>2+</sup>	0	96
Mixture 3		
Ag <sup>+</sup>	90	5
Cu <sup>2+</sup>	0	99
Zn <sup>2+</sup>	0	97

<sup>a</sup>Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M various cation mixtures at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $C_{20}H_{26}O_4S_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in 1,2-DCE; receiving phase, 20 mL of 0.01 M  $S_2O_3^{2-}$  at pH 5; time of transport, 4 h

studied cations interferes with Ag<sup>+</sup>. The selectivity of the membrane system was also studied under optimum conditions by undertaking competitive transport experiments with equimolar concentrations of different transition and heavy metal ions such as Cr<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>.

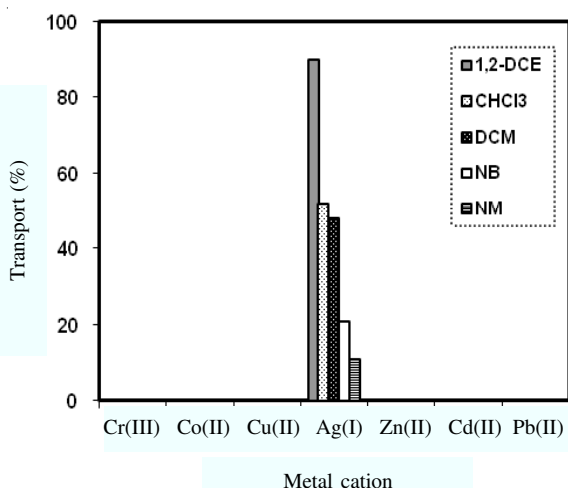


Fig. 8. The results of metal ion transport. Experimental conditions: source phase, 10 mL of  $5 \times 10^{-4}$  M of metal cations at pH 6; liquid membrane phase, 50 mL of  $2 \times 10^{-3}$  M  $C_{20}H_{26}O_4S_2$  carrier and  $4 \times 10^{-3}$  M of palmitic acid in different organic solvent; receiving phase, 20 mL of 0.01 M  $S_2O_3^{2-}$  at pH 5; time of transport, 4 h

## Conclusion

The present study demonstrates that the new synthetic acyclic thioether ligand, *i.e.*, 2,9-dihydroxy-1,10-diphenoxy-4,7-dithia decane ( $C_{20}H_{26}O_4S_2$ ), is an excellent carrier for selective and efficient transport of Ag<sup>+</sup> cation through 1,2-dichloroethane bulk liquid membrane containing this carrier and palmitic acid. The presence of  $S_2O_3^{2-}$  as cation acceptor in the receiving phase, the efficiency and transport of Ag<sup>+</sup> greatly increases without affecting the selectivity. This study also demonstrates the usefulness of the liquid membrane technique for making it possible to combine extraction and stripping opera-

tions in a single process and reducing the solvent inventory requirements. In conclusion, the above system, which is specific for silver(I) cation is a potential candidate for practical use in silver(I) cation separation, especially as it has the advantages of low solvent requirement, high precision, efficiency, selectivity, simplicity and speed.

## ACKNOWLEDGEMENTS

The authors acknowledged the support of this work by Ferdowsi University of Mashhad, Mashhad, Iran.

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