



Efficient and Selective Transport of Silver(I) Cation Across a Bulk Dichloromethane Membrane Using 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane as a Carrier

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Abstract: 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix 5) was used as a highly efficient carrier for the transport of silver(I) cation through a dichloromethane (DCM) bulk liquid membrane. In order to achieve the highest transport efficiency of Ag^+ cation across the bulk liquid membrane system, the influence of different parameters was studied. These include: the nature of various organic solvents as liquid membrane phase, concentration of the carrier in the membrane phase, concentration of picric acid as counter anion in the source phase, type of various stripping agents in the receiving phase, concentration of thiosulfate anion ($\text{S}_2\text{O}_3^{2-}$) as a suitable stripping agent, pH of the source and receiving phases, volume of the receiving phase and equilibrium time of transport which were optimized. In the optimum procedure conditions, the transport of a 3×10^{-4} M solution of silver(I) cation was observed ($88.03 \pm 0.82\%$) after 4 hours. The selectivity of Ag^+ transport from aqueous solutions containing equimolar concentration of other metal cations such as Pb^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} and Fe^{3+} was also investigated.

Key words: Silver (I) cation, Kryptofix 5, Dichloromethane, Bulk liquid membrane transport.

Introduction

Silver is used widely in the production of coins, jewellery, tableware and alloys, and in the manufacture of electrical apparatus, mirrors and chemicals for photographic processes. Additionally, it is used in the production of dental amalgams and burn creams as silver sulfadiazine cream (SSD), due to its antibacterial properties [1-3]. Silver metal is practically non toxic, acute toxicity by ingestion is low. However, chronic absorption may cause "Argyria" a blue/grey discoloration of various tissues, ocular injury, leukopenia, and toxicity

in kidney, liver, and neurologic tissues [4]. Thus, the determination of silver in various media is of importance.

Membrane extraction is a promising technique for removal of valuable metal ions from diluted solutions [5,6]. A liquid membrane is a layer of an organic solvent separating two aqueous solutions. Compounds, promoting the transport of substances from one aqueous solution to another, may be dissolved in the organic phase. Liquid membranes have a lot of advantages over traditional solvent extraction, such as low capital and operating costs, combination of extraction and stripping processes into a single stage and small amounts of extractants. Liquid membranes can be classified as bulk, supported and emulsion membranes. Bulk liquid membranes are relatively thick (0.01-1 cm) and stable. The main issue for all types of supported liquid membranes is short lifetime of these membranes. Emulsion liquid membrane process is much more complex than that of the bulk liquid membrane.

Nowadays many compounds have been designed and synthesized to form remarkably stable and selective complexes with heavy metal ions such as Schiff bases [7], podands [8], cyclams [9] and calixarenes [10]. Among them cryptands and crown ethers are of special interest as they exhibit extremely high affinities toward heavy metal ions such as Ag^+ , Hg^{2+} and Pb^{2+} [11-13]. Their selectivities and coordination abilities with transition metal ions depend on ring cavity size, ligand rigidity, the nature of donor atoms and their disposition [14]. In recent years, many crown ethers have been synthesized and successfully utilized for highly selective binding with heavy metal cations in diversal processes such as ion transports through artificial and natural membranes, liquid-liquid phase-transfer reactions and isotope separations [15-17].

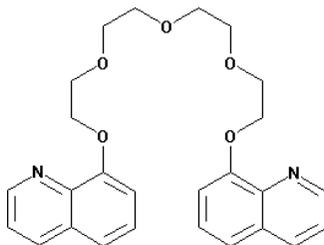
In our early experiments, we tested the competitive transport of Co^{2+} , Fe^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ and Pb^{2+} metal cations from an aqueous source phase into an aqueous receiving phase through NB, CHCl_3 , DCM and 1,2-DCE organic solvents as liquid membranes containing kryptofix 5 ligand at ambient temperature [18]. The obtained results show that this ligand is a highly selective ionophore for Ag^+ cation among the other metal cations and the sequence of transport efficiency for Ag^+ cation in these organic solvents was found to be: $\text{DCM} > \text{CHCl}_3 > 1,2\text{-DCE} > \text{NB}$.

In this work, we employed kryptofix 5 as an excellent specific ion carrier for the highly efficient and selective transport of Ag^+ metal cation through a bulk dichloromethane membrane. 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 of Ag^+ metal cation was verified and the influence of effective parameters was optimized.

Experimental

Reagents and solvents

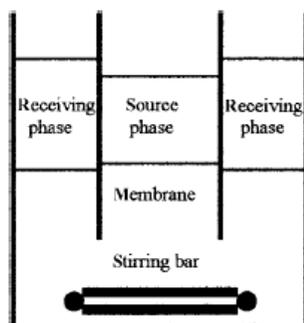
1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix 5) (Scheme 1), silver(I) nitrate, iron(III) nitrate, cadmium(II) nitrate, zinc(II) nitrate, copper(II) nitrate, cobalt(II) nitrate, lead(II) nitrate, sodium acetate, acetic acid, sodium hydroxide, formic acid, picric acid, sodium thiosulfate, sodium sulfite, sodium thiocyanate, sodium pyrophosphate, EDTA and thiourea all purchased from Merck and used without further purification. Dichloromethane (DCM), chloroform (CHCl_3), nitrobenzene (NB) and 1,2-dichloroethane (1,2-DCE) (all from Merck) were used with the highest purity. All aqueous solutions were prepared using double distilled deionized water.



Scheme 1. Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix 5).

Apparatus

The determination of silver(I) content was carried out by a Shimadzu AA-670 atomic absorption spectrometer (AAS) equipped with an Ag-hallow cathode lamp. The pH measurements were made with a Metrohm 692 pH-meter using a combined glass electrode. A bulk liquid membrane cell was used in all transport experiments (Scheme 2).



Scheme 2. Representation of the bulk type liquid membrane cell used.

Procedure

Bulk liquid membrane (BLM) transport measurements were performed 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(I) nitrate (10 ml, 3.0×10^{-4} M) and picric acid (3.0×10^{-3} M). The outer aqueous phase (receiving phase, RP) was a $\text{Na}_2\text{S}_2\text{O}_3$ solution (5 ml, 1.0×10^{-3} M). The transport process was maintained by the buffering the aqueous source and receiving phases. The membrane phase (MP) contained 50 ml of 1.0×10^{-3} M kryptofix 5 as carrier in organic solvent. The membrane phase was magnetically stirred by a Teflon-coated magnetic bar. 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. Determination of the silver(I) concentration in both aqueous phases was carried out by AAS. The data points reported are averages of at least three replicate measurements.

Results and discussion

Effect of organic solvent as membrane phase

The nature of the membrane solvent is one of the main factors in establishing transport efficiency. Several parameters whose values depend on the membrane solvent can affect the

transport of metal cations through bulk liquid membranes. 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. The organic solvent which should be immiscible with water and non-volatile must have a suitable polarity related to an optimal value of the association constant of the complex. A solvent of low viscosity must be chosen to obtain the highest rate of transport possible in a particular system [19,20].

In the present work, we have examined the influence of some organic solvents as membrane phase. The data for selective transport of Ag^+ cation from an aqueous source phase through DCM, 1,2-DCE, CHCl_3 and NB organic membranes containing kryptofix 5 at ambient temperature is given in Table 1. As is seen, the transport efficiency of Ag^+ cation by kryptofix 5 as carrier is varied in order: $\text{DCM} > \text{CHCl}_3 > 1,2\text{-DCE} > \text{NB}$. According to the physicochemical properties of the solvents, these results may be attributed to the lower viscosity of DCM ($\eta = 0.39$) which leads to increase the rate of ion transfer in this organic solvent compared to the other three organic solvents. Moreover, the low donor number (DN) of dichloromethane ($\text{DN} = 1$) results in decreasing the competition between the solvent and the ligand molecules for the metal cation which leads to increase the stability of the complex formed between the Ag^+ cation and the ligand and, therefore, increasing the transport rate of silver(I) cation in this organic solvent. In addition, the lower dielectric constant of DCM ($\epsilon = 8.93$) than those of 1,2-DCE ($\epsilon = 10.66$) and NB ($\epsilon = 34.80$), may aid the ion-pair formation in DCM which results in a better transfer rate in this membrane system.

Table 1. Effect of the organic solvent on Ag^+ cation transport^a.

Organic solvent	Transported into receiving phase (%)	Remaining in source phase (%)
DCM	88.05	1.36
CHCl_3	64.51	15.43
1,2-DCE	6.17	26.92
NB	4.84	54.72

^aExperimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in different organic solvents; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

Effect of carrier concentration in the membrane phase

As expected, it has been found that the nature of the ligand used as a carrier in the organic membrane phase has a significant effect on the efficiency and selectivity of metal cation transport [21,24].

In our early experiments, we tested the kryptofix 5 ability to transport of Co^{2+} , Fe^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ and Pb^{2+} metal cations from an aqueous source phase into the aqueous receiving phase through DCM, 1,2-DCE, CHCl_3 , and NB organic solvents as membrane. The obtained results showed that this ligand is a highly selective ionophore for Ag^+ cation among the other metal cations. The attachment of phenyl groups to this ligand increases its lipophilicity, thus increasing its solubility and effectively trapping it in the organic phase into one or both of aqueous phases. In addition, the interaction of π -electron system presents in aromatic rings with the silver(I) cation may be effective on complexation process between this metal cation and the ligand [25,26]. Therefore, it seems that silver(I) cation gets self encapsulated by the ligand and hence shows maximum transport efficiency.

The effect of concentration of the ligand in the organic membrane phase on the transport efficiency of Ag^+ metal cation was studied (Figure 1). As is obvious from this Figure, while

the transport of Ag^+ cation in the absence of the carrier is very low, but, the transport efficiency of this cation increases sharply with increasing the concentration of carrier in the membrane phase. The maximum transport occurs at 1.0×10^{-3} M of the carrier.

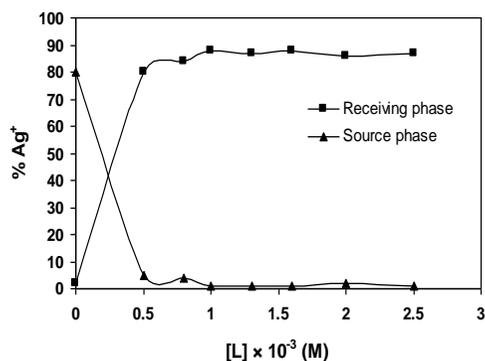


Figure 1: Effect of carrier concentration on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of varying concentration of carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

Effect of picric acid in the source phase

In preliminary experiments, it was found that the nitrate ion is not a suitable counter anion to accompany the (ligand- Ag^+) complex into the organic phase, only 23.48% of Ag^+ cation was transported into the receiving phase. However, addition of picric acid to the source phase increased the Ag^+ cation transport. The influence of the concentration of picric acid in the source phase on the silver(I) cation transport was investigated and the results are shown in Figure 2. The optimum concentration of picric acid was found to be 3.0×10^{-3} M. As seen from this Figure, the efficiency of Ag^+ cation transport increases with increasing picric acid concentration up to 3.0×10^{-3} M, but further increase in the concentration of picric acid caused a pronounced decrease in the transport efficiency of Ag^+ cation. This behavior maybe due to the competition of picric acid with Ag^+ cation for transport process. Similar behavior has been observed for selective transport of silver(I) cation through liquid membranes [27].

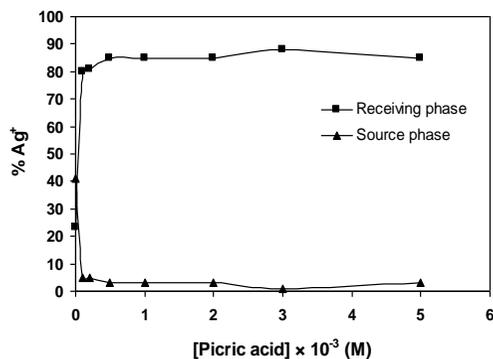


Figure 2. Effect of picric acid concentration on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and varying concentration of picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

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

Permeability of the membrane system for Ag^+ cation was found to be largely dependent on the nature and concentration of stripping ligand used in the receiving phase. As is evident from Table 2, the use of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) as stripping agent in the receiving phase caused a rather large increase in the efficiency of Ag^+ cation transport. While the presence of other stripping agents such as SO_3^{2-} , SCN^- , $\text{P}_2\text{O}_7^{4-}$, EDTA and thiourea results in diminished transport efficiency. The optimum concentration of thiosulfate anion in the receiving phase was investigated (Figure 3) and it was found to be 1.0×10^{-3} M. It is worthily to note that in the absence of the stripping agent on the receiving phase, the silver(I) cation transports only 11.17% into the receiving phase.

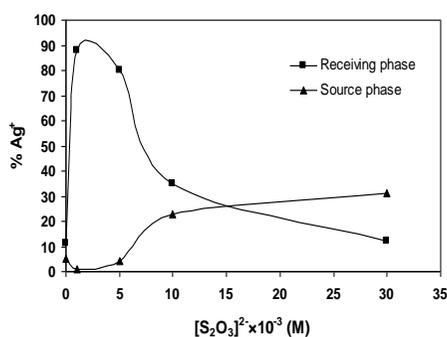


Figure 3. Effect of thiosulfate anion ($\text{S}_2\text{O}_3^{2-}$) concentration in the receiving phase on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of varying concentration of $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

Table 2. Effect of different stripping agents present in the receiving phase on Ag^+ cation transport^a.

Nature of stripping agent	Transported into receiving phase (%)	Remaining in source phase (%)
$\text{S}_2\text{O}_3^{2-}$	88.64	1.21
SO_3^{2-}	— ^b	5.43
SCN^-	—	70.33
$\text{P}_2\text{O}_7^{4-}$	—	26.70
EDTA	—	25.34
Thiourea	72.04	20.50

^aExperimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M of different stripping agents at pH 3; time of transport, 4 hours.

^bThe hyphenated symbols mean that the values are about zero.

Effect of pH

The influence of pH of the source phase and receiving phase on the transport efficiency of Ag^+ cation was studied and the results are shown in Figures 4 and 5, respectively. As is evident from these Figures, the maximum silver(I) cation transport occurs at pH 4 of the source phase and pH 3 of the receiving phase.

Effect of receiving phase volume

The influence of the receiving phase volume on the transport efficiency of silver(I) cation was investigated (Figure 6). As is obvious in this Figure, the optimum volume of the receiving phase is 5 ml. Therefore, the separation and preconcentration of Ag^+ cation occur during this technique.

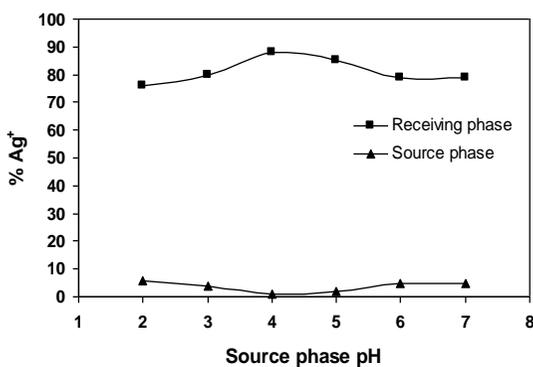


Figure 4. Effect of pH in source phase on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid with various pH; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

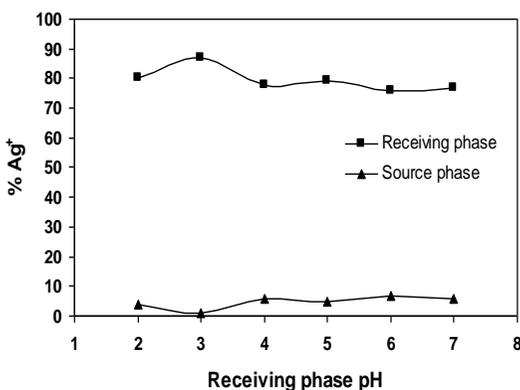


Figure 5. Effect of pH in receiving phase on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ with various pH; time of transport, 4 hours.

Effect of time

A series of cells were designed for the transport of Ag^+ cation and each cell examined after a certain time of stirring. Figure 7 shows the time dependence of Ag^+ 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, it was confirmed that about 88.52% of Ag^+ cation was transported from the source phase into the receiving phase after 4 hours.

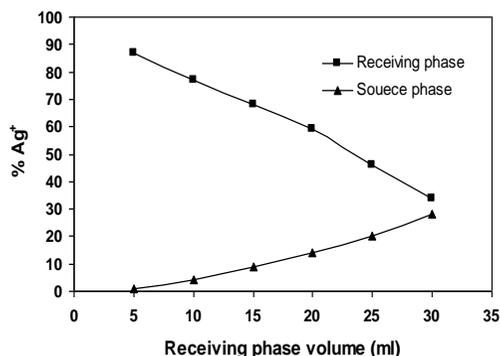


Figure 6. Effect of receiving phase volume on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, varying volume of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

Reproducibility of the bulk liquid membrane transport

The reproducibility of Ag^+ cation transport was investigated and the percent of Ag^+ cation transported after 4 h from six replicate measurements was found to be: $88.03 \pm 0.82\%$.

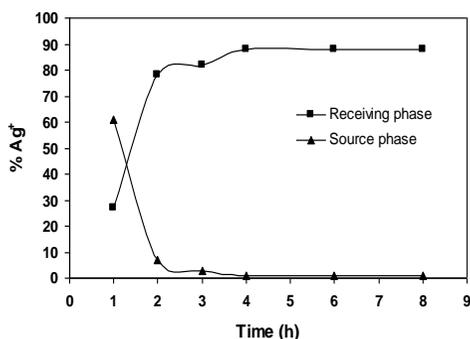


Figure 7. Effect of time on Ag^+ cation transport. Experimental conditions: source phase, 10 ml of 3.0×10^{-4} M Ag^+ cation and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3.

Transport selectivity

We also investigated the effect of various metal cations such as Pb^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} and Fe^{3+} on the selectivity of liquid membrane for Ag^+ cation. The results are given in Table

3. As is seen in this Table, with the exception of Pb^{2+} cation, no interfering effect was observed by other metal cations in transport efficiency of silver(I) cation.

Table 3. Amount of cations transported from various cation mixtures through DCM membrane^a

<i>Mixture</i>	<i>Transported into receiving phase (%)</i>	<i>Remaining in source phase (%)</i>
Mixture 1	73.59	5.22
Ag^+	11.18	75.50
Pb^{2+}	— ^b	80.95
Co^{2+}		
Mixture 2	75.30	4.41
Ag^+		
Zn^{2+}	3.68	30.44
Cd^{2+}		26.14
	1.15	
Mixture 3	73.77	4.62
Ag^+		
Cu^{2+}		71.09
Fe^{3+}	2.30	
	—	60.23

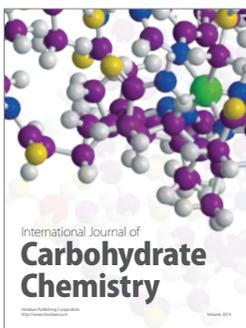
^aExperimental conditions: source phase, 10 ml of 3.0×10^{-4} M various cation mixtures and 3.0×10^{-3} M picric acid at pH 4; liquid membrane phase, 50 ml of 1.0×10^{-3} M carrier in DCM; receiving phase, 5 ml of 1.0×10^{-3} M $\text{S}_2\text{O}_3^{2-}$ at pH 3; time of transport, 4 hours.

^bThe hyphenated symbols mean that the values are about zero.

Recommended mechanism

The recommended mechanism for the transport of Ag^+ cation through bulk liquid membrane, which operated in this study, is shown in Scheme 3. Movement of the charge species through the hydrophobic organic membrane is accomplished by the presence of host ligand, ion paired with picrate as a suitable counter anion. The picrate ion not only neutralizes the charged (ligand- Ag^+) complex, but also induces a more lipophilic character to the Ag^+ complex so that it can be readily extracted into the membrane phase. After complexation of Ag^+ cation with the carrier on the source side of the membrane, the

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