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Article

Selective Transport of Silver(I) Cation Across a Bulk Liquid Membrane Containing Bis-β-enamino Ester as Ion Carrier

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Facilitated transport of silver(I) cation across a bulk liquid membrane by two synthesized ligands, bis-β-enamino ester (BBEE) and bis(benzoic acid) trioxaheptane (BBAT), as carriers dissolved in dichloromethane has been investigated. BBEE was used as a specific ion carrier for the transport of silver(I) ion. The influence of experimental parameters affecting the transport efficiency of silver(I) ion have been studied. In the presence of thiosulfate as a suitable metal ion acceptor in the receiving phase and picrate ion as ion pairing agent in the source phase, the amount of silver(I) ion transported across the liquid membrane after 120 min was found to be 97%. Tolerance to the presence of different ions was investigated and it was found that silver(I) cation transport was not affected even in the presence of 10-fold concentration of these metal cations in solution. This system was applied for the recovery of silver(I) cation from silver plating and photographic waste solution.

Keywords: facilitated transport, silver(I), bulk liquid membrane

Introduction

Silver is an important element that is mainly used in photographic and imaging industry, dental and medical products, electrical and electronic equipment and other products like jewelry, coins, and mirrors.[1-4] It is an important ion in some drugs like silver sulfadiazine cream that has been a standard treatment for burns over the past decades and silver deposition has been found in the skin, gingiva, cornea, liver, and kidney of patients.[5,6] It is reported that the concentration of silver(I) cation in water higher than 0.17 μg L^{-1} is toxic to fish and microorganisms. It has also been found that silver is toxic to humans at a concentration as high as 97.2 μg L^{-1} in drinking water.[7-10] On the other hand, owing to the fact that Ag^+ has moderate coordination ability, it is quite difficult to be discriminated from other chemically similar toxic elements. Therefore, separation and recovery of silver from waste and industrial sources are environmentally and economic important.

The solvent extraction process has already been industrially applied to the recovery of precious metal ions.[11,12] However, the extraction rate of precious metals is understood to be kinetically very slow, and as a result a huge amount of extractant and interfacial area are required to operate the process efficiently.

Compared with solvent extraction, liquid membranes have shown great potential since they combine the process of extraction and stripping in a single unit operation[13,14] especially in the case where the solute concentration is relatively low and other techniques cannot be applied efficiently. The extraction chemistry of liquid membrane is similar to that found in classical liquid-liquid extraction, but the transport process is governed by kinetic rather than equilibrium parameters, under non-equilibrium mass transfer.[15] Bulk liquid membrane (BLM) is one of the simplest designs for performing liquid membrane processes, which are often used to investigate the complexation and transport properties of synthetic and natural ionophores with metal salts.[16-18]

The carrier in the liquid membrane phase plays an important role in the liquid membrane process, which must: (*i*) provide a very high extraction distribution coefficient from dilute solutions; (*ii*) react reversibly with the metal so that the metal can be recovered by a stripping reaction; (*iii*) have reasonably fast extraction and stripping kinetic; and (*iv*) have very low solubility in the aqueous phase for economic and environmental reasons.[19] There has been a number of papers dealing with Ag^+ transport through different liquid membrane configurations using various

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kinds of carriers. The choosing of the type of carrier is important in the design of metal separation.

In a study by Altin *et al.*[20] transport of Ag^+ ion was investigated in HNO_3 solution through a flat-sheet supported liquid membrane (SLM) process containing the membrane liquid prepared from a mixture of DC18C6 and toluene. Under optimum conditions, 94% of Ag^+ ions are carried from the feeding phase to the receiving phase. Amiri *et al.*[21] have investigated selective transport of silver ion through supported liquid membrane using calix (4) pyrroles as a suitable ion carrier. Furthermore, it has been reported that various parameters such as carrier concentration in the membrane phase, thiosulfate concentration in strip phase, picric acid concentration in the feed phase, stirring speed and the type of solvent affect the transport of silver ion.

Also López-López *et al.*[22] used tri-isobutylphosphine sulfide (TIBPS) as a carrier for the determination of total silver ion concentration in freshwaters by a bulk liquid membrane (BLM) system. High and selective Ag^+ bulk liquid membrane transport with *N*,*N*-diethyl-*N*'-camphanyl thiourea as a carrier has been studied by Berhe *et al.*[23] Vajda *et al.*[24] used Cyanex471X as a carrier in a bulk liquid membrane system. They observed that silver(I) ion transport increases as the HNO_3 concentration in the aqueous phase and the carrier concentration in the solvent increases. In our previous works, we have transported efficiently the silver ion through bulk liquid membranes using different acyclic and cyclic ligands as carriers.[25,26]

In the present paper, we report the results of a selective and efficient bulk liquid membrane system containing bis-β-enamino ester (BBEE) as a synthesized carrier for transport of silver(I) ion. The parameters influencing the efficiency of the transport are verified. The selectivity of the method was checked by performing the competitive transport experiments of silver ions from its mixtures with some suspected interfering ions. The applicability of the proposed method was tested for recovering of silver ions in plating and photographic waste solution.

Experimental

Reagents

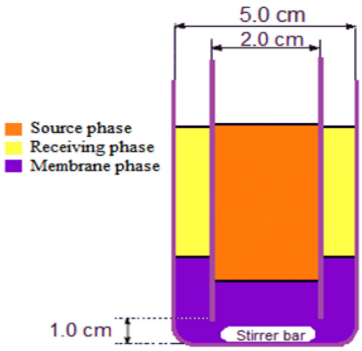
The carriers BBEE and bis(benzoic acid) trioxaheptane (BBAT) were synthesized by H. Eshghi research Group (Department of Chemistry, Ferdowsi University of Mashhad). Reagent grade dichloromethane (Aldrich), 1,2-dichloroethane (Merck) and chloroform (Merck) were tested as organic phases. Analytical grade silver nitrate (Merck), sodium thiosulfate (Merck) and all other chemicals were of the highest purity available and used without further purification. Doubly distilled deionized water was used throughout all experiments.

Apparatus

The determination of silver(I) content was carried out by a Shimadzu AA-670 atomic absorption spectrometer equipped with an Ag-hallow cathode lamp (HCL) and was made under the recommended conditions for silver cation. The pH measurements were accomplished with a Metrohm model 692 pH/ion meter equipped with a combined glass-Ag/AgCl electrode. The membrane phase was stirred including a Teflon-coated magnetic bar by magnetic stirrer (Daihan MSH-20D). A bulk type liquid membrane cell was used in all transport experiments.

Procedure

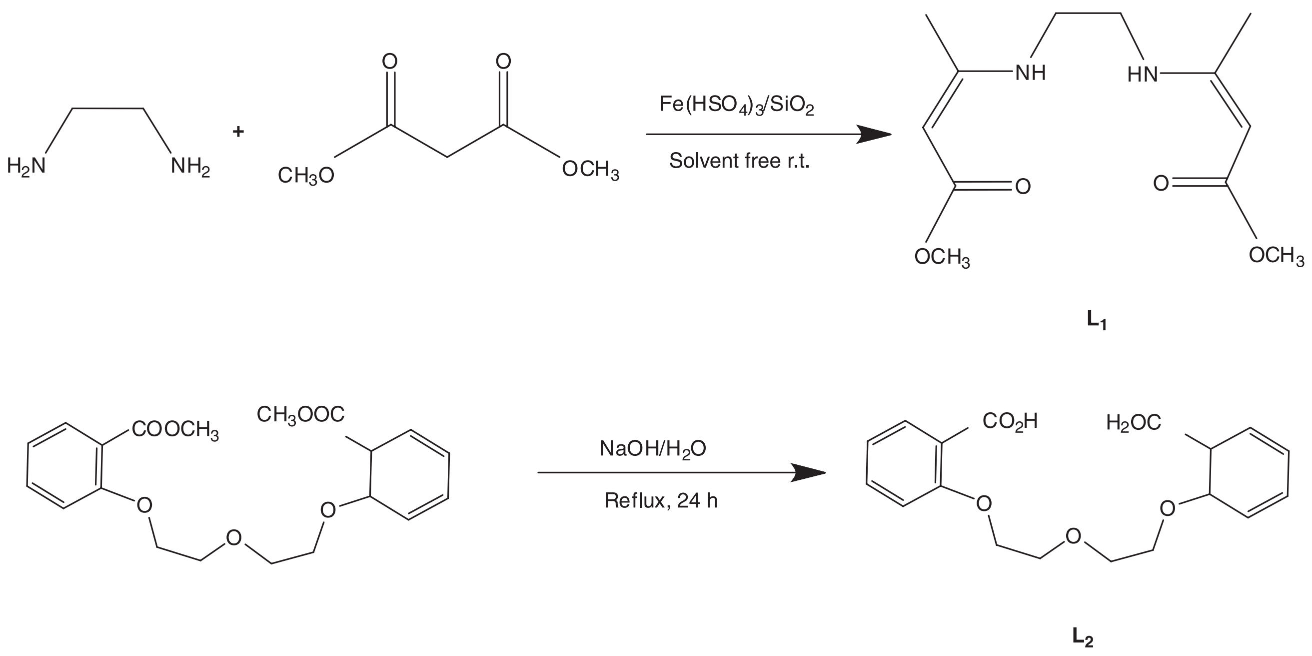
A glass cylindrical cell (internal diameter-i.d. 5.0 cm) holding a glass tube (i.d. 2.0 cm) which separates the source and receiving aqueous phases was used for the transport experiments (Scheme 1). The source (feed) phase consisted of 10 mL of buffer solution at pH 5.0 ± 0.1 containing silver nitrate (5×10^{-5} mol L^{-1}).



Scheme 1. Experimental set-up for the transport experiments.

The receiving (strip) phase included 30 mL of buffer solution at pH 5.0 ± 0.1 containing sodium thiosulfate solution (0.02 mol L^{-1}). A dichloromethane layer (50 mL) containing 8×10^{-4} mol L^{-1} of the ligand lay below these two aqueous phases and bridged them. The pH of each source and receiving phases were adjusted using CH_3COOH/CH_3COONa buffer solution. The cells were covered with cover slips in order to prevent evaporation of solvents and then entirely covered by aluminum foil in order to prevent the light-induced reduction of Ag^+ in the source phase.

All transport experiments were carried out at ambient temperature. The organic phase was magnetically stirred



Scheme 2. Synthetic pathway for the preparation of BBEE (L_1) and BBAT (L_2).

by a Teflon-coated magnetic bar at 300 rpm. All transport runs were terminated after 120 min and samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy. The reproducibility was performed under optimized conditions and the transport process was investigated by performing five replicate transport experiments. The relative standard deviation was found to be 1.5%.

Synthesis

The synthesis of BBEE and BBAT ligands is depicted in Scheme 2. These carriers were prepared according to the literature methods.[27,28]

Synthesis of bis-β-enamino ester (BBEE)

A mixture of the dimethyl malonate (4 mmol), ethylene diamine (2 mmol) and $Fe(HSO_4)_3.SiO_2$ (0.22 g containing 0.25 mmol of $Fe(HSO_4)_3$) was stirred in solvent-free conditions at room temperature for 10 min. After completing the reaction as indicated by thin layer chromatography (TLC), the mixture was diluted by ethyl acetate (15 mL). The insoluble catalyst was separated by filtration and rinsed with ethyl acetate and dried. The solvent was evaporated from the filtrate and the crude product was purified by recrystallization from $EtOH/H_2O$ (1:1). Yield: 98%; mp 137-139 °C; IR (KBr) ν / cm^{-1} 3308, 2957, 1656, 1582, 1279, 1171; ^1H NMR (100 MHz, $CDCl_3$) δ 8.6 (b, 2H), 4.5 (s, 2H), 3.6 (s, 6H), 3.35 (m, 4H), 1.9 (s, 6H).

Synthesis of 1,7-bis(2'-benzoic acid)-1,4,7-trioxaheptane (BBAT)

A solution of 1,7-bis(2'-methyl benzoate)-l,4,7-trioxabeptane (37.5 g, 0.1 mol) in 10% aqueous NaOH (500 mL) was refluxed for 24 h. The mixture was cooled and washed with chloroform (2 × 100 mL) and acidified with HCl (6 mol L^{-1}) and extracted with CH_2Cl_2 (5 × 150 mL). The solvent was evaporated and the white solid was recrystallized from CH_2Cl_2 to give white crystal of BBAT. Yield: 34.5 g (100%); mp 105 °C; IR (KBr) ν / cm^{-1} 1700; ^1H NMR (100 MHz, $CDC1_3$), δ 3.85 (t, 4H, J 4.5 Hz), 4.20 (t, 4H, J 4.5 Hz), 6.8-7.1 (m, 4H), 7.35 (dt, 2H, J_1 8, J_2 2 Hz), 7.9 (dd, 2H, J_1 8, J_2 2 Hz), 8.3 (b, 2H).

Results and Discussion

The liquid membrane technique is composed of two processes in a single stage: extraction of an ion from aqueous feed (donor) solution to organic phase containing the carrier molecules (membrane) and back extraction of this ion from the membrane to aqueous strip (acceptor) phase. The overall transport process consists of a diffusion step and a complexation/decomplexation reaction at two independent and different interfaces. The membrane studies were carried out because simple and energy efficient systems are necessary in a practical application point of view.

Chelating agents containing sulfur or nitrogen atoms as coordination sites possess great affinity toward d10 transition metal ions like Ag^+. Thus, the formation of complex with metal cations may be primarily attributed to the affinity of the metal ion for nitrogen atoms.[29,30] Of course, the relative size of the metal ion and cavity of the ligand can also play an important role in the selectivity of the resulting complex.

In preliminary experiments, BBEE and BBAT ligands were tested as silver ion carriers. Among these ligands examined, BBEE was used as a carrier for the selective and efficient transport of Ag^+ across a bulk liquid membrane. Meanwhile, the experimental variables were optimized in order to achieve the highest efficiency in the transport of silver(I) cation.

Nezhadali *et al.*[31] applied a bulk liquid membrane for selective separation of Ag^+ cation using 1,1'-(1,3-phenylene) bis(3-allylthiourea) as a carrier and their results, showed that the transport efficiency of this metal cation for the five replicate measurements after 4 h, was 92.3 ± 5.3%. The results obtained in our experiments, show a better efficiency and precision for selective transport of Ag^+ ion through bulk liquid membrane using bis-β-enamino ester (BBEE) ligand. To our knowledge, the transport of silver(I) cation across the bulk liquid membranes using this synthesized ligand, has not been reported.

Effect of the nature of the carrier and its concentration

The permeability of the membrane system used for transport of Ag^+ ion also depends largely on the nature of ligand used as carrier in the organic membrane phase. As it is seen from Table 1, under similar experimental conditions, the efficiency of silver ion transport decreases in the order $L_1 > L_2$. This is presumably related to the increased stability of the AgL_1^+ complex in comparison with the corresponding complex with L_2 ligand, the observed trend may also be originated from the suitable lipophilic-hydrophobic balance and flexibility which allow sufficiently fast exchange rates of AgL_1^+ for loading and unloading in order to avoid carrier saturation.

In order to investigate the effect of the concentration of L_1 on the transport of silver(I) ion, the experiments were run at different carrier concentrations and the transport procedure was followed. As it is seen from Figure 1, silver(I) ion transport increases with increasing the concentration of L_1 in the membrane phase up to an 8.0×10^{-4} mol L^{-1} level. While a further increase in the carrier concentration not only has no improved effect on the percentage of transported silver ion, but also results in a slight decrease in extraction efficiency. As is evident in Table 1 and Figure 2, in the optimized concentration of the ligand, the transport efficiency of Ag^+ cation through DCM liquid membrane is about 97%.

Table 1. Effect of carrier structure on silver(I) transport[a]

Carrier	Percentage transported into strip phase	Percentage remaining into feed phase
BBEE	97	2
BBAT	25	60

[a]Conditions: feed phase, 10 mL of 5×10^{-5} mol L^{-1} Ag^+, 6.0×10^{-3} mol L^{-1} of picric acid; membrane phase, 8.0×10^{-4} mol L^{-1} carriers in DCM; strip phase, 30 mL of 0.02 mol L^{-1} sodium thiosulfate; time of transport, 120 min; stirring speed, 300 rpm; BBEE: bis-β-enamino ester; BBAT: bis(benzoic acid) trioxaheptane.

A similar behavior for the carrier concentration in the LM has already been reported in the literature.[32] This could be due to the more difficult release of the cation into the receiving solution, as a result of its firm bounding to the carrier, and/or the increased viscosity of the membrane with increasing carrier concentration.

In addition, a blank experiment was performed in which the membrane contained no carrier. No detectable transport of the silver(I) ions through the liquid membrane was found in the blank experiment, suggesting that the transport of the silver ions through the liquid membrane was fulfilled by the carrier. Therefore, the carrier is essential to transport the silver(I) ions from the feed phase.

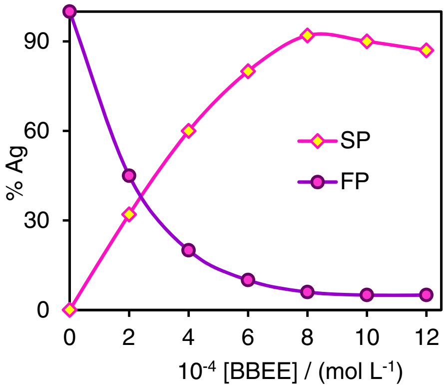


Figure 1. Effect of carrier (L_1) concentration in the membrane phase on silver ion transport. Conditions: feed phase, 10 mL of 5×10^{-5} mol L^{-1} Ag^+, 6.0×10^{-3} mol L^{-1} of picric acid; membrane phase, varying concentrations of L_1 in DCM; strip phase, 30 mL of 0.02 mol L^{-1} sodium thiosulfate; time of transport, 120 min; stirring speed, 300 rpm.

Effect of picric acid concentration in the feed phase

In preliminary experiments, it was found that nitrate ion is not a suitable counter ion to accompany the AgL_1^+ complex into the membrane phase, and the transport of silver ion through the BLM used was found to be negligible. However, addition of picric acid to the feed solution resulted in a further increase in transport efficiency so that > 90% silver transport was obtained after 120 min. It is well known that the soft, polarizable and weakly hydrated picrate ion is a convenient counter ion that provides greater distribution ratios and membrane transport rates for metal ion-neutral ligand complexes than do inorganic ions such as NO_3^- and ClO_4^-.[33]

For this reason, picrate ion was selected as a suitable counter ion. Then, the influence of the picric acid concentration in the feed phase on the silver ion transport was studied. It was found that, the efficiency of silver ion transport increases with increasing picric acid concentration up to 6.0×10^{-3} mol L^{-1} concentration is reached. However, a further increase in the concentration of picric acid caused a decrease in the percentage transport of silver ion, most possibly due to the fact that the picric acid itself competes with silver nitrate for transport through the BLM system.

Effect of organic solvent in the membrane phase

In order to study the influence of the organic solvent on transport efficiency, dichloromethane (DCM), 1,2-dichloroethane (DCE) and chloroform ($CHCl_3$) were used as organic membranes. From the results which are summarized in Table 2, it can be seen that the order of the amount of the Ag^+ released into the receiving phase varies as: $CHCl_3$ << DCE < DCM. The highest transport efficiency was obtained in the case of DCM. Chloroform was found to be an unsuitable solvent for the transport of Ag^+ cation. Considering the polarity of the organic solvents, one can attribute that the viscosity and polarity are essential factors for solvent selection for BLM phenomena. This is consistent with the literature reported.[34]

Table 2. Effect of organic solvent on silver(I) transport[a]

Solvent	Percentage transported into strip phase	Percentage remaining into feed phase
Dichloromethane	95	3
Dichloroethane	69	23
Chloroform	20	71

[a]Conditions similar to those mentioned in Table 1, except for solvent type.

Effect of stripping agent in receiving phase

The strength of the acceptor phase (strip phase) for the transport of Ag^+ ion is significant on both efficiency and selectivity of the transport. If the metal ion-complex is not completely stripped into the receiving phase, the membrane phase becomes saturated with the complex and, therefore, the transport rate will decrease.[35]

The percentages of silver ion transport in the presence of different stripping agents such as SCN^-, $S_2O_3^{2-}$, CN^-, thiourea, ethylenediamine tetraacetic acid (EDTA) and $P_2O_7^{2-}$, were determined under similar experimental conditions.

The results showed that among the studied stripping agents, the presence of thiosulfate $(S_2O_3)^{2-}$ in the receiving phase showed the highest transport efficiency for silver(I) cation.

In some cases, the total percentage of the silver ion in the feed and strip phases is not equal to 100, due to the fact that some reasonable amount of the silver(I) cation is remained in the membrane phase, especially when the stripping agent does not have high enough tendency to completely release the silver ion from the $(AgL_1^+)Pic^-$ adduct from the membrane phase into the receiving phase.

The optimum concentration of sodium thiosulfate in strip phase was investigated and it was found to be: 0.02 mol L^{-1} (Figure 2). It should be noted that, in the absence of $S_2O_3^{2-}$ ion in the strip phase, no measurable transport occurred in a time period of 120 min. However, the transport process of the Ag^+ ion through the membrane phase decreases at lower or higher concentrations of $Na_2S_2O_3$. In the studies by Nowier *et al.*[36] and Altin *et al.*[20] it was reported that increasing stripping phase concentration facilitates achieving an optimum permeability value. The reason for this may be explained as the concentration of the solute increases, the solution reaches saturation value and, therefore, the solubility decreases. In this case, the amount of $(S_2O_3)^{2-}$ ions which would form a complex with the silver ions in the membrane/stripping interface decreases.

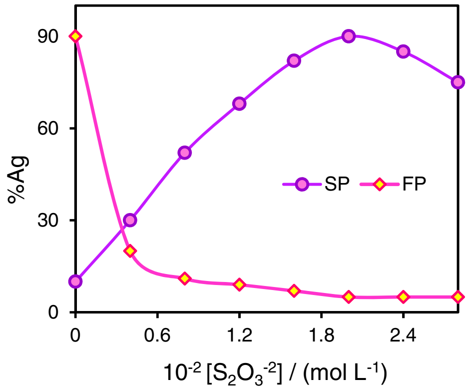


Figure 2. Effect of thiosulfate ion concentration in the strip phase on silver ion transport. Conditions: feed phase, 10 mL of 5.0×10^{-5} mol L^{-1} Ag^+, 6.0×10^{-3} mol L^{-1} of picric acid; membrane phase 8.0×10^{-4} mol L^{-1} L_1 in DCM; strip phase, 30 mL of varying concentration of sodium thiosulfate; time of transport, 120 min; stirring speed, 300 rpm.

Effect of pH of the feed and striping phases

The influence of pH of the source and receiving phases on the transport efficiency of Ag^+ ion was studied in pH range 3-8 and it was found that maximum transport of this metal occurs at pH 5. This shows that the transport does not follow a proton driven mechanism.[25]

Effect of the stirring speed

In order to explore the effect of stirring speed on the Ag^+ transport, several transport experiments were performed with different stirring speeds (50-400 rpm) and the results indicate that the stirring speed affects the transport efficiency of Ag^+ ion through the organic membrane phase.

The percentage of transported Ag^+ ion increases up to about 300 rpm and then decreases. However, further increase in the stirring rate results in some decrease in the transport efficiency of the metal cation owing to the high turbulence flow caused by stirring, which possibly causes the displacement of some carrier molecules from the membrane. Similar behavior has been observed by Muthuraman *et al.*[37] at higher stirring speed.

Time dependency of the transport process

The experimental results obtained for investigate the effect of time on the transport efficiency show that the amount of Ag^+ ion extracted from the source phase into the receiving phase increases with time (Figure 3). It was found that, under the optimum experimental conditions, the transport of Ag^+ ion is almost quantitative after 120 min.

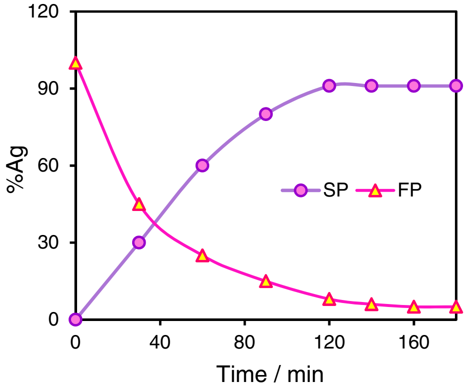


Figure 3. Time dependence of silver ion transport. Conditions: feed phase, 10 mL of 5.0×10^{-5} mol L^{-1} Ag^+, 6.0×10^{-3} mol L^{-1} of picric acid; membrane phase, 8.0×10^{-4} mol L^{-1} L_1 in DCM; strip phase, 30 mL of 0.015 mol L^{-1} sodium thiosulfate; varying time of transport; stirring speed, 300 rpm.

Reproducibility of the liquid membrane system

Under optimum conditions, the reproducibility of the method was investigated and the percent of the silver(I) ion transported after 120 min from 5 replicate measurements was found to be 97% with a standard deviation of ± 1.5%.

Selectivity of bulk liquid membrane system

The selectivity of a BLM system is a parameter that allows the evaluation of the degree of purification of a target analyte with respect to the other species present in solutions. The selectivity of the process towards silver ion was tested by performing the transport of Ni^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+} metal cations containing Ag^+ ion in their mixtures. The results are summarized in Table 3. It was found that even in the presence of 10-fold concentrations of these metal ions with respect to Ag^+ ion, there is no serious interference in the transport process of this heavy metal ion.

Table 3. Percentages of cation transported from various cation mixtures through the BLM system[a]

Mixture of cations	Percentage transported into strip phase	Percentage remaining in feed phase
Mixture 1		
Ag^+	93	5
Cd^{2+}	3	95
Zn^{2+}	4	82
Mixture 2		
Ag^+	93	4
Pb^{2+}	7	87
Fe^{2+}	0	99
Cu^{2+}	5	92
Mixture 3		
Ag^+	94	3
Co^{2+}	3	94
Ni^{2+}	0	97
Mn^{2+}	0	98
Mixture 4		
Ag^+	95	2
Fe^{3+}	0	98
Cr^{3+}	0	99
Al^{3+}	0	98
Mixture 5		
Ag^+	95	2
K^+	0	98
Ca^{2+}	0	99

[a]Conditions similar to those mentioned in Table 1.

Suggested mechanism

The transport of silver ion by using the BBEE ligand, obeys a facilitated co-transport. As is shown in Figure 4, the silver ion forms a single charge complex at the interface between the source phase and membrane phase and after forming a hydrophobic ion pair with picrate ion, the resulting ion-paired complex diffuses through the complex with thiosulfate ion (L_1-Ag-thiosulfate). Then the free carrier diffuses back across the liquid membrane and the cycle starts again. The net result is the transport of silver ion from the source phase to the receiving phase across the membrane.

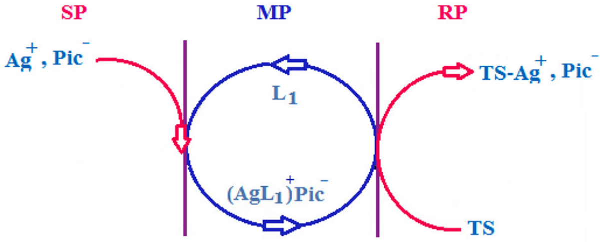


Figure 4. Simplified representation of the transport mechanism of silver ion by carrier (L_1). Source phase (SP), membrane phase (MP), receiving phase (RP).

Application of BLM for silver plating and photographic waste solution

The BLM system used for Ag^+ ion extraction has been applied for recovery of Ag^+ ions from silver plating and photographic waste solutions. The composition of silver plating and photographic waste solution is shown in Table 4. Under optimized experimental conditions, the Ag^+ ions were removed up to 95% in a time interval of 120 min and the results indicate that only the silver ion is transported which show that the selectivity and efficiency of this method are high for silver ion recovery in these real samples.

Table 4. Composition of silver plating and photographic waste solution

Sample	Metal ion	Concentration in feed solution (× 10^{-4} mol dm^{-3}) / (mol L^{-1})	Concentration in strip solution (× 10^{-4} mol dm^{-3}) / (mol L^{-1})
Silver plating waste	Ag	5.75	5.50
	Cu	0	0
	Zn	0	0
	Bi	0	0
	Cr	0	0
Photographic waste	Ag	4.12	3.95
	Fe	3.85	0
	Mg	1.51	0
	K	23.2	0

Conclusions

The quantitative transport of Ag^+ ion through a dichloromethane bulk liquid membrane containing bis-β-enamino ester (BBEE) as a carrier was studied and it was found that this ligand is an excellent carrier for selective and efficient transport of silver(I) cation. The optimum conditions of the transport was found as 5.0×10^{-5} and 6.0×10^{-3} mol L^{-1} for Ag^+ and picric acid, respectively, in the source phase (pH 5), 8.0×10^{-4} mol L^{-1} BBEE in the dichloromethane membrane, 2.0×10^{-2} mol L^{-1} thiosulfate in the receiving phase (pH 5), stirring speed of 300 rpm and a transport time period of 120 min. The excellent efficiency and high degree of selectivity for the silver(I) cation transport by the proposed BLM system, reveals its potential application for the selective removal, concentration and purification of silver ion from its different mixtures. Up to 95% of Ag^+ ion has been removed from silver plating and photographic waste solutions, which indicates that this technique can be used for recovery of Ag^+ ion from industrial wastes effluents. This method offers important advantages such as simplicity, low cost and high selectivity.

Acknowledgments

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