

Selective Separation of Silver(I) Ion Through a Bulk Liquid Membrane Containing 1,1'-(1,3-Phenylene)bis(3-allylthiourea) as Carrier

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The competitive bulk liquid membrane transport of six metal cations from an aqueous source phase (SP) containing Ag⁺, Pb²⁺, Cu²⁺, Zn²⁺, Co²⁺ and Ni²⁺ through an organic membrane phase (MP) facilitated by 1,1'-(1,3-phenylene)bis(3-allylthiourea) as a carrier into an aqueous receiving phase (RP) was studied and compared. Fluxes and selectivities for competitive metal cation transport have been determined in a variety of source solution pH and membrane solvent types. The obtained results showed that the carrier is selective for Ag⁺ cation. The effect of different experimental conditions that affect the transport efficiency were studied and optimized. In the optimum condition, the transport of a 5 × 10⁻⁴ mol L⁻¹ solution of Ag⁺ cations was observed 92.3 ± 5.3% after 4 h in the presence of equimolar concentrations of other metal cations. A possible application of this carrier system and transport process for separation and recovery of Ag⁺ cation from real samples has also been examined.

Keywords: 1,1'-(1,3-phenylene)bis(3-allylthiourea), bulk liquid membrane, atomic absorption spectrometry

Introduction

Nowadays, rapid industrial development and the diversified character of the world economy led to handle with the large volumes of different types of wastewaters. Wastewaters are a potential source of organic and metal pollutants and discharging them into the environment without prior treatment is a serious problem of concern. Furthermore, the presence of metal ions in wastewater might inhibit biodegradation of organic pollutants which are present in the wastewater.¹ Separation of metal ions is not only a very incident event in biological systems as well as in large scale industrial applications.² Therefore, separation and removal of metal ions from industrial effluents is of interest in recovering the metal ions as well as for abating the environmental pollution problems.³ Silver is one of the most ancient metal used in the production of jewellery, coins, tableware, alloys and arts. Also, it is used in the manufacture of electrical apparatus, light sensitive device, mirrors, electroplating and photographic materials, dental amalgams and burn creams.⁴⁻⁶ Different

separation techniques have been used for separation and recovery of this precious and toxic metal ion from industrial water such as solvent extraction,⁷⁻⁹ adsorption,¹⁰⁻¹² cloud point extraction¹³⁻¹⁵ and membrane separation.¹⁶⁻¹⁹ The main properties of membrane separations are expressed as simultaneous removal and recovery of pollutants and materials in a single unit, simple in concept and operation, easy to scale-up, non-equilibrium mass transfer, high selectivity, high fluxes, reusability and low energy consumption; make them ideal for industrial applications.²⁰ Among other membrane separation techniques, liquid membrane transport includes processes incorporating liquid-liquid extraction and membrane separation in one continuously operating device. Liquid membrane system involves an organic liquid membrane which is an immiscible with the two aqueous source phase (SP) and receiving phase (RP) that serves as a semipermeable barrier between these two aqueous phases. The mechanism of the extraction is basically the same as that of the liquid-liquid extraction except that the transport process is governed by kinetic rather than equilibrium parameters, under non-equilibrium mass transfer.²¹ In this method, solute species dissolve in the membrane and diffuse across the membrane

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due to an imposed concentration gradient.²² The efficiency and selectivity of transport across the membrane not only depends on the solubility and diffusion coefficient of solute in the membrane, but also enhances by the presence of a mobile complexation agent in the membrane which reacts rapidly and reversibly with the solute to form a complex. The best carrier is a compound that formed remarkably stable and selective complexes and the rate of the transport increases with the increase of stability constant of complexes.^{23,24}

Unquestionably, design and synthesis of the reagents for the formation of remarkably stable and selective complexes with metal cations is very significant in the efficient transport of cations through the liquid membrane system in a range of industrial and analytical applications. The interaction of the ligand and metal cation not only depends on the nature of the metal cation, but also depends on the number, distance and orientation of the donor atoms of the ligand that are structurally accessible to the complexed cation.²⁵⁻²⁷ A large number of synthetic ionophores such as podands, cryptands, crown ethers and Schiff base ligands are known which transport metal ions selectively across liquid membrane in various configurations and applied in separation science.²⁸⁻³⁰ However, the development of selective techniques for the separation and recovery of transition and post transition heavy metal cations is a challenging task.^{31,32}

In this present study, we studied the competitive bulk liquid membrane transport of six metal cations involving Ag^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} with 1,1'-(1,3-phenylene)bis(3-allylthiourea) as a carrier using chloroform (CHCl_3), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and nitrobenzene (NB) as an membrane phase (MP). When DCM was used as an MP, a good transport selectivity has been observed for silver(I) cation over several other cations. The influence of different experimental conditions such as pH of the SP, type of the MP, carrier concentration in the MP, concentration of picric acid in the SP, type and concentration of stripping agents in the RP, stirring rate and time was investigated. Also, a possible application of this carrier-facilitated transport system to separation and recovery of Ag^+ cation from real and industrial samples was examined.

Experimental

Reagents and materials

All chemicals and reagents used in this study were commercially available grade and were purchased from either Aldrich (Saint Louis, MO, USA) or Merck (Darmstadt, Germany). CHCl_3 , DCM, 1,2-DCE and NB with highest

purity were used as liquid membrane. Nitrate salts of silver, lead, copper, cobalt, nickel and zinc were the highest purity and used without any further purification. The stock solutions of metal ions were prepared by direct dissolution of proper amount of nitrate salts of them in 1% nitric acid solution. The fresh standard and working solutions were obtained daily by appropriately diluting of the stock solutions with deionized water. The pH of aqueous solutions was adjusted by the buffering of aqueous SP and RP.

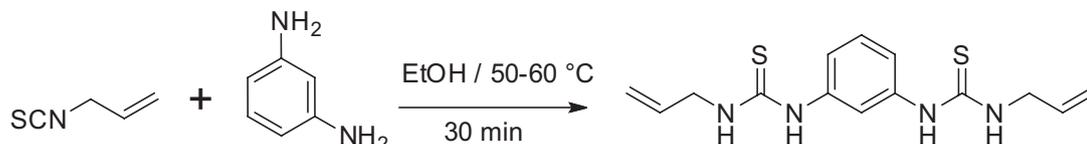
Instrumentation

All UV-Vis spectra were recorded on a computerized double-beam 1601pc Shimadzu spectrophotometer (Tokyo, Japan) using two matched 1 cm quartz cells. In a typical experiment, 2.5 mL of ligand solution (1.0×10^{-5} mol L^{-1}) in acetonitrile was placed in the spectrophotometer cell and the absorbance of the solution was measured. Then a known amount of the solution of Ag^+ ions in acetonitrile (1.0×10^{-4} mol L^{-1}) was added stepwise using a 10 μL Hamilton syringe. The electronic absorption spectra of solution were measured after each addition at 270 nm. The Ag^+ ion solution was continually added until the desired metal to ligand mole ratio was achieved.

The infrared (IR) spectra were recorded with Shimadzu IRPrestige-21 FTIR instrument (Tokyo, Japan) in the solid state as KBr discs. The determinations of the metal ion concentrations were performed on a GBC Sens AA flame atomic absorption spectrometer (Victoria, Australia) equipped with D_2 lamp background correction and hollow cathode lamps at respective wavelengths as radiation sources. An air-acetylene flame atomizer was used for all atomic absorption measurements under the recommended instrumental conditions for each metal ion. The pH measurements were made with a Metrohm 744 digital pH meter (Herisau, Switzerland) using a combined glass-calomel electrode.

Ligand preparation

The preparation of ligand containing nitrogen and sulfur donor atoms was performed as described in the previous work.³³ In a typical procedure, 2 mmol of allyl isothiocyanate was added dropwise to a stirred ethanol solution of 1 mmol of 1,3-phenylenediamine. The reaction mixtures were heated at 50-60 °C for about 30 min and the mixture was kept at room temperature for 24 h. Then, the final product was filtered and washed with ethanol, recrystallized from ethanol:water (1:1) to give corresponding dithiourea, which was used as a suitable carrier in the transport experiments.



Scheme 1. Synthesis of 1,1'-(1,3-phenylene)bis(3-allylthiourea).

Bulk liquid membrane transport

Transport measurement was performed in a 'U' shape glass cell³⁴ in which the SP (5 mL) and RP (5 mL) were separated by an MP (10 mL) (Figure 1). The inner dimension of the transport apparatus was 10 mm diameter \times 150 mm depth. The SP containing an equimolar mixture of metal nitrate salts (1.0×10^{-3} mol L⁻¹) and picric acid (1.25×10^{-3} mol L⁻¹) was buffered at pH 5 using CH₃COOH/CH₃COONa buffer solution and placed in one limb of the 'U' cell. The MP contained 6.0×10^{-4} mol L⁻¹ of carrier which was placed at the bottom of the 'U' shape cell. The RP containing a concentration of 5.0×10^{-3} mol L⁻¹ of thiourea was buffered at pH 3 using HCOOH/HCOONa buffer solution and placed in the other limb of the 'U' cell. The MP was magnetically stirred by a Teflon-coated magnetic bar. All transport experiments were carried out at ambient temperature and after each experiment, both aqueous phases were analyzed for determination of metal content by flame atomic absorption spectroscopy. A similar transport experiment was also performed in the absence of the carrier as a reference, and no leakage of metal ions from SP into the RP was observed. To check the reproducibility, all measurements were carried out in duplicate.

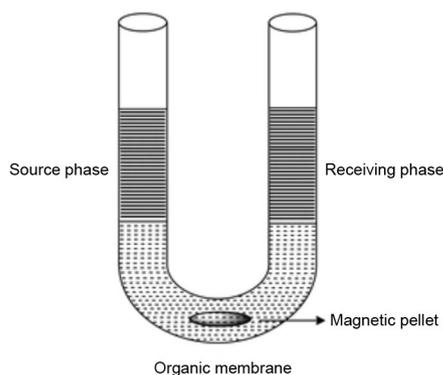


Figure 1. Representation of the bulk type liquid membrane cell.

Results and Discussion

Study of complexation between 1,1'-(1,3-phenylene)bis(3-allylthiourea) and Ag⁺

Selective transport of metal cations by carrier-mediated liquid membrane depends on the nature of the ligand used

as a carrier in the membrane.^{35,36} The investigations have established that the kind, number, distance and orientation of the donor atoms of the ligand that are structurally accessible to the complexed cation can affect the transport selectivity and efficiency.²⁵⁻²⁷ In the preliminary experiment, we tested the ligand ability for the competitive transport of Ag⁺ cation among some other metal cation such as Pb²⁺, Cu²⁺, Zn²⁺, Co²⁺ and Ni²⁺ from SP into the RP through DCM organic solvent as a MP. It was found that the ligand has the desired ability to transport Ag⁺ cations against its concentration gradient through bulk liquid membrane. In order to investigate the complexation process between 1,1'-(1,3-phenylene)bis(3-allylthiourea) and Ag⁺ cations, the spectrophotometric titration was utilized and the complexation procedures were analyzed in acetonitrile at 25 °C due to the absorbance alteration which occurs with the cation to ligand ([M]/[L]) ratio conversion. The electronic absorption spectra of ligand (1.0×10^{-5} mol L⁻¹) without and in the presence of Ag⁺ (1.0×10^{-4} mol L⁻¹) ions are exhibited in Figure 2. As can be seen, absorbance of the acetonitrile solution of ligand at wavelength of 270 nm decreased with the addition of Ag⁺ ions to the solution. On the other hand, the observed spectral evolution involved the formation of a well-defined isobestic point at around 250 nm, indicating the presence of one absorbing complex compound between ligand and Ag⁺ ions. The mole ratio method was also used for estimation of the stoichiometry of the Ag⁺-ligand complex and a typical mole-ratio plot is represented in Figure 3. The obtained results show that the slope of the curve changes at 1:1 [M]/[L], that indicate the stoichiometry of the complex formed between ligand and Ag⁺ cation is 1:1.

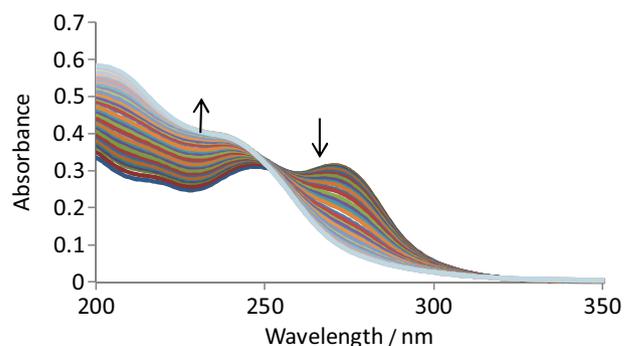


Figure 2. The spectrum of ligand solution (1.0×10^{-5} mol L⁻¹) in acetonitrile and increasing concentration of Ag⁺ ion solution (1.0×10^{-4} mol L⁻¹).

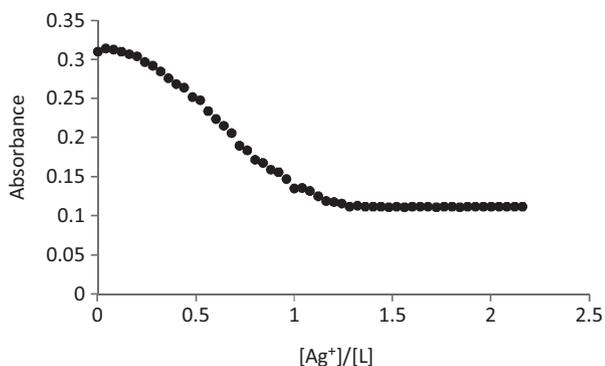


Figure 3. Mole ratio plots of absorbance as $[M]/[L]$ at 270 nm.

In addition, the Fourier transform infrared (FTIR) spectrophotometric technique was also applied to study the possible complexation reaction between Ag^+ and ligand. The FTIR spectra of the ligand and Ag^+ -ligand complex are shown in Figure 4.

Effect of pH of the SP on transport efficiency

Reported literatures in recent years is a conformation of achievable high enrichment factor for the liquid membrane transport technique with making a small pH difference between SP and the acidic RP.³⁷ When the transport mechanism has benefit from proton pump or pH gradient, pH difference leads to back diffusion of protons from the RP into the SP.³⁸ On the other hand, when a legating agent has used to transport a specific metal cation, pH can alter the conditional stability constant of the resulting metal complex.²⁴ Hence, pH is a dominant factor in the separation of metal cation using liquid membrane transport. The effect of pH on the

competitive transport of six-metal cations from SP at a pH ranges of 4-6.5 into acidic RP (pH 3) was investigated and the results are given in Table 1. It was found that maximum Ag^+ cation transport occurs at pH 5 of the SP. It seems that at lower pH values of the SP, the efficiency of silver transport decreased due to a subtraction in the hydroxide concentration for exchanging proton with Ag^+ or slow partition coefficients of the Ag^+ at the source/membrane phases interface. In other words, at higher pH values of the SP, the efficiency of Ag^+ transport decreased probably due to the complex formation of Ag^+ ion with hydroxide ion.

Effect of solvent on transport efficiency

Choosing the right organic membrane solvent is the prime issue in establishing transport efficiency.³⁹ The physicochemical properties of solvents play noticeable roles in solute-solvent and solute-solute interactions in solutions. The $\log K_f$ value for the formation of the cation-ligand complex in the organic membrane, the diffusion path length and diffusion coefficients of all mobile species in the unstirred boundary layers depend on the organic membrane solvent nature.⁴⁰ The thickness of boundary layers is a function of the viscosity of the solvent and the partitioning of the cations into the organic membrane should be affected by the dielectric constant of the solvent.^{41,42} The selected solvent should be immiscible with the water, has low viscosity and volatility and at the same time it must have a suitable polarity related to an optimal value of the association constant of the complex.^{43,44} The results of the competitive transport of six-metal cations from an aqueous SP through CHCl_3 ,

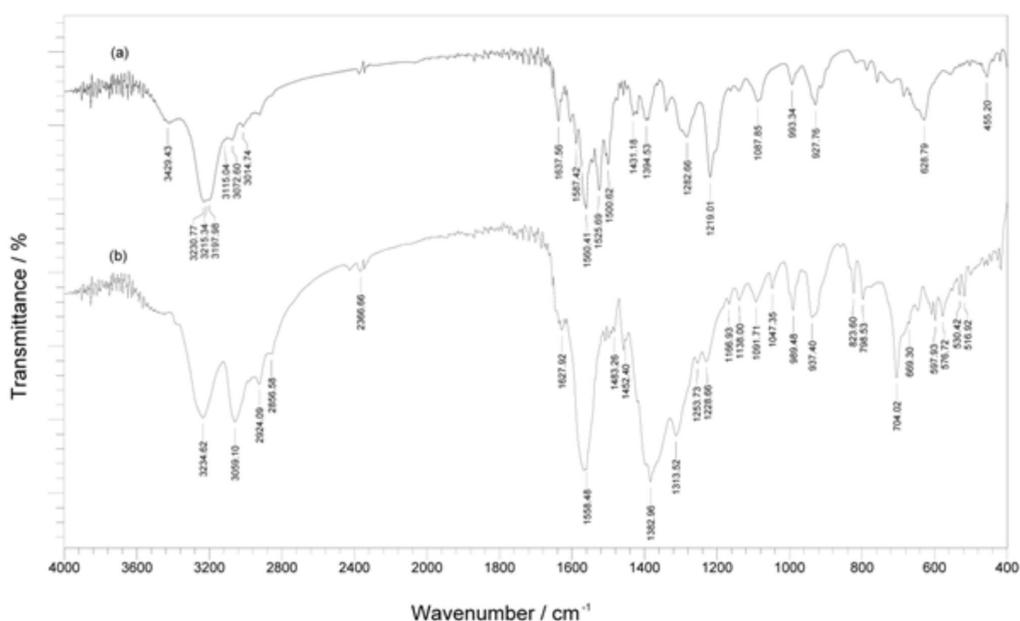


Figure 4. FTIR spectrum of (a) ligand and (b) Ag^+ -ligand complex.

Table 1. Effect of pH of the SP on the competitive transport of the six metal cations across DCM-MP using 1,1'-(1,3-phenylene)bis(3-allylthiourea) as a carrier

pH	Ag ⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺	Co ²⁺	Ni ²⁺
4						
Receiving ^a / %	8.54	– ^d	–	–	–	–
Membrane ^b / %	3.37	0.12	1.98	0.23	–	–
J ^c / (mol per h)	1.78	–	–	–	–	–
4.5						
Receiving ^a / %	17.97	–	–	–	–	–
Membrane ^b / %	10.38	0.52	2.72	–	–	–
J / (mol per h)	3.74	–	–	–	–	–
5						
Receiving ^a / %	38.78	–	–	–	–	–
Membrane ^b / %	21.23	1.52	4.50	–	–	–
J / (mol per h)	8.08	–	–	–	–	–
5.5						
Receiving ^a / %	31.53	–	–	–	–	–
Membrane ^b / %	18.02	1.42	1.99	0.15	–	–
J / (mol per h)	6.57	–	–	–	–	–
6						
Receiving ^a / %	24.56	–	–	–	–	–
Membrane ^b / %	13.21	2.20	2.52	–	–	–
J / (mol per h)	5.12	–	–	–	–	–
6.5						
Receiving ^a / %	19.57	–	–	–	–	–
Membrane ^b / %	14.23	1.85	1.59	–	–	–
J / (mol per h)	4.08	–	–	–	–	–

^aPercent of total metal cations in the RP after 24 h; ^bpercent of total metal cations in the MP after 24 h; ^call J (flux rate) values are $\times 10^{-8}$; ^dthe hyphenated symbols means that the values are about zero or they are with high uncertainties.

1,2-DCE, DCM, and NB containing the ligand are given in Table 2. As shown, the transport efficiency of Ag⁺ ion by carrier is varied in order: DCM > CHCl₃ > 1,2-DCE > NB. DCM has the lowest viscosity ($\eta = 0.39$ mPa s) compared to the CHCl₃ ($\eta = 0.58$ mPa s), 1,2-DCE ($\eta = 0.73$ mPa s) and NB ($\eta = 1.62$ mPa s) which leads to increase the rate of the Ag⁺ transport in the organic MP. In addition, the solvating ability of a solvent plays a fundamental role in complexation reactions between metal cations and ligands. As expected, due to the low donor number (DN) of DCM (DN = 1.0) compared with those of CHCl₃ (DN = 4.0) and NB (DN = 4.4), the competition between solvent and the ligand for the metal cation decrease which leads to an increase in the stability of the formed complex between the Ag⁺ and the ligand. Also, the lower dielectric constant of DCM ($\epsilon = 8.93$) compared to the 1,2-DCE ($\epsilon = 10.66$) and NB ($\epsilon = 34.80$) possibly end up in stabilization of the ion-pair in the organic phase which results in a better transport rate in this liquid membrane.

Effect of the ligand concentration on transport efficiency

Carrier-facilitated transport system is a coupled transport process that combines a chemical coupling reaction with a diffusion process. In this system, the solute has first reacted with the carrier to form a solute-carrier complex, which then diffuses through the membrane to finally release the solute at the permeate side. Carrier is a water-immiscible complexation agent which dissolved in the MP and reacts selectively, rapidly and reversibly with the desired solute to form a complex. Hence, the efficiency and selectivity of transport across the MP might be markedly enhanced by the presence of a carrier in the MP. In this study, the effect of the concentration of ligand as a suitable carrier in the MP on the transport efficiency of Ag⁺ cations was investigated in the concentration range (5.0×10^{-5} to 1.0×10^{-3} mol L⁻¹) of ligand and the results are presented in Figure 5. It is seen that the percentage of Ag⁺ cation transport increases with an increase in ligand

Table 2. Data for six metal cations competitive transport across organic solvents as MP with ligand

Solvent	Ag ⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺	Co ²⁺	Ni ²⁺
CHCl ₃						
Receiving ^a / %	25.94	— ^d	1.23	—	—	—
Membrane ^b / %	17.89	1.95	6.80	—	—	—
J ^c / (mol per h)	5.40	—	0.26	—	—	—
1,2-DCE						
Receiving ^a / %	18.32	0.23	2.23	—	—	—
Membrane ^b / %	16.05	4.23	7.80	—	0.59	0.78
J / (mol per h)	3.82	0.05	0.46	—	—	—
DCM						
Receiving ^a / %	39.95	—	—	—	—	—
Membrane ^b / %	23.45	1.80	4.20	—	—	—
J / (mol per h)	8.32	—	—	—	—	—
NB						
Receiving ^a / %	15.26	4.8	3.23	—	—	—
Membrane ^b / %	23.21	6.80	8.47	—	0.42	—
J / (mol per h)	3.18	1.00	0.67	—	—	—

^aPercent of total metal cations in the RP after 24 h; ^bpercent of total metal cations in the MP after 24 h; ^call J (flux rate) values are $\times 10^{-3}$; ^dthe hyphenated symbols means that the values are about zero or they are with high uncertainties.

concentration in the MP and 6.0×10^{-4} mol L⁻¹ of ligand is much more effective in the efficient transport of Ag⁺ ions. The ligand concentration over this amount had no considerable effect on the transport efficiency. Therefore, the ligand concentration was fixed in 6.0×10^{-4} mol L⁻¹ at the subsequent experiments.

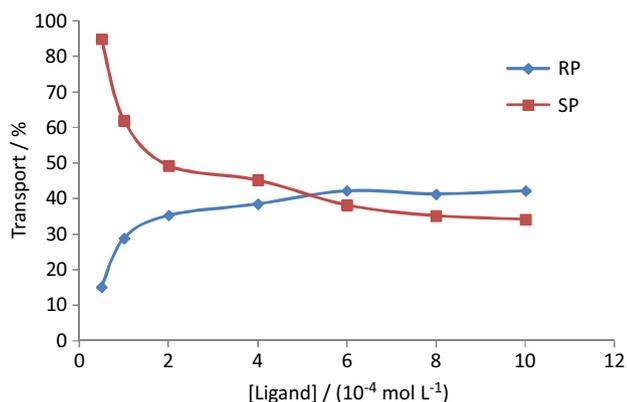


Figure 5. Effect of ligand concentration in the MP on the transport of Ag⁺ ions. SP: 5 mL solution containing 1.0×10^{-3} mol L⁻¹ of metal cations at pH 5; MP: 10 mL of ligand in DCM at different concentrations; RP: 5 mL solution containing thiourea (5.0×10^{-3} mol L⁻¹) at pH 3; stirred for 4 h at 400 rpm.

Effect of picric acid in the SP on transport efficiency

To maintain electroneutrality and solute uphill pumping, many carrier-facilitated membrane systems require a coupling ion to be counter- or co-transported along with

the solute ion. Since the coupling ion must also enter and cross the organic phase, it is bound to influence transport efficiency. Transport efficiency affected by several parameters such as anion hydration free energy anion lipophilicity, and anion interactions with the solvents. It seems that anion hydration free energy is the major determinant.²⁰ Christensen *et al.*⁴⁵ shows that transport rate of K⁺ with dibenzo-18-crown-6 as a carrier, decreased in the following order: picrate > PF₆⁻ > ClO₄⁻ > IO₄⁻ > BF₄⁻ > I⁻ > SCN⁻ > NO₃⁻ > Br⁻ > BrO₃⁻ > Cl⁻ > OH⁻ > F⁻ > acetate > SO₄⁻. This order is almost identical to that for increasing anion hydration free energy and demonstrates the strong correlation between anion hydration and transport efficiency: larger anions are more easily dehydrated and thus more readily enter the membrane to facilitate transport.

The results of the competitive transport of six metal cations from SP through DCM containing the ligand showed that the nitrate ion is not a suitable counter anion to accompany the ligand-Ag⁺ complex into the MP. Therefore, we used picric acid as counter ion in the SP to increase the Ag⁺ cation transport into the MP. The role of the picric acid may be to aid the transport process by providing a soft, polarizable and weakly hydrated counter ion in the membrane on proton loss to the aqueous phase, giving rise to charge neutralization of the Ag⁺ ion being transport through ion pair or adduct formation.^{32,46} The influence of the concentration of picric acid on the transport efficiency of Ag⁺ cation was investigated and the results are presented

in Figure 6. As can be seen, the efficiency of the Ag^+ cation transport increases sharply with increasing picric acid concentration up to $(1.25 \times 10^{-3} \text{ mol L}^{-1})$, and further increase in the concentration of picric acid caused a decrease in the percentage transport of the Ag^+ ion. This behavior maybe caused due to the competition of picric acid with Ag^+ ion for transport through the liquid membrane system.

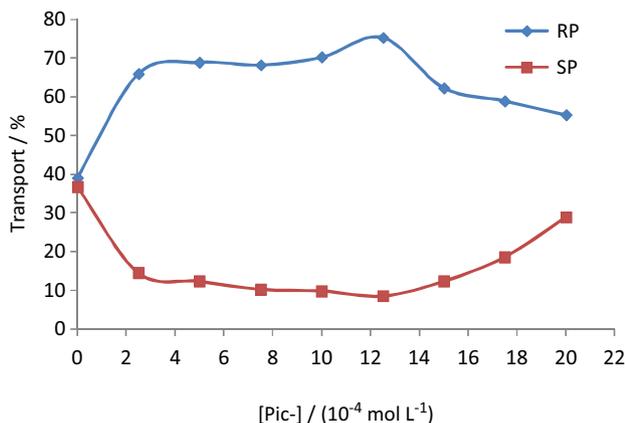


Figure 6. Effect of picric acid in the SP on the transport efficiency of Ag^+ ions. SP: 5 mL solution containing $(1.0 \times 10^{-3} \text{ mol L}^{-1})$ metal cations and different concentrations of picric acid at pH 5; MP: 10 mL of ligand in DCM at the concentration of $6.0 \times 10^{-4} \text{ mol L}^{-1}$; RP: 5 mL solution containing thiourea $(5.0 \times 10^{-3} \text{ mol L}^{-1})$ at pH 3; stirred for 4 h at 400 rpm.

Effect of stripping agent type and its concentration in the RP on transport efficiency

In the preliminary experiments, it was found that the permeability of the membrane system for Ag^+ cation is extremely dependent on the nature and composition of the stripping agent used in the RP. As it is observed in Table 3, among the different stripping agents used in these experiments, thiourea, with the increased complexing ability towards Ag^+ cation, acts as the most suitable receiver for the release of Ag^+ cation from the MP into the RP.

Table 3. Effect of type of stripping agent on the Ag^+ transport

Stripping agent	Concentration / (mol L^{-1})	Percentage transported into RP / %	Percentage remaining in SP / %
KSCN	0.01	48.52	32.84
EDTA	0.01	11.23	56.21
Na_2SO_3	0.01	32.23	25.32
Thiourea	0.01	73.20	8.52
$\text{Na}_2\text{S}_2\text{O}_3$	0.01	53.25	37.51

The influence of the concentration of thiourea in the RP on the transport efficiency of Ag^+ was also evaluated and the results are shown in Figure 7. According to the obtained results, the optimum concentration of thiourea

in the RP was found to be $5.0 \times 10^{-3} \text{ mol L}^{-1}$. It should be noted that in the absence of the stripping agent on the RP, the Ag^+ cation transports only 39% into the RP. Thus, $5.0 \times 10^{-3} \text{ mol L}^{-1}$ thiourea concentration was used for further experiments.

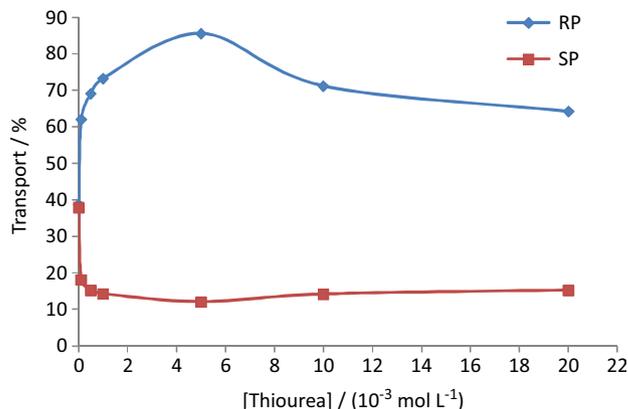


Figure 7. Effect of thiourea concentration in the RP in the transport of Ag^+ ions. SP: 5 mL solution containing $(1.0 \times 10^{-3} \text{ mol L}^{-1})$ metal cations and $(1.25 \times 10^{-3} \text{ mol L}^{-1})$ picric acid at pH 5; MP: 10 mL of ligand in DCM at a concentration of $6.0 \times 10^{-4} \text{ mol L}^{-1}$; RP: 5 mL solution containing different concentrations of thiourea at pH 3; stirred for 4 h at 400 rpm.

Effect of time on transport efficiency

The time required for maximum transport of Ag^+ cation through the bulk liquid membrane was inspected under the experimental conditions. The results demonstrated the acceptable transport of Ag^+ cation from the aqueous SP into the RP and maximum transport of Ag^+ cation was achieved in about 4 h. Therefore, further experiments were carried out for a period of 4 h.

Effect of stirring rate on transport efficiency

In order to explore the effect of stirring speed on the Ag^+ transport, several transport experiments were performed with different stirring speeds (100-600 rpm) and the results are presented in Figure 8. As can be seen, the transport efficiency of Ag^+ ions through the MP augments with acceleration of stirring speed which reveals that diffusion was the rate limiting step in the transport of Ag^+ from the SP to RP. The transport efficiency increases at lower stirring speeds (100-400 rpm) and then it is nearly constant at higher stirring speeds (500-600 rpm).

Recommended mechanism

The Ag^+ ion is transported from the SP into the RP via a DCM membrane with the simultaneous counter-transport of proton. Movement of the charge species through the

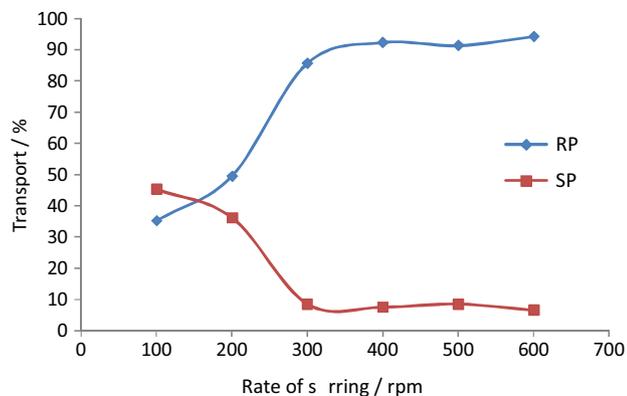
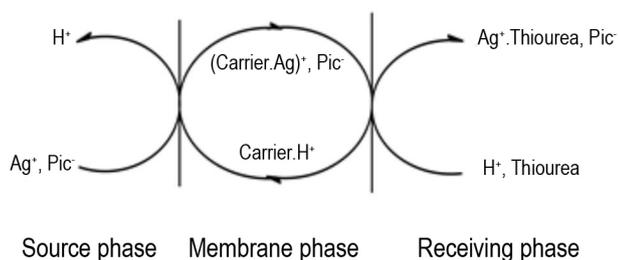


Figure 8. Effect of the stirring speed on the transport efficiency of Ag^+ ions. SP: 5 mL solution containing ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) metal cations and ($1.25 \times 10^{-3} \text{ mol L}^{-1}$) picric acid at pH 5; MP: 10 mL of ligand in DCM at a concentration of $6.0 \times 10^{-4} \text{ mol L}^{-1}$; RP: 5 mL solution containing thiourea ($5.0 \times 10^{-3} \text{ mol L}^{-1}$) at pH 3; stirred for 4 h at different stirring speed.

hydrophobic organic membrane is accomplished by the presence of the host ligand, ion paired with picrate ion as a suitable counter ion. The picrate ion not only neutralizes the charged Ag^+ -ligand complex, but also induces a more lipophilic character to the Ag^+ complex so that it can be readily extracted into the MP. During the complexation process of Ag^+ ion with the ligand on the source side of the membrane, the ligand splits off protons into the SP and the formed complex diffuses across the membrane. On the other side of the membrane, the release of the Ag^+ ion into the RP occurs via the formation of complex between Ag^+ ion and thiourea as a stripping agent. At this moment, the ligand associates with proton from the RP and the free ligand diffuse back across the membrane and cycle start again. A schematic diagram of this mechanism is shown in Scheme 2.



Scheme 2. Schematic diagram of liquid membrane system for transport of Ag^+ ions.

Limit of detection

The blank determination was performed using bulk liquid membrane system at optimum condition of experiments. The blank value was $0.12 \pm 0.18 \text{ mg L}^{-1}$ of Ag^+ for 5 replicates experiment and the limit of detection (calculated as 3 times of the standard deviation) was 0.54 mg L^{-1} of Ag^+ ion.

Real water analysis

Three real environmental water samples, including ground, river and tap water spiked with an equimolar mixture of six metal cations as nitrate salts ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) separated using this membrane system under the optimal conditions of the experiments. Tap water and ground water were collected from Payame Noor University of Ardabil (Iran), and river water was collected from the Baliqly Chay River in Ardabil (Iran). The results are given in Table 4. It is obvious that Ag^+ is successfully transported and purified using this membrane system. In addition, to show practical utilization of this bulk liquid membrane system, it was used for recovery of Ag^+ ions from silver plating and photographic waste solutions. The composition of each waste solution is given in Table 5. The obtained results indicate that only silver is transported, which shows the selectivity and efficiency of this bulk liquid membrane system for silver recovery.

Table 4. Recovery (%) and relative standard deviation (RSD, %) of real environmental water samples

Water sample	Recovery / %	RSD / %
Tap water	92.3	5.3
River water	89.2	8.5
Ground water	83.2	4.8

RSD: relative standard deviation.

Table 5. Application of proposed methodology for recovery of Ag^+ from silver plating and photographic waste solutions

Sample	Metal ion	[M] in SP / ($10^{-4} \text{ mol L}^{-1}$)	Recovery / %
Silver plating	Ag^+	4.87	89.32
	Cu^{2+}	0.60	0
	Pb^{2+}	ND	–
	Zn^{2+}	0.23	0
Photographic waste	Ag^+	3.02	91.06
	Fe^{2+}	3.56	2.10
	Mg^{2+}	1.17	0
	K^+	25.63	4.61

[M] in SP: metal concentration in source phase.

Conclusion

The present study demonstrates that the 1,1'-(1,3-phenylene)bis(3-allylthiourea) is an excellent carrier for selective transport of Ag^+ cation. The results of the competitive bulk liquid membrane transport of Ag^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} metal cations using this

ligand in various organic membranes showed that the rates of the cation transport are strongly influenced by the nature of the organic solvent. The efficiency of the method depends on effective parameters such as pH of the SP, carrier concentration, concentration of picric acid as counter anion, type and concentration of stripping agent, stirring rate and transport time. At the optimum conditions of transport experiments, the proposed method was triumphantly used for the separation of (5.0×10^{-4} mol L⁻¹) Ag⁺ from real water samples in the presence of equimolar concentration of some other metal cations and found that the recoveries for tap, river and ground water after 4 h were 92.3 ± 5.3 , 89.2 ± 8.5 and $83.2 \pm 4.8\%$, respectively. Also, this bulk liquid membrane system was successfully utilized for recovery of Ag⁺ ions from silver plating and photographic waste solutions.

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