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Selective Separation and Transport of Ag^+ ion Through a Bulk Liquid Membrane by Bis-2,6-dihydroxymethyl-4-haloanisole as Carrier

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ABSTRACT

In this work, carrier-facilitated transport of Ag^+ ion from an aqueous source phase (SP) containing Hg^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Co^{2+} through an against its concentration gradient from aqueous 5 ml (5.0×10^{-4} mol L^{-1}) hydrochloric acid solution across a liquid membrane containing through an organic membrane phase (MP), 10 ml Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA) (3.8×10^{-4} mol L^{-1}) solution as a carrier into an aqueous receiving phase (RP), 5 ml Sodium thiocyanate (4.0×10^{-4} mol L^{-1}) solution was the most efficient receiving phase agent among several aqueous reagents tested. Fluxes and selectivities for competitive metal cation transport have been determined in a variety of source solution pH and membrane solvent types. The mobile carrier in chloroform has been investigated. The obtained results showed that the carrier is selective for Ag^+ ion. The effect of different experimental conditions that affect the transport efficiency were studied and optimized. In the optimum condition, the transport of an Ag^+ ion across the liquid membrane is more than 92% after 2.5 h. The carrier, DABDAMA, selectively and efficiently could able to transport Ag^+ ion in the presence of other associated metal ions in binary system.

Keywords: Silver (I) ion, Bulk Liquid Membrane, Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA), Atomic Absorption Spectrometry

1. INTRODUCTION

Silver is an important element that is widely used for human life. Because of its bacteriostatic properties, silver compounds are often used in filters and other equipment to purify swimming pool and drinking water, and is used in the processing of foods, drugs and beverages [1]. Silver is usually found at extremely low concentrations in natural waters because of its low crustal abundance and low mobility in water. It is obvious that in order to monitor silver concentration in natural waters and to study silver toxicity effects on bio organisms in oceanographic research and survey work, highly sensitive and selective methods for silver determination are required. A variety of methods, including spectrometric and electrochemical techniques, have been

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proposed for the determination of silver in different environmental samples [2-5]. However, aforementioned methods, except for Flame Atomic Absorption Spectrometry (FAAS), involve a greater cost and increased instrumentation complexity, limiting its widespread application to routine analytical work. Direct determination of trace amounts of metal ions in some samples by FAAS is difficult because of low sensitivity. Thus, pre-concentration procedures are often required. Different techniques, such as solvent extraction [6], adsorption [7], liquid–liquid extraction [8], dispersive liquid–liquid micro extraction [9, 10], solid-phase extraction [11, 12], cloud point extraction [13,14], flotation [15], other pre-concentration methods of silver involve batch adsorption [16,17] and membrane separation [18,19]. 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 due to an imposed concentration gradient [22].

Bulk liquid membrane (BLM) is one of the simple, lowest and efficient types of liquid membranes [23]. In this technique similar to liquid membrane configurations, (viz ion transport across membranes) combine the extraction, diffusion, and back extraction of analytes are particularly drawing maximum attention. BLM constitute the cheapest separation techniques because of their relatively small inventory and low capital cost [24].

In a BLM, a relatively thick layer of immiscible fluid is used to separate the source and receiving phase. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility. A recent development in liquid membranes is the incorporation of selective carriers within the liquid membrane phase which selectivity and efficiency via chemical reaction facilitate the transport of a specific compound across the membrane [25].

Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery of target compound. The selective transport of metal ions across a membrane is 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. However, the development of selective techniques for the separation and recovery of transition and post transition heavy metal cations is a challenging task [26,27].In this present study, we studied the competitive bulk liquid membrane transport of six metal cations involving Ag^{+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Co^{2+} with Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA), as a carrier using chloroform ($CHCl_3$), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and acetonitryl (AN) as an membrane phase (MP). When $CHCl_3$was used as an MP, a good transport selectivity has been observed for Ag (I) ion 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 hydrochloric 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^+ ion from real and industrial samples was examined [28, 29].

2. EXPERIMENTAL

2.1. Reagents and materials

All chemicals and reagents used in this study were prepared of the analytical grade purchased from Merck Company, solution (Merck, Darmstadt, Germany). The solutions were prepared with doubly distilled water. The concentrations of the stock solutions were as follows: $CHCl_3$ (69%), MP Bis-2, 6-dihydroxymethyl-4-haloanisole (DABDAMA), RP with highest purity were used as liquid membrane. Nitrate salts of silver (99%), mercury (97%), lead (98%), cadmium (98%), copper (99%), and zinc (99%), were the highest purity and used without any further purification. 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.

2.2. Instrumentation

All the determinations of the analytes were carried out using a sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources was used for the determinations of silver. The optimum conditions for FAAS are given in (Table. 1). The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A pH meter (Metrohm 691 pH Meter) was also used. Transport experiments were conducted using a thermostated (Grants Instruments, model W14, Cambridge, England) apparatus at 298 K and transport experiments were carried out in a U-type cell (Fig. 1) [30].

Table 1: Operating parameters for silver analysis by FAAS

Parameters	
Wavelength,, nm	328.1
Lamp current, mA	4.0
Acetylene flow rate, $Lmin^{-1}$	2.0
Slit width, nm	0.5
Air flow rate, $Lmin^{-1}$	13.5
Background correction	Deuterium

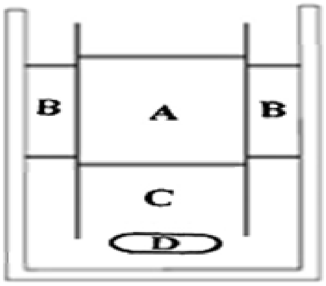


Figure 1: Representation of the bulk type liquid membrane cell used, (A) source phase; (B) receiving phase; (C) membrane phase; (D) magnetic stirrer.

2.3. Synthesis of Ligand Bis-2,6-dihydroxymethyl-4-haloanisole DABDAMA.

Bis-2,6-dihydroxymethyl-4-haloanisole was prepared according to one of our previous reports. In a round-bottomed flask equipped with a condenser and a magnetic stirrer, calcium hydrogen sulfate (0.468 g, 2.0 mmol) was added to a solution of 4-bromo-2,6-bis(hydroxymethyl)anisole (0.247 g, 1.0 mmol) in CH_3CN (4.0 mL). The mixture was stirred at 80°C for 2 h.

Then, the mixture was concentrated under reduced pressure and H_2O (20 mL) was added to the resulting mixture upon which precipitates were formed. The precipitates were filtered, washed with water and dried. Recrystallization from ethanol gave 0.27 g (82%) of DABDAMA. The ligand information is below and a schematic diagram for its scheme synthesis is shown in (Fig. 2) [31].

m.p.: 230 °C; IR (KBr): 3300, 3102, 2946, 1667, 1552, 1464, 1375, 1291, 1220, 1175, 1012 cm^{-1}.

H (NMR): 1.93 (S, 6H, 2* CH3CO), 3.76 (S, 3H, CH3O), 4.30 (d, 4H, J = 5.7 Hz, 2* CH2), 7.32 (S, 2H, ArH), 8.35 (b, 2H, 2* NH).

2.4. Pretreatment of real samples

2.4.1. Water samples

Analysis of water samples for determination of Ag (I) ion content was performed as following: 200 mL of sample was poured in a beaker and 8 ml concentrated HNO_3 and 3 ml of H_2O_2 of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value were performed according to general described procedure [32].

2.4.2. Blood, amalgam and waste radiographic samples

Real samples including blood samples were treated as described previously. Then the Test Procedure described above was applied. For the application of the present procedure to amalgam alloy, an accurately weighed 0.4 g portion of each amalgam alloy sample was digested as described previously [33]. and dissolved in the smallest volume of water, and the solution was transferred to a 100 mL volumetric flask by adjustment of the pH of the solution to the desired value; then the Test Procedure described above was carried out. The waste radiographic samples were prepared for the measurement of their silver content as follows. To 20 mL sample were added about 10 mL 3M nitric acid and 10 mL water. The solution was boiled until its volume was reduced to 20 mL solution. The resulting solution was neutralized with NaOH solution to the desired pH value and filtered. The filtrate and washings were diluted to 50 mL in a volumetric flask, and then the test procedure described above was applied [34].

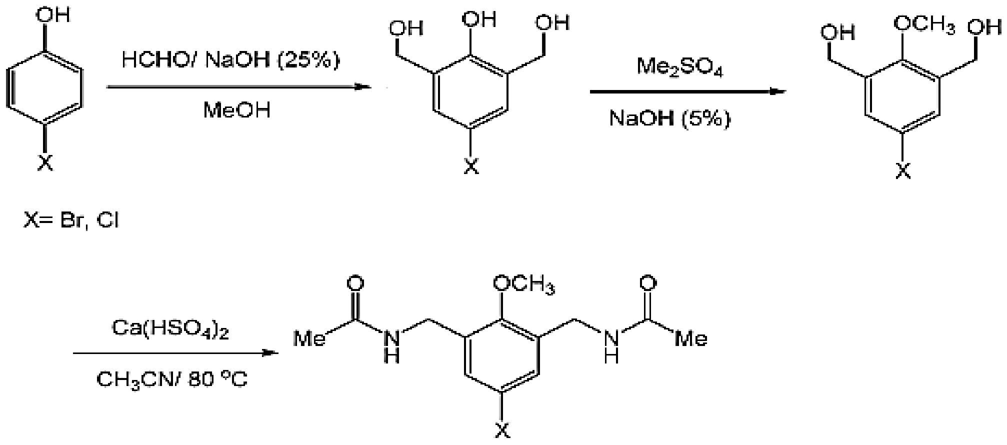


Figure. 2: Scheme synthesis and structure of Ligand Bis-2,6-dihydroxymethyl-4-haloanisole.

2.4.3. Dryer agents and colored human hair samples

The determination of silver in colored hair samples of human was performed as the following: prior to analysis, each individual hair sample was cut into a size less than 1cm and mixed to make a representative hair sample. After washing, the sample was dried in an oven at 50°C for 5 minutes. 100 mg of the sample was heated in the presence of 10 mL concentrated nitric acid on a hot plate for about 20 minutes. After a clear solution was formed, 1 mL of H_2O_2 30% was added and again heated to one-fourth [35]. Then its pH was adjusted and the procedure in section 2.4.3 was repeated.

2.5. Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (Fig. 1) (inside diameter, 4.0 cm) holding a glass tube (inside diameter, 2.0 cm) which separates the two aqueous phases, was used. The inner aqueous phase (source phase, SP) contained an equimolar mixture of metal nitrate salts (1.0×10^{-3}mol L^{-1}) and hydrochloric acid (5 mL, 5.0×10^{-4} molL^{-1}). The MP contained (3.8×10^{-4} molL^{-1}) Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA) in chloroform of carrier which was placed at the bottom of the cell. The RP containing a concentration of (4.0×10^{-3} mol L^{-1}) of sodium thiocyanate was buffered at pH 6 using was buffered at pH 6 using CH_3COOH/CH_3COONa buffer solution and placed in one limb of the cell. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (2.0 × 5 cm, diameter). Under these conditions, while is the mixing process perfect, the interfaces between the organic membrane and the two aqueous phases remained flat and well defined. Determination of the silver ion concentration in both aqueous phases was carried out by CV-AAS. A similar transport experiment was carried out in the absence of the carrier for reference [36].

3. Results and Discussion

3.1. Procedure Detection measurements

Study of complexation between Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA) and Ag^+ ion selective transport of metal cations by carrier-mediated liquid membrane depends on the nature of the ligand used as a carrier in the membrane [37]. 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 [38]. In the preliminary experiment, we tested the ligand ability for the competitive transport of Ag^+ ion among some other metal cation such as Hg^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Co^{2+} from SP into the RP through CH_3CN organic solvent as a MP. It was found that the ligand has the desired ability to transport Ag^+ ion against its concentration gradient through bulk liquid membrane. In order to investigate the complexation process between Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA) and Ag^+ ion, 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 spectrum of Ag^+ ion solution (1.0×10^{-4} mol L^{-1}) at wavelength of 425 nm decreased with the addition of ligand to the solution. It is exhibited in (Fig. 3). 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 (Fig. 4). As can be seen, absorbance of the acetonitrile solution of ligand at wavelength of 360 nm decreased with the addition of Ag^+ ion to the solution. On the other hand, the observed spectral evolution involved the formation of a well-defined isobestic point at around 430 nm, indicating the presence of one absorbing complex compound between ligand and Ag$^+$ ion.

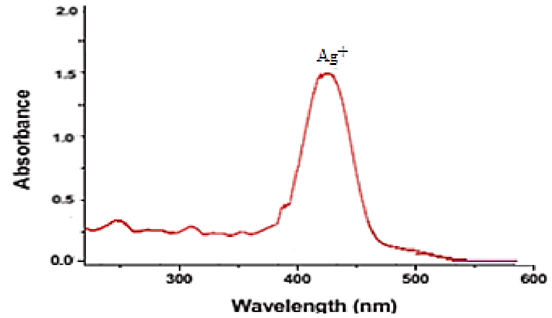
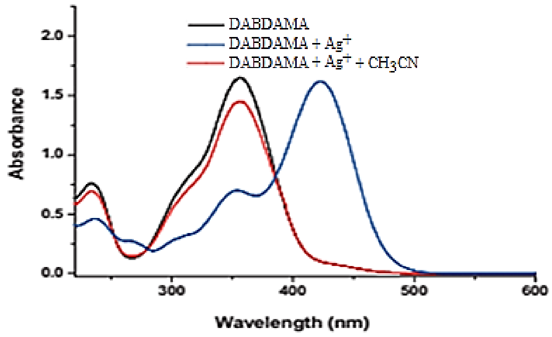


Fig 3: The spectrum of Ag$^+$ ion solution (1.0×10^{-4} mol L^{-1}).



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

3.2. Effect of pH

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. 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. 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 [39, 40]. 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 0.1-8.0 into acidic RP investigated and the results are given in Figure 5. It was found that maximum Ag$^+$ cation transport occurs at (pH 6) of the SP. It seems that at lower pH values of the SP, the efficiency of Ag$^+$ transport decreased due to a subtraction in the hydroxide concentration for exchanging proton with Ag$^+$ or slow partition coefficients of the Ag$^+$ ion at theource/membrane phase 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 shown in (Fig. 5).

Effect of solvent on transport efficiency choosing the right organic membrane solvent is the prime issue in establishing transport efficiency. 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. 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 [41].

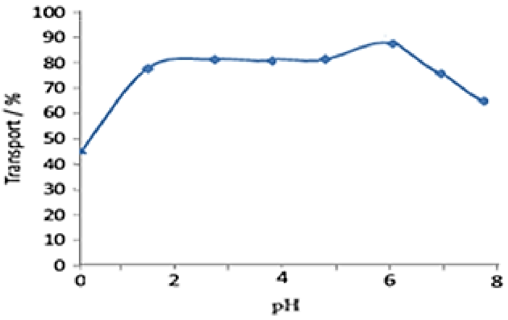
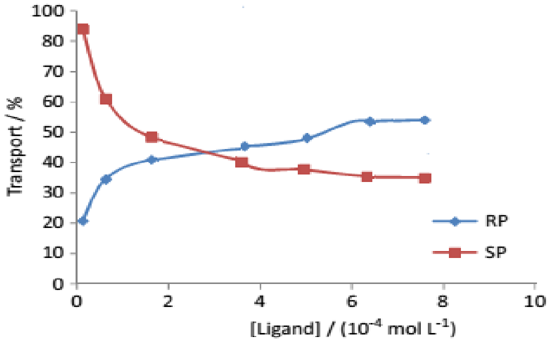


Fig 5: Effect of pH of the source phase on the tran t of Ag$^+$ ion. SP: Conditions; source phase, 5 mL solution containing 1.0×10^{-3}mol L^{-1} of Ag (I) ion at various pH, MP: 10 mL of ligand in

$CHCL_3$ at different concentrations; RP: 5 mL solution containing Sodium thiocyanate (4.0 × 10^{-3}mol L^{-1}), stirred for 2.5 h at 350 rpm.

3.3. Effect of the ligand concentration on transport efficiency

The preferential binding of sulfur containing ligands towards Ag^+ ion has been reported in the literature. The influence of the concentration of DABDAMA in the organic phase on the transport efficiency of Ag^+ ion was studied. It was seen that the percentage of transport of Ag^+ ion increases with an increase in DABDAMA concentration in the organic phase [42]. 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^+ ion 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 6. It is seen that the percentage of Ag^+ ion transport increases with an increase in ligand concentration in the MP and (3.8 × 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 (3.8 ×10^{-4} mol L^{-1}) at the subsequent experiments shown in (Fig. 6) [43].



Fi. 6: Effect of ligand concentration in the MP he transport of Ag^+ ion. SP: 5 mL solution containing 1.0 × 10^{-3} mol L^{-1} of metal cations at pH 6; MP: 10 mL of ligand in $CHCL_3$ at different concentrations; RP: 5 mL solution containing Sodium thiocyanate (4.0 × 10^{-3} mol L^{-1}) at pH 6, stirred for 2.5 h at 350 rpm.

3.4. Effect of hydrochloric acid in the SP on transport efficiency

Most chelating ligands are conjugate bases of weak acid groups and accordingly, have a very strong affinity for hydrogen ions. Therefore the pH, play an important role in the complexation of metal ions by chelation. The pH will determine the values of the conditional stability constants of the complexes of metal ions with a desired ligand. It was expected that the efficiency of transport at higher pH values (>6.0) due to the formation of Ag(s) precipitate (white precipitate) at top of the chloroform between the source and membrane phases has been reduced. Therefore the source phase must be acidic. The effect of the presence of (5.0 × 10^{-4} mol L^{-1}) of different acids including HCl, $HClO_4$, HNO_3, H_2SO_4 and picric acidin the source phase on the transport of Ag^+ ion was studied and it was observed that the maximum transport occurs in the presence of (5.0 × 10^{-4} mol L^{-1}) HCl. It was found that nitrate ion is not a suitable counter anion to accompany the ligand-Ag^+ complex into the organic phase and only

70% of Ag^+ ion was transported into the receiving phase in a long time. The results of the competitive transport of six metal cations from SP through $CHCL_3$ 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 hydrochloric acid as counter ion in the SP to increase the Ag^+ ion transport into the MP. The role of the hydrochloric 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 [44, 45]. The influence of the concentration of hydrochloric acid on the transport efficiency of Ag^+ ion was investigated in the concentration range (1.0×10^{-5} to 1.5×10^{-3} mol L^{-1}) of hydrochloric acid and the results are presented in (Fig. 7). As can be seen, the efficiency of the Ag^+ cation transport increases sharply with increasing hydrochloric acid concentration up to (5.0×10^{-4} mol L^{-1}), and further increase in the concentration of hydrochloric acid caused a decrease in the percentage transport of the Ag^+ ion. This behavior maybe caused due to the competition of hydrochloric acid with Ag^+ ion for transport through the liquid membrane system.

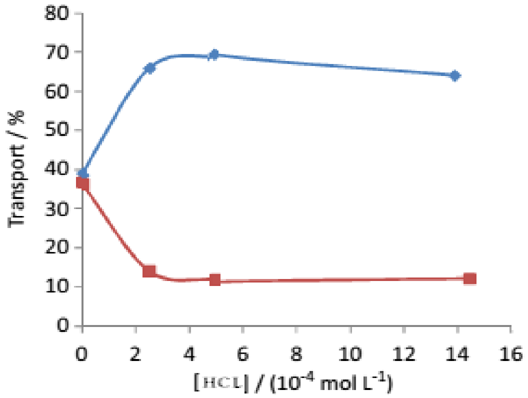


Figure. 7: Effect of hydrochloric acid in the SP on the transport efficiency of Ag+ ion. SP: 5 mL solution containing (1.0×10^{-3} mol L^{-1}) metal cations and different concentrations of hydrochloric acid at pH 6, MP: 10 mL of ligand in $CHCL_3$ at the concentration of 3.8×10^{-4} mol L^{-1}, RP: 5 mL solution containing Sodium thiocyanate (4.0×10^{-3} mol L^{-1}) at pH 6, stirred for 2.5 h at 350 rpm.

3.5. Effect of striping 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^+ ion is extremely dependent on the nature and composition of the stripping agent used in the RP. As it is observed in (Table. 2), among the different stripping agents used in these experiments, thiourea, with the increased complexing ability towards Ag^+ ion, acts as the most suitable receiver for the release of Ag^+ ion from the MP into the RP.

Table. 2: Effect of type of stripping agent on the Ag^+ ion transport

Stripping agent	**Concentration (mol L^{-1})**	**Percentage transported in to RP%**	**Percentage transported in SP%**
NaSCN	0.01	78.08	13.65
$Na_2S_2O_3$	0.01	16.17	45.51
Na_2SO_3	0.01	20.17	35.37
EDTA	0.01	37.46	30.16
Thiourea	0.01	62.46	28.04

The influence of the concentration of Sodium thiocyanate in the RP on the transport efficiency of Ag^+ ion was also evaluated and the results are shown in (Fig. 8). According to the obtained results, the optimum concentration of Sodium thiocyanate in the RP was found to be (5.0×10^{-3} mol L^{-1}). It should be noted that in the absence of the stripping agent on the RP, the Ag^+ ion transports only 78% into the RP. Thus, (4.0×10^{-3} mol L^{-1}) Sodium thiocyanate concentration was used for further experiments [43,44].

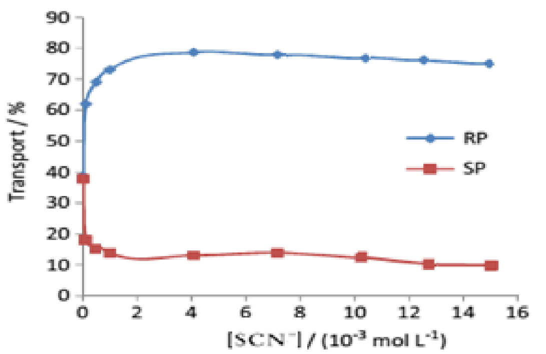


Figure. 8: Effect of Sodium thiocyanate concentration in the RP in the transport of Ag^+ ion. SP: 5 mL solution containing (1.0×10^{-3} mol L^{-1}) metal ion and (5.0×10^{-4} mol L^{-1}) hydrochloric acid at pH 6, MP: 10 mL of ligand in $CHCL_3$ at a concentration of (3.8×10^{-4} mol L^{-1}), RP: 5 mL solution containing different concentrations of Sodium thiocyanate at pH 6; stirred for 2.5 h at 350 rpm.

3.6. Effect of time on transport

In the (Fig. 9), shows the time dependence of copper transport through the liquid membrane under experimental conditions. It is obvious that the extraction of Ag^+ ion from the source phase into the organic membrane occurs almost completely after 100 min. However, the plot shows the transport rate decreases gradually with time and a steady state situation is reached in which the amount of Ag^+ ion in MP hardly changes, whereas the decrease in SP and increase in RP are constant and equal. After 2.5 h, the concentrations of Ag^+ ion were independent of time and transport was completed. It was found that, under the optimum conditions, the transport of silver ion from the aqueous source phase into the receiving phase after 2.5 h is almost quantitative [43,45].

3.7. 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 (100-550 rpm) and the results are presented in (Fig. 10). As can be seen, the transport efficiency of Ag+ ion 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 (100-350 rpm) and then it is nearly constant at higher stirring speeds (350-550 rpm) [45,46].

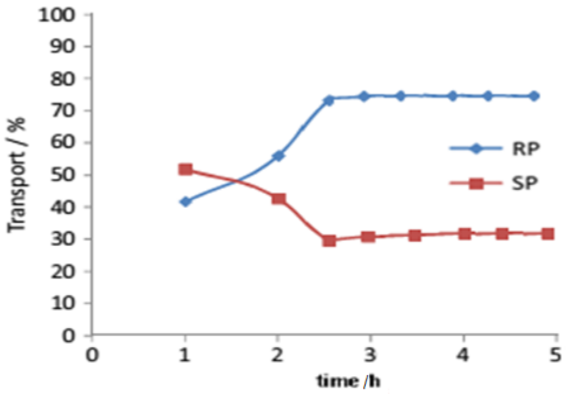


Figure. 9: Effect of the stirring speed on the transport efficiency of Ag^+ ion. SP: 5 mL solution containing (1.0×10^{-3} mol L^{-1}) metal cations and (5.0×10^{-4} mol L^{-1}) hydrochloric acid at pH 6, MP: 10 mL of 10 mL of ligand in $CHCL_3$ at a concentration of (3.8×10^{-4} mol L^{-1}), RP: 5 mL solution containing Sodium thiocyanate (4.0×10^{-3} mol L^{-1}) at pH 6, stirred at 350 rpm.

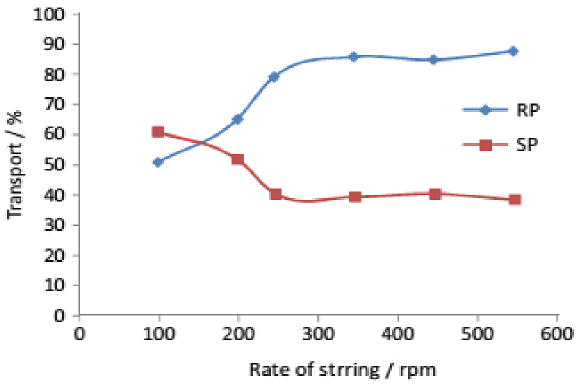


Figure. 10: Effect of the stirring speed on the transport efficiency of Ag^+ ion. SP: 5 mL solution containing (1.0×10^{-3} mol L^{-1}) metal cations and (5.0×10^{-4} mol L^{-1}) hydrochloric acid at pH 6, MP: 10 mL of 10 mL of ligand in $CHCL_3$ at a concentration of (3.8×10^{-4} mol L^{-1}), RP: 5 mL solution containing Sodium thiocyanate (4.0×10^{-3} mol L^{-1}) at pH 6, stirred for 2.5 h at different stirring speed.

2.8. Effect of temperature

The effect of temperature on the transport of the Ag^+ ion through the liquid membrane containing ligand DABDAMA in $CHCl_3$ was examined at 298, 305, 323 and 330 K, respectively. The experimental results are shown in (Fig. 11). It is quite obvious that transport increases with an increase in the temperature [46].

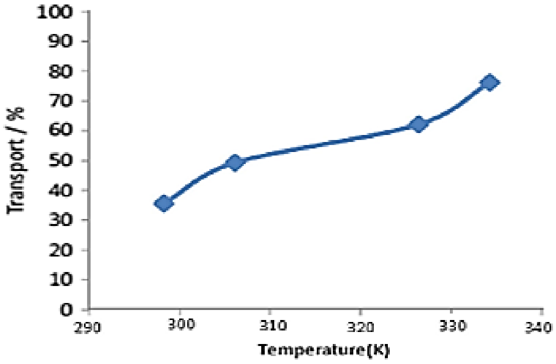
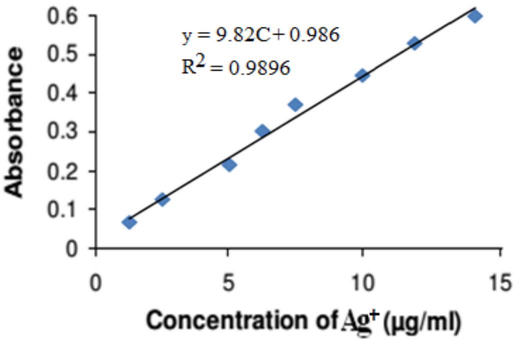


Fig. 11: Effect of temperature on the transport efficiency of Ag^+ ion.

3.9. Calibration graph and reproducibility

Our studies proved that the most sensitive pH for determination Ag^+ ion in pH 6.0. So we choose this pH using buffer solution in aliquots of solution of Ag^+ ion in assay procedure. A linear correlation was found between absorbance and concentration of Ag (I) ion in the range of (0.6-15 μg mL^{-1}) shown in (Fig. 12) [36,38]. The equation sensitive calibration curve is: A= 9.82 C + 0.986 R^2= 0.9896.

Where A and C correspond to absorbance and Ag^+ ion concentration in μg mL^{-1}, respectively. The correlation coefficient indicates excellent linearity. The molar absorptivity coefficient was found (2.8×10^3 $L.mol^{-1}.cm^{-1}$), and limits of detection (LOD) of (0.6 μmol L^{-1}), and quantification (LOQ) of (0.65 μmol L^{-1}) [42].



Fi. 12: Calibration curve of Ag^+ ion at pH 6.0.

3.10. Recommended mechanism

The Ag^+ ion is transported from the SP into the RP via a $CHCL_3$ membrane with the simultaneous counter-transport of proton. Movement of the charge species through the 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 (Fig. 13) [45,46].

3.10. 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 (5.0×10^{-4} mol L^{-1}) separated using this membrane system under the optimal conditions of the experiments. The proposed method was applied to the determination of total Ag^+ ion in tap water, river water, amalgam, waste radiographic, blood and colored human hair samples. In (Table. 3), the results obtained are shown, and compared with those obtained by atomic absorption spectrophotometry. The obtained results indicate that only silver is transported, which shows the selectivity and efficiency of this bulk liquid membrane system for silver recovery [38, 47].

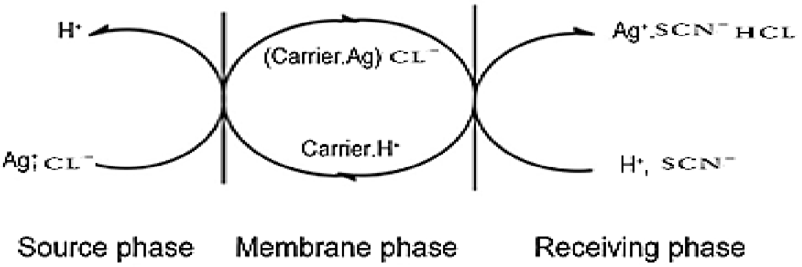


Figure 13: Schematic diagram of liquid membrane system for transport of Ag^+ ion.

Table 3: Recovery (%) and relative standard deviation (RSD, %) of real samples

sample	Added (ng L^{-1})	Founded (ng L^{-1})	RSD %	Recovery %
Tap water	0 10	1.03 1.62	1.1 1.8	--- 103
River water	0 10	0.62 1.64	1.1 1.3	--- 95.3
amalgam	0 10	0.67 2.28	1.7 2.7	--- 100.8
waste radiographic	0 10	4.40 12.38	1.7 2.7	--- 100.8
Blood	0 10	0.21 0.93	1.9 2.3	--- 102
colored human hair	0 10	1.11 2.14	1.0 0.8	--- 101.8

4. CONCLUSION

The present study demonstrates that the Bis-2,6-dihydroxymethyl-4-haloanisole (DABDAMA) is an excellent carrier for selective transport of Ag^+ ion. The results of the competitive bulk liquid membrane transport of Hg^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Co^{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 hydrochloric 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^+ ion 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 2.5 h were 92.3 ± 2.3, respectively. Also, this bulk liquid membrane system was successfully utilized for recovery of Ag^+ ion from plating and photographic waste solutions.

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جداسازی و انتقال انتخابی یون نقره از طریق غشای مایع حجیم توسط لیگاند بیس۲و٦ - دی هیدروکسی متیل ٤ - هالوآنیسول به عنوان حامل

فرزانه مراحل[*] و لیلا نیکنام

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چکیده

در این کار، انتقال یون نقره از یک منبع آبی توسط حامل تسهیل شده است. فاز (SP) حاوی Hg^{2+}، Pb^{2+}، Zn^{2+}، Cr^{3+} و Co^{2+} از طریق یک گرادیان غلظت در برابر آن از محلول آبی ۵ میلی لیتری با غلظت ($5/0 \times 10^{-4}$ مول بر لیتر) محلول اسید کلریدریک در یک غشای مایع حاوی فاز غشای آلی(MP)، ۱۰میلی لیتر لیگاند بیس۲و٦- دی هیدروکسی متیل ٤- هالوآنیسول (DABDAMA) با غلظت ($3/8 \times 10^{-4}$ مول بر لیتر) محلول به عنوان یک حامل به فاز دریافت کننده آبی(RP)، ۵ میلی لیتر تیوسیانات سدیم با غلظت ($4/0 \times 10^{-4}$ مول بر لیتر) محلول محلول کارآمدترین عامل فاز دریافتی در میان چندین معرف آبی آزمایش شده بود. شارها و گزینش‌پذیری‌ها برای انتقال رقابتی کاتیون‌های فلزی در انواع مختلف pH محلول منبع و انواع حلال‌های غشایی تعیین شده‌اند. حامل متحرک در کلروفرم مورد بررسی قرار گرفته‌است. نتایج به‌دست‌آمده نشان داد که حامل برای یون نقره انتخابی است. اثر شرایط تجربی مختلف که بر راندمان حمل و نقل تأثیر می‌گذارند مورد مطالعه و بهینه‌سازی قرار گرفت. در شرایط بهینه، انتقال یون نقره در غشای مایع پس از ۲/۵ ساعت بیش از ٪۹۲ حاصل گردید. محلول حامل بیس۲و٦- دی هیدروکسی متیل ٤- هالوآنیسول (DABDAMA) به طور انتخابی و کارآمد می‌تواند یون نقره را در حضور سایر یون‌های فلزی مرتبط در سیستم دوتایی انتقال دهد.

کلید واژه‌ها: یون نقره (I)، غشای مایع فله، محلول حامل بیس۲و٦ - دی هیدروکسی متیل ٤ - هالوآنیسول، طیف سنجی جذب اتمی.

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