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Highly facile supported liquid membrane transport and removal of silver ion using dibenzyldiaza-18-crown-6 dissolved in a supramolecular solvent as selective ion carrier

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ABSTRACT

Supported liquid membranes (SLM) using organic solvents are limited by their relative instability and high volatility. The use of supramolecular solvents (SUPRASs) as a liquid membrane phase could overcome these disadvantages due to their negligible vapor pressure and high viscosity. In the present study, a highly facile and selective transport of silver ions through a SLM using a SUPRAS composed of vesicles of decanoic acid was developed. The SLM used was a thin porous membrane impregnated with dibenzyl-diaza-18-crown-6 (DBzDA18C6), as a selective ion carrier, dissolved in the SUPRAS. Effective parameters including the concentration of picric acid, as a counter ion, in the source phase (SP), nature of solvent and amount and type of carrier in the membrane phase and nature and concentration of stripping agent in the receiving phase (RP), and nature and amount of stripping agent in the RP were investigated. In the presence of 8.85×10^{-5} M, picrate ion as a suitable bulky ion pairing agent in the SP, 0.008 M DBzDA18C6 dissolved in SUPRAS as a favorite carrier solution in the membrane phase and 0.5 M thiosulfate as a convenient metal ion acceptor in the RP, the silver ion transport was occurred quantitatively after only 45 min, which is highly improved over previously reported SLM systems for the transport of Ag^+ ion. The selectivity of silver transport from aqueous solution containing Pb^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, and Cr^{3+} ions was also investigated.

Keywords: Uphill transport of Ag^+ ion; Supported liquid membrane; Supramolecular membrane solvent; Dibenzyl-diaza-18-crown-6; Selectivity

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1. Introduction

Since silver ion possesses a well-known toxicity towards the aquatic plants and animals [1], and its presence in natural water and environment is of critical importance. The wastes of the medical and photographic industry and those from the electronics' manufacturing, silverware, and jewelry are the major sources of the environmental silver [2]. In fact, it is reported that about 150,000 kg of silver annually enters the aquatic environment from the mine tailings, photography industry, and electroplating systems [3]. Therefore, the separation and recovery of silver from industrial wastes is of increasing importance. Thus, an

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extensive research work has been devoted to the transport of silver from aqueous media through different liquid membranes, including bulk liquid membranes [4–8], emulsion liquid membranes [9], hollow fiber-supported liquid membranes (HFSLMs) [10,11], and supported liquid membranes (SLMs) [1,12–17]. The application of liquid membrane technology to the separation and recovery of heavy metals from diluted solutions has also been reported [18–21].

Compared to other liquid membrane methods, the major advantage of SLM, in which the solution of a selective ion carrier in an organic solvent is placed in a porous support material, is its need for much lower liquid membrane for the formation of the support matrix [22]. Moreover, low operating costs, minimum product contamination, no phase separation requirement, selectivity, and flexibility are the other advantages of SLMs [23]. However, the long-term stability of membranes, as the most important practical properties of SLMs, is usually affected by the chemical nature and textural characteristics of the polymeric support, nature of the organic membrane phase, and method of the preparation of membranes [24–26]. In order to overcome these problems and improve the practical efficiency of SLMs, a number of scientific parameters have been investigated; these include polymerization of the top membrane layers, [23,24,27,28] gelation of liquid membranes [29,30], use of materials of highly permeability [31], use of ionic liquid phases in SLM [32–34], and ultrasound-assisted preparation of SLMs [35].

For the first time, in this work we explored the suitability of supramolecular solvents (SUPRASs) composing of vesicles of decanoic acid as a potential solvent in SLM containing dibenzyl-diaza-18-crown-6 (DBzDA18C6) as a selective Ag^+ ion carrier. The solvent was prepared from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutyl ammonium ion (Bu_4N^+). The Bu_4N^+ is known to induce the liquid–liquid phase separation in vesicular solutions of alkyl carboxylic acids [36]. In practice, the SUPRASs as water-immiscible liquids are formed by dispersion of large surfactant aggregates in a continuous phase, mostly water [37].

Then, upon application of an external stimulus such as temperature, electrolyte, solvent, and pH, the SUPRASs are spontaneously formed in hydro-organic vesicular or micellar solutions. The formation of such larger aggregates will result in their separation from bulk solution via a coacervation process [38,39]. The highly ordered structures of aggregates of SUPRASs possess regions of different polarities, which result in variety of interactions with the analytes of interest in their solution [39], so that the type of analyte-SUPRASs interactions can be tuned via variations in the hydrophobic or the polar groups of the surfactants. Moreover, the SUPRASs contain high concentrations of amphiphiles and, consequently, possessing many binding sites, which permits them to achieve high extraction efficiencies by using low extractant volumes [40,41]. The above-mentioned characteristics of the SUPRASs make them potential candidates for use as suitable membrane solvents in SLMs for facilitated transport of metal ions.

2. Materials and methods

2.1. Reagents and chemicals

High purity dibenzyldiaza-18-crown-6 (DBzDA18C6) and other 18-crown derivatives including dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), benzo-18-crown-6 (B18C6) and diaza-18-crown-6 (DA18C6), tetrabutylammonium hydroxide (TBAH, 20% w/v in water), decanoic acid (DeA), picric acid, and nitrate salts of other cations (from Merck or Fluka) were used as received. Reagent grade toluene (TOL) and 2-nitrophenyloctyl ether (NPOE) (both from Fluka), kerosene (KS) (KS, low odor, 0.8 g cm^{-3}, Aldrich), octanol (OCT), 2-nitrophenylpentyl ether (NPPE), and dihexyl ether (DHE) (all from Sigma-Aldrich) were tested as organic phases, for comparative studies. Highest purity available silver nitrate, sodium dodecyl sulfate (SDS), and sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) were purchased from Merck and used without further purification.

2.2. Apparatus

A model AA-400 atomic absorption spectrometer (Varian Pty Ltd, Musgarave, Victoria, Australia) equipped with hollow cathode lamps and a deuterium lamp background was used for controlling the metal ion concentration of the aqueous solutions, under the recommended conditions. All pH measurements were made with a model 692 digital pH-meter (Metrohm, Herisau, Switzerland) equipped with a glass combination electrode. At regular time intervals, 1.0-mL aliquots of samples were withdrawn from the source and receiving phases (RPs) and the determination of silver and other cations used were carried out. The SLM cell used for this study consisted of two compartments, each having a volume of 150 mL (Fig. 1) was fabricated from Perpex material. The SLM with a contact area of 10 cm^2 was fixed between the two cell compartments containing source and RPs. Each compartment was equipped with a Teflon-coated magnetic stirrer for stirring the aqueous solutions and an inlet

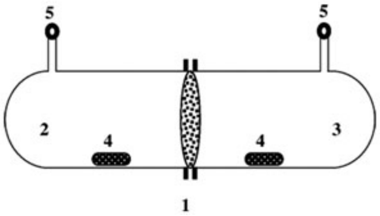

Fig. 1. Schematic representation of apparatus used for measurement of permeability of metal ions: (1) SLM: DBzDA18C6 dissolved in SUPRAS; (2) SP: Ag^+ and Pic^-; (3) RP: $S_2O_3^{2-}$; (4) Stir bar; (5) Sample port.

for filling and draining the source and receiving solutions. Each solution was stirred at optimum speed, while the speed of source phase (SP) was a little faster than RP.

2.3. Vesicular coacervate SUPRASs preparation

A 2:1 molar ratio of decanoic acid and tetrabutylammonium hydroxide mixture in distilled water at pH 7.0 was used for the preparation of vesicular coacervates. In order to have proper SUPRASs, at first a stable suspension of decanoic acid in distilled water at 40˚C was prepared and then Bu_4NOH was added at pH 7.0 (adjusted by NaOH solution). Centrifugation of the resulting mixture for 4,000 rpm at 10 min was applied for dissolution and liquid–liquid phase separation of decanoic acid. The coacervate, standing at the top of the solution, was withdrawn with a syringe and stored in a closed glass vial until use. The prepared SUPRASs were stable at room temperature for more than three months. It should be noted that the coacervate volume required is depended on the amount of decanoic acid used. Bendito and co-workers have already reported a linear relationship between the volume of coacervate and the amount of decanoic acid with a slope of $1.3 \pm 0.2\ \mu L\ mg^{-1}$ [42]. Typically, about 5 mL of the SUPRASs was prepared from 5.15 g of decanoic acid and 3.9 g of tetrabutylammonium hydroxide in 200 mL distilled water (see Fig. 2, upper phase). The density and viscosity of the SUPRASs prepared were evaluated as $0.86\ g\ mL^{-1}$ and 91 mPa s, respectively. Meanwhile, the highly ordered structures of aggregates of SUPRASs provided them with regions of different polarities, which result in variety of interactions with the analytes of interest in their solution [38,39]. In fact, the type of analyte-SUPRASs interactions can be tuned via variations in the hydrophobic or the polar groups of the surfactants used.

Fig. 2. Photograph of decanoic acid coacervate on its suspension, as upper layer.

2.4. SLM system

In preparation of an SLM it is primarily necessary to immobilize an organic solution containing a suitable ion carrier in the pores of a hydrophobic microporous membrane [14–17]. In this study, a Celgard K-256 microporous polypropylene membrane with a thickness of 38 μm, a porosity of 60% and an effective pore size of 0.05 μm (Asahi Chemical Co., Ltd, Osaka, Japan) was used as the supporting membrane for immobilization of DBzDA18C6 dissolved in the SUPRASs prepared. The membrane was cut into circular pieces of 4.0 cm diameter and was preliminary immersed in 5 mL acetone and taken in an ultrasonic bath at 40˚C for 10 min to remove any contaminant. After that, the membrane was socked in the SUPRASs containing DBzDA18C6 at atmospheric pressure over night. It was then taken out of the solution and the excess solution present the surfaces were removed with a filter paper.

3. Results and discussion

Selection of the best conditions for the SLM transport silver ion through a microporous polypropylene membrane system based on the first use of a SUPRASs as membrane solvent was the main objective of this study. Then, based on some preliminary experiments showing the suitability of the system for facilitated transport of silver ion, the important parameters affecting the uphill Ag^+ transport through the SLM system designed were optimized.

3.1. Supramolecular solvent composition

The SUPRASs used in this study was prepared from aqueous mixtures containing protonated (DeA) and deprotonated (De^-) forms of decanoic acid in the presence of tetrabutyl ammonium ion in the micro and nanoscale regimes, as reported before [40]. Here, the possible driving forces for the formation of these vesicular aggregates include the hydrogen bond formation between the carboxylic and carboxylate groups of the protonated and deprotonated forms of decanoic acid, hydrophobic interactions between the hydrocarbon chains of DeA and De^- molecules, and the electrostatic interactions between negatively charged carboxylate group and positively charged Bu_4N^+ ion. It is well known that the carboxylic acid molecules are strongly hydrogen-bonded to each other so that such interamolecular hydrogen bond forces increase the cohesion between molecules and, thus, it seems to be mainly responsible for the drop formation in the reverse micelle- and vesicles-based coacervates [36].

Meanwhile, the sample aqueous solution pH determines the state of DeA and, therefore, it is expected to play an important role in the stability of vesicles in aqueous samples [41]. The experimental results showed that the maximum amount of stable vesicles can be formed at $pH = pK_{a,DA}$ of ~7, in which the decanoic acid and decanoate are present in equimolar amounts. Under such experimental conditions, the DeA-Bu_4N-De vesicles formed are easily separated from the aqueous solution as an immiscible liquid (the SUPRASs) with lower density than water (i.e. 0.86 g mL^{-1} in this case). On the other hand, the vesicular coacervate composition is well known to be mainly depended on the $(DeA+De^-)/Bu_4N^+$ molar ratio (w/w) in the bulk solution [41]. Accordingly, our experimental studied revealed an optimum $(DeA+De^-)/Bu_4N^+$ molar ratio of two is suitable for successful preparation of the SUPRASs of interest. Here, Bu_4N^+ ion acts as a coacervating agent, so that in its absence, only an aqueous suspension of DeA/De^- vesicles is formed, while in its presence large water-immiscible vesicles are produced. This is mainly due to the neutralization of decanoate ions, which eliminates the repulsive electrostatic interactions between De^- anions in the aggregate [40]. However, the prepared SUPRASs showed a decreased stability at higher molar ratios, most probably due to some cation-π interactions between Bu_4N^+ and non-bonded De^- ions.

Finally, the SUPRASs thus prepared and characterized were used as suitable solvent in membrane phase of a SLM for facilitated transport of Ag^+ ion. It was found that, in the membrane phase, the carrier DBzDA18C6 and its Ag^+ ion complex can be easily dissolved in the SUPRASs via formation of proper hydrogen bond, hydrophobic, and π-cation interactions, as schematically shown in Fig. 3. It should be noted that the hydrophobic and polar/charged solutes can be dissolved into the hydrocarbon and polar regions of the amphiphile constituted SUPRAs, respectively, independent of their type. Hydrophobic compounds can interact with SUPRASs via dispersive, dipole–dipole, and dipole-induced dipole interactions and driving forces for the polar compounds extraction are ionic, π-cation, and hydrogen bonding, which is more important than the two other interactions [41,42].

3.2. Effect of nature of carrier solvent in MP on silver ion transport

In SLM membrane systems, a polymer-based hydrophobic microporous support is usually used to separate the aqueous source and RPs. In conventional SLM method, the use of volatile organic solvents of low viscosity which leads to high transport rate is impracticable, mainly because the solvent cannot completely remain in the pores of the solid support during the transport, which resulted in the SLM instability. In addition to non-volatility, the organic solvent used in SLM should be thoroughly immobilized in the pores of support and completely immiscible with water as it

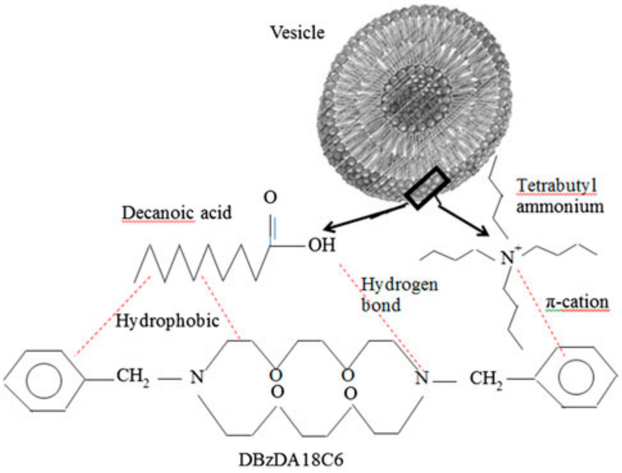

Fig. 3. Schematic representation of the intermolecular forces responsible for dissolution of DBzDA18C6 in decanoic acid vesicles.

serves as a barrier between two aqueous source and RPs. Besides, the solvents for SLMs should also meet four important requirements: (1) low toxicity, (2) low cost, (3) satisfactorily dissolving the ionophore, and (4) ability for efficient extraction of the metal ion–carrier complex and metal ion–carrier–counter ion ionic pair [17]. Based on these parameters, the number of organic solvents suitable for use in SLMs is limited.

In our preliminary experiments, it was found that the transport efficiency of silver ion largely depends on the nature of the organic phase. Since the membrane solvent must have both high dielectric constant and low water-solubility, in order to achieve a highly stable and permeable SLM [15–17], we examined TOL, KS, NPPE, NPOE, OCT, DHE, and SUPRASs (synthesized in our laboratory), as membrane solvents in the SLM. The important properties of these solvents are compared in Table 1 [43–49].

Among the seven selected solvents, the SUPRASs found to be the most suitable solvent for the SLM system (see Fig. 4). Beside of the lower transport efficiency of silver ion, in other organic solvents than the SUPRASs, they have some disadvantages such as notable toxicity (in the cases of TOL, KS, OC, and DHE) and high cost (in the cases NPOE, NPPE, and DHE). The dielectric constant of a solvent is known as a relative measure of its chemical polarity, and polar and non-polar solvents possess high and low dielectric constants, respectively. For instance, water (dielectric constant of 80.1) and n-hexane (dielectric constant of 1.89) are known as polar and non-polar solvents, respectively. But some interactions between solvent and water, like hydrogen bonding, results in unexpected results. For example, dichloromethane and tetrahydrofuran with dielectric constants of 9.08 and 7.52, respectively, have completely different solubilities in water. The former is rather poorly soluble in water, while the latter is completely miscible with water. This is mainly due to hydrogen bonding between water and oxygen atom in tetrahydrofuran [46]. Although polar solvents with high dielectric constants such as NPOE, NPPE, OC, and DHE have high affinity to extract ion-pairs, their high viscosity induces slow transport rates. On the other hand, the polar nature of these solvents results in poor wetting ability for the polymeric support. Although both TOL and KS are non-polar solvents with low dielectric constants and have no favorable extraction properties for ion-pairs, as is seen in Fig. 4, the transport rate of

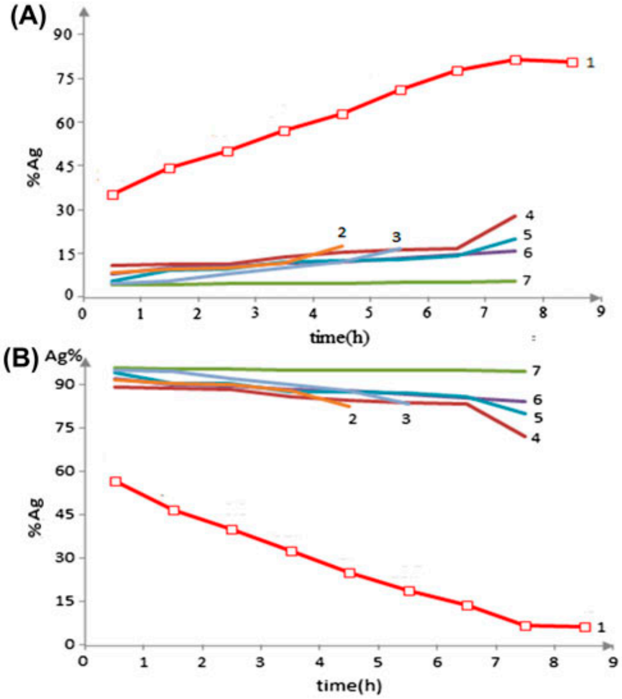

Fig. 4. Effect of the carrier solvent on silver ion transport in the SLM system: (1) SMS, (2) OCT, (3) DHE, (4) TOL, (5) NPOE, (6) NPPE, and (7) KS. (A) %Transported into RP and (B) %Remaining in SP. Conditions: SP, 150 mL of 2 ppm Ag^+, 0.004 M PA at pH 2.8; membrane phase, 3.0×10^{-3} M DBzDA18C6 in different organic solvents; RP, 150 mL of 0.02 M $Na_2S_2O_3$ at pH 5.4.

Table 1
Some properties of the solvents used in this work

Solvent	Density (g mL^{-1})	Viscosity (mPa s)	Polarity[a]	Water solubility (g L^{-1})	Refs.
NPOE	1.04	12.35	P (31.8)	Immiscible	[43,44]
TOL	0.87	0.59	NP (2.4)	0.52	[45]
OC	0.82	7.4	P (10.3)	0.46	[46,53]
DHE	0.79	1.7	P (–)	Immiscible	[48]
NPPE	1.09	7.58	P (29.1)	Immiscible	[4,49]
KS	0.8	1.64	NP (1.8)	Immiscible	[17,46]
SUPRAMSs	0.86	91	Tunable polarity	Immiscible	This work

[a] P: polar; NP: non-polar. Values in parentheses are dielectric constants.

silver ion through the SLM containing TOL is faster and more efficient than that through KS. This can be mainly contributed to the favorable viscosity of TOL. On the other hand, faster transport of solutes through the membrane and more stable SLM can be observed in the presence of organic solvents with lower and higher viscosities in the membrane phase, respectively [45,47,50–53]. The observed superiority of the SUPRASs is due to their high boiling point, complete water-immiscibility, high viscosity, and high tendency in dissolving both DBzDA18C6 and Ag^+-DBzDA18C6-Pic^- ion pair via different interactions between the solutes and the existing binding sites in SUPRASs. As it is seen in Table 1, although SUPRASs possess high viscosity (i.e. 91 mPa s), not only form a stable SLM, but also results in fast transport of silver ion through the SUPRASs-SLM. This is mainly due to the multiple binding sites with different polarities which exist in the vesicles of decanoic acid [40]. Besides these relative advantages, the SUPRASs can be easily prepared and its preparation is neither expensive nor time-consuming. Meanwhile, the environmentally friendly nature of the SUPRASs has made them excellent candidates as organic membrane solvent in the SLM systems.

3.3. Effect of nature and concentration of stripping agent on silver ion transport

As expected, the nature and composition of ligand used as scavenger in the RP solution for the release of silver ion from MP into the RP are known to have a significant effect on both efficiency and selectivity of the transport [13]. The percentages of silver ion transported to RP and remaining in MP and SP in the presence of different potential stripping agents, under similar experimental conditions, are listed in Table 2. As seen, the use of thiosulfate as a silver ion receptor and SDS as MP/RP interface modifier in the strip solution caused a large enhancement in the efficiency and selectivity of silver ion transport, as compared with NaCN, KSCN, and NH_3 as stripping agents. This is corresponded to the previous results reported in the literature [1,2,4–6,14,15].

In the next step, the effect of $Na_2S_2O_3$ concentration in the RP, in the range of 0.02–0.7 M, was studied and the results are shown in Fig. 5. As seen, the transport efficiency was increased with increasing thiosulfate concentration up to 0.5 M, and diminished at higher thiosulfate concentration. The observed decrease at >0.5 M could possibly be due to reaching a saturation value, which results in decreased amount of free $(S_2O_3)^{2-}$ ions necessary for its efficient complex formation with the silver ions in the MP/RP interface [1]. It should be noted that the amount of silver transport was found to be negligible in the absence of a metal ion receptor in the receiving solution. Moreover, the influence of RP pH, in the range of 6–10, on silver ion transport was studied and negligible effect on the cation transport was observed [17].

3.4. Effect of nature and concentration of carrier on silver ion transport

The ligands to be used as suitable Ag^+ ion carriers in membrane transport studies are expected to fulfill the following conditions. They should behave selectively for Ag^+ ion over other metal ions, they should possess rapid exchange kinetics and, finally, they should be lipophilic in nature to avoid leaching into the aqueous source and RPs. The complexing agents containing sulfur and nitrogen coordination sites are known to possess high affinities toward d^{10} transition metal ions such as Ag^+. On the other hand, in the case of macrocyclic ligands, the cavity diameter of ligand and ionic size of the cation should be approximately close to each other to a form quite stable 1:1 complex in the MP [14–17]. In the case of metal ions with dimensions that have best match with the ligand cavity, a more stable complex at a molar ratio of unity is achieved. This is mainly due to the enthalpy term indicating greater electrostatic interactions between

Table 2
Effect of nature stripping agent in RP on Ag^+ transport. Conditions: SP, 150 mL of 2 ppm Ag^+ and 4.0×10^{-3} M picric acid at pH 4; MP, 1.0×10^{-3} M DBzDA18C6 in SUPRSs; RP, 150 mL of 0.5 M of each stripping agent; time of transport 1 h

Stripping agent	Ag transported to RP (%)	Ag remaining in SP (%)	Ag remaining in MP (%)
$Na_2S_2O_3$, pH 5.4	98.3	0.7	1.0
NaCN, pH 10.7	55.0	24.4	20.6
KSCN in 0.2 M H_2SO_4, pH 0.9	25.2	48.9	25.9
NH_3, pH 10.9	17.4	16.6	66.0

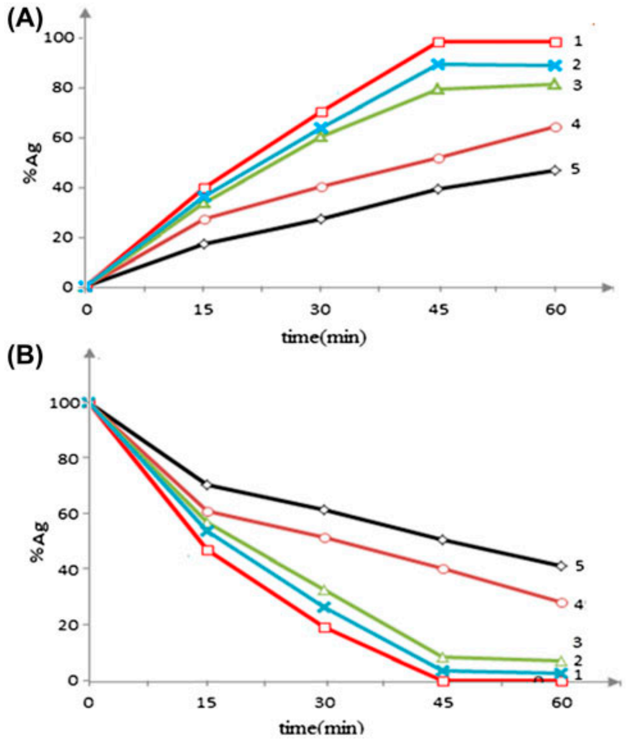

Fig. 5. Effect of sodium thiosulfate concentration in RP on silver ion transport in the SLM system: (1) 0.5 M, (2) 0.7 M, (3) 0.3 M, (4) 0.1 M, and (5) 0.02 M. (A) %Transported into RP and (B) %Remaining in SP. Conditions: SP, 150 mL of 2 ppm Ag^+, 8.85×10^{-5} M picric acid at pH 4.0; membrane phase, 8.0×10^{-3} M DBzDA18C6 in SUPRASs; RP, 150 mL of varying concentration of $Na_2S_2O_3$ (0.02–0.7 M) at pH 5.4.

donating sites in crown ether, as a host, and acceptor orbitals of cation, as a guest [54]. In this work, we studied the use of five macrocyclic derivatives of 18-crown-6, with the close cavity radii of about 1.34–1.43 Å [54,55], suitable for Ag^+ ion with a radius of 1.15 Å, but with different donating atoms and different cavity substituents, namely DBzDA18C6, DA18C6, DC18C6, DB18C6 and B18C6, and the results are summarized in Table 3.

As can be seen from Table 3, among different macrocyclic carriers studied, the use of aza-substituted macrocycles (i.e. DBzDA18C6 and DA18C6) resulted in a considerable increase in transport efficiency of the membrane system for Ag^+ ion over other 18-crown derivatives. This is presumably related to the increased stability of the complexes of Ag^+ ion, as a soft acid, with the aza-substituted crown ethers, containing two donating nitrogen atoms as soft bases [6,43,56]. While, due to the weak interactions between hard nature of oxygen donating atoms of DC18C6, DB18C6, and B18C6 and the soft character of the cation, the transport efficiency of the silver ion with these ligands is significantly diminished. However, despite the formation of stable complexes with transition metal ions, DA18C6 is not an effective carrier for these cations, compared to DBzDA18C6, because of the considerable solubility of this ligand and its complexes in aqueous phases [4]. Such high water solubility of aza-substituted crowns can be overcome by appending some lipophilic groups, such a benzyl group, to the crown ether moiety [54]. Thus, DBzDA18C6 containing two lipophilic benzyl groups on its macrocyclic cavity were used as a suitable selective carrier for silver ion transport through the designed SLM.

In the next step, the influence of DBzDA18C6 concentration on the permeation of silver ion was investigated. The supported membrane was soaked in SUPRASs solutions of the carrier with varying concentrations, in the range of 3.0×10^{-3}–1.0×10^{-2} M, and the transport procedure was followed. Fig. 6 shows the influence of the concentration of DBzDA18C6 in the SUPRASs membrane on the transport efficiency of silver ion. As it is seen from Fig. 6, the efficiency of silver transport increases with increasing carrier concentration in the MP up to 8.0×10^{-3} M. Beyond this limit, the transport efficiency of silver ion is decreased slightly. A similar behavior for the effect of carrier concentration on the SLM transport has already been reported in the literature [15,45]. This could be due to more difficult release of the cation into the RP as a result of its firm bounding to the carrier, and/or the increased viscosity of the SUPRASs membrane phase with increasing carrier concentration.

3.5. *Effect of picric acid concentration in SP on silver ion transport*

In this work, picrate ion was selected as a lipophilic counter anion in SP, which can form a stable neutral ion pair with positively charged Ag^+-DBzDA18C6 complex, suitable for its quantitative extraction into the MP [14–17]. Then, the influence of the picric acid concentration in the SP, in the range of 1.85×10^{-5}–4.00×10^{-3} M, on the transport of silver ion was investigated and the results are shown in Fig. 7. As it is seen from Fig. 7, in the absence of picric acid in the SP, the silver transport efficiency is relatively low. While, the efficiency of silver transport increases with increasing picric acid concentration up to 8.85×10^{-5} M. However, a further increase in the concentration of picric acid (up to 0.004 M) resulted in a pronounced decrease in the percentage of silver transport. This is most probably due to the competition of picric acid itself with silver nitrate for transport

Table 3
Effect of nature of carrier in MP on Ag^+ transport. Conditions: SP, 150 mL of 2 ppm Ag^+ and 4.0×10^{-3} M picric acid at pH 4; MP, 1.0×10^{-3} M of each carrier in SUPRS; RP, 150 mL of 0.5 M $Na_2S_2O_3$ at pH 5; time of transport, 1 h

Carrier	Ag transported to RP (%)	Ag remaining in SP (%)	Ag remaining in MP (%)
DBzDA18C6	98.1	0.66	1.24
B18C6	14.3	66.7	19
DA18C6	65.3	22.1	12.6
DB18C6	8.7	69.8	21.5
DC18C6	27.4	46.7	25.9

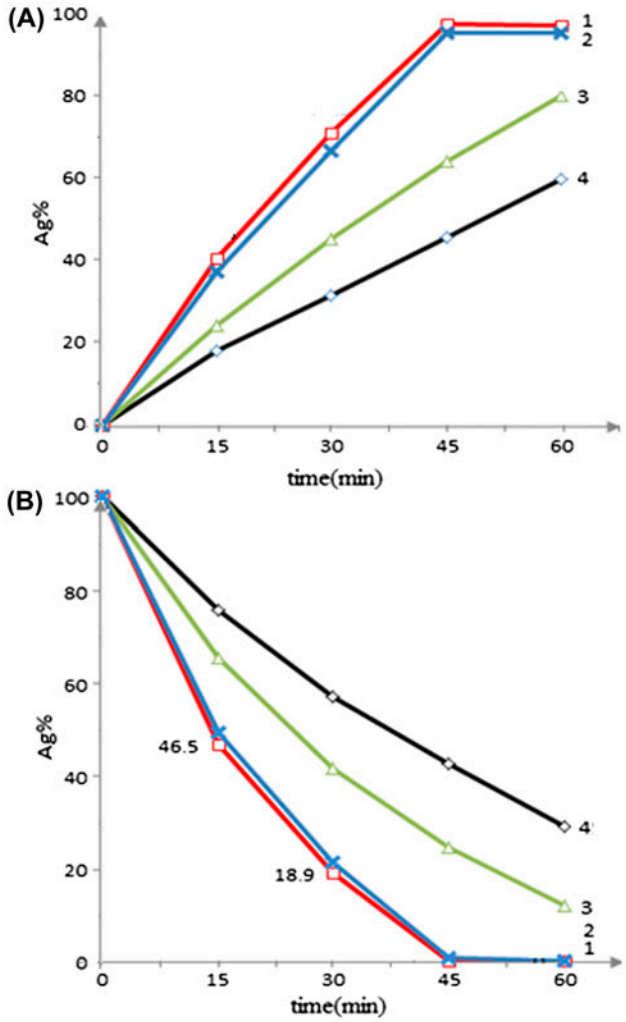

Fig. 6. Effect of DBzDA18C6 concentration in MP on silver ion transport in the SLM system: (1) 0.008 M, (2) 0.010 M, (3) 0.005, and (4) 0.003. (A) %Transported into RP and (B) %Remaining in SP. Conditions: SP, 150 mL of 2 ppm Ag^+, 8.85×10^{-5} M picric acid at pH 4.0; membrane phase, varying concentration of DBzDA18C6 in SUPRASs; RP, 150 mL of 0.5 M $Na_2S_2O_3$ at pH 5.4.

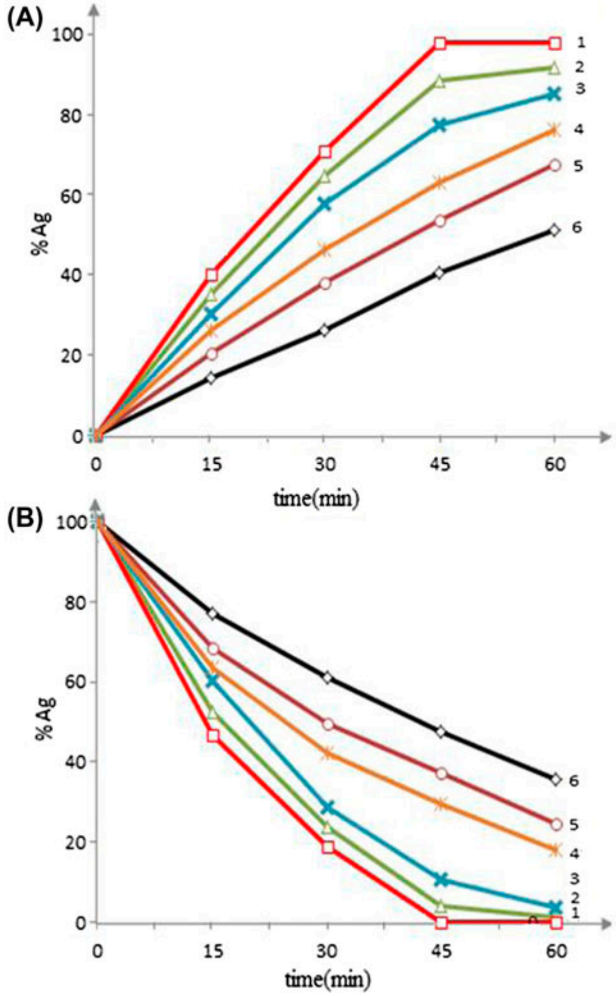

Fig. 7. Effect of picric acid concentration on silver ion transport in the SLM system: (1) 8.85×10^{-5} M, (2) 6.85×10^{-5} M, (3) 1.85×10^{-4} M, (4) 4.00×10^{-3} M, (5) 1.85×10^{-5} M, and (6) 0.00 M. (A) %Transported into RP and (B) %Remaining in SP. Conditions: SP, 150 mL of 2 ppm Ag^+, varying concentration of picric acid at pH (4.0–2.8); membrane phase, 8.0×10^{-3} M DBzDA18C6 in SMS; RP, 150 mL 0.5 M $Na_2S_2O_3$ at pH 5.4.

through the SLM system. The occurrence of such ion aggregate transport was also supported by the accumulation of a significant amount of picric acid in RP after the course of the transport experiment [14]. On the other hand, picrate ions can be easily dissolved in vesicular and reverse micelle of decanoic acid, so that there should be a strong competition between the transport of $AgDBzDA18C6^{+}pic^{-}$ ion pair and picric acid through the SLM at higher concentrations.

3.6. Time dependence of SLM transport

Fig. 8 shows the percentage of silver ion remaining in the SP and membrane MP phases and that transported into the RP, in the course of Ag^{+} transport through the SLM system designed, under optimal experimental conditions. It is quite obvious that both the extraction and release of Ag^{+} ion from the SP into the MP and RP phases occur very quickly so that the transport rate is fast and the transport process is completed after a short time of about 45 min.

Table 4 compared the transport efficiency and the time of silver transport through the proposed SLM and those of some published SLM systems in the literature [1,12–15,17,56–58]. It is obvious that, while the efficiency of silver ion transport of our SLM system is among the best cases, its time of transport is much lower than that of all cases summarized in this table. On the other hand, since the hydrophobic polymeric support could be completely wet with the SIUPRASs used, through the hydrophobic interactions, the new SLM is more stable than other organic SLMs.

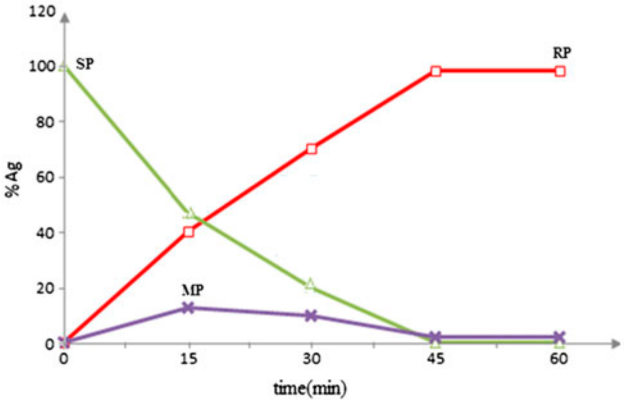

Fig. 8. Time-dependence of silver ion transport through the SUPRASs-SLM. Conditions: SP, 150 mL of 2 ppm Ag^{+}, 8.85×10^{-5} M picric acid at pH 4.0; membrane phase, 8.0×10^{-3} M DBzDA18C6 in SUPRSs; RP, 150 mL of 0.5 M $Na_2S_2O_3$ at pH 5.4.

3.7. The SLM stability

It is noteworthy that, in spite of their excellent advantages, the SLM systems suffer from instability with time. This is mainly due to the gradual bleeding of the carrier and/or membrane solvent from the MP, which can strongly influence both the flux and selectivity of the membrane [22]. In order to investigate the stability of the SLM system designed, the stirring rates of aqueous source and RPs were varied in the range of 350–600 rpm and negligible differences in Ag^{+} ion transport into RP and remaining in SP between runs were observed, supporting the high stability of the SLM used [54]. To obtain an experimental clue about the membrane stability, a single membrane was used five times for transport experiments, via the repeated-run method, after keeping it for 10 min in an acetone ultrasonic bath at 40°C, between the runs, and the results are shown in Fig. 9. As it can be seen in Fig. 9, there are no significant differences in transport efficiency of sliver ion through the SLM between the first and fifth runs. Therefore, a thoroughly stable SLM is obtained using SUPRASs as the MP solvent. This is mainly due to the promising characteristics of SUPRASs including high water-immiscibility low vapor pressure and high tendency to dissolve the carrier and its metal ion complex and high wet-ability of the polymeric support. In fact, the unexpectedly high viscosity of the prepared SUPRASs (i.e. 91 mPa s) greatly hinders the diffusion of the dissolved silver ion carrier DBzDA18C6 from micron pores of the supported membrane into the surrounding aqueous phases and, thus, results in the formation of a highly stable SUPRASs-SLM system. It should also be noted that the SUPRASs prepared by decanoic acid vesicles and reverse micelles are quite environmentally friendly solvents. This is because of their water-immiscibility, non-volatility, and non-flammability [40].

3.8. The SLM selectivity

The SLM selectivity is an effective parameter that allows for the evaluation of the purification degree of a species with respect to others. The selectivity of the SLM system designed for the transport of Ag^{+} ion over other transition and heavy metal ions, including Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Cr^{3+}, present at equimolar concentrations in four different mixtures in the SP solution, is illustrated in Table 5. As seen, none of the metal ions used interfere with the transport of silver ion by the SLM system proposed. The high selectivity of silver transport over the other cations studied is mainly due to the increased affinity of the carrier DBzDA18C6 for Ag^{+} ion over other

Table 4
Comparison of the proposed method with other SLM methods developed for silver ion transport

Source phase	Receiving phase	Membrane phase (carrier/solvent)	Transport Ag^+ into RP (%)	Time of transport	Refs.
Ag^+ in 1 M HNO_3	1.5 M KCN	Triethanolamine (TEA)/cyclohexanon	>99	5 h	[12]
Ag^+ in 0.015 M HNO_3	0.08 M $Na_2S_2O_3$	DC18C6/toluene	81	240 min	[1]
Ag^+ in 0.75 M HNO_3	1 M NH_3	Tri-n-dodecylamine/ cyclohexane	98	200 min	[13]
Ag^+ in 0.008 M picric acid	0.015 M $Na_2S_2O_3$	Calix[4]pyrole/kerosene	97	75 min	[17]
Ag^+ in 10^{-4} M picric acid	0.03 M $Na_2S_2O_3$	Mixed aza-thioether crown containing a 1,10-phenantroline sub-unit/nitrophenyloctyl ether (NPOE)	98	3 h	[15]
Ag^+ in 10^{-3} M picric acid	0.01 M $Na_2S_2O_3$	Hexathia-18C6/NPOE	98	3 h	[14]
Ag^+ at pH 6	1 M HNO_3	Thiacalix[4] arene/NPOE	23	24 h	[56]
Ag^+ in 0.1 M HNO_3	0.5 M $Na_2S_2O_3$	APTS4(podand)/m-chlorotoluene	40	8 h	[57]
Ag^+ in 0.1 M CN^- as $Ag(CN)_3^{2-}$ at pH 11	Distilled water	K^+–DB18C6/mixture of ethanol and chloroform	35	6 h	[58]
Ag^+ in 8.85×10^{-5} M picric acid	0.5 M $Na_2S_2O_3$	DBzDA18C6/SUPRASs	98	45 min	This study

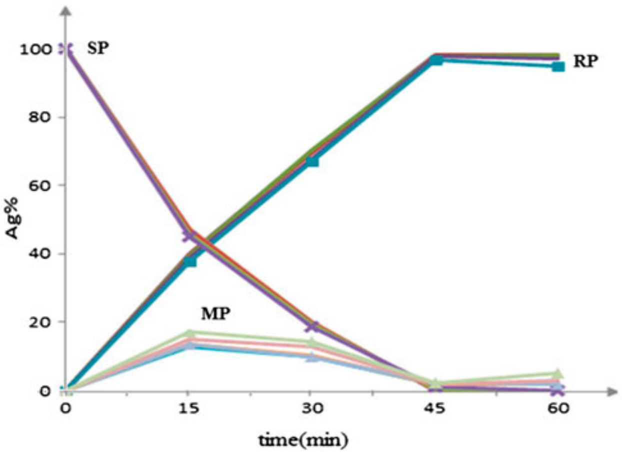

Fig. 9. Results of five repeated transport experiments with the same membrane phase. Conditions: SP, 150 mL of 2 ppm Ag^+, 8.85×10^{-5} M picric acid at pH 4.0; membrane phase, 8.0×10^{-3} M of DBzDA18C6 in SUPRASs; RP, 150 mL of 0.5 M $Na_2S_2O_3$ at pH 5.4.

cations studied [54,55], With the exception of Pb^{2+} ion with size of 1.19 Å, other cations mentioned in Table 5 (i.e. Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cr^{3+}, and Ni^{2+} ions) possess smaller ionic radii (over the range of 0.63–0.95 Å) than that of Ag^+. Silver ion, as a larger cation in comparison of others, is able to coordinate more donor atoms inside the cavity of DBzDA18C6, which leads to larger stability constant and higher selectivity over the smaller ones. On the other hand, smaller cations with larger ionic charges (i.e. 2+ and 3+) can be solvated more strongly and, in general, complexes formed with macrocycles are less stable than those formed by the single charged larger ones [54]. Although Pb^{2+} ion with a proper ionic radius can fit inside the cavity of DBzDA18C6, its complex with DBzDA18C6 is not as strong and selective as $AgDBzDA18C6^+$ complex. This is significantly attributed to the more hard nature of lead ion incorporating with the soft nature of two nitrogen donor atoms inside the carrier [55]. Moreover, the use of thiosulfate as a selective silver ion receptor in the RP, as compared with other cations, causes a pronounced increasing effect on the efficiency and selectivity of silver ion released into the RP [1].

3.9. Transport mechanism

Transport of silver ions using the proposed SUPRASs-SLM system obeys a facilitated counter ion co-transport mechanism (Fig. 10). As it is seen from

Table 5
Amount of cation transported from different cation mixtures through the SUPRA SLM under optimal experimental conditions mentioned in Fig. 9

Mixture	M transported to RP (%)	M remaining in SP (%)	M remaining in MP (%)
Mixture 1			
Ag^+	96.8	0	3.2
Pb^{2+}	0	91.7	8.3
Cu^{2+}	1.01	98.09	0.9
Mixture 2			
Ag^+	96.4	0	3.6
Mn^{2+}	0	99.2	0.8
Ni^{2+}	0.5	99.3	0.7
Mixture 3			
Ag^+	96.7	0	3.3
Pb^{2+}	0	97.4	2.6
Co^{2+}	0	98.9	1.1
Cd^{2+}	1.3	98.0	0.69
Mixture 4			
Ag^+	96.8	0	3.2
Cr^{3+}	0	98.7	1.3
Cu^{2+}	1.3	97.8	0.9
Ni^{2+}	0	98.9	1.1

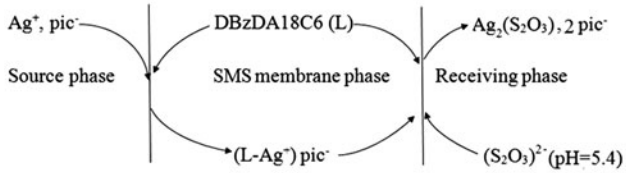

Fig. 10. Mechanism of the SLM system for transport of silver ions.

Fig. 10, the mechanism of silver ion transport can be explained as follows: (1) the Ag^+ ion forms a single charge complex with the membrane carrier (DBzDA18C6) at the interface of SP-MP, (2) in the presence of picrate ion as a suitable counter ion, a stable neutral $AgDBzDA18C6^+$ Pic^- ionic-pair is formed in MP and preferentially diffuses across the organic membrane. It should be noted that, since the SUPRASs possess the ability to dissolve compounds with a wide range of different polarities, the solubility and diffusion of the complexed silver ion pair in MP will be enhanced [37–40], (3) at the MP-RP interface, the release of silver ion is facilitated via formation of a stable and selective $\left[Ag(S_2O_3)_2\right]^{3-}$ complex. This stage is supported by the fast formation of a yellow color in the RP after transport, (4) finally, the free carrier (DBzDA18C6) diffuses back across the SMS membrane and the silver ion transport cycle starts again.

4. Conclusions

In this work, for the first time, we explored the suitability of SUPRASs composed of vesicles of decanoic acid as a potential solvent in SLM containing DBzDA18C6 as a selective carrier for transport of Ag^+ ion. The SUPRASs possess a unique array of physicochemical properties which make them very attractive for replacement with organic solvents in analytical separations. These solvents combine the capability of solubilizing solutes with wide polarity ranges and the ability to achieve high transport efficiencies in short periods of time, mainly due to the mixed-mode mechanisms and multiple binding sites that they can provide. The vesicular coacervate phase used in this work possesses a relatively high viscosity and low vapor pressure, which make its use very attractive in obtaining stable SLM systems. Moreover, using SUPRASs as membrane phase, the need for using toxic and expensive organic solvents is eliminated. On the other hand, since the SUPRASs can dissolve the lipophilic ion carrier ligands such as crown ethers with different polarities, it can be a promising solvent in SLM systems for the selective and efficient ion transport over a short period of time.

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