PHYSICOCHEMICAL INVESTIGATION OF SYSTEMS AND PROCESSES

Highly Efficient and Selective Membrane Transport of Silver(I) Using 15-Crown-5 as a Selective Ion Carrier

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Abstract—Selective transport of Ag^+ cation through a nitrobenzene bulk liquid membrane with 15-crown-5 as an efficient carrier was studied. The maximum transport value of $88.02 \pm 0.78\%$ was observed for Ag^+ ion after 8 h at Ag^+ concentration of 4×10^{-4} M. The selectivity and efficiency of Ag^+ cation transport from aqueous solutions containing equimolar amounts of Cr^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} cations were also investigated.

The rapidly increasing environmental consciousness has led to significantly tightened environmental standards in most of countries. The production of hazardous industrial wastes, especially of those containing heavy metals, will become a serious problem all over the world in the near future. It is suggested that silver might pose a potential risk as water pollutant because of the lack of recycling of mixed silver [1].

Liquid–liquid extraction and separation of silver(I) ion in the presence of classical [2] and macrocyclic ligands [3] is reported in the literature. However, a considerable limitation in traditional solvent extraction processes is that a large amount of high-purity solvents (and carriers) is required, especially when processing dilute solutions. Additional concern is the disposal of the solvents used, which creates a serious environmental problem. Among the separation techniques, ion transport is a selective, efficient and simple method. Selective transport of transition metal cations through liquid membranes attracts growing researchers' attention [4]. The principles of selective transport of cations were formulated in [5].

Among three basic types of liquid membranes, bulk liquid membranes, emulsion liquid membranes, and supported liquid membranes, bulk liquid membranes appear to be the most easily operated. The latter two types of liquid membranes have been studied extensively. Their main drawback is limited stability. Bulk liquid membranes, in turn, have simple configuration and provide reproducible experimental data.

A number of synthetic ionophores such as crown ethers, cryptands, and podands are known. They transport metal ions selectively across various liquid membranes and are widely applied in separation and in construction of ion-selective electrodes [6]. Crown ethers are the most widely used carriers in liquid membrane systems. Due to high selectivity of crown ethers, they have been extensively used as extractants in solvent extraction and as ion carriers in transport across liquid membranes [7–9].

Despite the biological and industrial importance of silver ions, information about their transport across liquid membranes is scarce as compared to other transition metal ions [10]. Studies on Ag^+ selective membrane transport using various carriers are few [11]. Macrocyclic reagents with S, N, and O donor atoms are used as selective carriers for Ag^+ [12]. Since their use in commercial processes may be too expensive or impossible at all because of the complexity of their syntheses, interest in using simple complexants for the selective transport of silver ions increases.

15-Crown-5 has not been used for previously for

the transport of cations through bulk liquid membrane systems. In this paper, we report on efficient and selective transport of Ag$^+$ cations through a bulk nitrobenzene membrane containing 15-crown-5 as specific ion carrier.
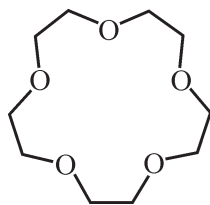
15-Crown-5

The parameters influencing the efficiency of the Ag$^+$ transport, such as the type and concentration of stripping agent in the receiving phase, carrier concentration in the membrane phase, concentration of picric acid as counteranion in the source phase, type of the membrane solvent used, pH of the receiving and source phases, volume of the receiving phase, and equilibrium time of transport process, have been optimized.

EXPERIMENTAL

Ni(NO$_3$)$_2$, Pb(NO$_3$)$_2$, Co(NO$_3$)$_2$, and Cr(NO$_3$)$_3$ were purchased via BDH Chemicals Catalog; Cd(NO$_3$)$_2$ was purchased from Riedel. AgNO$_3$, Zn(NO$_3$)$_2$, Ch$_3$COOH, CH$_3$COONa, HCOOH, NaOH, picric acid, sodium thiosulfate, sodium hydroxide, sodium sulfite, sodium pyrophosphate, EDTA, thiourea, and sodium thiocyanate (Merck) were used without additional purification.

Nitrobenzene, dichloromethane, chloroform, and 1,2-dichloroethane (Merck) were of the highest purity grade. All aqueous solutions were prepared using double-distilled deionized water.

The Ag(I) content was determined with a Shimadzu AA-670 atomic absorption spectrometer (AAS) equipped with an Ag hollow cathode lamp.

The pH measurements were made with a Metrohm 827 pH-meter using a combined glass electrode. A bulk liquid membrane cell was used in all transport experiments (Fig. 1).

Bulk liquid membrane transport experiments were performed at ambient temperature in a cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside diameter 2 cm). The inner aqueous source phase contained AgNO$_3$ (10 mL, 4.0 × 10^{-3} M) and picric acid (8.0 × 10^{-3} M). The outer aqueous receiving phase was a Na$_2$S$_2$O$_3$ solution (5 mL, 1.0 × 10^{-3} M). The membrane
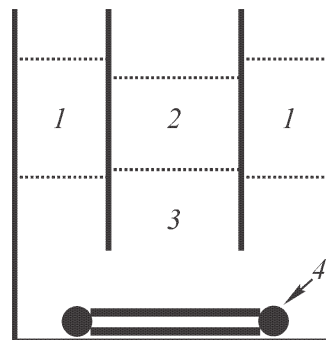

Fig. 1. Schematic of the bulk type liquid membrane cell used. (*1*) Receiving phase, (*2*) source phase, (*3*) bulk liquid membrane, and (*4*) magnetic stirrer.

phase contained 50 mL of a 5 × 10^{-4} M solution of 15-crown-5 (15C5) as carrier in an organic solvent. The membrane phase was magnetically stirred by a Teflon-coated magnetic bar. Under these conditions, not only the mixing is efficient, but also the interfaces between the organic membrane and the two aqueous phases remain flat and are well defined. The data points reported are averages of at least three replicate measurements.

RESULTS AND DISCUSSION

Preliminary, to evaluate the suitability of 15C5 as phase-transfer catalyst to separate Ag$^+$ cation from bulk liquid membrane system, we examined the dependence of the molar conductivity (Λm) on the ligand-to-cation molar ratio ([L]$_t$/[M]$_t$) by conductometric titration in acetonitrile at 25°C. The formation constant of the 15C5–Ag$^+$ complex, K_f, was calculated from the dependence of Λm on [L]$_t$/[M]$_t$ using GENPLOT program [13]; log K_f was found to be 2.76 ± 0.07. The value of log K_f indicates that 15C5 is a suitable carrier for selective transport of Ag$^+$ cation through the organic membrane.
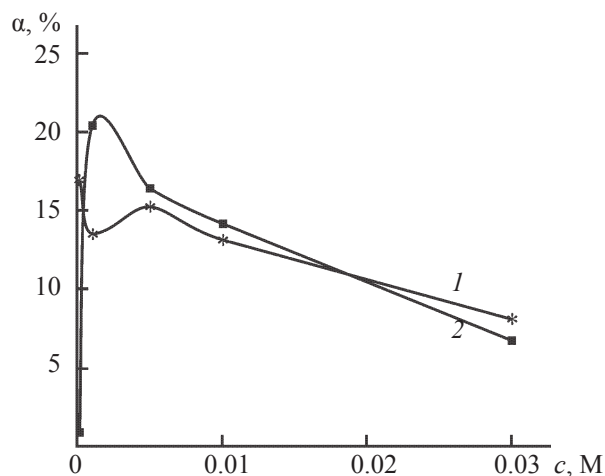
According to [14], the cavity size of 15-crown-5 is 1.7–2.2 Å, and the Ag$^+$ ion with an ionic radius of 1.26 Å well fits in the cavity of 15C5. Therefore, the Ag$^+$ ion forms a fairly strong complex with this ligand, which ensures higher transport efficiency for this metal cation compared to the other metal cations.

The solvent characteristics determine not only the lifetime of the liquid membrane, but also the solubility of the complex formed and the penetration coefficient. The energy effect in complex formation depends not only on the physical and chemical properties of the components

of complexes, but also on the properties of the medium in which the process takes place. Therefore, the effect of the organic membrane solvent on the efficiency and kinetics of Ag+ transport was studied. Apparently, the polarity and viscosity of the organic phase strongly affect the ion transport.

The transport efficiency of Ag+ cation with 15-crown-5 as ion carrier varies in the order nitrobenzene > dichloromethane > chloroform > 1,2-dichloroethane. This result can be attributed to higher polarity of nitrobenzene ($\mu = 4$), leading to acceleration of the ion transfer in this solvent compared to the other three solvents ($\mu = 1.55$, 1.35, and 1.86, respectively). Probably, nitrobenzene solvates the 15C5–Ag+ complex in the membrane phase more strongly, thus ensuring higher transport rate. On the other hand, the acceptor number of nitrobenzene (AN = 14.8) is lower than those of dichloromethane (20), chloroform (23.1), and 1,2-dichloroethane (16.7). Therefore, the ligand is weakly solvated in this solvent, which enhances the stability of the 15C5–Ag+ complex in nitrobenzene compared to the three other organic solvents.

The transfer of metal ions into the organic phase is also influenced by the viscosity of the organic solvent. The decrease in Ag+ transport efficiency in the order dichloromethane > chloroform > 1,2-dichloroethane can

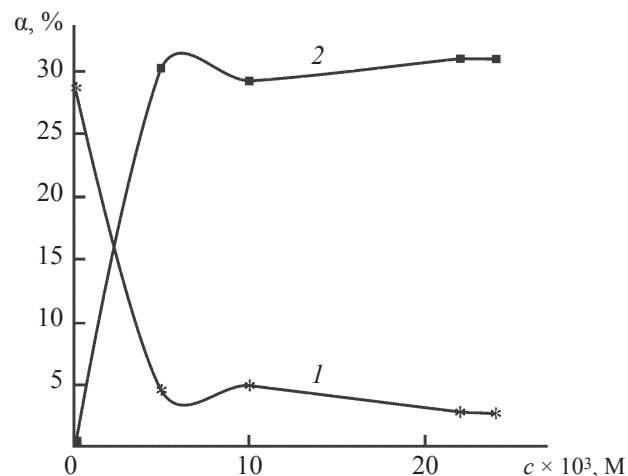be attributed to an increase in the viscosity in this series ($\eta = 0.39$, 0.58, and 0.73, respectively), decelerating the transport of Ag+ ions.

It was found that the permeability of the membrane system to Ag+ cation can be strongly influenced by the nature of the stripping ligand in the receiving phase. The percentages of the silver ions transported in the presence of different stripping agents under similar experimental conditions are listed in Table 1.

As expected, the nature and composition of the stripping agent in the receiving phase significantly affect the efficiency and selectivity of the transport process. Addition of sodium thiosulfate to the receiving phase increased the extent of silver transport significantly. The influence of the concentration of thiosulfate ion in the receiving phase on the silver(I) ion transport was investigated. The results are shown in Fig. 2. The effect of the other tested stripping agents on the transport of Ag+ ions was less significant. The optimum concentration of sodium thiosulfate in the receiving phase was found to be 0.001 M (Fig. 2).

High selectivity and efficiency of transport can only be achieved by properly selecting the carrier and its concentration. An increase in the carrier concentration will increase the transport efficiency, but the amount of the expensive carrier should be optimized to avoid its excessive consumption. The effect of the 15-crown-5

Fig. 2. Influence of the concentration c of thiosulfate ions in the receiving phase on the Ag+ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag+, 8.0×10^{-3} M picric acid, pH 4; liquid membrane phase: 50 mL of 0.5×10^{-3} M carrier in nitrobenzene; receiving phase: 5 mL of thiosulfate solution, pH 3; time of transport: 8 h. (*1*) Source phase and (*2*) receiving phase; the same for Figs. 3–7. (α) Recovery of Ag+ ions; the same for Figs. 3–7.

Fig. 3. Influence of the 15-crown-5 concentration c on the Ag+ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag+, 8.0×10^{-3} M picric acid, pH 4; liquid membrane phase: 50 mL of carrier solution in nitrobenzene; receiving phase: 5 mL of 10×10^{-3} M thiosulfate, pH 3; time of transport: 8 h.
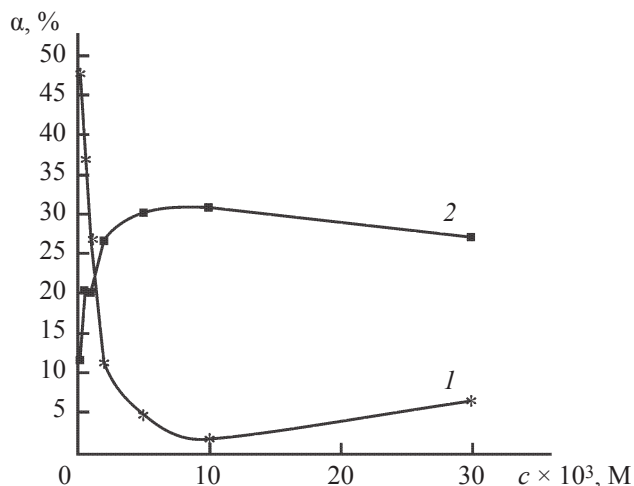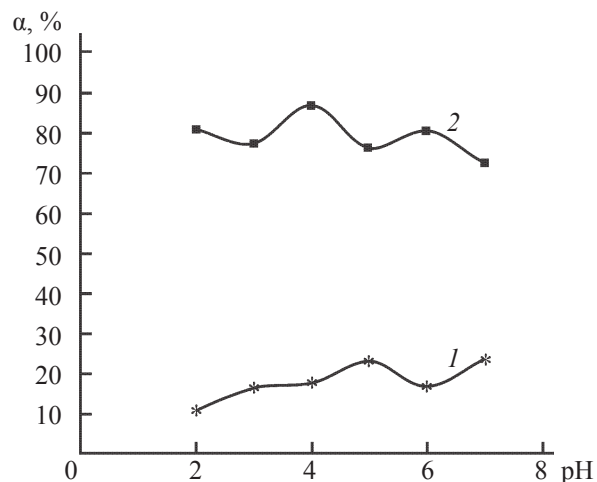
Fig. 4. Influence of the picric acid concentration c on the Ag$^+$ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag$^+$, picric acid, pH 4; liquid membrane phase: 50 mL of 0.5×10^{-3} M carrier in nitrobenzene; receiving phase: 5 mL of 10×10^{-3} M thiosulfate, pH 3; time of transport: 8 h.

Fig. 5. Influence of pH of the source phase on the Ag$^+$ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag$^+$, 8.0×10^{-3} M picric acid; liquid membrane phase: 50 mL of 0.5×10^{-3} M carrier in nitrobenzene; receiving phase: 5 mL of 10×10^{-3} M thiosulfate, pH 3; time of transport: 8 h.
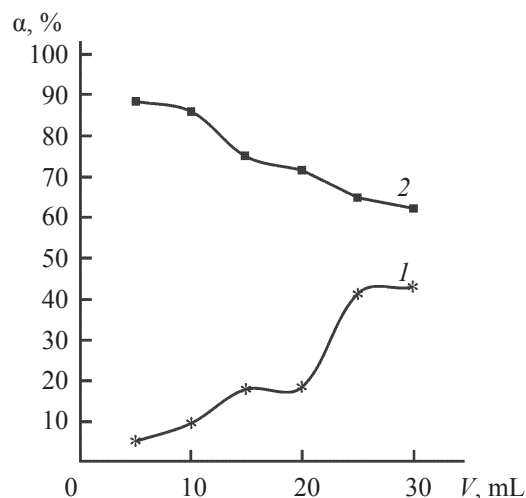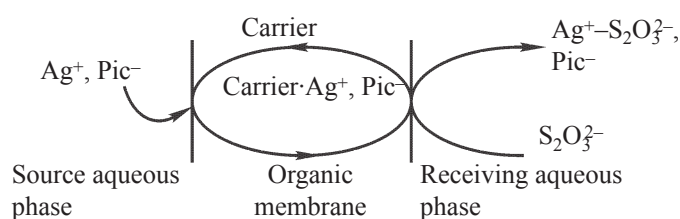

Fig. 6. Influence of the volume V of the receiving phase on the Ag$^+$ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag$^+$, 8.0×10^{-3} M picric acid, pH 4; liquid membrane phase: 50 mL of 0.5×10^{-3} M carrier in nitrobenzene; receiving phase: 10×10^{-3} M thiosulfate, pH 3; time of transport: 8 h.

concentration in the organic membrane phase on the transport efficiency of Ag$^+$ cation was studied (Fig. 3). As can be seen, the increase in the 15-crown-5 concentration in the membrane phase leads to an increase in the recovery of Ag$^+$ cations. The transport efficiency reached a maximum at a 15-crown-5 concentration of 4×10^{-3} M.

As shown earlier, the efficiency of the metal ion transfer from an aqueous solution into an organic phase not only depends on the cation type, stripping agent, and carrier concentration, but also can be influenced by the counteranion with which the 15C5–Ag$^+$ complex passes into the organic phase. Addition of picric acid to the source phase increased the Ag$^+$ cation transport. As seen from Fig. 4, the efficiency of the Ag$^+$ cation transport increases with an increase in the picric acid concentration up to an optimum value (10×10^{-3} M), after which the transport efficiency decreases, probably because of the competing effect of picric acid on the Ag$^+$ cation transport.

The influence of pH of the source and receiving phases on the Ag$^+$ transport efficiency was studied in the pH range 2–7. The maximum Ag$^+$ transport occurs at pH 4 for both the source and receiving phases (Fig. 5). This pH value was adjusted with CH$_3$COOH/CH$_3$COONa buffer solution. At lower and higher pH values, the transport efficiency decreases. At decreased

pH values, this may be due to protonation of the carrier in the membrane phase, leading to washout of the carrier from the membrane phase. Also, the deprotonation of picric acid becomes hindered. Furthermore, thiosulfate ion decomposes in strongly acidic solutions.

The volume of the receiving phase was also optimized. As seen from Fig. 6, the optimum volume of the receiving phase is 5 mL.

Scheme. Mechanism of the Ag$^+$ cation transport

The amount of Ag$^+$ ions transported through the bulk liquid membrane increased with time in the course of the first 8 h (Fig. 7). By this time, 88% of the Ag$^+$ ions were transported to the receiving phase, and beyond this time the degree of transport changed insignificantly. The mean degree of Ag$^+$ transport in 8 h in five replicate experiments was 88.02 ± 0.78 %. The relative standard deviation was found to be 0.78%.

The selectivity of the transport of Ag$^+$ ions through
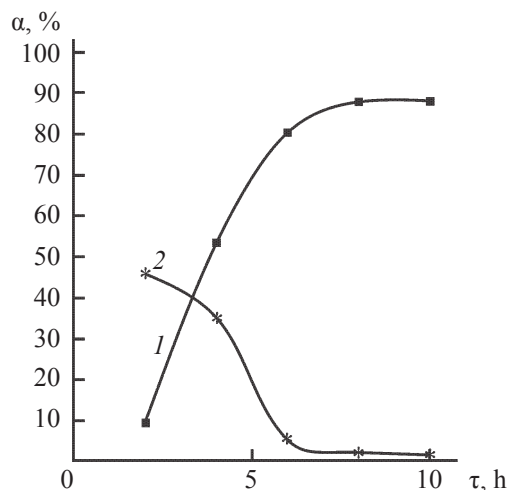
Fig. 7. Influence of time τ on the Ag$^+$ cation transport. Source phase: 10 mL of 4.0×10^{-4} M Ag$^+$, 8.0×10^{-3} M picric acid, pH 4; liquid membrane phase: 50 mL of 0.5×10^{-3} M carrier in nitrobenzene; receiving phase: 5 mL of 10×10^{-3} M thiosulfate, pH 3.

Table 1. Effect of stripping agents in the receiving phase on the Ag$^+$ cation transport

Stripping agent	Transferred to receiving phase, %	Remained in source phase, %
$S_2O_3^{2-}$	87.54	1.89
SCN	56.09	30.62
SO_3^{2-}	51.42	32.14
$P_2O_7^{4-}$	38.76	43.58
EDTA	32.08	37.04
Thiourea	13.45	63.72

Table 2. Degree of cation transfer from various mixtures through nitrobenzene membrane

Cation mixture	Transferred to receiving phase,%	Remained in source phase, %
Mixture no. 1		
Ag$^+$	87.04	1.69
Cr^{3+}	0	95.29
Co^{2+}	0	94.64
Mixture no. 2		
Ag$^+$	87.04	1.69
Cd^{2+}	0	94.87
Pb^{2+}	0	92.45
Mixture no. 3		
Ag$^+$	87.04	1.69
Ni^{2+}	0	96.32
Zn^{2+}	10.12	82.91

the bulk liquid membrane in the presence of Cr^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} cations in the source phase was investigated. The results are given in Table 2. As can be seen, only the Zn^{2+} ions are transported to small extent together with Ag^+ ions.

The suggested mechanism of the transport of Ag^+ ions through the bulk liquid membrane is shown in the scheme. After the Ag^+ cation forms a charged species with the carrier molecule on the source side of the membrane, the resultant complex is ion-paired with picrate as a counteranion and moves across the organic membrane. Then the formed complex diffuses down its concentration gradient to the receiving side of the membrane, and the metal ion is released into the receiving phase as $Ag–S_2O_3^{2-}$ complex. The picrate ion neutralizes the charged $15C5–Ag^+$ complex, making it lipophilic, so that it can be readily extracted into the hydrophobic organic membrane. Then the free carrier diffuses back across the membrane and the cycle starts again.

CONCLUSIONS

(1) A study of the competitive bulk liquid membrane transport of Ag^+ cation in the presence of Cr^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} cations shows that 15-crown-5 as carrier is highly selective to Ag^+ ions. The silver transport efficiency decreases in the order nitrobenzene > dichloromethane > chloroform > 1,2-dichloroethane. Thus, 15-crown-5 is an excellent carrier for selective and efficient transport of Ag^+ ions with nitrobenzene used as the membrane phase.

(2) To achieve the best transport efficiency and high selectivity to Ag^+ cation, the choice of the appropriate counterions in the source and receiving phases and of the concentration of the neutral carrier in the membrane phase are important factors. Under the optimized experimental conditions (picric acid concentration 10×10^{-3}, 15-crown-5 concentration 4×10^{-3} M, process time 8 h), the maximum degree of transport of Ag^+ cation through nitrobenzene bulk liquid membrane was found to be ~88%.

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