Highly Selective and Efficient Membrane Transport of Silver as AgBr_2^- Ion Using K^+ -decyl-18-crown-6 as Carrier

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Potassium-decyl-18-crown-6 was used as a highly selective and efficient carrier for uphill transport of silver as AgBr_2^- complex ion through a chloroform bulk liquid membrane. When thiosulfate anion was used as a metal ion acceptor in the receiving phase the amounts of silver transported across the liquid membrane after 120 and 180 min were $87.0 \pm 1.8\%$ and $96.0 \pm 1.9\%$, respectively. The selectivity and efficiency of silver transport from aqueous solution containing Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} and Fe^{3+} ions were investigated. In the presence of EDTA at pH = 4 as suitable masking agent in the source phase, the interfering effects of Pb^{2+} and Fe^{3+} ions were diminished drastically.

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Introduction

Among the separation techniques, ion transport is a highly selective, efficient and very simple method. Ion transport is inherently a reaction based method, and its advantages are due to controllability of the carrier reaction conditions.¹ In solving analytical and technological problems, it is sometimes desirable to obtain an aqueous rather than an organic solution of the recovered component. This can be achieved by liquid membrane processes. An efficient separation process combines a high transport rate with a high selectivity.² After reports of Pedersen and others³⁻⁵ about synthesis and the selectivity toward alkali metal ion, many researchers have become interested in using crown ethers as a selective carrier in membrane transport separation method.^{1-2,6-10}

Among the heavy metals, silver is an element of important commercial value. It is valuable because of its resistance to corrosion and its usefulness in alloys and jewelry. Improved procedures for extracting it from its ores and for recovering it from wastewater would be valuable. However, despite the biological and industrial importance of silver ions, information about its transport across liquid membranes in comparison with other transition metal ions is sparse.¹⁰⁻²⁰ In this paper, we describe a new selective and efficient liquid membrane system containing potassium-decyl-18-crown-6 for the uphill transport of silver ion as AgBr_2^- counter ion. The receiving phase contains the thiosulfate anion, which was found to play an important role in the transport process.

Experimental

Reagents and chemicals

Reagent-grade decyl-18-crown-6, benzo-15-crown-5 (B15C5), 18-crown-6 (18C6) dibenzo-18-crown-6 (DB18C6),

dicyclohexyl-18-crown-6 (DC18C6), and dibenzopyridino-18-crown-6 (DBPY18C6) were purchased from Merck and were used as received. Analytical grade sodium bromide, sodium thiosulfate, silver nitrate and the nitrate salts of other cations used (all from Merck) were of the highest purity available and were used without any further purification except for vacuum drying over P_2O_5 . Extra pure chloroform (Merck) was used as organic phase. Doubly distilled deionized water was used throughout.

Apparatus

A bulk liquid membrane cell was used in this study.^{19,21} The atomic absorption spectrophotometer used for the measurements of the metal concentration in the aqueous phases was a Perkin Elmer 3800 instrument.

Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used. The inner aqueous phase (source phase, SP, 5 ml) contained silver nitrate (1.0×10^{-4} M), sodium bromide (5.0×10^{-1} M), and potassium nitrate (2.0×10^{-1} M). The outer aqueous phase (receiving phase, RP) contained sodium thiosulfate (10 ml, 1.0×10^{-3} M). The membrane phase (MP) contained 20 ml of 6.0×10^{-3} M decyl-18-crown-6 in chloroform. It lay below the source and receiving phases, and bridged these aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (2.0 cm $\times$ 5 mm) at 150 rpm. Under these conditions, not only is the mixing process perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined. Determination of the metal ion concentration in both aqueous phases was carried out by AAS. Reproducibility was confirmed as 2% or better. A similar transport experiment was carried out in the absence of the carrier for reference. Detailed conditions are included in the tables of the text.

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Structure 1

Results and Discussion

It is well known that the complexing ability of ordinary crown ethers towards soft heavy metal ions as Ag^+ is quite low.^{22,23} This problem has been overcome through using anionic complexes by M^{n+} -crown ether carriers (M^{n+} is co-transported cation).^{24,25} Previously 18-crown-6 has been used as a carrier for both cationic and anionic forms of metal ions, but its low lipophilicity caused substantial bleeding from the membrane phase into the aqueous phase and the efficiency of the membrane gradually decreased.^{18,20,26} For overcoming this, and enhancing the efficiency of carrier, we chose decyl-18-crown-6 (I) as a carrier in the form of M^{n+} -18-crown-6 for liquid membrane transport of silver ion. Because of the good fit of potassium ion into the 18-crown-6 ring,²² K^+ has been used as co-transported cation. Previous study shows that AgBr_2^- transport rate increases as the stability constant for M^{n+} -18-crown-6 complex increases, with the greatest percentage of Ag transport occurring when $\text{M}^{n+} = \text{K}^+$.²⁴ Consequently, the amount of complex cation available to form an ion-pair with AgBr_2^- will be greatest in the case of K^+ , resulting in the largest extent of partitioning into the organic layer.²⁷ In the presence of excess bromide ion, Ag^+ will form a relatively stable and bulky anion AgBr_2^- with $\log \beta_2 = 7.34$ and low hydration energy,²⁷ which can easily accompany K^+ -18-crown-6 cations into the membrane phase.

The influence of the concentration of KNO_3 in the source phase on silver ion transport was investigated; results are shown in Fig. 1. It is evident that the percentage of transported silver increases with increasing concentration of KNO_3 . Maximum transport occurs when the concentration of the salt is 0.2 M. A further increase in the concentration of potassium nitrate has very little effect on the transport efficiency. In the absence of KNO_3 , the extraction of ions *via* $(\text{Ag}^+ \text{-decyl-18C6})(\text{NO}_3^-)$ ion pairs into the membrane is not negligible but is small.

The best pH region of the source phase for the quantitative transport of Ag^+ ion was studied. It was found that, over a wide pH range of 4.0 – 10.0 for both source and receiving phases, the transport of silver ion into receiving phase is semi-quantitative and the variation of pH caused a negligible change in the transport efficiency. The results of pH effect are shown in Table 1.

The effect of sodium thiosulfate concentration in the receiving phase on silver transport was investigated; the results are shown in Fig. 2. Obviously, maximum silver transport occurs at a concentration of 1.0×10^{-4} M. Notably, the absence of a metal ion acceptor in the receiving phase resulted in partitioning of silver into the membrane, but with negligible silver transport into RP. As expected, it was found that the nature and composition of the ligand used as scavenger for the transported metal ion in the receiving phase could have a significant effect on the efficiency and selectivity of transport.^{10-20,28-31} In Table 2 are listed the percentages of silver ion transported in the presence of different stripping agents under similar experimental conditions. The use of $\text{S}_2\text{O}_3^{2-}$ ion as stripping

Fig. 1 The effects of potassium ion concentration in the source phase on silver ion transport. Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ 0.5 M NaBr and varying concentrations of K^+ ion (as KNO_3); membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M sodium thiosulfate; time of transport, 120 min.

Fig. 2 The effect of thiosulfate ion concentration in the receiving phase on silver ion transport from chloroform membrane. Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of varying concentration of sodium thiosulfate; time of transport, 120 min.

ligand in the receiving phase caused a large enhancement in the efficiency of Ag^+ transport, as compared with the case of other receiving agents such as thiourea, EDTA, KSCN and NaI. In some cases, the total percentage of silver ion in both source and receiving phases are not equal to 100, this is due to some silver ions remaining in the liquid membrane, especially when the type of stripping agent does not perfectly interact with the silver ion under the conditions used.

As expected, the nature of the macrocyclic crown ether used as carrier in the organic membrane phase was found to have a pronounced effect on the permeability of the membrane system

Table 1 Effect of pH of receiving phase on silver transport

pH of receiving phase	Percentage transported into receiving phase	Percentage remaining in source phase
2	80	13
5	83	11
7	87	9
9	76	12
11	71	14

Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ , 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M stripping agent; time of transport, 120 min.

Table 2 Effect of the stripping agent nature in the receiving phase on silver transport

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
Thiourea	3	12
EDTA	3	15
KSCN	9	13
NaI	3	11
$\text{Na}_2\text{S}_2\text{O}_3$	8	79

Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ , 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M stripping agent; time of transport, 120 min.

Table 3 Effect of carrier structure on silver transport

Carrier	$\log K_{\text{K}^+\text{-crown}}^a$	Percentage transported into receiving phase	Percentage remaining in source phase
DBPY18C6	4.15 ^b	15	85
DB18C6	5.0 ^c	24	76
DC18C6	6.0 ^c	73	14
18C6	6.1 ^c	78	14
B15C5	2.8 ^c	28	72
Decyl-18C6	6.1 ^c	87	9

Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ , 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml of 6.0×10^{-3} M of each carrier in chloroform; receiving phase, 10 ml of 1.0×10^{-3} M sodium thiosulfate; time of transport, 120 min.

a. Logarithm of stability constants of K^+ -crown in methanol.

b. Ref. 32.

c. Ref. 22.

designed for silver transport. In other experiments (and under the same experimental conditions) we tried several crown ethers as carrier for the transport of AgBr_2^- anions in the presence of K^+ ions, results are shown in Table 3. As can be seen, decyl-18C6, 18C6, DC18C6 are the most suitable carriers for the anionic transport of silver, mainly due to their proper cavity size for K^+ ion,²² and consequently, the highest stability of the complexes in the series. Some increased transport efficiency of decyl-18C6 over that of 18C6 as mentioned before is related to lower solubility of the former crown ether into the aqueous phases. It is noteworthy that, DB18C6 and DBPY18C, despite their proper cavity size for K^+ ions, showed much lower transport efficiencies in comparison with the three other 18-crowns used. This is related to the diminished stability of their

Fig. 3 The effect of decyl-18C6 concentration in the membrane phase on silver ion transport from chloroform membrane. Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ , 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml varying concentration of carrier in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M sodium thiosulfate; time of transport, 120 min.

Fig. 4 The time dependence of silver ion transport from chloroform membrane. Conditions: source phase, 5 ml of 1.0×10^{-4} M Ag^+ , 0.5 M NaBr and 0.2 M KNO_3 ; membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M sodium thiosulfate.

K^+ complexes because of substitution of benzo and both benzo pyridyl groups, respectively.^{22,32,33} However, in the case of macrocycle of smaller ring size such as B15C5 the improper cavity size for K^+ decreased the stability of complex, and transport of silver ion diminished drastically through the liquid membrane.²²

The effect of concentration of decyl-18C6 in the membrane phase on the transport of silver ion was studied; the results are shown in Fig. 3. It is obvious that the percentage transport of silver increases with increasing concentration of macrocycle in chloroform. Maximum transport occurs at a concentration 6.0×10^{-3} M.

The time dependence of silver transport through the liquid membrane proposed was investigated under the optimal experimental conditions (Fig. 4). It can be seen that the

Table 4 Amount of cations transported from various cation mixtures through the liquid membrane

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Ag ⁺	86	11
Cu ²⁺	0	100
Ni ²⁺	0	100
Zn ²⁺	7	90
Mixture 2		
Ag ⁺	87	9
Cd ²⁺	0	100
Mixture 3		
Ag ⁺	88	9
Pb ²⁺	81	5
Mixture 4		
Ag ⁺	50	10
Fe ³⁺	90	2
Mixture 5 ^a		
Ag ⁺	60	15
Pb ²⁺	0	100
Mixture 6 ^b		
Ag ⁺	83	15
Fe ³⁺	6	75

Conditions: source phase, 5 ml of 1.0×10^{-4} M of each cation, 0.5 M NaBr and 0.2 M KNO₃; membrane phase, 20 ml of 6.0×10^{-3} M decyl-18C6 in chloroform; receiving phase, 10 ml of 1.0×10^{-4} M sodium thiosulfate; time of transport, 120 min.

a. In the presence of 0.01 M EDTA at pH = 4.0.

b. In the presence of 0.005 M EDTA at pH = 4.20.

extraction of silver from source phase into the organic membrane and release of silver into the receiving phase occur at about the same rate. Formation and dissociation of the metal complexes of crown ethers and similar compounds are generally fast processes,³³ in other words generally the transport rate is limited by the exchange rate of species at phase boundaries (diffusion controlled). It is found that, under the optimum conditions, the transport of silver ion from source phase into the receiving phase after 120 and 180 min was 88% and 96%, respectively. The reproducibility of silver transport was investigated and the percent of metal ions transported after 120 min obtained from six replicate measurements was found to be $86.4 \pm 1.8\%$.

In order to study the selectivity of the membrane system for the silver ions, the percentage transport of Ag⁺ and Mⁿ⁺ cations, which were present with silver ions in equimolar concentration (SP: 5 ml of 1.0×10^{-4} M of Ag⁺ and each other cation), into receiving phase were determined and the results are summarized in Table 4. As can be seen, among a variety of cations studied, only Pb²⁺ and Fe³⁺ ions show some potential interfering effect. The interfering of Fe³⁺ may be due to the formation of mixed complexes of Fe³⁺ and Ag⁺ such as [FeBr₄]Ag,³⁴ which has no tendency to interact with K⁺-decyl-18C6, this effect is absent in the case of Pb²⁺. The high selectivity of silver transport over the other cations used can be primarily related to the higher stability of the AgBr₂⁻ compared to those of the other metal-bromide complexes.³¹ On the other hand, the high affinity of thiosulfate for silver ions over most of other cations tested is another important factor in determining the efficiency of Ag⁺ ion transport.

As can be seen from Table 4 (both Mixture 3 and Mixture 4) the interference effects of Pb²⁺ and Fe³⁺ can be eliminated in the presence of EDTA (0.01 M at pH = 4.0 for Pb²⁺ and 0.005 M at

pH = 4.20 for Fe³⁺) as a proper masking agent in the source phase. It is interesting to note that, under optimal experimental conditions, most of the Mⁿ⁺ cations used revealed no measurable interfering effect.

Conclusions

The proposed system in this paper is selective transport of silver ion as AgBr₂⁻ by using K⁺-decyl-18C6 as carrier. The interferences of some metal ions such as Pb²⁺ and Fe³⁺ could be removed through using EDTA at pH = 4.0. Under the optimum conditions (0.5 M NaBr, 0.2 M KNO₃ in source, 6.0×10^{-3} M decyl-18-crown-6 in liquid membrane, 1.0×10^{-3} M sodium thiosulfate in receiving phase), 87% of silver ion could be selectively transported across the chloroform liquid membrane after 120 min.

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