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Highly Efficient and Selective Membrane Transport of Silver(I) Ion by a Cooperative Carrier Composed of Aza-18-crown-6 and Palmitic Acid

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A given mixture of aza-18-crown-6 and plamitic acid was found to be an excellent cooperative carrier for the efficient transport of Ag^+ ions through a bulk liquid membrane. In the presence $S_2O_3{}^{2-}$ ion, as a suitable metal ion acceptor in the receiving phase, the amount of silver transported across the liquid membrane after 90 min was 93.6±1.5%. The selectivity and efficiency of silver transport from aqueous solutions containing other cations such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Fe^{2+} ions were investigated. In the presence of diphosphate as a suitable masking agent in the source phase, the interfering effect of Cd^{2+} ion was eliminated.

Carrier-mediated transport of metal ions through bulk liquid membranes is not only interesting for its potential as a model for a biological membrane, but also for its potential applications to selective removal, concentration and purification of metal ions from their mixtures.[1,2] During the past two decades, there has been increasing interest in the possible use of artificial membranes in specific separation procedures of biological and industrial importance.[2—4] Among a wide variety of artificial ionophores used for this purpose, crown ethers and their related open-chain analogues have been shown to be good carriers, especially for alkali and alkaline earth metal ions.[5,6] However, in comparison, much less attention has been focused on the transport of transition and heavy metal ions.[7—12] Especially, despite the biological and industrial importance of silver ion, information about its transport across liquid membranes is quite sparse.[13—15]

One of the serious problems associated with the use of crown ethers of lower lipophilicity as carriers in the organic membranes is their substantial bleeding from the membrane phase into the aqueous phases.[7] Nevertheless, it has been shown that the addition of long chain fatty acids to the membrane phase not only significantly reduces the degree of carrier loss, but also could have a coorperative effect in the uphill transport of metal ions through the liquid membranes.[7—9] In this paper, we describe a highly efficient and selective method for the transport of Ag^+ ions through a bulk liquid membrane containing a mixture of 16-aza-1,4,7,10,13-pentaoxacyclooctadecane (aza-18-crown-6) and palmitic acid (PA). The receiving phase contains thiosulfate ions which were found to play an important role in the transport process.

Experimental

A18C6 and other macrocyclic ligands used were purchased from Merck company and used as received. Reagent grade chloroform (Merck) was used as the membrane organic solvent. All other chemicals used in this study were of the highest purity available and were used without further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

A bulk type liquid membrane cell[5,16] was used in all experiments. pH measurements of the aqueous phases were performed with a Corning 125 pH meter using a combined glass electrode. A philips Pye Unicam SP9 atomic absorption spectrophotometer was used for monitoring the metal content of the aqueous phases.

All transport experiments were carried out at ambient temperature (i.e. 23±1°C). 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) contained silver nitrate (5 cm^3). The outer aqueous phase (receiving phase) contained sodium thiosulfate (10 cm^3). The chloroform membrane phase (30 cm^3) containing 2.5×10^{-3} M A18C6 and 1.0×10^{-3} M PA (M=mol dm^{-3}) lay below these aqueous phases, and bridged the two aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (3 cm×5 mm diameter). Samples of both aqueous phases were analyzed for metal content by AAS. reproducibility was confirmed as ±5% or better.

A similar transport experiment was carried out in the absence of the coorperative carriers for reference. The detailed conditions are included in the tables of the text. It should be mentioned that the final pH of both aqueous phases were determined after each transport experiment, and it was found that,it all cases studied, the difference between initial and final pH values is negligible.

Results and Discussion

The membrane system operated here is illustrated schematically in Fig. 1. After complexation of the carrier with silver ion on the left side of the membrane, the complex formed diffuses down its concentration gradient. On the right side of the membrane, the metal ion would be released into the receiving phase via formation of a ternary complex (carrier-metal ion-thiosulfate). At this stage, the carrier diffuses back across the membrane. The net result is

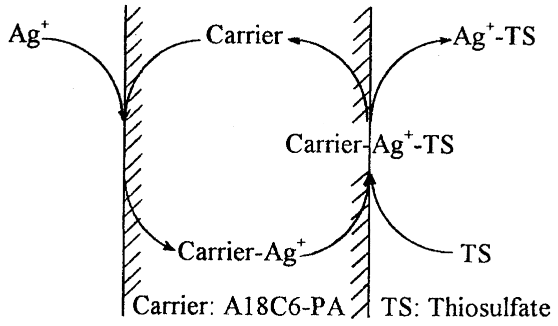

Fig. 1. Liquid membrane system for transport of Ag^+ ions.

the transport of Ag^+ ion from the aqueous source phase to the aqueous receiving phase across the bulk of the organic phase (the membrane).

In preliminary experiments, it was found that aza-18-crown-6 alone was not an effective carrier for the efficient transport of Ag^+ ion through the bulk liquid membrane. This is mainly due to the considerable solubilities of the free and complexed forms of the macrocyclic ligand in aqueous phases.[7,11] However, a mixture of aza-18-crown-6 and PA appeared to be much more promising in efficient transport of Ag^+ ion. A possible reason for this cooperative behavior would be the existence of some proton donor-proton acceptor interactions between the fatty acid (as donor) and the nitrogen atom of the crown ether (as acceptor) which can impart a grater degree of lipophilicity to the crown ether–metal ion complex, in order to facilitate the cation transport through the liquid membrane.[8] Another possibility is that the PA would form an inverse micelle,[17,18] inside of which the crown ether molecules may be trapped. The crown ether may then be easily transported across the membrane inside the inverse micelle.

The membrane system was then optimized with respect to the relative concentrations of aza-18-crown-6/PA, by keeping the amount of one of the constituents constant and varying the concentration of the other one. The results are give in Tables 1 and 2. As is seen, while aza-18-crown-6 and PA alone can transport 69 and 2% of silver after 80 min, respectively, a given mixture of them (about 2.5×10^{-3} mol dm^{-3} aza-18-crown-6 + 1.0×10^{-3} mol dm^{-3} PA) is much more effective in the efficient transport of silver.

Table 1. Effect of Relative Concentration of Aza-18-crown-6 on Silver Transport[a)]

Concentration of aza-18-crown-6 $\times10^3$(mol dm^{-3})	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	2	60
1.0	50	25
2.0	79	20
2.5	84	15
3.0	84	14
4.0	84	14
5.0	84	14
6.0	84	14
7.5	85	13

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} Ag^+; membrane phase, 30 cm^3 of 9.0×10^{-3} mol dm^{-3} PA and varing concentration of aza-18-crown-6 in chloroform; receiving phase, 10 cm^3 of 0.1 mol dm^{-3} $S_2O_3{}^{2-}$; time of transport, 80 min.

Permeability of the membrane system for Ag^+ ion was found to be largely dependent on the nature and concentration of stripping ligand used in the receiving phase. Use of $S_2O_3^{2-}$ as receiving agent caused a rather large enhancement in the efficiency and selectivity of Ag^+ transport, while the presence of other stripping agents such as bromide, iodide, thiocyanate and phenanthroline in the receiving phase resulted in a pronounced decrease in the selectivity of silver transport by increasing the interfering effect of cations such as Cu^{2+}, Cd^{2+}, and Zn^{2+}. The optimum concentration of sodium thiosulfate in the receiving phase was investigated (Table 3) and found to be 0.1 mol dm^{-3}. It is interesting to note that absence of a metal ion receptor in the receiving phase resulted in no measurable silver transport even for much longer periods of time; while some 75% of silver ion is extracted from the source phase into the membrane phase. This indicates that the stability of Ag^+-aza-18-crown-6 complex in chloroform solution could be very high.

The influence of the pH of the receiving phase on the transport efficiency of Ag^+ ion was studied in the pH 5.0—10.0 range. The results revealed that, in this range, the pH of the receiving phase does not have any considerable effect on the transport efficiency of silver ions. Furthermore,

Table 2. Effect of Relative Concentration of Palmitic Acid on Silver Transport[a)]

Concentrarion of PA $\times$ 10^{-3}(mol dm^{-3})	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	69	26
0.5	79	20
0.8	84	15
0.9	84	15
1.0	85	14
1.5	85	15
2.0	85	14

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} Ag^+; membrane phase, 30 cm^3 of 2.5×10^{-3} mol dm^{-3} aza-18-crown-6 and varying concentration of PA in chloroform; receiving phase, 10 cm^3 of 0.1 mol dm^{-3} $S_2O_3{}^{2-}$; time of transport, 80 min.

Table 3. Effect of $S_2O_3{}^{2-}$ Concentration in Receiving Phase on Silver Transport[a)]

Concentration of $S_2O_3{}^{2-} \times 10^2$(mol dm^{-3})	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	0	25
0.1	69	22
5.0	75	20
8.0	84	15
10	94	6
15	93	7
20	92	8

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} Ag^+; membrane phase, 30 cm^3 of 2.5×10^{-3} mol dm^{-3} aza-18-crown-6 and 1.0×10^{-3} mol dm^{-3} PA in chloroform; receiving phase, 10 cm^3 of varying concentration of $S_2O_3^{2-}$; time of transport, 90 min.

in order to check the possibility of any counter-transport between Ag^+ ions and protons, the concentration of HCl in the receiving phase was raised to 1.0 mol dm^{-3} and the transport experiment was carried out in the absence of any thiosulfate ion in this phase. The results showed only a negligible transport of Ag^+ ion (i.e. $<5\%$) which emphasizes the absence of a counter-transport system between silver ions and protons, even under such a high pH gradient.

Moreover, the silver transport efficiency was found to be critically dependent on the nature of macrocycle used in the binary carrier and, to a much lower extent, on the structure of fatty acid. In other experiments (and under the same experimental conditions) we tried several macrocyclic ligands other than aza-18-crown-6 as well as four different fatty acids as carrier for the transport of Ag^+ ion. The results are summarized in Table 4. As is seen, with the exception of aza-18-crown-6 and 4,7,13,16,21,24-hexacosa-1,10-diazabicyclo[8,8,8]hexacosane (cryptand 222), in all other cases the results show just a negligible amount of silver transport. Thus, it seems reasonable to assume that only those macrocycles containing nitrogen atoms as proton acceptors in their rings can act cooperatively in the presence of fatty acids, as proton donor centers, for the efficient transport of Ag^+ ions. As was mentioned before, the data seem to support the necessity of some proton donor–proton acceptor interactions between the two components of the binary carrier for its cooperative action in metal ion processes.

It is interesting to note that, in the case of cryptand 222, despite the very high stability of the resulting silver complex, its efficiency for membrane transport of silver is some 10% less than that of aza-18-crown-6 which forms a much less stable complex with Ag^+ ion. the data given in Table 4 indicate, after 80 min the extraction of silver cryptate into the organic phase is almost complete, emphasizing its good extractability into the membrane phase. However, the slow rate of release of silver from its 222 cryptate into the receiving phase seems to be responsible for the lower transport efficiency observed. There is actually a proposed hypothesis[19)] that predicts the existence of an optimum value for the stability of metal ion-carrier complex above or below which the

Table 4. Effect of the Carrier Structure on Sliver Transport[a)]

Carrier		log K_f of crown − Ag^+ complex in water[b)]	Percentage transpoted into receiving phase	Percentage remaining in source phase
Crown ether	Fatty acid			
Dibenzo-18-crown-6	Palmitic acid	1.4	4	32
18-Crown-6	Palmitic acid	1.5	11	41
Benzo-18-crown-6	Palmitic acid	—	5	38
Dibenzo-24-crown-8	Palmitic acid	—	2	69
15-Crown-5	Palmitic acid	0.9	6	53
Cryptand 222	Palmitic acid	9.6	74	4
Aza-18-crown-6	Palmitic acid	3.3	85	15
Aza-18-crown-6	Oleic acid	=	83	17
Aza-18-crown-6	Lauric acid	=	83	16
Aza-18-crown-6	Stearic acid	=	79	19

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} Ag^+; membrane phase, 30 cm^3 of 2.5×10^{-3} mol dm^{-3} crown ether and 1.0×10^{-3} mol dm^{-3} fatty acid in chloroform; receiving phase, 10 cm^3 of 0.1 mol dm^{-3} $S_2O_3{}^{2-}$; time of transport, 80 min. b) Data taken from Ref. 19. dibenzo-18-crown-6=2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctade-2,11-cene, 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, benzo-18-crown-6 = 2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctade-2-cene, dibenzo-24-crown-8 = 2,3,14,15-dibenzo-1,4,7,10,13,19,22-octaoxacyclotetracosane, 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane, cryptand 222 = 4,7,13,16,21,24-hexacosa-1,10-diazabiyclo[8,8,8]hexacosane, aza-18-crown-6 = 16-aza-1,4,7,10,13-pentaoxacyclooctadecane.

rate of ion transport decreases.

In addition, the nature of fatty acid used shows a rather small influence on the flux of silver transport. Table 4 indicates that the rate of Ag$^+$ transport varies in the order : palmitic acid > oleic acid > lauric acid > stearic acid. Based on the above discussion, both the acidity and lipophilicity of fatty acids are expected to somehow influence the transport efficiency.

Figure 2 shows the time dependence of Ag$^+$ ion transport through the liquid membrane under optimal experimental conditions. It is obvious that both the extraction of Ag$^+$ from the source phase into the membrane and its release from the membrane into the receiving phase are quite fast, so that some 99.5% silver transport occurs after 120 min under the optimal conditions. The reproducibility of silver transport was investigated and the percent of transport after 90 min form twelve replicate measurements was found to be 93.6±1.5.

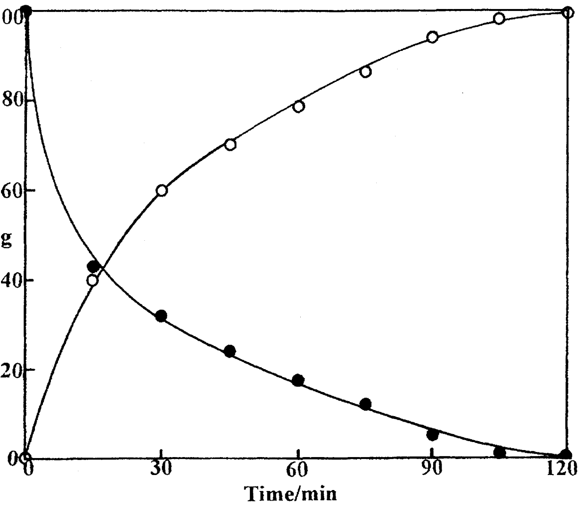

Fig. 2. Time dependence of silver transport: ○, transported; ●, remaining. Conditions: similar to those mentioned in Table 5.

Table 5. Amount of Cation Transported from Different Cation Mixtures through the Membrane[a)]

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Ag$^+$	95	4
Zn^{2+}	0	10
Cu^{2+}	4	7
Mixture 2		
Ag$^+$	96	4
Co^{2+}	0	12
Ni^{2+}	5	13
Mixture 3		
Ag$^+$	96	3
Cd^{2+}	75	7
Mixture 4		
Ag$^+$	97	2
Pb^{2+}	0	5
Mixture 5		
Ag$^+$	94	4
Fe^{2+}	0	5

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} of each cation; membrane phase, 30 cm^3 of 2.5×10^{-3} mol dm^{-3} aza-18-crown-6 and 1.0×10^{-3} mol dm^{-3} PA in chloroform; receiving phase, 10 cm^3 of 0.1 mol dm^{-3} $S_2O_3{}^{2-}$; time of transport, 90 min.

Table 6. Amount of Cation Transported from a Cation Mixture through Membrane in the Presence of Varying Concentration of $P_2O_7{}^{4-}$ as a Masking Agent[a)]

Cation	Percentage transported into receiving phase	Percentage remaining in source phase	Concentration of $P_2O_7{}^{4-}$ in source phase, (10^4mol dm^{-3})
Ag$^+$	96	3	0.0
Cd^{2+}	75	7	
Ag$^+$	95	4	2.0
Cd^{2+}	25	60	
Ag$^+$	95	5	5.0
Cd^{2+}	10	80	
Ag$^+$	94	5	8.0
Cd^{2+}	4	90	

a) Conditions: source phase, 5 cm^3 of 7.4×10^{-5} mol dm^{-3} of each cation; membrane phase, 30 cm^3 of 2.5×10^{-3} mol dm^{-3} aza-18-crown-6 and 1.0×10^{-3} mol dm^{-3} PA in chloroform; receiving phase, 10 cm^3 of 0.1 mol dm^{-3} $S_2O_3{}^{2-}$; time of transport, 90 min.

In Table 5 are listed the percentage transport of Ag$^+$ and M^{n+} cations, which were present with silver ion in equimolar concentrations, into the receiving phase. As can be seen, among different cations tried, Cd^{2+} ion interfere seriously in the transport of silver ions. This would be, at least in part, due to the higher tendency of cadmium ion for complex formation with thiosulfate ion, in comparison with the other cations tried.[20)] However, the interfering effect of Cd^{2+} ion on the silver transport was significantly decreased by addition of sodium diphosphate as a suitable masking agent in the source phase. The influence of increased concentration of $P_2O_7^{4-}$ ion on the interfering effect of cadmium ion is shown in Table 6. It is obvious that, in the presence of 8.0×10^{-4} mol dm^{-3} concentration of diphosphate, the interfering effect of cadmium ion has been eliminated almost completely, while the efficiency of silver transport will remain unchanged.

References

1) R. Painter and B. C. Pressman, *Top. Curr. Chem.*, **101**, 83 (1982).

2) B. G. Cox and H. Schneider, "Coordination and Transport Properties of Macrocyclic Compounds in Solution. In Studies in Physical and Theoretical Chemistry, " Elsevier, Amsterdam (1992), Vol. 76.

3) P. R. Danesi, *Sep. Sci. Technol*, **19**, 857 (1984).

4) M. Okahara and Y. Nakatsuji, *Top. Curr. Chem.*, **128**, 37

(1985).

5) R. M. Izatt, G. A. Clark, J. S. Bradshaw, J. D. Lamb, and J. J. Christensen, *Sep. Purif. Methods*, **15**, 21 (1986).

6) M. Dozol, "Possible Applications of Crown-Ethers to Metal Extraction Using Liquid Membrane Technology. A Literature Survey. In New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications," ed by L. Cecille, M. Casaraci, and L. Pietrelli, Elsevier, Amsterdam (1991), pp. 163—172.

7) L. F. Lindoy and D. S. Baldwin, *Pure Appl. Chem.*, **61**, 909 (1989).

8) S. Dadfarnia and M. Shamsipur, *Bull. Chem. Soc. Jpn.*, **65**, 2779 (1992).

9) S. Dadfrania and M. Shamsipur, *J. Membr. Sci.*, **75**, 61 (1992).

10) H. Parham and M. Shamsipur, *J. Membr. Sci.*, **86**, 29 (1994).

11) H. Parham and M. Shamsipur, *J. Membr. Sci.*, **95**, 21 (1994).

12) M. Akhond and M. Shamsipur, *Sep. Sci. Technol.*, **30**, 3061 (1995).

13) R. M. Izatt, G. A. Clark, and J. J. Christensen, *J. Membr. Sci.*, **24**, 1 (1985).

14) K. I. Kinner, J. C. Lochhart, and D. J. Rushton, *J. Chem. Soc., Dalton Trans.*, **1990**, 1365.

15) C. Sirlin, M. Burgard, and M. J. F. Leroy, *J. Membr. Sci.*, **54**, 299 (1990).

16) R. M. Izatt, F. C. LindH, A. L. Bruening, J. S. Bradshaw, J. D. Lamb, and J. J. Christensen, *Pure Appl. Chem.*, **58**, 1453 (1986).

17) M. J. Rosen, "Surfactants and Interfacoal Phenomena," Wiley, New York (1978).

18) D. Myers, "Surfactant Science and Technology," VCH Publishers, Weinheim (1988).

19) J. D. Lamb, J. J. Christensen, J. J. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt, *J. Am. Chem. Soc.*, **102**, 6820 (1980).

20) J. Inczedy, "Analytical Applications of Complex Equilibria," Ellis Horwood, Chichester (1976).

21) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, **85**, 271 (1985).