

Highly Efficient and Selective Membrane Transport of Silver(I) Using Dibenzodiaza-15-crown-4 as a Selective Ion Carrier

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A chloroform membrane system containing dibenzodiaza-15-crown-4 was found to be a highly efficient and selective transport of Ag^+ ions through a chloroform liquid membrane. In the presence of thiosulfate ion as a suitable ion stripping agent in the receiving phase, the amount of silver transported across the liquid membrane after 105 min is $95 \pm 1.3\%$. The selectivity of Ag^+ transport from aqueous solutions containing Tl^+ , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , K^+ , Ca^{2+} , Sr^{2+} , Hg^{2+} , Zn^{2+} , Cu^{2+} was investigated. The interfering effect of Cu^{2+} ions was drastically diminished in the presence of EDTA as a proper masking agent in the source phase.

Keywords: Liquid membrane; Ag^+ ion transport; Azacrown ether.

INTRODUCTION

The silver content of environmental samples is increased with the increasing use of silver compounds and silver-containing preparations in industry and in medicine.^{1,2} Silver can enter the environment via industrial waste water because it is often an impurity in copper, zinc, arsenic and antimony ores.³ Thus, separation, concentration and sensitive determination of Ag^+ ion are of increasing interest.

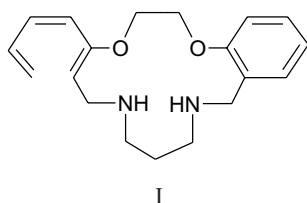
Compared with solvent extraction, liquid membrane transport for the selective removal and purification of the given metal ions from their mixtures or recovery of valuable resources have the advantage that the amounts of organic solvents and metal ion complexing agents are markedly reduced.⁴⁻⁵ However, despite the biological and industrial importance of silver ions, information about its transport across liquid membranes, in comparison with other transition metal ions,⁵⁻¹² is sparse. During the past decade, there have been some studies on Ag^+ -selective membrane transport using neutral ionophors,¹³⁻¹⁵ although a few proton-driven Ag^+ transport using potential anionic carriers have also been reported.^{16,17} However, most of these transport systems suffer problems like the interfering effect of some transition and heavy metal ions, partial bleeding of the carrier into the aqueous phases, long transport time, or

relatively high concentration of the ion carriers in the membrane phase.

Among the ion carriers used for the transport experiments, the strong binding of the cyclic and bicyclic polyether macrocyclic ligands with alkali and alkaline earth metal ions has been well documented;¹⁸ however, such ligands generally held very weak complexes with transition metal ions. Nevertheless, incorporation of donor atoms other than oxygen in the backbone of polyether ligands tends to increase considerably their affinity for the latter ions. For example, it has been demonstrated that the O_2N_2 -donor ligands, incorporating 14- to 17-membered macrocyclic rings, form stable complexes with a range of transition (and post transition) metal ions.¹⁹⁻²¹

In this investigation we employed dibenzodiaza-15-crown-4 (DBDA15C4, I) as a specific ion carrier for the highly efficient and selective transport of Ag^+ ions through a bulk chloroform membrane. In the presence of thiosulfate as a suitable metal ion acceptor in the receiving phase, a concentration of DBDA15C4 as low as 7.0×10^{-4} M was found to transport the silver ion quantitatively and selectively across the liquid membrane at 105 min. It should be noted that we have recently used the carrier I in the presence of histidine as a very efficient stripping agent for the transport of zinc ions through a bulk liquid membrane.²²

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EXPERIMENTAL

Reagents

Reagent grade dibenzodiaza-15-crown-4 (DBDA15C4), 18-crown-6 (18C6), dibenzopyridino-18-crown-6 (DBPy18C6), dicyclo-18-crown-6 (DC18C6), benzo-15-crown-5 (B15C5), dibenzylidiaz-18-crown-6 (DBzDA18C6) and dibenzo-18-crown-6 (DB18C6) were purchased from Aldrich or Fluka chemical companies and used as received. Analytical grade sodium perchlorate, sodium thiosulfate, silver nitrate and the nitrate salts of other cations used (all from Merck) were of highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Extra pure chloroform (Merck) was used as the organic phase. Doubly distilled and deionized water was used throughout.

Apparatus

A bulk type liquid membrane cell was used in this study.^{23,24} The atomic absorption spectrophotometer used for the measurement of metal concentration in the aqueous phases was a Shimadzu AA-760 instrument. The atomic absorption measurements were made under the recommended conditions for each metal ion.

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.^{16,23,24} The inner aqueous phase (source phase, SP) contained silver nitrate (5 mL, 1.0×10^{-4} M) and sodium perchlorate (4.0×10^{-2} M). The outer aqueous phase (receiving phase, RP) contained sodium thiosulfate (10 mL, 1.0×10^{-2} M). The membrane phase (MP) containing 20 mL of 7.0×10^{-4} M DBDA15C4 in chloroform lay below these aqueous phases and bridged the two aqueous phases. 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 $\pm 1.3\%$ 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. The data points reported are averages of three replicate measurements.

RESULTS AND DISCUSSION

Ligands for use as suitable Ag^+ -ion-carriers in a liquid membrane system should fulfil certain conditions. They should be selective for Ag^+ over other metal ions, have rapid exchange kinetics and be sufficiently lipophilic to avoid leaching into the aqueous source and receiving phases.

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 ternary complex (DBDA15C4- Ag^+ -thiosulfate). At this stage, the carrier diffuses back through the membrane. The net result is the transport of silver ions from the aqueous source phase to the aqueous receiving phase across the bulk liquid membrane.

Effect of the composition of the ligands as ion carriers on ion transport

The permeability of the membrane system used for transport of Ag^+ ions is found to be significantly dependent

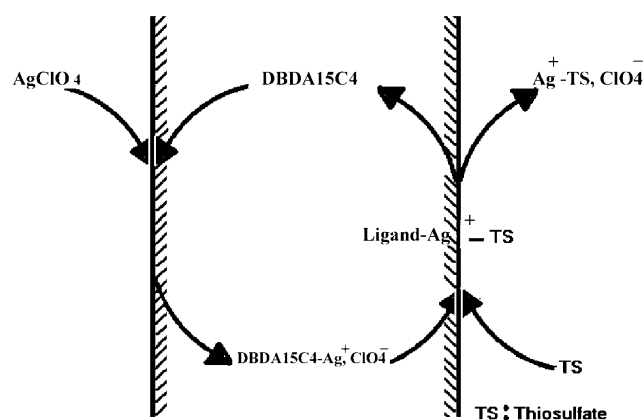


Fig. 1. Liquid membrane system for transport of Ag^+ ion with DBDA15C4 as carrier.

on the nature of the macrocyclic ligand. We tried six macrocyclic ligands other than DBDA15C4 as carrier for the transport of silver ions, and the results are given in Table 1. As seen, in the case of B15C5, DC18C6, 18C6 and DB18C5 the transport efficiency is low, mainly due to incomplete extraction of Ag^+ . On the other hand, the use of aza-substituted macrocycles (i.e., DBzDA18C6 and DBPy18C6) will result in a considerable increase in transport efficiency of the membrane system. This is presumably related to the increased stability of Ag^+ ion as a soft acid with the aza-substituted crown ethers, containing some donating nitrogen as soft base, over the Ag^+ -ordinary macrocycle complexes.^{18,19,25}

The influence of the concentration of DBDA15C4 in the organic membrane phase on the transport efficiency of silver was also investigated (Fig. 2). As seen, while no measurable silver transport occurs in the absence of the carrier, the percentage transport of Ag^+ ions increases sharply with the increasing concentration of DBDA15C4, and quantitative transport of silver ions occurs at 7.0×10^{-4} M of the carrier.

Effect of anion in source phase on transport efficiency

In preliminary experiments, it was found that nitrate

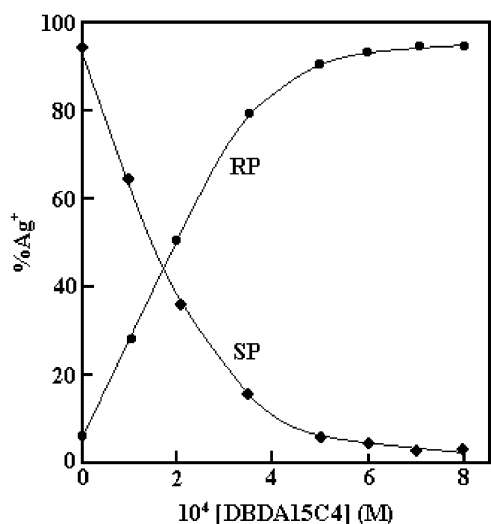


Fig. 2. Effect of DBDA15C4 concentration on silver transport. Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag^+ and 0.04 M NaClO_4 ; membrane phase, 20 mL of varying amounts of DBDA15C4 in CHCl_3 ; receiving phase, 10 mL of 0.01 M thiosulphate; time of transport, 105 min.

Table 1. Effect of the carrier structure on silver transport^a

Carrier	Percentage transported into receiving phase	Percentage remaining in source phase
DB18C6	6	89
18C6	15	84
DBPy18C6	45	45
DBzDA18C6	75	4
DC18C6	10	90
B15C5	6	92
DBDA15C4	95	3

^a Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag^+ and 0.04 M NaClO_4 ; membrane phase, 20 mL of 7.0×10^{-4} M macrocycle in CHCl_3 ; receiving phase, 10 mL of 0.01 M thiosulphate; time of transport, 105 min.

ion is not a suitable counter ion to accompany the Ag^+ -DBDA15C4 complex into the membrane-phase; only 2% of Ag^+ was transported into the receiving phase in a time period of 105 min in the presence of nitrate. As shown earlier, metal ion transfer efficiency from aqueous solution into the organic phase not only depends on the cation type and properties of the ionophore, but also may be influenced strongly by properties of the anion.^{26,27} However the addition of sodium perchlorate to the source phase increased the extent of silver transport significantly. Similar influence of perchlorate ion on the solvent extraction of the Ag^+ -HT18C6 complex has been reported in the literature.^{28,29} It has been suggested that the crown ether incorporates the Ag^+ ion into its cavity, and the counter anion is coordinated in the axial position forming a lipophilic neutral complex that is suitable for transfer into transfer organic phase. Thus, the degree of extraction increases with increasing hydrophobicity of the anion.

The influence of the concentration of perchlorate ion in the source phase on the silver ion transport was investigated, and the results are shown in Fig. 3. As seen, the percentage of silver ion transported in the receiving phase increases with an increase in perchlorate ion concentration in the source phase. Maximum transport occurs when the sodium perchlorate transport concentration is 0.04 M (i.e., $[\text{ClO}_4^-]/[\text{Ag}^+]$ ratio of 57).

Effect of stripping agent in the receiving phase on transport of silver ion

As expected, it was found that the nature and composition of stripping agent for the transported metal ion in the receiving phase could have a significant effect on the efficiency and selectivity of transport.^{9-11,21,22,30} In Table 2 are

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

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
L-cysteine	35	10
NH ₄ SCN	83	12
Thiourea	6	13
Na ₂ S ₂ O ₃	85	12
EDTA	4	13
Na ₂ C ₂ O ₄	45	17

^a Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag⁺ and 0.04 M NaClO₄; 20 mL of 7.0×10^{-4} M macrocycle in CHCl₃; receiving phase, 10 mL of stripping agent; time of transport, 105 min.

listed the percentages of silver ion transported in the presence of different stripping agents under similar experimental conditions. The use of S₂O₃²⁻ ion as stripping ligand in the receiving phase caused a large enhancement in the efficiency of Ag⁺ transport when compared with the case of other receiving agents. The optimum concentration of sodium thiosulfate in the receiving phase was investigated (Fig. 4) and found to be 0.01 M.

Time dependence of silver ion transport

Fig. 5 shows the time dependence of Ag⁺ ion trans-

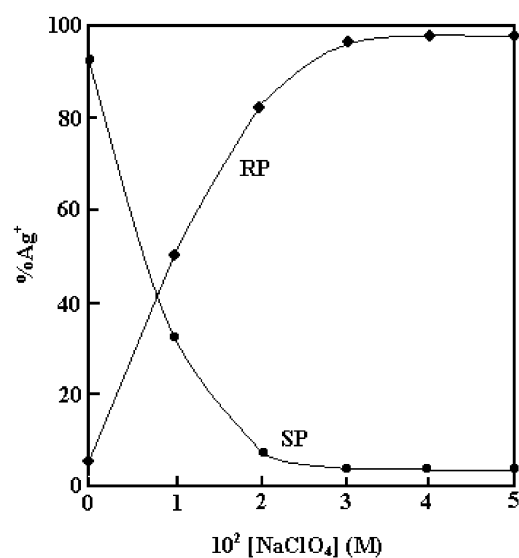


Fig. 3. Effect of perchlorate ion concentration in the source phase on silver transport. Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag⁺ and varying concentrations of NaClO₄; membrane phase, 20 mL of 7.0×10^{-4} M DBDA15C4 in CHCl₃; receiving phase, 10 mL of 0.01 M thiosulphate; time of transport, 105 min.

port through the liquid membrane under optimal experimental conditions. The reproducibility of silver transport was investigated, and the percentage of Ag⁺ transported after 105 min obtained from eight replicate measurements was found to be $95.0 \pm 1.3\%$.

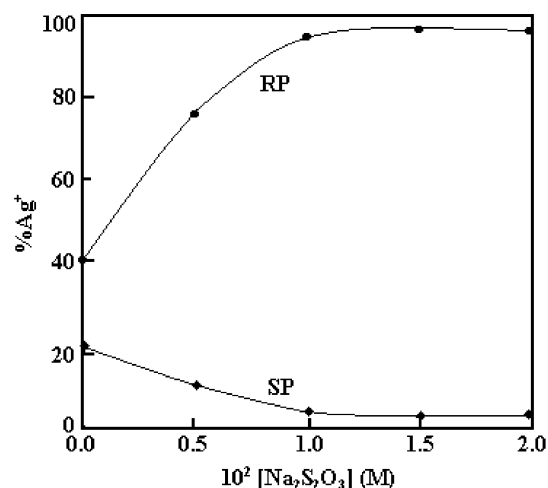


Fig. 4. Effect of thiosulfate concentration in the receiving phase on silver transport. Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag⁺ and 0.04 M NaClO₄; membrane phase, 20 mL of 7.0×10^{-4} M DBDA15C4 in CHCl₃; receiving phase, 10 mL of varying amounts of thiosulphate; time of transport, 105 min.

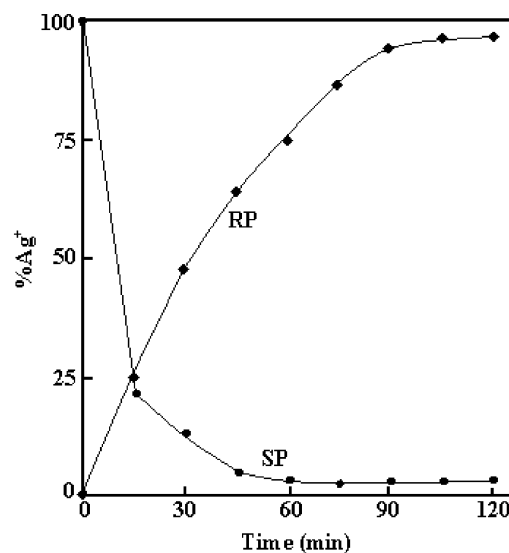


Fig. 5. Time dependence of silver transport. Conditions: Source phase, 5 mL of 1.0×10^{-4} M Ag⁺ and 0.04 M NaClO₄; membrane phase, 20 mL of 7.0×10^{-4} M DBDA15C4 in CHCl₃; receiving phase, 10 mL of 0.01 M thiosulphate.

Transport selectivity

In Table 3 are listed the transport percentages 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, Cu^{2+} ions interfere seriously in the transport of silver ions. This is most possibly due to strong complexation of copper with the macrocycle I.²⁴ However, the interfering effect of Cu^{2+} ion on the silver transport was significantly eliminated by addition of EDTA as a suitable masking agent in the source phase. Table 3 shows that, in the presence of 5.0×10^{-4} M EDTA, the interfering effect of $\text{Cu}(\text{II})$ on the transport of silver ion has been decreased from 56% to 13%, while there is only a 4% decrease in the transport of silver ion. Although mercury ion cannot be transported under this condition, it was found to decrease the transport efficiency of Ag^+ to 78% in 105 min. This is most possibly because the sites of DBDA15C4 are occupied by mercury ions and caused a decrease in the Ag^+ transport efficiency.

Table 3. Amount of cation transported from various cation mixtures through the membrane^a

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
mixture 1		
Ag^+	95	1
Tl^+	0	95
Pb^{2+}	5	2
mixture 2		
Ag^+	83	7
Cd^{2+}	1	98
Ni^{2+}	4	95
Co^{2+}	6	91
mixture 3		
Ag^+	98	1
K^+	3	97
Ca^{2+}	8	75
Sr^{2+}	0	78
mixture 4		
Ag^+	81	5
Hg^{2+}	9	68
Zn^{2+}	1	70
mixture 5		
Ag^+	87	2
Cu^{2+}	56	5
mixture 6 ^b		
Ag^+	82	1
Cu^{2+}	13	79

^a Conditions similar to those mentioned in Table 1.

^b In the presence of 0.0005 M EDTA in source phase.

Application

In order to assess the applicability of the proposed membrane system to the selective separation of silver from real samples, it was applied to the recovery of silver ion from developed radiological films.

A 69 cm² sheet of a developed radiological film was left in a furnace for two hours at 700 °C. The residue was dissolved in hot 1:1 nitric acid-water, and the pH of the resulting solution was adjusted to about 5 by a NaOH solution. Finally, the solution was completely transferred into a 250 mL volumetric flask and diluted to the mark with water. The silver content of the solution as determined by AAS was found to be 5.0×10^{-5} (equivalent to 196 mg silver per square meter of film). The transport of silver ion from the final solution through the proposed liquid membrane was carried out according to the recommended procedure. Average recovery of 92% and mean standard deviations of 1.4% were obtained.

CONCLUSION

The results show that, by using sodium perchlorate in the source phase and sodium thiosulfate in the receiving phase, silver ions can be transported through a chloroform membrane containing DBDA15C4 as ion carrier, by formation of $\text{Ag}^+ \text{-DBDA15C4-C1O}_4^-$ complexed ion pair. The simplicity of method, low cost, short time, and high efficiency for Ag^+ ion transport obtained by the BLM system studied demonstrate its potential applicability to selective removal and purification of silver from its mixtures.

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REFERENCES

1. *Treatise on Analytical Chemistry*; Kolthoff, I. M.; Elving, P. J., Eds.; Vol. 4, Part II; Interscience: New York, 1966.
2. Rener, H. In *Ulmans Encyclopadie der Tehnischen Chemie*; 4th ed., Vol. 21, Verlag Chemie: Weinheim, 1982.
3. Oager, S. R. *Metallic Raw Materials Dictionary*; Bank Tobel: Zürich, 1984.
4. Masuda, Y.; Sekido, E. *Bunseki Kagaku*. **1990**, *39*, 683.
5. Masuda, Y.; Zhang, Y.; Yan, C.; Li, B. *Talanta* **1998**, *46*, 203.
6. Akhond, M.; Shamsipur, M. *J. Membr. Sci.* **1996**, *117*, 1223.
7. Izatt, R. M.; Lamb, J. D.; Bruening, R. L.; Wang, C.; Edge,

- N.; Bradshaw, J. S. *Sep. Sci. Technol.* **1993**, 28, 283.
8. Oue, M.; Akama, K.; Kimura, K.; Tanaka, M.; Shono, T. *J. Chem. Soc. Perkin Trans. 1.* **1989**, 1675.
9. Painter, R.; Pressman, B. C. *Top. Curr. Chem.* **1982**, 101, 83.
10. Okahara, M.; Nakatsuji, Y. *Top. Curr. Chem.* **1985**, 128, 37.
11. Sevdic, D.; Mieder, H. *J. Inorg. Nucl. Chem.* **1977**, 39, 1409.
12. Dadfarnia, S.; Shamsipur, M. *Bull. Chem. Soc. Jpn.* **1992**, 73, 61.
13. Akhond, M.; Shamsipur, M. *Sep. Sci. Technol.* **1995**, 30, 3061.
14. Zoltov, Y. A. *Macrocyclic Compounds in Analytical Chemistry*; John Wiley & Sons: New York, 1997.
15. Saito, K.; Taninaka, I.; Murakami, S.; Muramatsu, A. *Talanta* **1998**, 46, 1187.
16. Sevdic, D.; Fekete, L.; Mieder, H. *J. Inorg. Nucl. Chem.* **1980**, 42, 885.
17. Mohapatra, P. K.; Manchanda, V. K. *Radiochim. Acta* **1991**, 55, 193.
18. Izatt, R. M.; Bradshaw, J. S.; Lamb, J. D.; Christensen, J. J. *J. Chem. Rev.* **1985**, 85, 271.
19. Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, 91, 1721.
20. Adam, K. R.; Anderegg, G.; Lindoy, L. F.; Lip, H. C.; Mcpartlin, M.; Rea, J. H.; Smith, R. J.; Tasker, P. A. *J. Inorg. Chem.* **1980**, 19, 2956.
21. Lindoy, L. F.; Lip, H. C.; Mcpartlin, M.; Rea, J. H.; Henrick, K.; Tasker, P. A.; Lip, L. C. *Inorg. Chem.* **1980**, 19, 3360.
22. Fakhari, A. R.; Rajabi Khorrami, A.; Shamsipur, M. *Sep. Purif. Technol.* **2006**, 50, 77.
23. Kazemi, S. Y.; Shamsipur, M. *Bull. Korean. Chem. Soc.* **2005**, 26, 930.
24. Kazemi, S. Y.; Shamsipur, M. *Sep. Purif. Technol.* **1999**, 17, 181.
25. Jaiswal, P.; Ijeri, V.; Srivastava, A. *J. Incl. Phenom.* **2004**, 49, 219.
26. Olsher, U.; Hankins, M. G.; Kim, Y. D.; Bartsch, R. A. *J. Am. Chem. Soc.* **1993**, 115, 3370.
27. Shamsipur, M.; Kazemi, S. Y.; Azimi, G.; Madaeni, S. S.; Lippolis, V.; Garau, A.; Isaia, F. *J. Member. Sci.* **2003**, 215, 87.
28. Ishikawa, J.; Sakamoto, H.; Mizuno, T.; Otomo, M. *Bull. Chem. Soc. Jpn.* **1995**, 68, 3071.
29. Shamsipur, M.; Khayatian, G. *Indian J. Chem. Sec. A* **2001**, 40, 594.
30. Talanova, G. G.; Elkarim, N. S. A.; Talanov, V. S.; Hanes, R. E.; Hwang, H.-S.; Bartsch, R. A.; Rogers, R. D. *J. Am. Chem. Soc.* **1999**, 121, 11281.