

## Highly Selective Transport of $\text{Ag}^+$ Ion through a Liquid Membrane Containing 2-Mercaptobenzothiazole as a Carrier

Morteza Akhond<sup>\*</sup> and Javad Tashkhourian

Department of Chemistry, Faculty of Science, Shiraz University, Shiraz 71454, I.R. Iran

Received October 21, 2002

2-Mercaptobenzothiazole was used as a highly selective and efficient carrier for the uphill transport of silver ion through a chloroform bulk liquid membrane. In the presence of thiosulfate ion as a suitable metal ion acceptor in the receiving phase, the amount of silver transported across the liquid membrane after 180 min was  $90 \pm 3.0\%$ . The selectivity and efficiency of silver ion transported from aqueous solutions containing equimolar mixtures of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$  were investigated.

**Key Words :** Liquid membrane, Silver transport, Separation, 2-Mercaptobenzothiazole

### Introduction

A great deal of research work on ion transport published in last three decades<sup>1-8</sup> testifies to the increasing interest existing among chemists, chemical engineers and biologists in understanding the transport processes occurring across the natural and artificial membranes.

Chemists and chemical engineers would like to understand the mechanism of transport so that with the knowledge obtained they would be able to fabricate membranes of desired properties. Biologists, however, would like to use these systems as simple models for the physiological membranes in order to understand the complex behavior of cell membranes in terms of established physicochemical principles.

The separation of chemical species from a complex mixture is often an important process in industry and chemical analysis. Liquid-membrane transport in which the extraction and stripping operations are combined in a single process reduces the solvent inventory requirement, and also allows the use of expensive and highly selective extractions, which otherwise would be uneconomic in solvent extractants. For these reasons, liquid-membrane transport has attracted worldwide attention, and much work has been directed toward developing methods for its application to the separation of various metal ions separations,<sup>9-15</sup> and to a lesser degree separation of organic substances.<sup>16-19</sup>

Low-level exposure to silver compounds is widespread owing to the use of soluble silver compounds to disinfect water for drinking and recreation purposes. It is suggested<sup>20</sup> that silver might pose a potential risk as water pollutant because of the lack of recycling of mixed silver. Silver also enters the environment through industrial wastes because it often exists as an impurity in Zn, Cu, As, and Sb ores.

It is well known that sulfur ligands coordinate with transition metal cations as exclusive donor atoms. In this

respect, macrocyclic and noncyclic thio compounds have attracted widespread attention owing to the unique properties of these compounds.<sup>21</sup> In aqueous solution, little or no reaction occurs between the sulfur-containing ligands and either alkali or alkaline earth metal ions, but the stability of the complexes with  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  are enhanced markedly.<sup>22,23</sup> Therefore, we were prompted to investigate the behavior of 2-mercaptobenzothiazole.

2-Mercaptobenzothiazole reacts with a wide variety of soft metal ions to form yellow to yellow-orange insoluble complexes and has been used as a gravimetric reagent and as an extraction photometric reagent for some metal ions.<sup>24-25</sup> It has been used in separation and preconcentration of metal ions,<sup>26,27</sup> and as carrier in construction of ion selective electrode.<sup>28</sup>

In this paper, we describe a highly efficient and selective method for the transport of  $\text{Ag}^+$  ion through a liquid membrane containing 2-mercaptobenzothiazole as a carrier. The receiving phase contains  $\text{S}_2\text{O}_3^{2-}$  ion, which was found to play an important role in the transport process.

### Experimental Section

**Reagents.** 2-Mercaptobenzothiazole was purchased from Fluka chemical company. Reagent grade chloroform (Merck) was used as the membrane organic solvent. Silver nitrate, sodium thiosulfate and all other chemicals used in this study were of the highest purity available from either Merck or Fluka chemical companies and used without further purification. Triply distilled deionized water was used throughout.

**Apparatus.** A bulk type liquid membrane cell was used in this study.<sup>29</sup> The pH measurements were made with a Corning 125-pH meter using a combined glass electrode. The atomic absorption spectrophotometer used for the measurement of metal concentration in the aqueous phases was a Philips Pye Unicam SP9 instrument with cell for determining mercury. The atomic absorption measurements were made under the recommended conditions for each

<sup>\*</sup>Corresponding author. Phone: +98-711-2284822; Fax: +98-711-2280926; E-mail: akhond@chem.suse.ac.ir

metal.

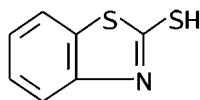
**Procedure.** All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used. The inner aqueous phase (source phase) contained silver nitrate (5 mL,  $7.42 \times 10^{-5}$  M). The outer aqueous phase (receiving phase) contained sodium thiosulfate (10 mL, 0.1 M). The pH values of the source and receiving phases were adjusted with either sodium hydroxide or nitric acid. The chloroform solution (30 mL) containing  $1.2 \times 10^{-4}$  M 2-mercaptobenzothiazole lay below these aqueous phases, and bridged the two aqueous phases. The organic layer was slowly stirred (150 rpm) by a Teflon-coated magnetic bar (3 cm  $\times$  5 mm diameter). Under these conditions, not only the mixing processes is 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 atomic absorption spectroscopy.

### Results and Discussion

2-Mercaptobenzothiazole that its structural formulas was shown in Figure 1 was used as a carrier for this study. In preliminary experiments, we found that the membrane containing this ligand is a suitable membrane for  $\text{Ag}^+$  transport.

The guest  $\text{Ag}^+$  ion is transported from one aqueous phase (the source phase) to the other aqueous phase (the receiving phase) *via* a chloroform membrane. Movement of the charged species through the hydrophobic membrane is accomplished by the presence of carrier (2-mercaptobenzothiazole). It seems more probable that the transport phenomenon is based on a deprotonation-protonation cycle of carrier in the membrane interfaces of the source and the receiving phases, respectively. The  $\text{Ag}^+$  ion forms a complex with a deprotonated ionophore to be extracted from the source phase into the membrane phase. In the interface between the membrane and the receiving phase that protonation of the carrier combined with a release of the silver ion and its complexation by thiosulfate occurs at the interface and then, the carrier diffuses back across the liquid membrane. The net result is the transport of  $\text{Ag}^+$  ion from the aqueous source phase to the aqueous receiving phase across the bulk of the organic phase (the membrane).

In the next steps, the experimental variables such as concentration of carrier (2-mercaptobenzothiazole) in the organic phase, nature and concentration of the stripping agent in the receiving phase, pH and buffer solutions of source, pH of receiving phase, and the effect of fatty acid on



**Figure 1.** The molecular structure of 2-Mercaptobenzothiazole.

$\text{Ag}^+$  transport and time of transport were optimized in order to achieve the highest efficiency in the transport of a  $7.42 \times 10^{-5}$  M solution of  $\text{Ag}^+$  across the membrane system used.

The influence of the concentration of 2-mercaptobenzothiazole in the organic phase on the transport efficiency of silver was studied and the results are shown in Table 1. It is clear that, the percentage of transported silver increases with increasing concentration of carrier in organic phase. The maximum transport rate lies between concentration range  $1.2 \times 10^{-4}$  M to  $2.4 \times 10^{-4}$  M. As it is seen, a further excess of carrier has considerable effect on the transport efficiency.

In some systems that carrier has nitrogen atom in its structure like amino and imino groups were observed that carrier alone was not an effective carrier for the transport of  $\text{M}^{II}$  ions through the bulk liquid membrane. This is mainly due to the considerable solubilities of the free and complexed forms of carrier into aqueous phases.<sup>10-15,32-34</sup> It has been shown that this problem can be overcome by appending long chain aliphatic groups to the carrier backbone to increase the lipophilicity of the system.<sup>29,32,33</sup> However, this synthetic procedure is often not straightforward. A simpler alternative is the addition of a long chain fatty acid to the organic phase to decrease the extent of carrier bleeding into the aqueous phases.<sup>10-15,30-34</sup> In our system we used different fatty acids such as palmitic acid, oleic acid, stearic acid and lauric acid but it wasn't seen any considerable change in transport percentage of silver. This proved that there is no bleeding of carrier in source and receiving phases.

Table 2 shows that the permeability of the membrane system for  $\text{Ag}^+$  ion is considerably dependent on the nature of stripping agent for  $\text{Ag}^+$  ion in the receiving phase. In the presence of thiosulfate in the receiving phase, 85% of  $\text{Ag}^+$  ion transported through the membrane during 150 min while the use of other reagents resulted in much lower percentage

**Table 1.** Effect of 2-mercaptobenzothiazole concentration in the membrane phase on silver transport<sup>a</sup>

Concentration of carrier (M)	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	3	90
$1.2 \times 10^{-6}$	25	45
$5.0 \times 10^{-6}$	27	36
$1.1 \times 10^{-5}$	41	25
$4.0 \times 10^{-5}$	59	10
$6.0 \times 10^{-5}$	65	7
$8.0 \times 10^{-5}$	75	5
$1.2 \times 10^{-4}$	82	5
$2.4 \times 10^{-4}$	83	6
$3.4 \times 10^{-4}$	76	5
$7.9 \times 10^{-4}$	65	6
$1.2 \times 10^{-3}$	61	3

<sup>a</sup>Experimental conditions: Source phase, 5 mL of  $7.42 \times 10^{-5}$  M  $\text{Ag}^+$ ; membrane phase, 30 mL of varying concentration carrier in chloroform; receiving phase, 10 mL of 0.1 M  $\text{S}_2\text{O}_3^{2-}$ ; time of transport, 150 min.

**Table 2.** Effect of various compounds as receiving phase<sup>a</sup>

Nature of stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
$\text{SO}_3^{2-}$	53	11
$\text{C}_2\text{O}_4^{2-}$	— <sup>b</sup>	6.5
$\text{S}_2\text{O}_3^{2-}$	83	5
Phenantroline	2	6.7

<sup>a</sup>Experimental conditions: Source phase, 5 mL of  $7.42 \times 10^{-5}$  M  $\text{Ag}^+$ ; membrane phase, 30 mL of  $1.2 \times 10^{-4}$  M 2-mercaptobenzothiazole in chloroform; receiving phase, 10 mL of 0.1 M various compound; time of transport 150 min. <sup>b</sup>Can not be detected.

**Table 3.** Effect of  $\text{S}_2\text{O}_3^{2-}$  concentration in receiving phase on silver transport<sup>a</sup>

Concentration of $\text{S}_2\text{O}_3^{2-}$ (M)	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	— <sup>b</sup>	8
$1.0 \cdot 10^{-2}$	10	5
$2.0 \cdot 10^{-2}$	10	5
$4.0 \cdot 10^{-2}$	37	5
$6.0 \cdot 10^{-2}$	53	4
$8.0 \cdot 10^{-2}$	80	3
$1.0 \cdot 10^{-1}$	82	2
$2.0 \cdot 10^{-1}$	83	3

<sup>a</sup>Experimental conditions: Source phase, 5 mL of  $7.42 \times 10^{-5}$  M  $\text{Ag}^+$ ; membrane phase, 30 mL of  $1.2 \times 10^{-4}$  M 2-mercaptobenzothiazole in chloroform; receiving phase, 10 mL of varying concentration of  $\text{S}_2\text{O}_3^{2-}$ ; time of transport, 150 min. <sup>b</sup>Can not be detected.

of transported silver ion.

The optimum concentration of thiosulfate in the receiving phase was also investigated (Table 3) and found to be 0.1 M. Notably, the absence of a metal ion acceptor in the receiving phase resulted in no appreciable transport of silver even in much longer periods of time.

The influence of pH of source phase on the transport efficiency of  $\text{Ag}^+$  ion was studied in the pH range 2.7–10.3 (Table 4) and it was found that maximum  $\text{Ag}^+$  transport occurs at distilled water at pH range 5.5–6.

According to the couple-proton mechanism that we

**Table 4.** Effect of pH in source phase on silver transport<sup>a</sup>

pH of source	Percentage transported into receiving phase	Percentage remaining in source
2.7	35	27
3.9	38	15
4.9	64	13
5.9 <sup>c</sup>	81	2
6.3	55	5
7.1	39	16
7.6	8	37
9.0	3	58
10.3	— <sup>b</sup>	78

<sup>a</sup>Experimental conditions: Source phase, 5 mL of  $7.42 \times 10^{-5}$  M  $\text{Ag}^+$  with various pH; membrane phase, 30 mL of  $1.2 \times 10^{-4}$  M 2-mercaptobenzothiazole; receiving phase, 10 mL of 0.1 M  $\text{S}_2\text{O}_3^{2-}$ ; time of transport, 150 min. <sup>b</sup>Can not be detected. <sup>c</sup>Distilled water.

**Table 5.** Effect of various buffers on silver transport<sup>a</sup>

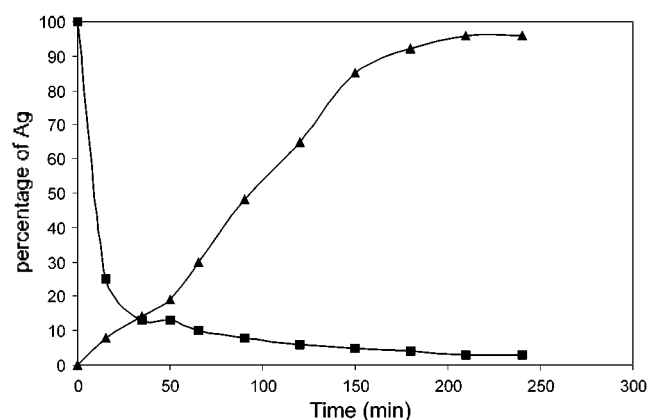
Buffer	Percentage transported into receiving phase	Percentage remaining in source phase
Citrate buffer	44	25
Acetate buffer	54	3.5
Phthalate buffer	36	27
Phosphate buffer	— <sup>b</sup>	—
Titrosol buffer	73	26

<sup>a</sup>Experimental conditions: Source phase, 5 mL of  $7.42 \times 10^{-5}$  M  $\text{Ag}^+$  with various buffer (pH=5.8); membrane phase, 30 mL of  $1.2 \times 10^{-4}$  M 2-mercaptobenzothiazole in chloroform; receiving phase, 10 mL of 0.1 M  $\text{S}_2\text{O}_3^{2-}$ ; time of transport, 150 min. <sup>b</sup> $\text{Ag}^+$  precipitates in phosphate buffer.

suggested for the  $\text{Ag}^+$  transport, we should adjust a basic media for the source phases. It was observed that the carrier is soluble in basic media therefore we had to work in pH of distilled water. Also the pH of receiving phase was studied and it was seen that the suitable pH was the pH of distilled water, because of the thiosulfate solution decomposes in acidic solution. For further studies the thiosulfate was omitted and the receiving phase with difference pH was used and the transport efficiency was investigated. The results shows that thiosulfate has an important role for silver transport and acidic receiving solution is not suitable for silver transport itself.

The influence of the buffer solution in source phase was studied and the results are shown in Table 5. We adjusted the pH of source phase with various buffer. It was found that the percentage of transport decreased, probably the species in the buffer solution affect on  $\text{Ag}^+$  transport. Therefore, it was preferred to work in distilled water without addition any buffer solution.

Figure 2 shows the time dependence of silver transport through the liquid membrane under the optimal experimental conditions. It is obvious that an increase in time increased the percentage transport of silver ion to receiving phase, and decreased the percentage of silver ion remaining in the source phase. According to the results the extraction of  $\text{Ag}^+$  from the source phase into the organic membrane is fast and its release from the organic phase into the receiving phase is to some extent quick, that the silver transport seems to be

**Figure 2.** Percentage of  $\text{Ag}^+$  vs. time in source (■) and receiving phases (▲).

**Table 6.** Amount of cation transported from various cation mixtures through membrane<sup>a</sup>

Cations	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Ag <sup>+</sup>	80	2
Zn <sup>2+</sup>	3	94
Cu <sup>2+</sup>	— <sup>b</sup>	11
Mixture 2		
Ag <sup>+</sup>	82	2
Co <sup>2+</sup>	—	93
Ni <sup>2+</sup>	—	90
Mixture 3		
Ag <sup>+</sup>	82	4
Cd <sup>2+</sup>	—	93
Mixture 4		
Ag <sup>+</sup>	86	6
Pb <sup>2+</sup>	—	—
Mixture 5		
Ag <sup>+</sup>	75	5
Fe <sup>3+</sup>	—	98
Mixture 7		
Ag <sup>+</sup>	70	9
Bi <sup>3+</sup>	—	40
Mixture 10		
Ag <sup>+</sup>	70	5
Fe <sup>3+</sup>	—	78
Mixture 11 <sup>c</sup>		
Without Ag <sup>+</sup>		
Pd <sup>2+</sup>	—	—
Mn <sup>2+</sup>	—	100
Mixture 12 <sup>c</sup>		
Without Ag <sup>+</sup>		
Hg <sup>2+</sup>	12	10
Sr <sup>2+</sup>	—	30
Mixture 13		
Ag <sup>+</sup>	85	7
Li <sup>+</sup>	—	100
Na <sup>+</sup>	—	100
K <sup>+</sup>	—	100
Mixture 14		
Ag <sup>+</sup>	83	5
Mg <sup>2+</sup>	—	100
Ca <sup>2+</sup>	—	100

<sup>a</sup>Experimental conditions: source phase, 5 mL of  $7.42 \times 10^{-5}$  M of each cation; membrane phase, 30 mL of  $1.2 \times 10^{-4}$  M of 2-mercaptobenzo-thiazole in chloroform; receiving phase, 10 mL of 0.1 M S<sub>2</sub>O<sub>3</sub><sup>2-</sup>; time of transport, 150 min. <sup>b</sup>Can not be detected. <sup>c</sup>Chloride salts of these cations were applied.

completed above 4 hr.

The reproducibility of silver transport was investigated and the percent of Ag<sup>+</sup> ion transported after 180 min from ten replicate measurements was found to be  $90 \pm 3.0$ .

In Table 6 the percentage transport of Ag<sup>+</sup> and various M<sup>n+</sup> cations are listed, which were initially present with Ag<sup>+</sup> in equimolar concentrations except of mixtures 11 and 12 that there is no any Ag<sup>+</sup> in them. According to the Table 6 in the presence of Fe<sup>2+</sup>, Fe<sup>3+</sup>, Bi<sup>3+</sup> the percentage of transport decrease and in other hand it is clear that most of the cations

do not interfere seriously in the transport of Ag<sup>+</sup>.

In order to suggest a mechanism for the transport of Ag<sup>+</sup>, the pH values of source and receiving phases were measured before and after Ag<sup>+</sup> transport. The increase in the pH of source phase and decrease of pH of receiving phase proves that the mechanism is proton driven.

## Conclusion

The high efficiency and excellent degree of selectivity for Ag<sup>+</sup> ion transport shown by the membrane system introduced demonstrate its potential to selective removal, concentration or purification ion from different samples.

**Acknowledgments.** The authors wish to express their gratitude to Shiraz University Research Council for the support of this work.

## References

- Morf, W. F.; Ammang, D.; Bissig, R.; Pretsch, E.; Simon, W. *Progress in Macrocyclic Chemistry*. Izatt, R. M.; Christensen, J. J., Eds.; Interscience: New York, 1979; Vol. 1, pp 1-61.
- Mc Bride, D. W.; Izatt, R. M.; Lamb, J. D.; Christensen, J. J. *Inclusion Compounds*. Atwood, J. L.; Davies, J. F. D.; MacNicol, D. D., Eds.; Academic press: Orlando, FL, 1984; Vol. 3, pp 571-628.
- Marr, R.; Kopp, A. *Int. Chem. Eng.* **1982**, 22, 44.
- Ishikawa, J.; Sakamoto, H.; Otomo, M. *Analyst* **1997**, 122, 1383.
- Guyon, F.; Parthasarathy, N.; Buffle, J. *Anal. Chem.* **1999**, 71, 819.
- El Aamran, F. Z.; Kumar, A.; Beyer, L.; Florido, A.; Sastre, A. M. *J. Membr. Sci.* **1999**, 152, 263.
- Safavi, A.; Shams, E. *Talanta* **1999**, 48, 1167.
- Goering, R. M.; Bowman, C. N.; Koval, C. A.; Noble, R. D.; Ashley, M. E. *J. Membr. Sci.* **2000**, 172, 49.
- Safavi, A.; Rastegarzadeh, S. *Talanta* **1995**, 42, 2039.
- Akhond, M.; Shamsipur, M. *J. Chin. Chem. Soc.* **1996**, 43, 225.
- Akhond, M.; Shamsipur, M. *J. Membr. Sci.* **1996**, 117, 221.
- Hiratani, K.; Takahashi, T.; Sughara, H.; Kasuga, K.; Fujiwara, K.; Hayashi, T.; Bartsch, A. *Anal. Chem.* **1997**, 69, 3002.
- Akhond, M.; Shamsipur, M. *Sep. Sci. Technol.* **1997**, 32(7), 1223.
- Akhond, M.; Shamsipur, M. *Sep. Sci. Technol.* **1995**, 30, 3061.
- Akhond, M.; Shamsipur, M. *Bull. Chem. Soc. Jpn.* **1997**, 70, 339.
- Audunsson, G. *Anal. Chem.* **1986**, 58, 2714.
- Kuo, Y.; Geger, H. P. *Sep. Sci. Technol.* **1983**, 18, 421.
- Stehle, R. G.; Higuichi, W. I. *J. Pharm. Sci.* **1967**, 56, 1367.
- Behr, J.; Lehn, J. J. *Am. Chem. Soc.* **1973**, 95, 6108.
- Mahmoud, M. E.; Gohar, G. A. *Talanta* **2000**, 51, 77.
- Kamata, S.; Murata, H.; Kubo, Y.; Bhale, A. *Analyst* **1989**, 114, 1029.
- Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, 85, 271.
- Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, 91, 1721.
- Diamantatos, A. *Anal. Chim. Acta* **1973**, 66, 147.
- Diamantatos, A. *Anal. Chim. Acta* **1973**, 67, 317.
- Khan, M. R.; Khoo, S. B. *Anal. Chem.* **1996**, 68, 3290.
- Chwastowska, J.; Rogowoska, A.; Sterlinska, E.; Dudek, J. *Talanta* **1999**, 49, 837.

28. Mazloum, M.; Amini, M. K.; Mohammadpoor-Baltork, I. *Sensors and Actuators B* **2000**, *63*, 80.
  29. Izatt, R. M.; Lindh, G. C.; Bruening, R. L.; Bradshaw, J. S.; Lamb, J. D.; Christensen, J. J. *Pure Appl. Chem.* **1986**, *11*, 1453.
  30. Dadfarnia, S.; Shamsipur, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2779.
  31. Dadfarnia, S.; Shamsipur, M. *J. Mem. Sci.* **1992**, *75*, 61.
  32. Lindoy, L. F.; Baldwin, D. S. *Pure Appl. Chem.* **1989**, *61*, 909.
  33. Izatt, R. M.; Clark, G. A.; Bradshaw, J. S.; Lamb, J. D.; Christensen, J. J. *Sep. Purif. Methods* **1986**, *15*, 21.
  34. Inokuma, S.; Uabusa, K.; Kuwamura, T. *Chem. Lett.* **1984**, 607.
-