Selective Transport of Silver(I) Ion Through Polymer Membranes Containing Thioether Donor Macrocycles as Carriers

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Abstract: The Preparation of polymer membrane and its selectivity to silver(I) ion from an aqueous solution containing seven metal cations, Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Pb(II), was studied. The source phase contained equimolar concentrations of the above mentioned cations with the source and receiving phases being buffered at pH 5.0 and 3.0 respectively. The effect of variation in the number of the macrocyclic sulfur atom donor set and the size of ring 9 and 16 member macrocycles on transport efficiency is presented. Silver(I) ion transport occurred (at 25 °C) from the aqueous source phase across the polymer membrane (derived from cellulose triacetate) containing ligands 9-membered, S₃-donor and 16-membered S₄-donor macrocycles as the ionophors in separate experiments into the aqueous receiving phase. Clear transport selectivity for silver(I) ion was observed using both thioether donor macrocycles. The efficiency of transport rate for silver(I) ion with using 9-membered S₃-donor macrocycle as carrier was better than 16-membered S₄-donor.

Keywords: Membrane; Silver(I); Cellulose triacetate; Transport of silver ion

Introduction

The selectivity transport of silver(I) ion from the solutions containing heavy metal cations through bulk liquid membranes using wide range of macrocyclic and acyclic ionophores containing sulfur, nitrogen and oxygen donor atoms have been reported¹⁻⁷. The differences between single- species and competitive solvent extraction using crown ethers for some metal cations have also been studied⁸. The transport of cations through supported liquid membrane mediated by neutral carriers can be regarded as a sequential process including phase transfer of salt, Complexation/ decomplexation, and diffusion steps. The rate of transport depends on the mentioned process⁹. Polymer inclusion membranes are gel-like membranes incorporating into their matrix plasticizer(s) and ionophore. In previous investigation it has been employed

cellulose triacetate based membranes in transport experiments involving selective transport of Cu(II) ion from a solution containing seven metal cations¹⁰. Polymer inclusion membranes show a number of advantages over more traditional member systems. The incorporation of the ionophore into a polymer inclusion membrane tend to 'secure' it and hence inhibit leaching into the aqueous phases without the need for increased lipophilicity of the ligand or the addition of a lipophilic acid as often employed in the bulk liquid membrane systems. The more durable polymer inclusion membranes have also been shown to exhibit higher rates of transport for Group 1 metal ions than thin supported liquid membranes under defined conditions¹¹. It has also been demonstrated that transport rates are dependent on the concentration of an ionophore and the plasticizer in the polymer membrane¹¹⁻¹⁶.

In the present report, the results of competitive metal polymer inclusion transport involving Co(II), Ni(II), Zn(II), Cu(II), Ag(I), Cd(II) and Pb(II) using carriers **1** and **2** (Diagram I) are presented.

Diagram I.

Experimental

Reagents

All reagents were of analytical grade and were used without further purification. The ligands also were obtained commercially.

Transport experiments

The polymer membranes using ligands **1** and **2** were made based on that described previously¹⁰. The source phase was buffered at pH 5.0 (CH₃COOH/CH₃COONa). The metal ions present at a concentration of 0.01M were cobalt(II), nickel(II), copper(II), zinc(II), silver(I), cadmium(II) and lead(II), all as their nitrate salts. The receiving phase was buffered at pH 3.0 (HCOOH/HCOONa). The transport cell was based on that described previously¹⁰. The volume of each of the source and receiving phases was 130mL. The transport runs were carried out for a period of 24h and the stirring speed was 50rpm at 25 °C. The metal ion concentrations in the both receiving and source phases after each transport was determined using PU9100X Philips atomic absorption spectrometer. The transport results are quoted as average values obtained from triplicate runs.

Results and Discussion

The 9 and 16 membered ligands **1** and **2** were used as selective extractant for Ag(I) ion from a solution containing seven metal cations. The results of competitive transport experiments are shown in Table 1. As it is shown in Table 1 both ligands completely preference for the transport of silver(I) ion across the polymer membrane. This is similar to the behaviour observed in the corresponding competitive similar membrane transport studies. The Selectively bulk liquid membrane transport of silver(I) ion with macrocycles **1** and **2** have been reported previously⁵. As it is shown in Table 1, ligand **1** transport silver(I) ion across the polymer membrane more than **2**.

Table 1. Transport fluxes for silver(I) in seven-metal competitive transport across a polymer membrane employing 1 and 2 as ionophores (25 °C).

Cation	Flux (mol/h)	
	1	2
Co(II)	—	—
Ni(II)	—	—
Cu(II)	—	—
Zn(II)	—	—
Cd(II)	—	—
Ag(I)	8.42×10^{-7}	6.96×10^{-7}
Pb(II)	—	—

The previous studies⁵ show that the nine-membered, S₃-donor ligand (**1**) is a little better ionophor for transport of silver (I) ion across the chloroform membrane with flux rate of $105 \times 10^{-7} \text{ mol(24h)}^{-1}$ (ligand **2** flux rate is $103 \times 10^{-7} \text{ mol(24h)}^{-1}$). The comparison of the flux rate of the competitive polymer membrane transports with ligands **1** and **2** and their bulk liquid transport for silver(I) ion show a similarity in the order of flux rates. It seems the formation of $[\text{Ag} \cdot \mathbf{1}_2]^+$ complex⁵ with ligand **1**, is the main reason of more transport of silver(I) ion with this ligand respect to **2** with a 1:1 complex between it and Ag(I) ion. Figures 1 and 2 show the curves of the results of the competitive metal ion polymer inclusion

Figure 1. The rate of transport (mol/h) for a competitive metal-ion transport (source/membrane/receiving) study, using **1** incorporated into a polymer inclusion membrane. Aqueous source phase: 130 mL, contains seven metal ions, each with initial concentration 0.01M prepared in a buffer solution (CH₃COOH/CH₃COONa) pH 5.0. Membrane polymer phase contain ligand (0.01M). Aqueous receiving phase: a buffer solution of HCOOH/HCOONa, pH 3.0 (130mL); both liquid phases stirred for 24 hours at 25 °C. The transport rate for Ag(I) is the average taken from a triplicate runs. transports. The observed Ag(I) transport rate are $J = 8.42 \times 10^{-7} \text{ mol/h}$ and $6.96 \times 10^{-7} \text{ mol/h}$ for ligands **1** and **2** respectively. The rate of transport for silver(I) ion using **1** is about 1.2 times of **2**.

Figure 2. The rate of transport (mol/h) for a competitive metal-ion transport (source/membrane/receiving) study, using **2** incorporated into a polymer inclusion membrane. Aqueous source phase: 130 mL, contains seven metal ions, each with initial concentration 0.01M prepared in a buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) pH 5.0. Membrane polymer phase contain ligand (0.01M). Aqueous receiving phase: a buffer solution of $\text{HCOOH}/\text{HCOONa}$, pH 3.0 (130mL); both liquid phases stirred for 24 hours at 25 °C. The transport rate for Ag(I) is the average taken from a triplicate runs.

Conclusion

All these results confirms that the both ligands are an efficient reagents showing high specificity for Ag(I) in both bulk liquid membrane and polymer inclusion transport experiments under the conditions employed. Also the more efficiency of **1** for the transport Ag(I) ion is observed.

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References

- Black D, Blacke A J, Finn RL, Lindoy L F, Nezhadali A, Rounaghi Gh, Tasker P A and Schroder M, *J. Chem. Soc. Chem. Commun.*, 2002, **4**, 340.
- Kim J, Leong A J, Lindoy L F, Kim J, Nachbaur J, Nezhadali A and Rounaghi Gh, Wei G, *J. Chem.Soc., Dalton Trans.*, 2000, **19**, 3453.
- Lee S S, Yoon I, Park K M, Jung J H, Lindoy L F, Nezhadali A and Rounaghi Gh, *J. Chem. Soc., Dalton Trans.* 2002, **10**, 2180.
- Chia P J K, Leong A J, Lindoy L F and Walker G W, *Aust. J. Chem.* 1995, **48**, 879.
- Melnikova M F, Lindoy L F, Liou S Y, Mcmurtrie J C, Green N P, Nezhadali A, Rounaghi Gh and Setzer W N, *Aust. J.Chem.* 2004, **57**, 161.
- Parthasarathy N, Pelletier M and Buffle J, *Analytica Chimica Acta* 1997, **350**, 183.
- Parthasarathy N and Buffle J, *Analytica Chimica Acta*, 1991, **245**, 9.
- Talanova G G, Elkarim N S A, Hanes R E, Hwang H S, Rogers R D and Bartsch R A, *Anal. Chem.* 1999, **71**, 672.
- Rechewein-Buitenhuis E G, Visser H C, Jong F and Reinhoud D N *J. Am. Chem. Soc.* 1995, **117**, 3913.
- Nezhadali A, *Incl. Phen. Mol. Recogn.*, 2006, 54,307.
- Lamb J D, Schow A J and Peterson T R *J. Membr. Sci.* 1996, **111**, 291.
- Sugiura M, *Sep. Sci. Technol.* 1990, **25**, 1189.
- Izatt R M, Lam J D and Bruending R L *Sep. Sci. Technol.* 1988, **23**, 1945.
- Ruppert M, Draxler J and Marr R, *Sep.Sci. Techanal.* 1988, **23**, 1654.
- Sugiura M and Kikkawa, *Sep.Sci.Techanal.* 1987, **22**, 2263.
- Sugiura M, *Sep.Sci.Techanal.*1992, **27**, 269.