Selective and Efficient Transport of Silver as $Ag(CN)_2^-$ Ion Using Malachite Green as Carrier

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The facilitated transport of Ag^+ from cyanide solutions through bulk liquid membrane is reported. The organic phase consisted of a chloroform solution of malachite green as carrier. The effect of pH of source phase, potassium cyanide concentration in source phase, malachite green concentration in organic phase and sodium hydroxide in receiving phase on efficiency of transport process are examined. Under optimum conditions, the extent of $Ag(CN)_2^-$ transport across the liquid membrane is about 90% after 240 min. The carrier can selectively and efficiently transport $Ag(CN)_2^-$ ion from aqueous solutions containing other cations such as alkali and alkaline earth, Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Fe^{2+}, Ni^{2+} and Pd^{2+}.

Key Words: Silver cyanide, Transport, Malachite green.

INTRODUCTION

The increased use of metals as non-renewable resources has resulted in an urgent demand for the development of new techniques either for their recovery, separation and concentration, or for their purification. Solvent extraction is widely applied in the recovery and separation of metal species from aqueous solutions[1]. Metal ions separation by selective permeation of liquid membranes has several advantages over solvent extraction[2]. So, the use of liquid membrane technique for the extraction of metallic species has been widely investigated during the last decades and many applications in hydrometallurgy have been proposed[3–5].

Precious metal and metal impurities such as copper, nickel and iron are usually present in anionic form after hydrometallurgical extraction of precious metal ores[6] which can be extracted *via* an ion pair extraction process. The corresponding co-cation can be of various types such as quaternary amines, protonated amines, solvated cations and cationic metal complexes[7]. It would be desirable to be able to preferentially and selectively transport these metal anionic complexes so that selective liquid membrane separation could be achieved for the recovery of precious metals.

Cationic dyes tend to form an extractable ion-pair with anionic metal complexes of halide, cyanide, thiocyanate and other inorganic or organic anionic ligands. The extraction of anionic complexes with various cationic dyes has been

extensively studied[8]. However, the study of the permeation of anionic complexes through liquid membranes has drawn less attention[9-11].

Malachite green (MG) is a cationic dye which tends to form an ion pair with bulky anions. To the best of our knowledge no work on use of MG as a carrier in transport system has been reported previously. In this paper, the transport of silver as $Ag(CN)_2^-$ in bulk liquid membranes with MG as a carrier is described.

EXPERIMENTAL

Malachite green (MG) was purchased from Fluka and used as received. Stock solutions of silver were prepared by dissolving silver nitrate (Merck). Reagent grade chloroform (Merck) was used as the membrane organic solvent. All other chemicals used in this study were of the highest purity available from either Merck or Fluka and used without further purification. Doubly distilled deionized water was used throughout. The atomic absorption spectrophotometer used for the measurements in aqueous phases was a Shimadzu AA-670 instrument. pH measurements were made with a Metrohm 713 pH meter using a combined glass electrode.

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 phases (source phase, 5 mL) contained Ag^+ (1×10^{-4} M) and 0.002 M KCN buffered at pH 6 with phosphate buffer. The chloroform solution (25 mL) containing 1.2×10^{-4} M of MG lay below these aqueous phases and bridged them. The organic layer was stirred by a teflon-coated magnetic bar. Determination of metal ion concentration in aqueous phases was carried out by AAS. Reproducibility was confirmed as 15% or better. A similar experiment was carried out in the absence of the carrier for reference.

RESULTS AND DISCUSSION

Aqueous cyanide leaching solutions are common in hydrometallurgy of silver. This metal is present in solution as dicyanoargentate anion $Ag(CN)_2^-$ which can be extracted *via* an ion-pair extraction process. The corresponding co-cation can be of various types[12-14]

Malachite green (MG) is a cationic dye with a hydrophobic moiety which can form an ion pair with bulky anions. Thus, it is a desirable carrier for transport of bulky anions such as silver cyanide. The process of the formation of an ion pair at the aqueous source phase-organic layer membrane interface and the dissociation process of the ion pair at the membrane-receiving phase interface are sufficiently fast.

In preliminary experiments, it was found that the MG mediated transport of $Ag(CN)_2^-$ to a neutral aqueous receiving phase is quite low. However, in the presence of NaOH in the receiving phase, $Ag(CN)_2^-$ is replaced by OH^- in the receiving phase and the efficiency of the transport process is increased. In the

next step, the experimental variables such as the pH of the source phase, the concentration of NaOH in the receiving phase and the concentration of the carrier in the organic layer were optimized in order to achieve the highest selectivity and efficiency for the transport of Ag(CN)$^{2-}$ across the membrane.

Effect of the pH of the source phase: Table-1 shows the effect of pH of the source phase on the efficiency of silver transport. The results revealed that the maximum silver transport occurs at pH 6. At lower pH values there was a decrease in the percentage of transport of silver probably due to decomposition of Ag(CN)$_2^-$. The efficiency of transport decreases at higher pH values, probably due to the competition of OH$^-$ with Ag(CN)$_2^-$. From the results, a pH 6 was selected for further studies.

TABLE-1

EFFECT OF pH OF SOURCE PHASE ON THE TRANSPORT
OF Ag(CN)$_2^-$ ION[a]

pH	Transported (%)
4.0	15.0
4.7	77.0
5.0	81.2
5.3	84.5
6.0	88.0
6.2	85.0
6.7	81.2
7.0	78.0
8.0	78.0

[a] Experimental conditions: Source phase, 5 mL of 1×10^{-4} M Ag(CN)$_2^-$ and 0.05 M KCN; Liquid membrane phase, 25 mL of 1×10^{-4} M of MG; Receiving phase, 10 mL of 0.05 M NaOH; Rate of stirring 250 rpm; Time of transport 2 h.

Effect of cyanide concentration in the source phase: Table-2 shows the influence of the concentration of cyanide in the source phase on silver ion transport. As it is seen, the percentage of silver ion transported into the receiving phase increases with an increase in cyanide concentration up to 0.002 M of potassium cyanide. At lower cyanide concentrations, there was a decrease in the percentage of transport of silver probably due to uncompleted formation of Ag(CN)$_2^-$. Thus, 0.002 M potassium cyanide concentration was adopted for further studies.

Effect of sodium hydroxide concentration in the receiving phase: Results obtained from the study of the effect of sodium hydroxide in the receiving phase on transport efficiency of Ag$^+$ (Table-3) revealed that an increase in hydroxide concentration up to 0.06 M increases the efficiency of silver transport. Further

increase in hydroxide concentration did not improve the efficiency of transport. For this reason 0.06 M sodium hydroxide concentration was selected for receiving phase.

TABLE-2

EFFECT OF CYANIDE CONCENTRATION IN THE SOURCE PHASE ON TRANSPORT OF $Ag(CN)_2^-$ ION[a]

[CN⁻] (M)	Transported (%)
0.000	5
0.001	82
0.002	82
0.003	80
0.005	80
0.008	64
0.010	56
0.030	36
0.050	38

[a] Experimental conditions: Source phase, 5 mL of 1×10^{-4} M $Ag(CN)_2^-$ at pH = 6; Liquid membrane phase, 25 mL of 1×10^{-4} M of MG; Receiving phase, 10 mL of 0.05 M NaOH; Rate of stirring 250 rpm; Time of transport 2 h.

TABLE-3

EFFECT OF SODIUM HYDROXIDE CONCENTRATION IN THE RECEIVING PHASE ON THE TRANSPORT OF $Ag(CN)_2^-$ ION[a]

[OH⁻] (M)	Transported (%)
0.00	0
0.008	70
0.01	72
0.02	74
0.03	80
0.04	82
0.05	83
0.06	85.5
0.08	83
0.10	82

[a] Experimental conditions: Source phase, 5 mL of 1×10^{-4} M $Ag(CN)_2^-$ and 0.002 M KCN at pH = 6; Liquid membrane phase, 25 mL of 1×10^{-4} M of MG; Rate of stirring 250 rpm; Time of transport 2 h.

Effect of malachite green concentration in the organic phase: The influence of the concentration of MG in the chloroform phase on the transport efficiency of silver was also studied (Table-4). As can be seen, the percentage

transport of silver increases with an increase in MG concentration in chloroform. Maximum transport occurs when the reagent concentration is about 1.2×10^{-4} M. Further excess of the carrier had no considerable effect on the transport efficiency. Thus, a concentration of 1.2×10^{-4} M of MG adopted for further studies.

TABLE-4

EFFECT OF MG CONCENTRATION IN THE ORGANIC PHASE ON THE TRANSPORT OF Ag(CN)$_2^-$ ION[a]

[MG$^-$](M)	Transported (%)
0	3
5×10^{-5}	15
8×10^{-5}	70
1.2×10^{-4}	90
3×10^{-4}	89
5×10^{-4}	90

[a] Experimental conditions: Source phase, 5 mL of 1×10-4 M Ag(CN)$_2^-$ and 0.002 M KCN at pH = 6; Liquid membrane phase, varying concentration of MG; Receiving phase, 10 mL of 0.06 M NaOH; Rate of stirring 250 rpm; Time of transport 2 h.

Effect of time: Fig. 1 shows the time dependence of Ag$^+$ ion transport through the liquid membrane under the optimal experimental conditions. It is obvious that increase in time increased the percentage of silver to receiving phase and decreased the percentage of silver remaining in the source phase up to 240 min. The transport was nearly complete (90%) after 240 min.
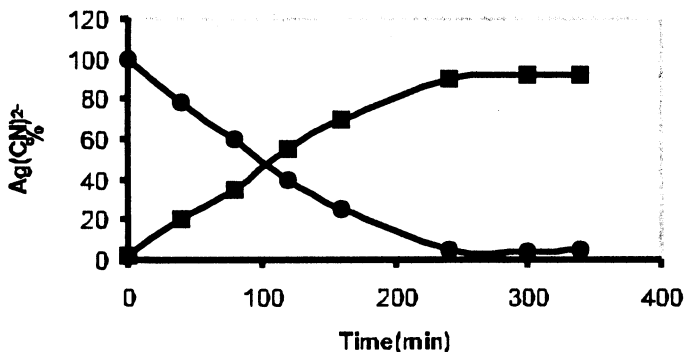

Fig. 1. Per cent of Ag(CN)$_2^-$ vs. time in receiving (■) and source (•) phases under optimum conditions.

Reproducibility of bulk liquid membrane technique: The reproducibility of the bulk liquid membrane technique was studied by performing six replicate transport experiments. The relative standard deviation was found to be 3%.

Selectivity of bulk liquid membrane technique: The per cent of transported Ag$^+$ and Mn$^+$ cations are listed in Table-5, which were present with silver in equimolar concentrations, into the receiving phase. In addition to the presented

cations, the interference effects of alkali and alkaline earth cations were also studied. All of these cations remained completely in the source phase. As is seen, the system is very selective and none of the cations studied interferes with this system.

TABLE-5

TRANSPORT OF Ag^+ FOR A COMPETITIVE EXPERIMENT WITH AN EQUIMOLAR MIXTURE OF FOREIGN IONS[a]

Mixture of cations	Cation	Transported (%)
$Ag^+, Hg^{2+}, Pd^{2+}, Cd^{2+}$	Ag^+	90
	Hg^{2+}	0
	Pd^{2+}	0
	Cd^{2+}	0
$Ag^+, Ni^{2+}, Co^{2+}, Fe^{2+}$	Ag^+	80
	Ni^{2+}	0
	Co^{2+}	0
	Fe^{2+}	0
$Ag^+, Zn^{2+}, Pb^{2+}, Al^{3+}$	Ag^+	85
	Zn^{2+}	0
	Pb^{2+}	0
	Al^{2+}	0

[a] Experimental conditions: source phase, 5 mL of 1×10^{-4} M $Ag(CN)_2^-$ and 0.002 M KCN at pH = 6; Liquid membrane phase, 25 mL of 1.2×10^{-4} M of MG; Receiving phase, 10 mL of 0.06 M NaOH; Rate of stirring 250 rpm; Time of transport 4 h.

Suggested mechanism: From the result obtained, the following mechanism is suggested for the transport of silver across a liquid membrane containing MG (Fig. 2). In the source phase silver forms an anionic complex $Ag(CN)_2^-$. MG is a
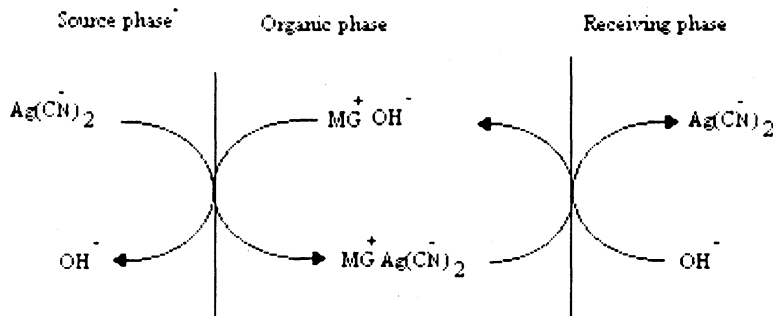

Fig. 2. Simplified representation of the transport mechanism of $Ag(CN)_2^-$ by Mg.

cationic dye with a single positive charge. In the source phase-organic phase interface MG forms an ion pair with silver cyanide and extracts it into the organic phase. At the receiving phase-organic phase interface, silver cyanide is abstracted from the organic phase while OH^- is given back to the carrier. A similar

mechanism has been reported previously for the transport of metal ion complex with thiocyanate[15].

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