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Javad Zolgharnein[a]; Akram Shahrjerdi[a]; Neda Asanjarani[a]; Gholamhassan Azimi[a]
[a] Department of Chemistry, Faculty of Science, Arak University, Arak, Iran

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Javad Zolgharnein, Akram Shahrjerdi, Neda Asanjarani, and Gholamhassan Azimi
Department of Chemistry, Faculty of Science, Arak University, Arak, Iran

Abstract: The facilitated transport of Au(III) through a chloroform bulk liquid membrane containing potassium-dicyclohexyl-18-crown-6 as a selective ion carrier was designed. Au(III) as $[AuBr_4]^-$, quantitatively transported across the liquid membrane. In the receiving phase, L-cysteine acts as a specific stripping agent. The amount of Au(III) transported through the liquid membrane after 120 minutes was $(96.2 \pm 1.3)\%$. The type of halide and its concentration, pH of source and receiving phase and also the type of stripping agents were optimized. The selectivity and efficiency of gold(III) transport from aqueous solutions containing various metal ions were investigated. The presence of EDTA in the source phase diminished drastically the competitive effect of interfering metals ion.

Keywords: Au(III)-transport, bulk liquid membrane, dicyclohexyl-18-crown-6, L-cysteine

INTRODUCTION

Gold is a metal with its beauty, permanency, and rarity; it is still the material of choice for jewelers and decoration articles. However, the unique chemical and physical properties of gold is the reason to use this element in many number of industrial and medical applications (1–3). Gold in a variety of forms has been used in medicine (4). Because of the importance of the functions of gold ion in human body, the transport

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Address correspondence to Javad Zolgharnein, Department of Chemistry, Faculty of Science, Arak University, Arak, Iran. Fax: +98 861 4173406. E-mail: J-zolgharnein@araku.ac.ir

of it through the human cell membrane may have great interest for research. The selective transport of metal ions across a cell membrane is known to play an essential role in biological processes (5). Among the separation methods ion-transport is much closer to the biological system (6). The recovery of metal ions from various wastes generated by industries is also of growing interest using ion-transport methods. In solving analytical and industrial problems, it is sometimes desirable to obtain an aqueous rather than an organic solution of the recovered component. This can be simply achieved by carrier-mediated transport through bulk liquid membrane processes (7). Macrocyclic compounds such as crown ethers have been well known as promising carriers, which is due to their highly selective interaction with many chemical species, particularly cations (8–10). In these respects, they resemble the naturally occurring antibiotic macrocycles, which have been shown to alter the permeability of biological membranes to certain cations (11–13). Ion transport is inherently a reaction based method, and its advantages are due to controllability of the carrier reaction conditions (14,15). Recently, we successfully used dibenzopyridino-18-crown-6, decyl-18-crown-6 and dicyclohexyl-18-crown-6, for selective and efficient ion-transport of the Pb^{2+}, Ag^{+}, and Tl^{+}, respectively through bulk liquid membrane (15–17). There is rarely a report about ion-transport of Au(III) through bulk liquid membranes (18,19). In this study, we have stimulated to design a new system, which is much closer to biological transports. We have designed an ion-transport of Au(III) through bulk liquid membrane containing potassium-dicyclohexyl-18-crown-6 as a selective and efficient ionophore. Au(III) as $[AuX_4]^{-}$ anion in the source and L-cysteine acts as a selective stripper in the receiving phase. L-cysteine is a sulphur containing amino acid such that the complexing ability of it is toward soft heavy metal ions such as Au(III) is quite high (20). This study demonstrates a new system for transport of Au(III) through bulk liquid membrane.

EXPERIMENTAL

Reagents and Chemicals

Reagent grade 18-crown-6 (18C6, **I**), dibenzo-18-crown-6 (DB18C6, **II**), dicyclohexyl-18-crown-6 (DC18C6, **III**), dibenzopyridino-18-crown-6 (DBPY18C6, **IV**), benzo-15-crown-5(B15C5,**V**), phenylaza-15-crown-5 (PhA15C5, **VI**), nitrobenzo-15-crown-5 (NB15C5, **VII**) were used (from Merck), their structure are shown in Fig. 1. The amino acids, salts of cations (nitrate, halides, sulphate, and thiosulphate), thiourea, EDTA, and extra pure chloroform (all from Merck) were used without any

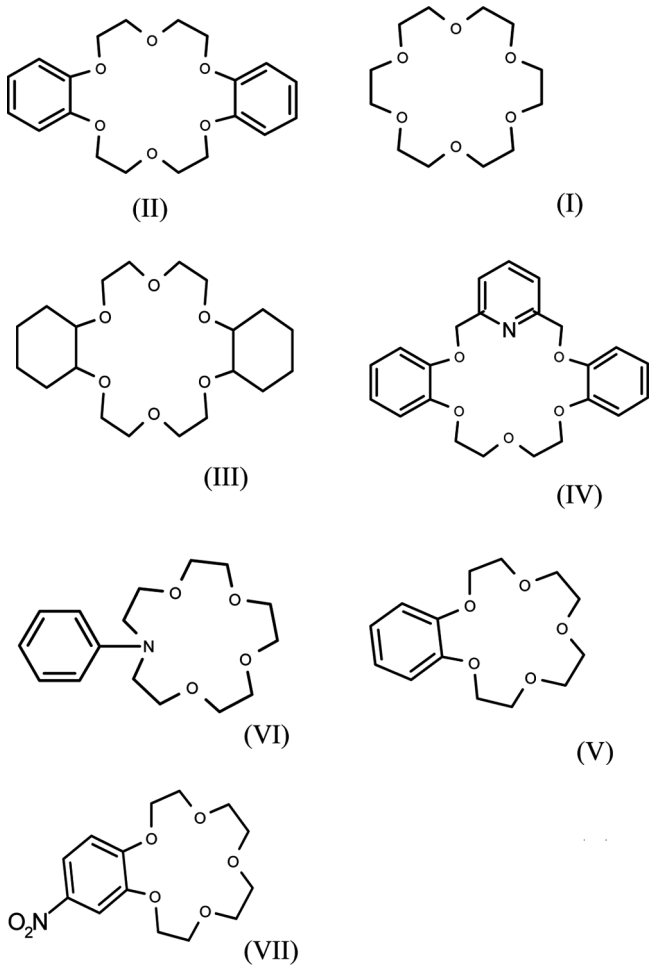

Figure 1. Structure of membrane carrier.

further purification except for vacuum drying of salts over P_2O_5. Au(III) bromide was from Aldrich Chemical Company. Doubly distilled deionized water throughout all experiment runs was used.

Apparatus and Procedure

A cylindrical glass cell (outside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used (21). The all influencing factors on selectivity and efficiency of

Au(III) transport have been optimized. In optimum conditions, the inner aqueous phase (source phase) contained 5 ml of 2.5×10^{-5} mol/L of Au(III) and 0.2 mol/L of potassium bromide. The outer aqueous phase (receiving phase) contained 10 ml of 6×10^{-3} mol/L of L-cysteine. The membrane phase contained 20 ml of 1.0×10^{-3} mol/L of DC18C6 in chloroform, which lies below the source and receiving phases, and bridged these aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (20×5 mm) at 120 rpm. All experiments were carried out at 25 ± 1°C. The Au(III) determinations were performed on a Perkin Elmer 2380 atomic absorption spectrometer. The wavelength set at 242.8 nm and the spectral band width at 0.7 nm. Determination of all other cations was carried out under the recommended conditions for each metal ion. A digital pH meter, Metrohm (model 691), equipped with a combined glass-calomel electrode was used for the pH adjustments. The pH values were adjusted by addition of 0.1 M of HNO_3 and sodium hydroxide solutions.

RESULTS AND DISCUSSION

Effect of Type and Concentration of Potassium Halide in Au(III) Transport

The Au(III) is more stable than Au(I), this has been convincingly ascribed to relativistic effects operating on S and P electrons (22). The high CFSE associated with square planer d^8 ions is a further factor favoring the +3 oxidation state (23). The square planer ions of type $[AuX_4]^-$ can be derived in which $X = F^-$, Cl^-, Br^-, and I^-. In designing of the ion-transport system for Au(III), the permeation of this highly charged ion through the organic liquid membrane such as chloroform is impossible. From another point of view, it is well known that the complexing ability of ordinary crown ethers toward soft heavy metal ions such as Au(III) is quite low (24,25). Since the Au(III) do not fit into the 18-crown-6 ring perfectly and according to the principal of Hard-Soft acid-base (26), interaction between Au(III) and oxygen atoms of 18-crown-6 ring is weak. This problem has been overcome by using anionic complexes of Au(III) and M^{n+} -crown ether carriers (M^{n+} is co-transported cation) (27,28). M^{n+} usually is an alkali or alkali earth cation, which forms more stable complex with ordinary crown ethers. Because of the goodness of fit of potassium ion into the 18-crown-6 ring (see next sub section), K^+ has been chosen as a co-transported cation. On the other hand, the Br^- has the most stability constant with Au(III) ($\log \beta = 31.5$) relative to other halide and low hydration energy (29). Because both Br^- and K^+ have the best criteria for changing Au(III) to an anionic complex, we preferred to

Table 1. Effect of halides in Au(III) transport

KX	[a]log β $[AuX_4]^-$	% transported into receiving phase	% remaining in Source phase
KF	–	85.3	13.8
KCl	21.3	95.1	2.9
KI	–	94.1	2.7
KBr	31.5	96.2	2.8

Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M KX; Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform; Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine; Time of transport: 120 min;
[a]Ref. (24).

choose the KBr for this purpose. The results obtained in Table 1, emphasizes the correction of this decision. This table shows the effect of type of halides (X^-) on formation of halide complex $[AuX_4]^-$. Therefore, we have designed a system for investigation the transport behavior of Au(III) as $[AuBr_4]^-$ through a bulk liquid membrane containing DC18C6 as a carrier in the form K^+-dicyclohexyl-18-crown-6.

The influence of the concentration of KBr in the source phase on Au(III) transport was investigated and the results are shown in Fig. 2. The transport of Au(III) increased as the concentration of KBr increases. The maximum transport of Au(III) occurs at a 0.2 mol/L of KBr in the source phase. A further increase in the concentration of potassium bromide has no significant effect on the transport efficiency. Without using of KBr, the extraction of ions via $[(Au(III)\text{-}DC18C6)^{3+}(Br^-)_3]$ ion-pairs into the membrane is negligible.

Effect of Type and Concentration of Carrier on Au(III) Transport

As we anticipated, the nature and type of the macrocycle used as carrier in the organic membrane phase has a very significant effect on the efficiency and selectivity of Au(III) transport. In another experiments (and under the same experimental conditions), several crown ethers as carrier for the transport of $[AuBr_4]^-$ anions in the presence of K^+ ions were examined. The results in Table 2, show that, among the 18-crown-6 series, DC18C6 is the most suitable carrier for the maximum transport of $K[AuBr_4]$, mainly due to its proper cavity size for K^+ ion. In addition, the presence of cyclohexyl groups which allows the pumping of the electrons into the ligand ring, increases the basicity of the oxygen atoms causes the more stability of K^+DC18C6 complex ($\log K = 4.96 \pm 0.03$) (30). It is noteworthy that, DB18C6 and DBPY18C6, despite their proper cavity size for K^+ ions,

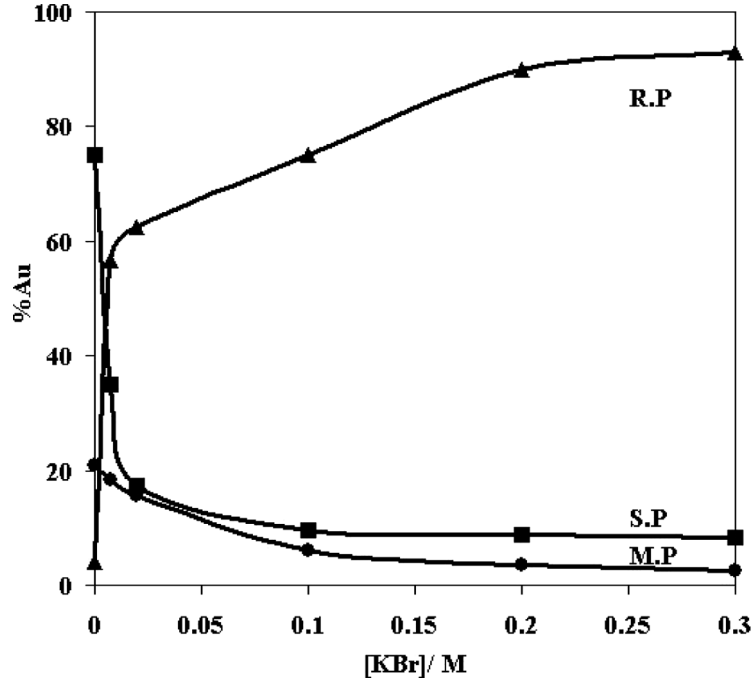

Figure 2. Effect of potassium bromide concentration in the source phase on Au(III) transport. Condition: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and varying concentration of KBr. Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform. Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine; Time of transport: 120 min.

Table 2. Effect of the carrier structure in the Au (III) transport

Carrier	% Transported into receiving phase	% Remaining in source phase	$LogK_{k+\text{-crown}}$
B15C5	60.1	16.9	2.8[a]
NB15C5	70.4	13.2	–
PhA15C5	66.0	30.2	–
DB18C6	70.9	15.3	4.86±0.04[b]
DBPY18C6	77.4	13.0	4.15±0.01[b]
18C6	81.8	10.3	5.06±0.07[b]
DC18C6	96.2	2.8	4.96±0.03[b]

Conditions: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M of KBr; Membrane phase: 20 ml of 1.0×10^{-3} M of examined carrier in chloroform; Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine; Time of transport: 120 min.

[a]Ref. (25).

[b]Ref. (30).

showed much lower transport efficiencies in comparison with DC18C6. This effect is related to the low stability of their K^+ complexes due to presence of more withdrawing electron group such as benzo and pyridyl into 18-crown-6 ring, (15,17,30). Some increasing transport efficiency of DC18C6 over the 18C6 is related to its lower solubility in the aqueous phase. In the case of macrocycles of smaller ring size such as B15C5, NB15C5, and PhA15C5, the improper cavity size for K^+ decreases the stability of $[Au(III)\text{-crown})^{3+}(Br^-)_3]$ complex. Thus, the transport of Au(III) through the liquid membrane diminishes drastically (17).

The influence of the concentration of DC18C6 in the organic membrane phase on the transport efficiency of Au(III) was also investigated. As seen in Fig. 3, the transport of Au(III) increases sharply by increasing the concentration of DC18C6 in the organic membrane. It is notable that, without the carrier the percentage transport of K^+ was negligible. The maximum transport of Au(III) occurs at a concentration more than a 1.0×10^{-3} mol/L of the carrier.

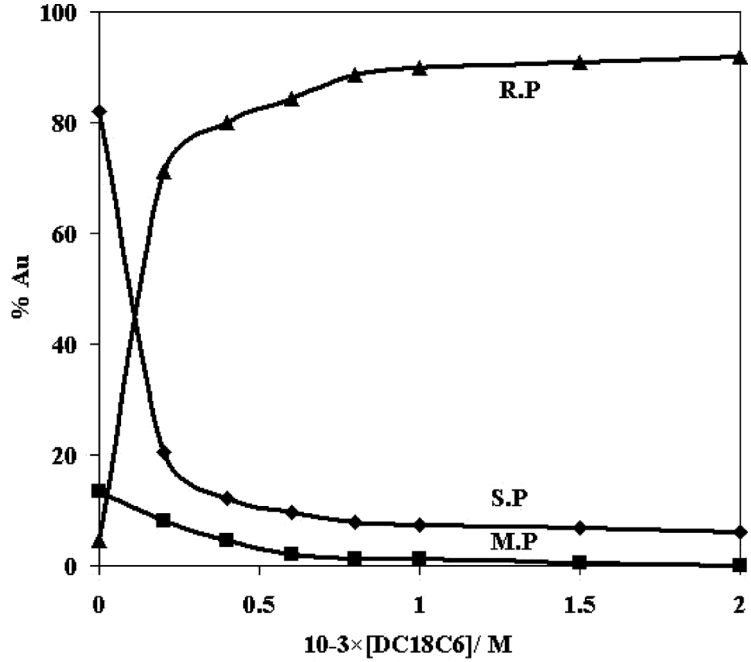

Figure 3. Effect of DC18C6 concentration in the organic phase in Au(III) transport. Condition: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M KBr. Membrane phase: 20 ml of varying concentration of DC18C6 in chloroform. Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine; Time of transport: 120 min.

Table 3. Effect of the receiving agent in Au(III) transport

Receiving agent	% Transported into receiving phase	% Remaining in source phase
Thiourea	55.8	28.7
$Na_2S_2O_3$	87.5	10.3
Na_2SO_3	66.6	12.4
L-glycine	74.0	5.6
Arginin	59.4	17.6
NaSCN	28.5	16.9
NaCl	55.5	3.7
NaI	50.6	9.4
L-cysteine	96.2	2.8

Conditions: Source phase: 5 ml of 2.50×10^{-5} M Au(III) and 0.2 M KBr; Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform; Receiving phase: 10 ml of 6.0×10^{-3} M of receiving agent; Time of transport: 120 min.

Effect of Type and Concentration of Receiving Agent in Au(III) Transport

Preliminary experiments revealed that the nature and composition of the receiving agent in the receiving aqueous phase could have a significant effect on the efficiency and selectivity of transport. The percentage of Au(III) transported in the presence of different receiving agent under similar experimental conditions is listed in Table 3. Among different receiving agent used, L-cysteine with high affinity to make stable complex with Au(III) acts as the most suitable receiver for the release of Au(III) cation from the membrane phase into the receiving phase. The log β for Au(III)-L cysteine is equal 14.85 (20,21). This amino acid has a sulphydryl group that the complexing ability of its toward soft heavy metal ions such as Au(III) accordance to HSAB principle is quite high (20,21,26).

The influence of the concentration of L-cysteine in the receiving phase on the transport efficiency of Au(III) was also studied and the results are shown in Fig. 4. The transport of Au(III) increases sharply by increasing the concentration of L-cysteine; The maximum of Au(III) transport occurs at a concentration of more than 6×10^{-3} mol/L.

Effect of the pH of Source and Receiving Phases in Au(III) Transport

In this study, the best pH region of the source and receiving phases in order to achieve quantitative transport of Au(III) was verified. Over a

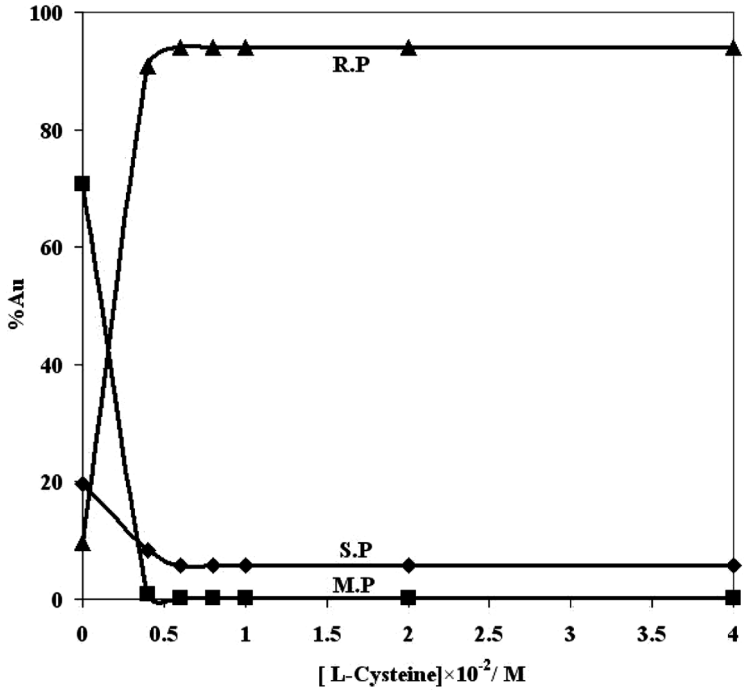

Figure 4. Effect of L-cysteine concentration in the receiving phase in Au(III) transport. Conditions: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M KBr. Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform. Receiving phase: 10 ml of varying concentration of L-cysteine. Time of transport: 120 min.

wide range of pH (3.0–11.0) of source, there is no significant variation on the transport efficiency of Au(III). Figure 5 shows the pH effect of the receiving phase on the transport of Au(III). As could be seen, the transport of Au(III) increased up to pH 8–9. At higher pH values there is a competitive reaction between different ionic forms of L-cysteine and OH^- for complexing Au(III) (20). This makes it difficult to assign the exact type of complexes in the solution. Therefore, the pH = 8–9 were chose as optimum pH in receiving phase.

Time Dependence of Au(III) Transport

The time dependence of Au(III) transport through the proposed liquid membrane was investigated. Figure 6 clearly shows that the extraction of Au(III) from the source phase into the organic membrane occurs

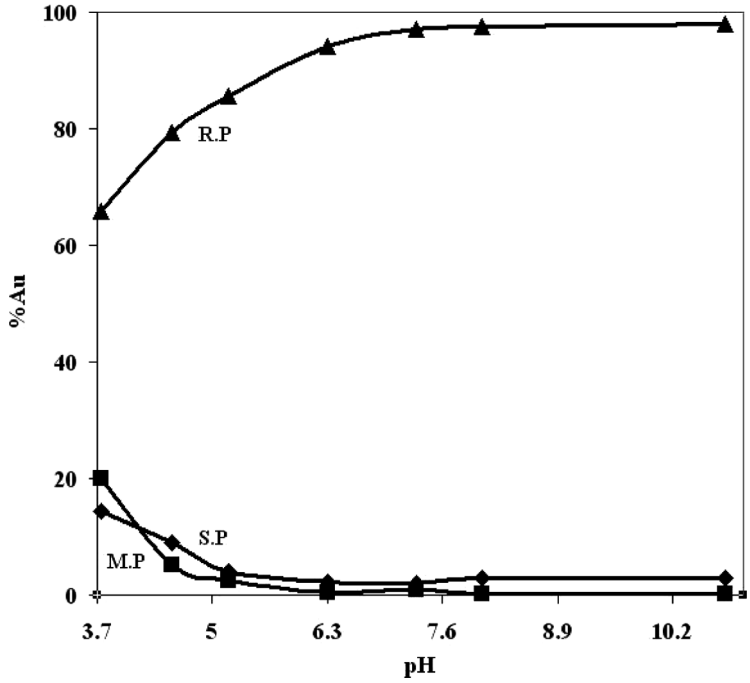

Figure 5. Effect of pH of the receiving phase in Au(III) transport. Conditions: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M KBr. Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform. Receiving phase: 10 ml of 6.0×10^{-3} M L-Cysteine; Time of transport: 120 min.

with a higher rate than releasing it into the receiving phase in the first 30 minutes of the experiment. However, the next releasing rate tends to be equal at even higher than extraction rate. Under optimum conditions, the transport of Au(III) from source phase into the receiving phase after 120 minutes equals 96.2%. The reproducibility of Au(III) transport was investigated and the amount of Au(III) transported through the membrane during 120 minutes in ten repeated measurements was $96.2 \pm 1.3\%$.

Competitive Effect of other Metal Ions

The selectivity of the designed membrane system was investigated under optimum experimental conditions. The equimolar concentrations of some M^{n+} cations such as: Tl^{+}, Ag^{+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+},

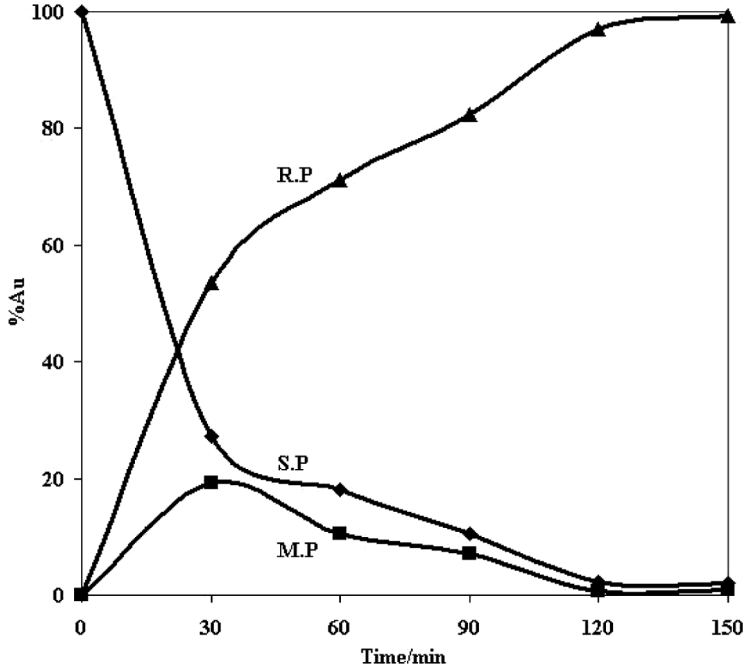

Figure 6. The time dependence of Au(III) transport from chloroform membrane. Conditions: Source phase: 5 ml of 2.5×10^{-5} M Au(III) and 0.2 M KBr. Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform. Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine; Time of transport: 120 min.

Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Fe(III), and Cr(III) in the presence of Au(III) undertaking competitive transport experiments using the optimized liquid membrane containing DC18C6.

It could be seen from the obtained results in Table 4, which among a variety of examined cations, Pb^{2+}, Zn^{2+}, Cu^{2+}, Ag^{+}, and Tl^{+} ions show some potential of the interfering effect. The high selectivity of Au(III) transport over the other used cations may be primarily attributed to the higher stability of the $[AuBr_4]^{-}$ compared to those of the other metal-bromide complexes (28). On the other hand, the high affinity of L-cysteine for Au(III) over most of other cations is another important factor in determining the efficiency of Au(III) transport (20). Table 4, shows the interferences effects of, Pb^{2+}, Zn^{2+}, Cu^{2+}, Ag^{+}, and Tl^{+}, which could be eliminated by the addition of EDTA (0.01 mol/L at pH = 4.5) as a proper masking agent to the source phase, under optimal experimental conditions.

Table 4. Amounts of cations transported from various cation mixtures through the liquid membrane

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
*Mixture **1***		
Au(III)	95	4
Ni^{2+}	0	100
Co^{2+}	4	95
*Mixture **2***		
Au(III)	84	16
Pb^{2+}	90	10
Tl^{+}	41	59
*Mixture **3***		
Au(III)	96	4
Cd^{2+}	1	99
*Mixture **4***		
Au(III)	96	3
Ca^{2+}	2	96
Mg^{2+}	1	98
*Mixture **5***		
Au(III)	97	3
Fe(III)	0	100
Cr(III)	0	100
*Mixture **6***		
Au(III)	95	4
Cu^{2+}	24	26
Zn^{2+}	52	33
Mixture 7		
Au(III)	97	2
Ag^{+}	94	3
*Mixture **8***		
Au(III)	97	2
Mn^{2+}	0	100
*Mixture **9***[b]		
Au(III)	95	3
Pb^{2+}	0	100
Tl^{+}	0	100
*Mixture **10***[b]		
Au(III)	97	3
Zn^{2+}	0	100
Cu^{2+}	0	100
*Mixture **11b***		
Au(III)	97	2
Ag^{+}	8	5

conditions: Source phase: 5 ml of 2.50×10^{-5} M Au(III), and equimolar of other metal ion used in each set and 0.2 M KBr; Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform; Receiving phase: 10 ml of 6.0×10^{-3} M L-cysteine. Time of transport: 120 min.

[b]in the presence of 0.1 M EDTA in source phase.

Recommended Transport Mechanism

The transport process follows such a sequence of steps; the source phase–membrane interface; the K^+-DC18C6 complex is formed (27). Because the $[AuBr_4]^-$ complex anion is less hydrated than other anions present in the source phase, it will form an ion pair with the potassium–crown complex cation. Partitioning of (K^+-DC18C6) $[AuBr_4]^-$ complex into the organic membrane. Diffusion of the [K^+-DC18C6] $[AuBr_4]^-$ across the membrane. The high affinity of L-cysteine for complexes with Au(III) releases it, K^+ and Br^- in receiving phase. Diffusion of DC18C6 back across the membrane to the source phase–membrane interface where the cycle is repeated.

CONCLUSIONS

A quantitative and facilitated selective system for transport of Au(III) through a chloroform bulk liquid membrane was designed. In this system, the K^+-DC18C6 was used as selective carrier for $[AuBr_4]^-$ transport. L-cysteine shows good affinity for extracting of Au(III) from membrane phase. All the influences parameters on transport efficiency were optimized. The interferences of some metal ions such as Pb^{2+}, Zn^{2+}, Cu^{2+}, Ag^+ and Tl^+ by using EDTA at pH = 4.5 diminished drastically. The maximum Au(III) could be selectively transported after 120 minutes.

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