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Bulk liquid membrane extraction of silver(I) with 2-mercaptobenzothiazole as a carrier: Kinetic approach

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ABSTRACT

The transport and separation of silver(I) ions across a bulk liquid membrane by 2-mercaptobenzothiazole (MBT) as carrier were investigated. The efficiency of Ag(I) transport was studied as a function of different parameters. The maximum of Ag(I) recovery was 85% in the presence of thiourea 0.1 M at pH 1, as complexing agent in the receiving phase, for a short extraction time of 4 h. A selective separation between Ag(I) and Mn(II) ions from equimolar mixture Ag–Cu–Mn solutions was performed. Besides, we have applied the kinetic model involving two consecutive irreversible first-order reactions to calculate the pseudo-first-order apparent membrane entrance and exit rate constants k_e and k_s, respectively. Under optimal conditions, the kinetic model curves of time dependence of silver concentrations (R) in the feed, membrane and receiving phases showed a good agreement with the experimental results. The apparent rate constants values were 6.93×10^{-3} min^{-1} for k_e and 6.81×10^{-2} min^{-1} for k_s. The transport of silver(I) is mainly controlled by the slow reaction of the formation of Ag–MBT complex at the membrane entrance.

Keywords: Bulk liquid membrane; Silver extraction; Apparent rate constants; 2-mercaptobenzothiazole; Thiourea stripping agent; Separation factor

1. Introduction

Silver is one of the first best-known noble metals used in various industrial applications (photography, electrochemical plating, chemical industry, etc.) that may be released into the environment through these industrial wastes. Silver is also used as an antibacterial agent for the purification of water. Today, it is well established that the silver ions are toxic to some aquatic species and can pose a serious threat to water pollution [1–3].

Hence, there is a necessity to develop selective methods for the preconcentration, separation and removal of silver metal from waste waters. Many of the conventional techniques for removing and recovering metal ions from aqueous effluents, such as precipitation, solvent extraction, electrochemical processes, ion exchange and electrodialysis have been reconsidered in view of their possible substitution by liquid membrane techniques [4–6]. Liquid membranes are

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interesting for metal extraction from aqueous media since this technology combines the extraction and stripping processes into a single unit operation and moreover, the metal extraction is facilitated by carrier-mediated transport [7,8].

The facilitated transport of silver(I) has been reported through various liquid membrane systems, (bulk liquid membrane (BLM)) [9–11], emulsion liquid membrane (ELM) [12,13], supported liquid membrane (SLM) [14–16] and plasticized inclusion membrane (PIM) [15,17,18]. Different types of carriers such as cyclic ligands crown ethers [9–14,16,19,20], cyanex [21] and D2EHPA [22,23] are used as carriers.

Among these liquid membrane processes, the BLM is a practical and simple system often used in laboratory to study and evaluate the complexation and the transport properties of synthetic and natural carriers [11,24], and to determine the rate constants of the extraction and stripping reactions that describe the kinetics of metal transport [25–29]. The high number of works describing the transport of silver through BLM is related to its preconcentration and separation with different carriers present in liquid membrane and to the effect of the feed and the receiving phase compositions that play a primordial role in the membrane transport [10,30,31]. Besides, in order to strip efficiently the silver ions from the membrane to the receiving phase and to avoid low transport time, complexing agents such as thiosulphate [10,20,32], EDTA [30], thiocyanate [30] and oxalate [10] have been used in the receiving phases. To date, only one work has shown the efficient transport of Ag(I) ions through BLM by the carrier 2-mercaptobenzothiazole (MBT) into a receiving phase constituted with thiosulphate, which was found to be a better complexing agent compared to EDTA, oxalate and thiocyanate [10]. MBT contains sulphur atoms that coordinate with metal ions as exclusive donor atoms and especially forms stable complexes with Hg^{2+} and Ag^{+} [10]. MBT has been widely used and grafted as selective ligand for adsorption of heavy metal ions on silica or alumina support [33–35], but only the work of Akhond and Tashkhourian [10] has described its behaviour in liquid membrane system. This study also reported on the selectivity of Ag(I) extraction from equimolar mixture of metal ions, but no kinetic study was performed to describe the mechanism of Ag(I) transport through the BLM.

In this paper, the liquid–liquid extraction and the transport of silver(I) ions were performed through BLM, containing 2-mercaptobenzothiazole (MBT) as carrier, from either single metal ions or equimolar mixture Ag–Cu–Mn aqueous solutions. Effects of the aqueous phases and membrane compositions were experimentally investigated to obtain the optimal efficiency of silver transport. The presence of thiourea, as complexing agent in the receiving phase was used to improve the efficiency of the extraction process. Besides, we have applied the kinetic model involving two consecutive irreversible first-order reactions to describe the reaction rates of Ag(I) and the MBT carrier at the interfaces by calculating the apparent rate constants k_e (extraction) and k_s (stripping). The results were simulated and fitted with the obtained experiment data of silver(I) under the optimal conditions of the transport.

2. Experimental

2.1. Reagents and metal ion solutions

The 2-mercaptobenzothiazole (MBT) was a commercial reagent from Fluka and was used without further purification. Chloroform ($CHCl_3$) from (Merck) was purified by washing with distilled water to remove the stabilizer. Silver nitrate, copper nitrate and manganese nitrate salts of the highest purity were purchased from Fluka and were prepared in distilled water or nitric acidic (Merck). The thiourea ($CS(NH_2)_2$) was obtained from Riedel-de Haen and was dissolved in water by adjusting the pH at 1 with HNO_3.

2.2. Procedure

2.2.1. Liquid–liquid extraction experiments

Extraction experiments were performed in a thermostated vessel (25 ± 1˚C) using equal volumes (10 mL/10 mL) of aqueous and chloroform organic phases shaken for a sufficient time (30 min) to reach equilibrium and then the separation of two phases was carried out by gravity. The metal ion concentrations were determined in the aqueous phase, after dilution in pure water, by atomic absorption with a Shimadzu 6800 spectrophotometer at a wavelength of 328.1 nm. The concentration of Ag(I) in the organic phase was obtained from a simple mass balance.

2.2.2. Transport experiments

The transport studies were carried out in a thermostatically controlled cylindrical glass cell at 25˚C, as described elsewhere [36]. The BLM, composed of the MBT carrier dissolved in chloroform ($V = 90$ mL), was put in the bottom of the cylindrical glass cell (Fig. 1). A glass cylinder tube was then placed vertically into the cell and filled by the feed phase. The receiving phase

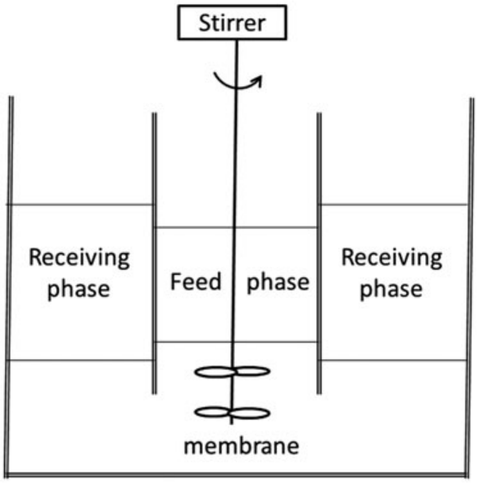

Fig. 1. Schematic representation of the BLM cell.

was thus introduced into the cell on the top of the organic phase. The presence of the cylinder tube allowed for separating the feed phase from the receiving phase. The volumes and the composition of the phases were as follows: the aqueous feed phase was 15 mL of $AgNO_3$ 10^{-3} M adjusted to the desired pH with nitric acid, the receiving phase (30 mL) contained either thiourea at different concentrations adjusted to pH 1, or pure water, or nitric acid 0.1 M. The stirring of the three phases was performed by a controlled rotation of the glass cylinder tube at 200 rpm. The surface areas of both interfaces feed phase-membrane (S_F) and membrane-receiving phase (S_R) were $S_F = 0.753$ cm^2 and $S_R = 18.08$ cm^2, respectively.

The metal concentration in both feed and receiving phases was measured by atomic absorption spectrophotometer at the wavelengths of 328.1 nm for silver and 324.7 nm for copper and 279.5 nm for manganese. The metal ion concentrations in the organic membrane phase were calculated from the mass balance. All the experiments have been repeated three times and the reproducibility was confirmed as ±5%.

2.3. Transport mechanism and kinetic model development

The silver(I) ions transport from feed phase to receiving phase via bulk chloroform membrane containing MBT as carrier can be explained by deprotonation–protonation of the carrier at the two membrane interfaces [10], where Ag^+ and H^+ ions are counter-transported. The mechanism can be described by the illustration in Fig. 2.

It was assumed that the facilitated transport of Ag(I) ions through bulk chloroform membrane obeys the kinetic model involving two consecutive irreversible first-order reactions, the extraction and the stripping defined by the first-order apparent rate constants k_e and k_s, respectively [37].

$$C_f \xrightarrow{k_e} C_m \xrightarrow{k_s} C_s$$

where C_o: initial silver(I) concentration in the feed phase at $t = 0$.

C_f, C_s and C_m: concentrations of metal ions in feed, receiving and membrane phases at t, respectively.

In order to determine k_e and k_s, three kinetic equations were used to fit the experimental data [25–29,38], based on the dimensionless concentrations R of Ag(I) in the feed, the BLM and the receiving phases:

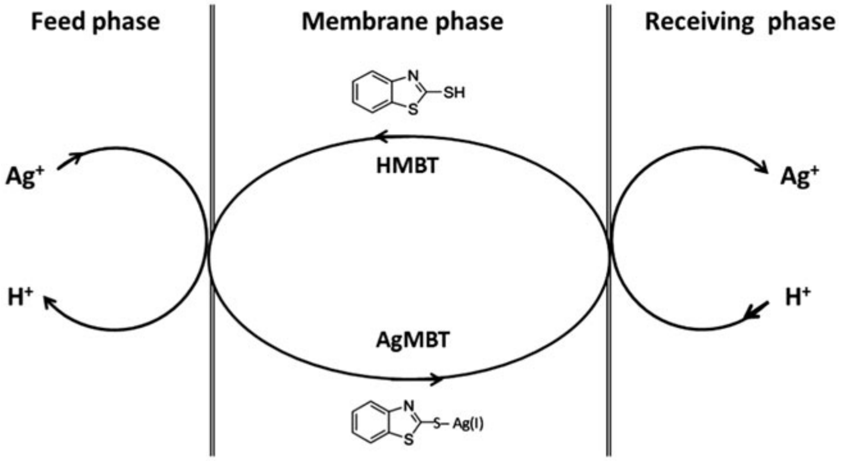

Fig. 2. Transport mechanism of Ag(I) through a BLM using MBT as carrier and H^+ as counter ions.

$$\frac{dR_f}{dt} = -k_e R_f \quad (1)$$

$$\frac{dR_m}{dt} = k_e R_f - k_s R_m \quad (2)$$

$$\frac{dR_s}{dt} = -k_s R_m \quad (3)$$

where $R_f = C_f/C_o$; $R_m = C_m/C_o$; $R_s = C_s/C_o$ and $R_f + R_m + R_s = 1$ according to the mass balance.

When $k_e \neq k_s$, the integration of these differential equations gives:

$$R_f = \exp(-k_e t) \quad (4)$$

$$R_m = \frac{k_e}{k_s - k_e}[\exp(-k_e t) - \exp(-k_s t)] \quad (5)$$

$$R_s = 1 - \frac{1}{k_s - k_e}[k_s \exp(-k_e t) - k_e \exp(-k_s t)] \quad (6)$$

These equations (R vs. time) show that R_f is monoexponential, whereas R_m and R_s are bi-exponential. In the case of accumulation of metal ions in the membrane phase, the maximum values of t_{max} and R_m can be evaluated when $dR_m/dt = 0$.

$$t_{max} = \frac{\ln\left(\frac{k_e}{k_s}\right)}{k_e - k_s} \quad (7)$$

$$R_m^{max} = \left(\frac{k_e}{k_s}\right)^{\frac{-k_s}{k_e - k_s}} \quad (8)$$

From combining Eqs. (7) and (8), the following relationship can be obtained:

$$k_s = \frac{\ln\left(\frac{1}{R_m^{max}}\right)}{t_{max}} \quad (9)$$

The apparent rate constants k_e and k_s, reported in Table 2, were obtained by fitting the equations.

3. Results and discussion

Preliminary experiments based on solvent extraction were performed in order to determine the stoichiometry of the extracted species. The extraction of Ag(I) ions from aqueous phase in chloroform by MBT at different concentrations was experimentally determined from the plots of the distribution curves log D vs. pH. The metal distribution coefficient (D) was calculated according to: $D = [M]_{org}/[M]_{aq}$, where $[M]_{org}$ and $[M]_{aq}$ represent the total metal concentrations in the organic and the aqueous phase, respectively. Fig. 3 shows that the slopes of the curves are equal to 1 confirming the 1:1 stoichiometry of the Ag–MBT complex for MBT concentrations varying from 5×10^{-5} to 5×10^{-4} M as reported in the literature [39].

In the next steps, several factors such as the composition of the aqueous and BLM phases were studied in order to study and to improve the efficiency of Ag(I) transport by the MBT carrier.

3.1. Effect of the receiving phase composition

The transport of metal ions across the liquid membrane is strongly influenced by the nature of the receiving phase, which plays an important role in the dissociation of the metal complex at the interface membrane-receiving phase. However, when the dissociation is not efficient, the membrane becomes saturated and the transport efficiency decreases. The transport of silver(I) through the BLM containing the MBT carrier concentration fixed at 5×10^{-4} M was studied in the presence of thiourea 0.1 M at pH 1 as stripping agent. The efficiency of the transport was compared to the stripping of Ag(I) into water or nitric acid 0.1 M receiving phases. The feed phase was composed of silver nitrate 10^{-3} M at pH 5.5. As shown in Table 1, the transport efficiency of Ag(I) decreases in the following order: thiourea > HNO_3 > water. The better efficiency of silver transport with HNO_3 than with water proves that the mechanism of transport is

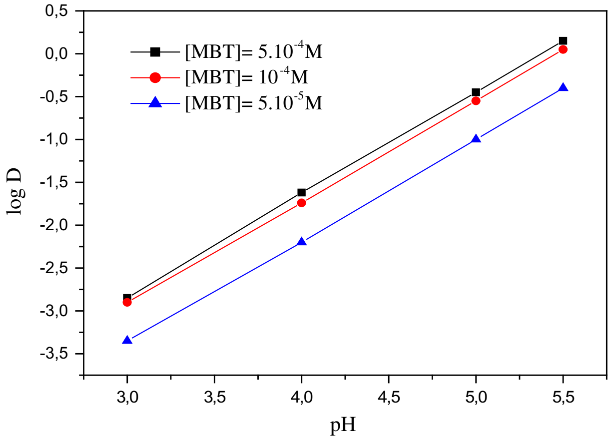

Fig. 3. Distribution coefficient of Ag(I) as a function of pH at variable concentrations of MBT. Aqueous phase: [Ag(I)] = 10^{-3} M; organic phase: [MBT] in chloroform.

Table 1
Effect of the receiving phase composition on the transport efficiency of silver (I). Feed phase: [Ag(I)] = 10^{-3} M at pH 5.5; membrane: [MBT/chloroform] = 5×10^{-4} M; receiving phase: water or nitric acid 0.1 M or thiourea 0.1 M at pH 1; time of the transport experiment 4 h

Receiving phase composition	Ag(I) % transported into receiving phase
H_2O	18
HNO_3 (0.1 M)	46
$CS(NH_2)_2$ (0.1 M)	85

proton driven, requiring a great difference of pH between the feed and receiving phases. The presence of thiourea significantly enhances the stripping of Ag(I) and leads to the highest Ag(I) transport efficiency compared to nitric acid and water. This fact could be related to the high ability of the thiourea to form a $Ag(CSN_2H_4)_3^+$ stable complex through either the sulphur atom or the nitrogen atom in acidic medium [14].

Besides, the transport efficiency of silver increases with increasing thiourea concentration from 0.01 to 0.3 M. Fig. 4 shows that an optimum transport efficiency of 85% is obtained for thiourea 0.1 M and remains constant when the thiourea concentration is increased above this critical concentration. In the following transport experiments, thiourea 0.1 M (pH 1) was thus introduced in the receiving phase.

3.2. Effect of pH of the feed phase on Ag(I) ions transport

Fig. 5 shows the extracted Ag(I) percentage into the receiving phase as a function of the pH of the feed phase in the range pH 2–9. The amount of extracted Ag(I) increases sharply with increasing pH values and reaches an optimum at 5.5. For pH values lower than 4.5 and higher than 6, one can notice a significant decrease in Ag(I) transport. As already mentioned, the sulphur atom of the MBT carrier coordinates with Ag(I) ions. However, at lower pH, the MBT remains preferentially in the protonated form and a lower amount of Ag(I) is extracted. This is an evidence of the influence of the pH of the feed phase on the interface reaction. On the contrary, for experiments conducted at pH values higher than 5.5 for the feed phase, the efficiency of the transport decreases due to the precipitation of Ag(I) metal ions as AgOH at higher values of pH.

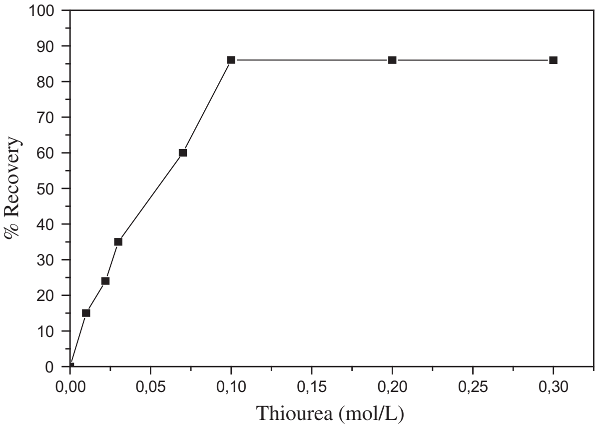

Fig. 4. Influence of the thiourea concentration in the receiving phase on the transport efficiency of silver(I). Feed phase: [Ag(I)] = 10^{-3} M at pH 5.5; membrane: [MBT/chloroform] = 5×10^{-4} M; receiving phase: thiourea at pH 1.

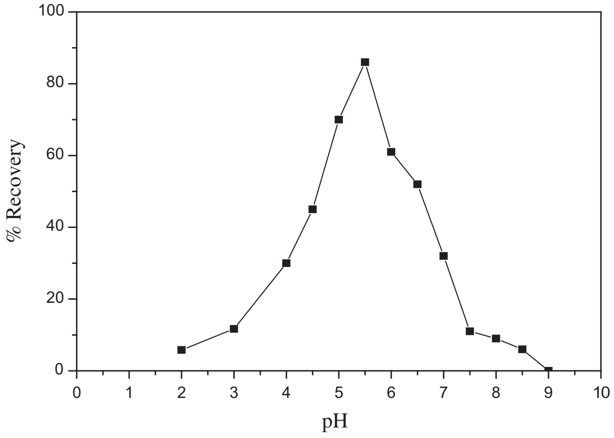

Fig. 5. Effect of pH in the feed phase on the Ag(I) ions transport to receiving phase via BLM. Feed phase: [$AgNO_3$] = 10^{-3} M at various pH; membrane: [MBT/chloroform] = 5×10^{-4} M; receiving phase: thiourea 0.1 M at pH 1.

3.3. Effect of carrier concentration

Transport experiments of Ag(I) ions were carried out at MBT concentrations ranging from 5×10^{-5} to 5×10^{-4} M. Fig. 6 shows that the recovery percentage of Ag(I) in the receiving phase increases slightly with increasing carrier concentrations and the maximum

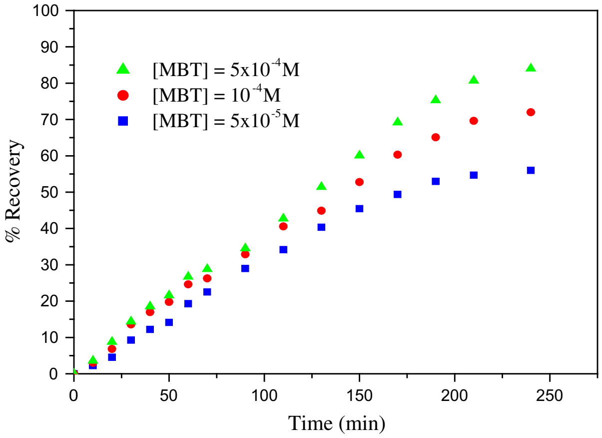

Fig. 6. Effect of MBT concentration on the Ag(I) recovery into the receiving phase. Feed phase: [$AgNO_3$] = 10^{-3} M at pH 5.5; membrane: MBT/$CHCl_3$; receiving phase: thiourea 0.1 M at pH 1.

recovery (85%) is reached for MBT 5×10^{-4} M after a transport time of 4 h.

3.4. Competitive transport of Ag(I) from Ag–Cu–Mn tertiary mixture

The competitive transport of silver(I) from feed phases also containing Cu(II) and Mn(II) ions at 10^{-3} M was investigated by BLM with MBT 5×10^{-4} M into thiourea 0.1 M at pH 1 as receiving phase. As observed in Fig. 7, effective separation occurs between Ag(I) and Mn(II) ions, while an insignificant separation of Ag(I) from copper(II) is obtained. The process selectivity decreases in the following order: Ag(I) (72%) > Cu(II) (45%) > Mn(II) (0.4%) after 4 h of transport experiments. This result can be explained by the high ability of Ag(I) to bond with sulphur donor atom of MBT compared to Cu(II) and Mn(II) [40].

The separation factor (SF) of Ag(I) from Cu(II) and Mn(II) mixture metals (M_m) was calculated for a transport time of 4 h and compared with reported works.

$$SF = ([Ag]/[M]_m)_{r,t}/([Ag]/[M]_m)_{f,0}$$

where the subscripts r, t indicate the receiving phase at time t ($t = 4$ h) and f, 0 indicate the feed phase at time 0 and m denotes mixture.

The value of the SF was 180 for Ag(I)/Mn(II), 1.6 for Ag(I)/Cu(II) and 113 for Cu(II)/Mn(II). A low selectivity between Ag(I) and Cu(II) ions (SF = 1.65) was also observed for the selective transport of silver from mixture containing Cu(II) and Zn(II) across SLM mediated by cryptand [2.2.2.] as a selective carrier into pure water as receiving phase [41]. Besides, in another work [18], a similar SF (2.63) was determined for the binary mixture Ag(I)–Cu(II) transported through a PIM containing the carrier calix[4] pyrrole[2] thiophene and in the presence of thiosulphate as complexing agent in receiving phase for a longer transport time of 24 h.

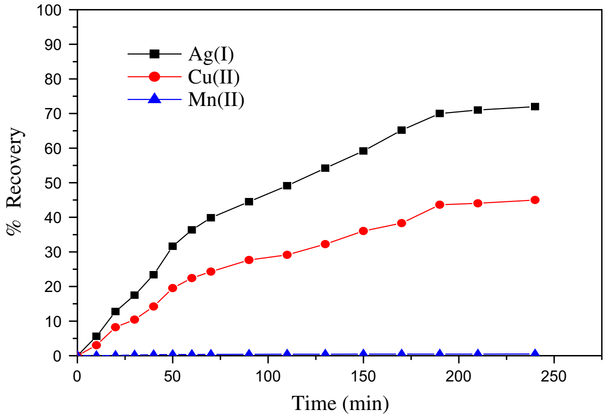

Fig. 7. Competitive transport of Ag(I), Cu(II) and Mn(II) from Ag–Cu–Mn equimolar mixture. Feed phase: [metal] = 10^{-3} M at pH 5.5; membrane: [MBT/chloroform] = 5×10^{-4} M; receiving phase: thiourea 0.1 M at pH 1; time of the transport experiment 4 h.

3.5. Kinetic transport

The concentration time profile of Ag(I) transport was carried out under optimum experiment conditions established previously. The evolution of the curves of the dimensionless concentrations (R) with time in the feed (R_f), membrane (R_m) and receiving (R_s) phases are reported in Fig. 8. As can be seen, R_f decreases mono-exponentially with time, and R_s increases continuously according to a sigmoid type curve. Besides, a low accumulation of the complex Ag–MBT occurs in the BLM during the first hour and then after 3 h, the mass transport is characterized by a quasi-stationary state. R_m presents a maximum (R_m^{max}) at t_{max} and decreases with time up to a constant level. The behaviour of the curves suggests thus that the Ag(I) transport obeys the kinetic model described by two consecutive irreversible first-order reactions [29,38] that can be calculated from equations (Eq. (4)) to (Eq. (9)). A good agreement is observed between the experimental and model data.

The obtained kinetic parameters k_s, k_e, t_{max} and R_m^{max} are presented in Table 2. The significant difference between the two rate constants k_e and k_s results in a lower complexation of the Ag(I)–MBT complex at

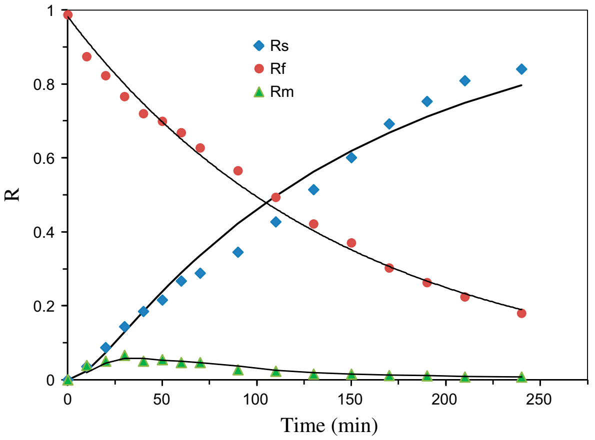

Fig. 8. Time dependence of dimensionless Ag(I) concentration (R): R_s in receiving phase, R_f in feed phase and R_m in membrane; points, experimental results; (▬) simulated results. Feed phase: $[AgNO_3] = 10^{-3}$ M at pH 5.5; membrane: $[MBT/CHCl_3] = 5 \times 10^{-4}$ M; receiving phase: thiourea 0.1 M at pH 1; time of the transport experiment 4 h.

Table 2
Apparent rate constants for extraction (k_e) and stripping (k_s) Ag(I) transport

k_e (min^{-1})	k_s (min^{-1})	t_{max} (min)	R_m^{max}
6.93×10^{-3}	6.81×10^{-2}	37	0.07

the interface of feed phase and BLM and a faster decomplexation rate at the interface of BLM and receiving phase that may be attributed to the presence of thiourea that promotes the decomplexation of the Ag(I) ions in the receiving phase. That is, the transport of Ag(I) is mainly controlled by the reaction rate at membrane–feed phase interface and the diffusion of Ag–MBT complex in BLM.

4. Conclusion

We have shown that BLM containing the carrier 2-mercaptobenzothiazole was an efficient liquid membrane system for the transport and separation of silver(I) ions. This process can be optimized from the concentration of the carrier in the BLM, the nature of the receiving phase and the feed acid concentration. The maximum of Ag(I) recovery was 85% in 4 h for MBT carrier concentration 5×10^{-4} M and in the presence of thiourea 0.1 M at pH 1 in the receiving phase.

The competitive transport of silver(I) from tertiary mixture Ag–Cu–Mn showed a good efficiency for silver transport and that the selective separation occurred between Ag(I) and Mn(II) ions, while no effective separation Ag(I)/Cu(II) was observed with the BLM.

We showed that the kinetic model based on the two consecutive irreversible first-order reactions when applied to Ag(I) transport gave a good fitting of the experimental data. The results of the experiments and the apparent rate constants values showed that the extraction of Ag(I) was mainly governed by the formation of the Ag–MBT complex at the interface of feed phase and membrane.

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