

Selective transport of Ag (I) ion across a bulk liquid incorporated with dibenzo 18-crown-6 (DB18C6) as carrier

Azizollah Nezhadali* and Fatemeh Moein Pour

* Department of Chemistry, Payame Noor University, Mashhad-868-31, Iran

*Corresponding author at: Department of Chemistry, Payame Noor University, Mashhad-868-31, Iran. Tel.: +98.511.8683968; fax: +98.511.8683001.
E-mail address: aziz_nezhadali@yahoo.com (A. Nezhadali).

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ABSTRACT

The competitive metal ion transport of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) cations with dibenzo-18-crown-6 (DB18C6) were studied and compared. The source phase contained equimolar concentration of the metal cation and the organic phase contained the ligand (DB18C6) in an organic solvent. The concentrations in the all transport experiments for the cations and ligand were 0.01 M and 1.0×10^{-3} M, respectively. The source phase solutions were buffered (acetic acid/sodium acetate) at pH = 4-6. The transports of Cu(II), Ag(I) and Co(II) with DB18C6 are possible in the mixture, but the transport efficiency for Ag(I) ion is much better than the other cations. The presence of dichloromethane and 1,2 dichloroethane were optimized in the organic phase. The results show the transport efficiency depends to the types of thiourea and potassium thiocyanate ligands in the receiving phase. The results show that the presence of palmetic acid in the membrane phase improves the efficiency of the transport for Ag(I) cation.

1. Introduction

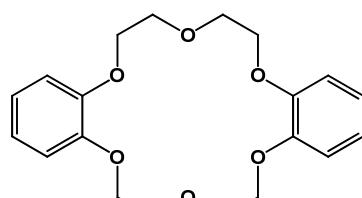
Among the separation techniques ion transport is a selective, efficient and simple method. The liquid membrane has widely been used to study ion transport with a concentration gradient [1-3]. The liquid membrane technique has been emerging as a method for the selective separation of the metal cations. It has several advantages such as, the extraction, stripping and regeneration operation are combined in single step [4].

In recent years, several investigations were carried out in the design and preparation of bulk liquid membranes [5-7]. Transport of metal ions across a membrane, plays an essential role in many biochemical processes and has useful practical applications in separation sciences. The stability constants of complexes have been used to understand the extraction equilibrium in different systems. As a rule, the rate of transport increases with rise in stability of complexes. The arrangement used in these systems involves three phases: aqueous source and receiving phases separated by an immiscible organic membrane phase incorporating the ionophore. For similar source and receiving phases, the presence of the ionophore in the organic phase may act as a 'carrier' for the metal ion until the concentrations in both aqueous phases equalizes and the system reaches equilibrium [8]. The investigations have established that the nature of a macrocyclic ionophore such as the ring size, the kind of donor atoms and substituting groups present in the ring has an important role in the cation transport [1-2]. The transport of cations through supported liquid membrane mediated by neutral carrier can be regarded as a sequential process including phase transfer of salt, complexation/decomplexation, and diffusion steps. The rate of transport depends to the above-mentioned process [8]. One of the specific characteristics of crown compounds is the ability to

selectively form complexes by capturing cations with an ionic diameter fitted to the cavity size of the crown compound. One of the crown ethers that used for separations as carrier in some extraction techniques is dibenzo-18-crown-6 (DB18C6) [8-9]. As of our knowledge, this ligand has not used in competitive bulk liquid membrane transport techniques for the mixture of transition and post transition metal cations. So, it seems to be a sufficient ligand for this purpose.

The variations in the nature of the solvent produce significant changes in the binding properties of the ligand and the efficiency of the transport [8]. In some researches using solvent binary mixtures in the membrane phase have improved the selectivity and efficiency of the ion transport [9].

In this study, we investigated competitive liquid membrane transport of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) cations using dibenzo-18-crown-6 as carrier (**Scheme 1**). The effect of some parameters and compounds like as pH, solvent, time, rate of shaking and addition of thiourea ($\text{CH}_4\text{N}_2\text{S}$) and potassium thiocyanate (KSCN) in receiving phase were studied and optimized.



Scheme 1

2. Experimental

2.1. Materials and solutions

All of the chemicals used were of analytical reagent grade (Merck). All of the aqueous solutions were prepared with double distilled deionized water. The standard stock solutions of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) were prepared by dissolving nitrate salts of them. 1×10^{-3} M Stock solutions of DB18C6 were prepared in chloroform, dichloromethane and 1,2 dichloroethane, separately.

2.2. Instrumentation

The metal ion concentrations in both source and receiving phases after each transport experiment were determined using a Philips PU9100X atomic absorption spectrometer. The buffer solutions prepared by controlling of them using Metrohm-691 pH meter.

2.3. Procedure

The transport experiments were carried out in a "concentric cell" in which the aqueous source (1 cm^3) and receiving (3 cm^3) phases were separated by an organic phase (5 cm^3). The organic phase was chloroform, dichloromethane or 1,2 dichloroethane in different experiments. The temperature of the cell was thermostated at 25°C . The aqueous source phase was containing the seven metal cations (1×10^{-2} M for each) and was buffered (acetic acid/sodium acetate) at pH = 4-6 during pH optimization step. The receiving phase was buffered (formic acid/sodium formate) at pH = 3.0. In separate experiments the transport of cations through the cell (no using of the ligand) was checked and observed no evidence of metal ion transport from source phase to the membrane or receiving phase. The effect of addition of thiourea ($\text{CH}_4\text{N}_2\text{S}$) and potassium thiocyanate (KSCN) to receiving phase and palmitic acid to organic membrane phase were studied. The stirring rate of the solution of the cell and volume percent of dichloromethane and 1,2 dichloroethane in the organic phase was optimized.

3. Results and discussion

3.1. pH Effect

The pH is a very important factor in the separation of metal ions using chelating agents. It will determine the values of the conditional stability constants of the metal complexes that effect on the transport efficiency. Thus, the effect of the results of pH on the transport experiments was studied. In the most cases of pH variation, the only transported cation is Ag(I), so the results of pH optimization are shown graphically for Ag(I) ion in Figure 1. As it is shown in Figure 1, the transport rates of Ag(I) ion are similar in the studied pHs (with a little bit more in pH = 5). This pH for the source phase is recommended by the researchers [2-4,9]. So, pH = 5 was used for the later experiments.

The reasons of this obvious may be depends to the present anion, solvent and size of cations. Nitrate anion is highly polarizable and interacts to a fair extent by dispersion forces with dichloromethane molecules. In the other words acceptor number of dichloromethane is big (20.4), this reason increase in negative free energy of salvation of Ag(I)-ion [10]. Also the other reason, for which transport rate for Ag^+ is better than other present metal cations, is its ionic size (0.126 nm). It is comfortable [11-12] with cavity size of the ligand (0.26-0.32 nm). So, Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) cations were considered as interfering ions in the competitive transport experiments.

The optimal value for pH was used to optimize the transport time. Alternatively, the obtained values were used in the optimization of stirring rate, composition (v/v, %) of binary mixtures, type of releasing agent in the receiving phase, the effect of palmitic acid in the membrane organic phase and finally, all these values were used to optimize the amount of palmitic acid. All of the transport experiments were done for triplicate runs.

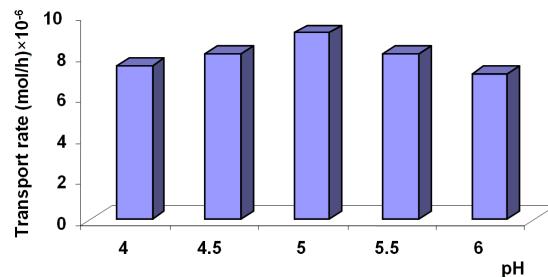


Figure 1. The results of competitive silver(I) ion transport using DB18C6 as a ligand vs. pH. The aqueous source phase was buffered at pH = 4.0, 4.5, 5.0, 5.5 and 6.0 with sodium acetate/acetic acid in separate experiments. The mixture of metal ions in source phase was 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in dichloromethane (5 mL). The cell was stirred for 24 h at 25°C .

3.2. Time effect

Figure 2, shows the time dependence of Ag(I) transport through the membrane cell under the experimental conditions using DB18C6. It was obtained that the transport of Ag(I) from the aqueous source phase into the receiving phase is very fast so, the transport time remains constant ($J \approx 9 \times 10^{-6} \text{ mol}/\text{h}$) after 3 h, under the experimental conditions.

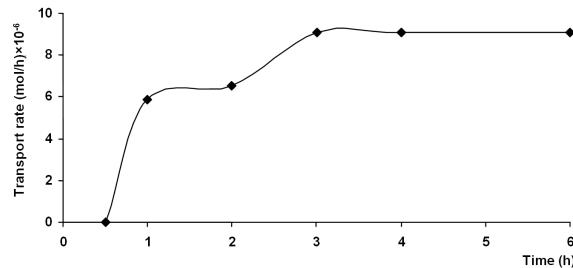


Figure 2. The results of competitive silver(I) ion transport using DB18C6 as a ligand vs. time. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in dichloromethane (5 mL). The cell was stirred at 25°C .

3.3. Stirring speed

In order to explore the effect of stirring speed, the transport experiments were performed at six different speeds, 100, 200, 300, 400, 500 and 600 rpm. The results in Figure 3, shows that the stirring speed affects the transport efficiency of Ag(I) ions through the organic membrane phase. The effect of the stirring speed on the diffusion of species through organic membrane is an important factor in order to minimize the diffusion layer at the interfaces. It was found that the transport efficiency increase is constant after 200 rpm.

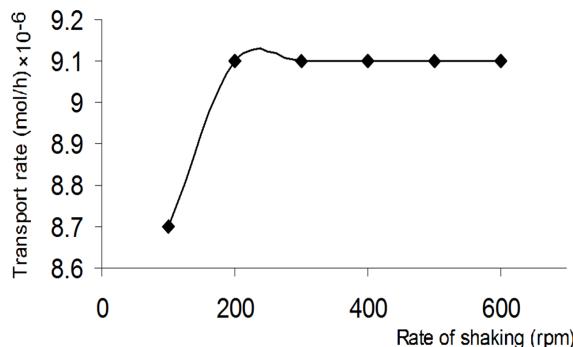


Figure 3. The results of competitive silver(I) ion transport using DB18C6 as a ligand vs. the rate of shaking. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in dichloromethane (5 mL). The cell was stirred for 3 h at 25 °C.

3.4. Effect of solvent

The goal of many studies involving complex formation in mixed solvent systems has been to investigate the effect of solvent composition on the stability and nature of the complex formed [9]. To investigate the effect of binary solvent mixture on the transport efficiency the volume percent (v/v, %) of dichloromethane in the organic phase was varied in different experiments and studied the effect of binary mixture effect on the transport rate of Ag(I) ion. The results of competitive transport of Ag(I) ion using DB18C6 as carrier are shown in **Figure 4**.

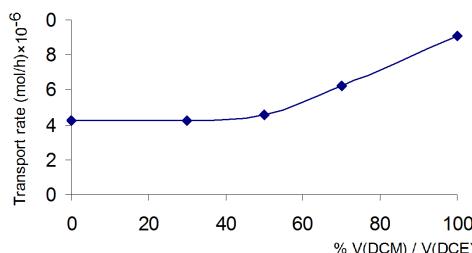


Figure 4. The results of competitive silver (I) ion transport using DB18C6 as a ligand vs. the volume percent of dichloromethane. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in different percent of dichloromethane (5 mL). The cell was stirred for 3 h at 25 °C.

As it was expected [9] the competitive transport results indicate, the transport rate depends to the volume percentage of the binary mixed solvents, under the optimal experimental conditions. As shown in **Figure 4**, the transport rate of Ag(I) ion increase with the volume percent of dichloromethane. The results show the transport rate depends to the volume percent of dichloromethane under the optimal experimental conditions. **Figure 4** shows that the transport rate of silver (I) ion increases with increasing the volume percent of dichloromethane.

According to the physicochemical properties of the solvents [11], the lower viscosity of dichloromethane (0.449) than 1,2 dichloroethane (0.73) and also the higher dielectric constant of 1,2 dichloroethane (1.86) than dichloromethane (1.14) can result in an increase of transport rate of the Ag⁺ ion. As shown in **Figure 4**, the transport rate of Ag(I) ion is sensitive to the solvent composition. Also, this behaviour may be due to the interactions between the dichloromethane and 1,2 dichloroethane molecules in their binary mixtures. The ionic

size of Ag(I) is 0.126 nm with one positive charge, therefore transport rate of Ag(I) increases to less polar solvent (1,2 dichloromethane).

3.5. Effect of thiourea concentration

The competitive silver(I) ion transport from the mixture of Ag(I), Cu (II), Ni(II), Zn(II), Mn(II), Cd(II) and Co(II) cations were done in different concentration of thiourea (1×10^{-5} to 0.01 M) at the optimal conditions of the pH, transport time and stirring rate. The results show that there was no more transport efficiency of Ag(I) ion after 1.5×10^{-4} M of thiourea concentration in the experimental conditions. So, the concentration of thiourea was selected 1.5×10^{-4} M as optimal value.

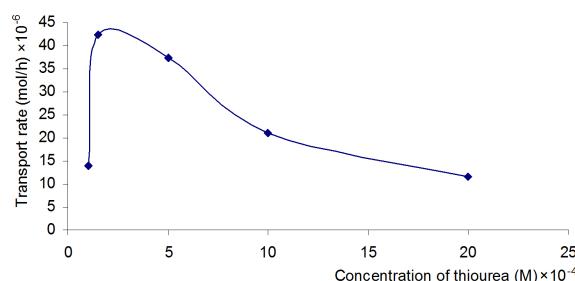


Figure 5. The competitive silver(I) ion transport using DB18C6 as a ligand vs. thiourea concentration in receiving aqueous phase. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in different percent of dichloromethane (5 mL). The cell was stirred for 3 h at 25 °C.

3.6. Effect of thiourea and potassium thiocyanate

In the separate experiments, the competitive metal ion transport process were employed with an aqueous receiving phase containing thiourea ($\text{CH}_4\text{N}_2\text{S}$) and potassium thiocyanate (KSCN) to improve the transport efficiency of Ag(I) ion. To comparing the effect of thiourea and potassium thiocyanate as complexing agents in the same conditions the concentration of these compounds were prepared 1.5×10^{-4} M (the optimal value of thiourea) in all separate experiments. The results of these compounds as complexing agents in the receiving phases for transport of Ag(I) ions are shown in **Figure 6**.

As it is shown in **Figure 6**, the transport rate of Ag(I) in the presence of thiourea is much more than potassium thiocyanate. **Figure 6** shows that there is no interfering of Cd(II), Ni(II), Zn(II) and Mn(II) cations in the transport of Ag(I) in these experiments. So, the Ag(I) transport was continued in the presence of thiourea in receiving phase as releasing agents.

The role of these additions is to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralization of the metal cations being transported through ion pairing [2-3]. Ion pair/adduct formation serves to inhibit any bleeding of partially hydrophilic species (such as the protonated ionophore and/or its corresponding charged metal ion complex) from the organic membrane either of aqueous phases [13] and this function in presence of thiourea is more effective. After complexation of the carrier with silver ion on the left side of the membrane (the boundary of source and organic phases), the formed complex diffuses down its concentration gradient. On the right side of membrane (the boundary of organic and receiving phases), the metal ion would be released into the receiving phase via formation of ternary complex (DB18C6-Mn⁺-thiourea) [14]. At this stage, the carrier diffuses back through the membrane. The net result is the

transport of cations from the aqueous source phase to the aqueous receiving phase across the BLM. Because of the ionic nature of KSCN this mechanism may be not happened for this releasing. In thiourea, there are [15] almost equal contributions from three canonical forms (**Scheme 2**).

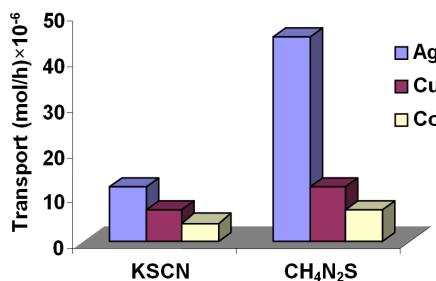
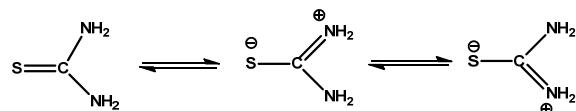


Figure 6. The results of competitive silver(I) ion transport using DB18C6 as a ligand vs. addition of thiourea ($\text{CH}_4\text{N}_2\text{S}$) and potassium thiocyanate (KSCN), both at 1.5×10^{-4} M concentrations to the aqueous receiving phase. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in different percent of dichloromethane (5 mL). The cell was stirred for 3 h at 25 °C.

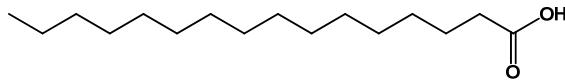


Scheme 2

Hence, thiourea is potentially capable of forming coordinate bonds through both sulphur and nitrogen even though the extremely low basicity of the ligand militates against the formation of nitrogen-metal bonds. In acidic medium, thiourea is protonated and the proton will be bonded to the sulphur atom favouring the bonding of the metal ions to nitrogen atoms. And then after, the proton is released in solution. Hence the formation of stable $[\text{Ag}(\text{Thiourea})]^+$ will be happen. In this case ML_n ($[\text{Ag}(\text{Thiourea})_n]^+$) complex could be formed [15]. This behaviour because of 1:1 complex formation in $\text{Ag}(\text{Thiocyanate})$ case is weak and thus the efficiency is high in the presence of thiourea as complexing agent in the receiving phase.

3.7. Effect of palmitic acid

A major role of the palmitic acid was to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase. This process could confirm rise to charge neutralization of the metal cation being transported through ion pairing or adduct formation. In separate experiments, competitive metal ion transport process employed with an organic phase containing palmitic acid (**Scheme 3**) and aqueous receiving phase containing thiourea (1.5×10^{-4} M) at the optimal conditions. The results are presented in **Figure 7**.



Scheme 3

Figure 7. shows that the transport of silver(I) ion has its maximum rate in the present of palmitic acid at concentration 3×10^{-3} M. The palmitic concentration at 3×10^{-3} M is three times

of DB18C6 ligand concentration; it means there are no more roles for palmitic acid in the transport experiments after this concentration of palmitic acid.

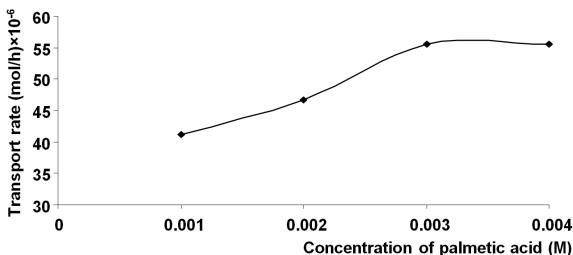


Figure 7. The results of competitive silver (I) ion transport using DB18C6 as a ligand vs. palmitic acid concentration in the organic membrane phase. The aqueous source phase was buffered at pH = 5.0 with sodium acetate/acetic acid. The metal ions were 0.01 M as their nitrate salts. The volumes of aqueous source and receiving phases were 1 and 3 mL, respectively. The receiving phase was buffered at pH = 3.0 with formic acid/sodium formate. The organic phase was containing 0.001 M ligand in different percent of dichloromethane (5 mL). The cell was stirred for 3 h at 25 °C.

4. Conclusion

Competitive metal ion transport of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) cations using DB18C6 (**Scheme 1**) as a carrier in organic phase showed that the transport rate of cations are strongly influenced by the nature of organic solvent. Dibenzo 18-crown-6 showed almost good selectivity for Ag(I) ion. The order of the transport rate of Ag(I) ion for different binary mixture in the organic phase was found to be: dichloromethane > 1,2 dichloroethane. A good transport rate was observed for Ag(I) ion in optimal conditions. The optimal values for pH of receiving phase, time of transport and stirring rate were 5.0, 3 h and 200 rpm, respectively. The experimental results obtained for the competitive transport of the studied metal cations with DB18C6 showed that the ion transport ability change in the presence of thiourea or potassium thiocyanate in the aqueous receiving phase.

Acknowledgments

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