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Spectrometric determination of Pb²⁺ cation after selective bulk liquid membrane transport using benzo-18-crown-6 as carrier

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ABSTRACT

Benzo-18-Crown-6 (B18C6) was used as a highly selective and efficient carrier for the transport of Pb^{2+} cation through a dichloromethane bulk liquid membrane (BLM). In order to achieve the highest transport efficiency of Pb^{2+} cation across the bulk liquid membrane system, the influence of different parameters on Pb^{2+} cation transport was investigated. This includes the nature of various organic solvents as liquid membrane phase, concentration of B18C6 in the membrane phase, concentration of picric acid as counter anion in the source phase, type of various stripping agents in the receiving phase, concentration of thiosulfate ion as a suitable stripping agent in the receiving phase, pH of the source and receiving phases and equilibrium time of transport which were optimized. In the optimum procedure conditions, the transport of a 1×10^{-4} M solution of Pb^{2+} cation was observed (88.0 ± 0.7%) after 4 hours. The selectivity and efficiency of Pb^{2+} cation transported from aqueous solutions containing equimolar mixtures of Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Ag^+ metal cations were investigated.

Keywords: bulk liquid membrane (BLM), transport, Benzo-18-Crown-6 (B18C6), Pb²⁺ cation, DCM.

INTRODUCTION

 Pb^{2+} is a toxic heavy metal cation that accumulates in soil and natural waters. Devices that will detect this metal at the trace level are the aim of numerous research groups. Crown ethers and, in particular, 18-Crown-6 have emerged as a potential recognition element in these devices for Pb^{2+} detection. Crown ethers are known to bind selectivity to cations based on macrocycle effect [1]. Selective transport of cationic substrates by membrane carriers is of great importance in chemistry, biology and separation sciences. Bulk liquid membrane is one of the simple and efficient types of liquid membranes [2]. In this technique similar to liquid membrane configurations, (vis ion transport across membranes) combine the extraction, diffusion, and back extraction of analytes are particularly drawing maximum attention [3].

Crown ethers as ion carriers were successfully used for metal ion separation in solvent extraction, transport through liquid membranes and ion exchange systems. These carrier compounds are dissolved in the liquid membrane and act as transport catalysts. Crown ethers and related compounds [4] have widely been used as complexing agents for metal selective extractions, phase transfer catalysis, membrane transport and as ionophore for the fabrication of ion-selective electrode. Macrocyclic crown ethers are well known as selective carriers for various ions. These compounds react with some bulky ions and the produced species were successfully used as neutral electrical carriers for some ions [5-6].

Ionophores for use in membranes should have rapid exchange kinetics and adequate complexation formation constants in the membrane. In addition, they should be well soluble in the membrane matrix and have a sufficient lipophilicity to prevent leaching from the membrane into the sample solution. These membrane systems have general configuration consisting of aqueous source and receiving phases separated by an organic liquid membrane [7]. Macrocycle-mediated cation transport by both neutral and proton-ionizable macrocycles in liquid membranes is often diffusion limited. Cation selectivities in competitive transport systems are determined by parameters such as: extraction constants for the interactions which occur at the membrane-aqueous phase interfaces, the concentration gradients in the species being transported between the two aqueous phases, and the equilibrium constants for any interactions occurring in the aqueous phases. Models which describe the macrocycle-mediated flux of cations through bulk liquid membranes indicate that membrane solvent exerts an important influence on membrane performance. Since the organic ligand is neutral, the cation carriers its counter anion with it across the membrane to maintain electral neutrality in the system. This process is commonly called passive transport. The concentration gradient of metal ions between two aqueous phases is a driving force for the transport process [8].

The water-dichloromethane-water liquid membrane system in this experiment was employed to collect data for single ion unitary transport of Pb^{2+} cation and for three cation ternary system involving Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ with Pb^{2+} cation. Our objective was to determine the effectiveness of organic membranes containing Benzo-18-Crown-6 (Scheme I) as a neutral macrocycle ligand in selectively transporting Pb^{2+} cation which is interest in relation to the environment and human toxicity.



Scheme I: Structure of Benzo-18-Crown-6

In our previously reported work [9], we investigated the competitive transport of Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ and Pb^{2+} metal cations from an aqueous source phase into the receiving phase through DCM, 1,2-DCE, CHCl₃ and NB solvents as organic membrane containing B18C6 as ionophore at ambient temperature. The obtained results showed that this membrane could transport the Pb²⁺cations nearly selective among other metal cations. In order to achieve the highest efficiency and selectivity in the transport of Pb²⁺cations across the membrane, the experimental variables were optimized.

MATERIALS AND METHODS

2.1. Reagents and solvents

Benzo-18-crown-6 (Merck), lead(II) nitrate (BDH), chromium(III) nitrate (BDH), cobalt(II) nitrate(BDH), copper(II) nitrate (BDH), zink(II) nitrate (Merck), cadmium(II) nitrate (Riedel), silver(I) nitrate (Merck), sodium acetate (Riedel), sodium hydroxide (Riedel), sodium thiosulfate (Na₂S₂O₃.5H₂O) (Merck), sodium thiocyanide (NaSCN) (Merck), sodium cyanide (NaCN) (Riedel), sodium sulfite (Merck), thiourea (Merck), EDTA (Riedel) were used as received. Dichloromethane(DCM), 1,2-dichloroethane(1,2-DCE), chloroform(CHCl₃), nitrobenzene(NB), nitromethane(NM), picric acid (2,4,6-Trinitrophenol), formic acid, acetic acid and nitric acid all purchased from Merck company. All aqueous solutions were prepared using deionized double distilled water.

2.2. Apparatus

The determination of lead (II) content was carried out by a Shimadzu AA-670 atomic absorption spectrometer equipped with a Pb-hallow cathode lamp (HCL) and was made under the recommended conditions for lead(II) cation. A pH meter, Metrohm 692 pH/ion meter equipped with a combined glass electrode was used for pH adjustments. A bulk liquid membrane cell was used in all transport experiments.

2.3. Procedure

Bulk liquid membrane (BLM) transport measurements were performed at ambient temperature in a cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside diameter 2 cm), thus separating the two aqueous phases. The inner aqueous phase (source phase, SP) contained 10 ml of lead(II) nitrate $(1 \times 10^{-4} \text{M})$ and picric acid $(1 \times 10^{-3} \text{M})$. The outer aqueous phase (receiving phase, RP) contained 30 ml of different stripping agents (5×10^{-2} M). The transport process was maintained by the buffering the aqueous source and receiving phases. The pH 5 was selected as optimum value for both aqueous phases using CH₃COOH/CH₃COONa 0.1M buffer solution. The membrane phase (MP) containing B18C6 $(1 \times 10^{-3} \text{M})$ as carrier in 50 ml of DCM, 1,2-DCE, CHCl₃, NB and NM as organic solvent lay below these aqueous phases which bridged these two phases. The membrane phase was magnetically stirred by a Teflon-coated magnetic bar. Under these conditions, not only the mixing process is perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined. The source and receiving phases were sampled and analyzed for the corresponding metal ion concentration by atomic absorption spectrophotometry. Reproducibility was confirmed as ±0.7 %. A similar transport experiment was carried out in the absence of the carrier for reference. Detailed conditions are included in the Tables and Figures in the text. The data points reported are averages of at least three replicate measurements.

3. Results and discussion

In our early experiments [9], we tested the B18C6 ability to transport of Pb^{2+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Ag^+ metal cations from an aqueous source phase into the receiving phase through DCM, 1,2-DCE, CHCl₃, and NB organic solvents as membrane. The obtained results showed that this ligand is a highly selective ionophore for Pb^{2+} cation among the other metal cations. A similar behavior has been observed for selective transport and extraction of Pb^{2+} cation through the liquid membrane containing 18-Crown-6 derivatives [10-12].

In order to increase the efficiency and selectivity of Pb^{2+} cation transport, we could use a particular stripping agent in the receiving phase. In the next step, variable parameters were optimized in order to achieve the highest efficiency in the transport of Pb^{2+} cation across the liquid membrane. Although the maximum percentage of Pb^{2+} cation that transports to the

receiving phase that contains buffer solution does not exceed 10% after 24 hours, but it exceeds 88% after 4 hours when 1×10^{-3} M of picric acid as counter anion was added to the source phase and 5×10^{-2} M of sodium thiosulfate as stripping agent, was added to the receiving phase, with DCM as membrane phase. The optimum transport conditions were established by the studies on the effect of pH, reagents concentration, organic solvent and time of transport.

As an additional experiments the above optimization processes was performed on 4 other concentrations of Pb^{2+} cation. The optimum conditions with respect to picric acid concentration in the source phase and sodium thiosulfate concentration in the acceptor phase and B18C6 in the membrane phase obtained for transport of 5×10^{-5} , 5×10^{-4} and 1×10^{-3} M of Pb^{2+} cation were similar to the optimum concentrations for the transport of the 1×10^{-4} M Pb^{2+} cation (i.e. 1×10^{-3} M of picric acid, 5×10^{-2} M of sodium thiosulfate and 1×10^{-3} M of B18C6). Thus, excess concentrations of picric acid, sodium thiosulfate and B18C6 do not affect the efficiency of the transport experiments. For these systems that displayed selective transport behaviour, sole selectivity for Pb²⁺ cation was observed under the employed experimental conditions in this investigation.

3.1. Effect of organic solvent

The nature of the membrane solvent is one of the main factors in establishing transport efficiency. Several parameters whose values depend on the membrane solvent can affect the transport of metal cations through bulk liquid membranes. The physical and chemical properties of solvents are closely related to their structures and play important roles in solute-solvent and solute-solute interactions in solutions. The organic solvent which should be immiscible with water and non-volatile must have a suitable polarity related to an optimal value of the association constant of the complex. A solvent of low viscosity must be chosen to obtain the highest rate of transport possible in a particular system [13-14].

In the present work, we have examined the influence of the membrane solvent. The data for selective transport of Pb^{2+} cation from an aqueous source phase through DCM, 1,2-DCE, CHCl₃, NB and NM organic membranes containing B18C6 at ambient temperature is given in Table 1. As is seen, the transport efficiency of the Pb^{2+} cations by B18C6 as carrier is varied in order: DCM>NB>1,2-DCE>CHCl₃>NM. According to the physicochemical properties of the solvents, these observations may be attributed to the lower viscosity of DCM that provides large diffusion through the membrane. Therefore, DCM has been used successfully as a solvent in our BLM system.

Organic	Transported into	Remaining in
Solvent	Receiving Phase/(%)	Source Phase/(%)
DCM	88	5
NB	53	21
1,2-DCE	47	26
CHCl ₃	31	44
NM	20	57

Table 1: Effect of the organic solvent on Pb²⁺cation transport ^a

^{*a*} Experimental Conditions: source phase, 10mL of $1 \times 10^{-4}M Pb^{2+}$ cation and $1 \times 10^{-3}M$ picric acid at pH 5; liquid membrane phase, 50mL of $1 \times 10^{-3}M$ B18C6 carrier in different organic solvent; receiving phase, 30mL of $5 \times 10^{-2}M$ $S_2O_3^{-2-}$ at pH 5; time of transport, 4 hours.

3.2. Effect of carrier concentration

Liquid membrane transport is related to liquid extraction, since passage through the membrane involves a similar sequence of chemical reactions. The major problem is membrane instability due to the leaching of the membrane compounds into the aqueous phases. Most attempts to

overcome this problem have tried to increase the membrane partition ratio by covalently attaching the transport carriers to highly lipophilic or polymeric chains. Carrier compounds are dissolved in the liquid membrane and act as transport catalyst [15].

The influence of carrier concentration in the organic phase on the transport efficiency of Pb^{2+} cation was studied and the graphical results are shown in Figure 1. The increase of carrier concentration in the membrane phase leads to an increase in the recovery of Pb^{2+} cation. The transport efficiency were increased with the concentration of B18C6 as carrier up to the optimum value $(1 \times 10^{-3} M)$, after while decreasing of the transport efficiency was observed. These results maybe were due to the adsorption of surface-active species at the liquid-liquid interface that can produce an interfacial resistance, which reduces the mass transfer rates of other compounds across the interface [16].



Figure 1: Effect of carrier concentration on Pb²⁺cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of varying concentration of B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M S₂O₃²⁻ at pH 5; time of transport, 4 hours.

3.3. Effect of picric acid in the source phase

For a neutral macrocyclic ligand which is devoid of ionizable hydrogen atoms, the metal ion-counter anion interaction is in general operative. In preliminary experiments, it was found that the nitrate ion is not a suitable counter anion to accompany the B18C6-Pb²⁺ complex into the organic phase, only 10 % of Pb²⁺cation were transported into the receiving phase after 24 hours. However, addition of bulky lipophilic anions such as picrate anion of picric acid (2,4,6-trinitrophenol), as the organophilic counter anion to the source phase increased the Pb²⁺cation transport.

The influence of the concentration of picric acid in the source phase on the Pb²⁺cation transport was investigated and the results are shown in Figure 2. The optimum concentration of picric acid was found to be 1×10^{-3} M. As seen from this Figure, the efficiency of Pb²⁺cation transport increases with increasing picric acid concentration until to 1×10^{-3} M, but further increase in the concentration of picric acid caused a pronounced decrease in the transport efficiency of Pb²⁺cation. This behaviour maybe due to the competition of picric acid with Pb²⁺cation for

transport process. Similar behaviour has been observed for selective transport of silver ion through a supported liquid membrane using Hexathia-18-Crown-6 [17].



Figure 2: Effect of picric acid concentration on Pb²⁺cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and varying concentration of picric acid at pH 5; liquid membrane phase,

50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M S₂O₃⁻² at pH 5; time of transport, 4 hours.

3.4. Effect of stripping agent type in the receiving phase

Table 2 shows that the permeability of the membrane system for Pb^{2+} cation is considerably dependent on the nature of stripping agent for this cation in receiving phase. It was seen a considerable change in transport percentage of Pb^{2+} cation in present of thiosulfate ion $(S_2O_3^{2^-})$ than the other stripping agents. In the presence of thiosulfate ions $(S_2O_3^{2^-})$ in the receiving phase, 88.0% of Pb^{2+} cation transported through the membrane during 4 hours, while the use of the other reagents such as $SO_3^{2^-}$, SCN⁻, CN⁻, EDTA and thiourea results in much lower transport efficiency of the Pb^{2+} cation. The optimum concentration of thiosulfate ion $(S_2O_3^{2^-})$ in the receiving phase was also investigated and it was found to be 5×10^{-2} M. The graphical results are shown in Figure 3. Notably, the absence of a metal ion acceptor in the receiving phase resulted in no appreciable transport of Pb^{2+} cation even in much longer periods of time.

Table 2: Effect of different stripping	agent present in the receiving	g phase on Pb ²⁺ cation transport ^a
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Nature of	Transported into	Remaining in
Stripping Agent	Receiving Phase/(%)	Source Phase/(%)
$S_2O_3^{2-}$	88	5
SO_{3}^{2}	32	28
SCN	37	32
CN ⁻	41	23
EDTA	28	37
Thiourea	15	51

^a Experimental Conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺ cation and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M of different stripping agent at pH 5; time of transport, 4 hours.



Figure 3: Effect of thiosulfate ion (S₂O₃²⁻) concentration in the receiving phase on Pb²⁺cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of varying concentration of S₂O₃²⁻ at pH 5; time of transport, 4 hours.



Figure 4: Effect of pH in source phase on Pb²⁺cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and 1×10⁻³M picric acid with various pH; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M S₂O₃²⁻ at pH 5; time of transport, 4 hours.

3.5. Effect of pH

The influence of pH of the source and receiving phases on the transport efficiency of Pb^{2+} cation was studied, and it was found that maximum transport of this cation occurs at buffer solution at pH 5 for both source and receiving phases that we adjusted with CH₃COOH/CH₃COONa buffer solution. The results are shown in Figures 4 and 5. It may be noted here, that the aqueous phase was fixed at 5 for most of the experiments due to the fact that higher pH values could result in the hydrolysis of the metal ion and lower pH values caused the protonation of crown compounds

and made the deprotonation of picric acid difficult. Furthermore the thiosulfate solution decomposes in more acidic solutions [18]. For further studies, the thiosulfate ion was omitted and the receiving phase with different pH was used and the transport efficiency was investigated. The results showed that thiosulphate ion has an important role for Pb^{2+} cation transport and more acidic receiving solution is not suitable for Pb^{2+} cation transport itself.



Figure 5: Effect of pH in receiving phase on Pb²⁺cation cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M S₂O₃²⁻ with various pH; time of transport, 4 hours.



Figure 6: Effect of time on Pb²⁺cation transport. Experimental conditions: source phase, 10mL of 1×10⁻⁴M Pb²⁺cation and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in DCM; receiving phase, 30mL of 5×10⁻²M S₂O₃²⁻ at pH 5.

3.7. Effect of time of transport

A series of cells were designed for the transport of Pb^{2+} cation and each cell examined after a certain time of stirring. Figure 6 shows the time dependence of Pb^{2+} cation transport through the liquid membrane under the optimal experimental conditions. It is obvious that the transport of

this cation into the receiving phase increases with time. According to the results obtained in this study, it was confirmed that about 88.0% of Pb^{2+} cation was transported from the source phase into the receiving phase after 4 hours.

3.8. Transport reproducibility

To find the reproducibility of the transport system under investigation, the experiment was repeated five times under the optimum conditions of transport. The results are illustrated in Table 3 and the transport reproducibility was confirmed as ± 0.7 %. Therefore, the percent of Pb²⁺cation transported after 4 hours from five replicate measurements was found to be (88.0 ± 0.7 %).

Table 5. Transport Reproducibility		
Run	Transported into	Remaining in
	Receiving Phase/(%)	Source Phase/(%)
1	87.40	5.62
2	88.15	4.25
3	86.73	7.19
4	87.58	6.52
5	88.31	3.80
	87.63 mean value	
	0.6 SD	
	0.7 RSD	

 Table 3: Transport Reproducibility ^a





Figure 7: The results of competitive metal ion transport. Experimental conditions: source phase, 10mL equimolar mixtures of Pb²⁺, Cr³⁺, Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Ag⁺ metal cations (1×10⁻⁴M) and 1×10⁻³M picric acid at pH 5; liquid membrane phase, 50mL of 1×10⁻³M B18C6 carrier in different organic solvents; receiving phase, 30mL of 5×10⁻²M S₂O₃²⁻ at pH 5; time of transport, 4 hours.

3.9. Transport selectivity

The water-DCM-water liquid membrane system in this experiment was employed to collect data for competitive transport of seven metal cations and also for three metal cation transport system involving Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ metal cations with Pb^{2+} cation. The selectivity of the above liquid membrane system for transport of Pb^{2+} cation over the other metal cations in equimolar mixtures at optimum conditions is illustrated in Figure 7. In another experiment, the

interference effects of these cations in ternary cation system were investigated. In Table 4 the percentage of cations transported into the receiving phase and remained in the source phase is investigated. The experimental data from this Figure and Table indicate that the system is very selective for Pb^{2+} cation, and none of the studied cations interferes with Pb^{2+} cation. High stability constant of Pb^{2+} cation with B18C6 and picrate ion in the source phase and thiosulfate ion in the receiving phase largely improved the method selectivity.

Cation	Transported into	Remaining in
	Receiving Phase/(%)	Source Phase/(%)
Mixture 1		
Pb^{2+}	88	5
Ag^+	2	92
Cd^{2+}	0	97
Mixture 2		
Pb ²⁺	88	5
Cr^{3+}	0	94
Co ²⁺	0	96
Mixture 3		
Pb^{2+}	88	5
Cu ²⁺	0	97
Zn^{2+}	0	95

Table 4: Amount of cations transported from various cation mixtures through the membrane ^a

^{*a*} Experimental Conditions: source phase, 10mL of 1×10^{-4} M various cation mixtures and 1×10^{-3} M picric acid at pH 5; liquid membrane phase, 50mL of 1×10^{-3} M B18C6 carrier in DCM; receiving phase, 30mL of 5×10^{-2} M S₂O₃²⁻ at pH 5; time of transport, 4 hours.



Figure 8: Transport mechanism of Pb²⁺cation through BLM process

3.10. Recommended mechanism

The recommended mechanism for the transport of Pb^{2+} cation through bulk liquid membrane, which operated in this study, is shown schematically in Figure 8. Movement of the charge species through the hydrophobic organic membrane is accomplished by the presence of host carrier B18C6 ion paired with picrate as a suitable counter anion. The picrate ion not only neutralizes the charged Pb^{2+} -B18C6 complex but also induces a more lipophilic character to the Pb^{2+} complex so that it can be readily extracted into the membrane phase. After complexation of Pb^{2+} cation with carrier on the source side of the membrane, the complex diffuses down its concentration gradient. On the receiving side of the membrane, the metal ion is released into the receiving phase via formation of a ternary complex (B18C6-Pb^{2+}-S_2O_3^{2-}). Then the free carrier

diffuses back across the membrane and cycle starts again. The net result is the transport of Pb^{2+} cation from the aqueous source phase to the aqueous receiving phase across the BLM.

CONCLUSION

The present study demonstrates that Benzo-18-Crown-6 is an excellent carrier for selective and efficient transport of Pb^{2+} cation through DCM bulk liquid membrane containing this carrier. Addition of picrate ion as a suitable counter anion to the source phase increased the Pb^{2+} cation transport efficiency. The presence of thiosulfate ion $(S_2O_3^{2-})$ as cation acceptor in the receiving phase greatly increases the efficiency of transport of Pb^{2+} cation without affecting the selectivity. The choice of the appropriate counter anions in the source and receiving solutions and the concentration of the neutral carrier in the membrane phase is particularly important in determining the efficiency and selectivity of the transport process of the Pb^{2+} metal cation. In conclusion, therefore, the above system, which is specific for Pb^{2+} cation, is a potential candidate for practical use in Pb^{2+} cation separation, especially as it has the advantages of high precision, efficiency, selectivity and simplicity.

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