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Kinetics study of selective removal of lead(II) in an aqueous solution containing lead(II), copper(II) and cadmium(II) across bulk liquid membrane

Sayed Yahya Kazemi · Akram Sadat Hamidi · Mohammad Javad Chaichi

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Abstract Transport of Pb(II) ion from equimolar aqueous solutions of Pb(II), Cu(II) and Cd(II) as well as from aqueous solutions containing only Pb(II) source phase $(C_{\text{metal}} = 1.0 \times 10^{-4} \text{ mol L}^{-1})$ through bulk liquid membranes containing crown ether and oleic acid as carrier has been investigated. The initial fluxes of transported metal ions depend on the hydrophile-lipophile balance (HLB) and molar volumes (Vx) of crown ethers. The initial fluxes of Pb(II), Cu(II), and Cd(II) decrease with increase of HLB value for azacrown ether, i.e., tetraaza-14-crown-4 (A_414C4) , L1 > benzo-15-crown-5 (B15C5), L2 > 4'-Aminobenzo-15C5, L3 > nitrobenzo-15-crown-5 (NB15C5), L4. The selectivity of the metal ions showed the following separation factors (SF): $SF_{Pb-Cu} = 2.15$, $SF_{Cu-Cd} = 2.10$, $SF_{Pb-Cd} = 4.52$. The highest transport recovery for Pb(II)was observed for L1 (99.3 %).

 $\begin{tabular}{ll} \textbf{Keywords} & Kinetic of transport \cdot Bulk liquid membrane \cdot \\ Transport of metal ions \cdot Transport selectivity \cdot \\ Crown ethers \end{tabular}$

Introduction

Lead is ubiquitous in the environment and has been used recklessly until very recently. All form of lead are toxic

S. Y. Kazemi (
) · A. S. Hamidi

Department of Basic Sciences, Sari Agricultural Sciences and Natural Resources University, P.O. Box 578, Sari, Iran e-mail: sykazemi@gmail.com

M. J. Chaichi Department of Chemistry, Mazandaran University, Babolsar, Iran e-mail: jchaichi@yahoo.com and adversely affect reproductive, nervous, immune, cardiovascular system as well as developmental process in children [1]. Due to its high toxicity, removal of lead ion from the environment has utilized a variety of separation techniques, such as adsorption, precipitation, and solvent extraction [2].

Compared with solvent extraction, liquid membranes have shown great potential since they combine the process of extraction and stripping in a single unit operation [3, 4]. Especially in the case where solute concentration is relatively low other techniques can not be applied efficiently. The extraction chemistry of liquid membrane is similar to what was found in classical liquid–liquid extraction [5]. Liquid membranes have been successfully used to treat aqueous streams contaminated with heavy metal ions like copper, zinc, cadmium, nickel, mercury, and lead [6–9].

Bulk liquid membrane (BLM) has been studied for preconcentration and separation of different metal ions with a variety of liquid membrane phases [10–12]. The carrier in the liquid membrane phase plays an important role in the liquid membrane process, which must (1) provide a very high extraction distribution coefficient from dilute solutions; (2) react reversibly with the metal ion so that it can be recovered by a stripping reaction; (3) have reasonably fast extraction and stripping kinetic; and (4) have very low solubility in the aqueous phase for economic and environmental reasons [13].

Metal ion separations using BLMs currently are receiving considerable attention. Recently, several acyclic and macrocyclic ligands with good selectivity for Pb(II) have been reported [14–16]. The coordination chemistry of Pb(II) have been reviewed by Parr [17]. From the relationship between ligand structure and the Pb(II) coordination behavior of several mixed nitrogen/oxygen/sulfur donor macrocyclic compounds, a preference of Pb(II) for



nitrogen donor atoms is clear. Macrocyclic compounds with only nitrogen donor atoms show extremely high complexation constants for Pb(II).

We previously examined four macrocyclic compounds (with nitrogen or oxygen donor atoms)/fatty acid carriers for competitive separation of Pb(II), Cu(II) and Cd(II). We investigated the influence of chemical parameters on the initial fluxes, selectivity coefficient and percentage removal of Pb(II), Cu(II) and Cd(II). We found that L1 has high efficiency, especially for Pb(II) transport [18]. In this paper we address the dependence of the initial fluxes of transported metal ions on the HLB and Vx of crown ethers L1–L4. The potential of these ligands for selective transport of Pb(II) across BLM will be discussed.

Experimental

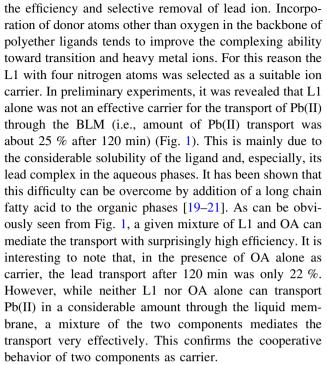
A₄14C4 (L1), B15C5 (L2), 4'-Aminobenzo-15C5 (L3) and NB15C5 (L4), were purchased from Fluka Chemical Company and used as received. Reagent grade chloroform (Merck) was used as the membrane organic solvent. All other chemicals used in this study were of highest purity available from either Merck or Fluka used without further purification except for vacuum drying over P₂O₅. Doubly distilled deionized water was used throughout.

A BLM cell was used in this study. The pH measurements were made with a Metrohm 744 pH meter using a combined glass electrode. The atomic absorption spectrophotometer used for the measurement of metal ion concentration in the aqueous phases was a Varian Specter AA10 instrument. The atomic absorption measurements were made under the recommended conditions for each metal ion.

All transport experiments were carried out using a BLM apparatus at ambient temperature. A cylindrical glass cell (inside diameter 5.0 cm) holding a glass tube (inside diameter 2.5 cm), thus separating the two aqueous phases was used. The source phase contained a mixture of 15 ml of metal ion nitrates and sodium perchlorate. The receiving phase included 15 ml of HCl as metal ion receptor. The membrane phase containing 25 mL of L1 and oleic acid (OA) in chloroform lay below these aqueous phases and bridged the two aqueous phases. The organic layer was magnetically stirred by Teflon-coated magnetic bar (2 cm × 5 mm diameter). The source and receiving phases were sampled and the corresponding metal ions concentration was determined by atomic absorption spectroscopy.

Results and discussion

As expected, the nature of the macrocycle used in the organic membrane phase has a very significant effect on



As shown earlier [18, 22] the metal ion transfer efficiency from aqueous solution source phase into the organic phase not only depends on the cation type and properties of the ionophore but also may be influenced strongly by properties of the anion. For this reason, the influence of the concentration of perchlorate ion in the source phase on the lead ion transport was optimized. The percentage of lead ion transported in the receiving phase increases with an increasing in perchlorate ion concentration in source phase. Thus, the degree of extraction increases with increasing hydrophobicity of the anion. Maximum transport occurs

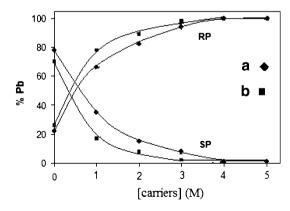


Fig. 1 Effect of A_4 14C4 and OA concentration on lead(II) transport; *filled diamond*, 10^{-4} [A₄14C4] and *filled square*, 3.0×10^2 [OA]. Conditions: source phase: 15 mL aqueous solution of Pb(II) 1.0×10^{-4} mol L⁻¹ and 1.5×10^{-2} mol L⁻¹ ClO₄⁻, membrane phase, **a**; 25 ml of 0.03 mol L⁻¹ OA and varying amount of A₄14C4, and **b**; 25 ml of 4.0×10^{-4} mol L⁻¹ A₄14C4 and varying concentration of OA in chloroform.; receiving phase, 15 mL of 0.3 mol L⁻¹ HCl, time of transport, 120 min



when the sodium perchlorate concentration is 1.5×10^{-2} mol L⁻¹. Similar influence of perchlorate ion on the solvent extraction of the Ag⁺-HT18C6 complex has been reported in the literature [23].

It is expected that the nature and composition of the striping agent -outer aqueous phase- could have a significant effect on the efficiency and selectivity of transport. Thus, the membrane system was optimized with respect to stripping agent concentration on the Pb(II) transport. The results show that an increase in hydrochloric acid concentration, up to $0.3 \text{ mol } \text{L}^{-1}$, increases the efficiency of lead transport. Figure 2 shows that further increases in HCl concentrations would not improve the efficiency of transport. For this reason, a $0.3 \text{ mol } \text{L}^{-1}$ of HCl was selected as the receiving phase. In the presence of chloride at concentrations >0.3 mol L^{-1} all the studied metals are in the form of chloride complex anions [24], which are attached to the donor nitrogen atoms of azacrown ether (L1).

Optimum transport conditions were found to be 1.0×10^{-4} mol L⁻¹ of Pb(II) ion and 1.5×10^{-2} mol L⁻¹ of ClO₄⁻, in the source phase, 0.03 mol L⁻¹ OA and 4.0×10^{-4} mol L⁻¹ L1, in the membrane phase, and 0.30 mol L⁻¹ of HCl, in the receiving phase. It was found that, under the optimum conditions, more than 99 % of total Pb(II) transported from the source phase into the receiving phase after 2 h. Meanwhile, the knowledge of the effect of kinetic parameters on lead transport in equimolar mixtures of Cu(II), Cd(II) and Pb(II) from aqueous source phase through BLMs is crucial for obtaining the selective removal condition of lead.

Thus, in this section, the relationship between $ln(C_0/C)$ and time for Pb(II) transport in the presence of equimolar concentration of Cu(II) and Cd(II) across the BLM containing L1–L4 macrocyclic crown ethers were examined

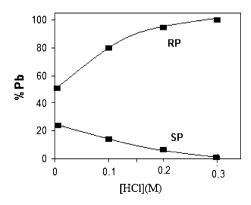


Fig. 2 Effect of HCl concentration in receiving phase on lead(II) transport. Conditions: source phase: 15 mL of Pb(II) 1.0×10^{-4} mol L $^{-1}$ and 1.5×10^{-2} mol L $^{-1}$ of ClO $_4$ $^-$, Membrane phase, 25 ml of 0.03 mol L $^{-1}$ OA and 4.0×10^{-4} mol L $^{-1}$ of A $_4$ 14C4 in chloroform; receiving phase, 15 mL of HCl, varying concentration; time of transport, 120 min

and the results are shown in Fig. 3. The transport of Pb(II) can be described by a first order kinetics in metal ion concentration changes. It is in accordance to the mathematical model proposed by Danesi [22]. The kinetic parameters for the transport of Pb(II) in the presence of Cu(II) and Cd(II) were calculated and summarized in Table 1 [8]. As can be seen, higher value of permeability coefficient, initial fluxes and recovery factor for Pb(II) were obtained for L1. It can be due to existence of four nitrogen atom in macrocyclic ring. The largely decreased efficiency of L2 to L4 seems to be due to oxygen as donor atoms and benzo groups which results in the enhanced configuration rigidity of the ligand [12]. The repulsion between perchlorate ions with π -electrons of benzene ring with amino group is more than the others (L2 and L4) [25]. Therefore, anion interaction with π -electrons in benzene

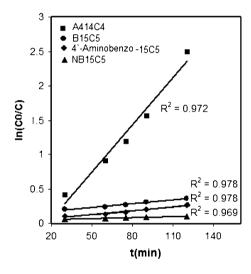


Fig. 3 Kinetics of Pb(II) ions transport across BLMs containing: source phase: 15 mL of Pb(II) 1.0×10^{-4} mol L⁻¹ and 1.5×10^{-2} mol L⁻¹ of ClO₄⁻, membrane phase, 25 ml of 0.03 mol L⁻¹ OA and 5.0×10^{-4} mol L⁻¹ of crown ethers, L1–L4 in chloroform, receiving phase, 15 mL of 0.4 mol L⁻¹ HCl, time of transport, 120 min

Table 1 Kinetics parameters: permeability coefficient (P), initial flux (J_i) , HLB, V_X and recovery factor (RF %) for lead ions transport across BLM with carriers L1–L4

Crown ethers	Permeability coefficient (µm/s)	Initial flux (µmol/ m ² s)	HLB	V _x	RF %
A ₄ 14C4, L1	11.680 (0.023)	1.168	6.91	430.08	91
B15C5, L2	1.066 (0.0020)	0.106	7.22	465.30	16
4'-Aminobenzo- 15C5, L3	0.914 (0.0018)	0.091	8.40	477.15	12
4'-NB15C5, L4	0.304 (0.0006)	0.030	11.57	495.80	9



ring can decrease the complex formation constant and then it decreases initial flux and P and RF% of L3 compared to L2. On the other hand electron withdrawing effect of nitro group considerably decreases the complex formation constant [26, 27]. Ulewicz, et al. found that the initial fluxes of transported metal ions under competitive conditions depend on the HLB of crown ethers [28]. The transport efficiency for metal ions was also found to be dependent on the structure of crown ether used. The crown ethers could be specifically characterized by means of their molar intrinsic volumes, Vx (cm³/mol), and HLB, both of which can be calculated with the equation presented by Mc Gowan et al. [29–31], as:

$$V_x = \sum n_i V_{x,i} - 6 \cdot 56 \times B \tag{1}$$

where $V_{x,i}$ is a volume specific for the *i*-th atom of the molecule, n_i is the number of *i*-th atoms, and B is the total number of bonds (irrespective whether single or multiple). The number of bonds could be easily calculated with the following equation:

$$B = N - 1 + R \tag{2}$$

where N and R stand for the total number of atoms and rings in the molecule, respectively.

The HLB value was calculated as:

$$HLB = 7 - 0.0337 \times V_x + 1.5 \times n \tag{3}$$

where n denotes the total number of oxygen and nitrogen atoms in the molecule.

The calculated values of V_x and HLB are shown in Table 1. The relationship between HLB and the transport fluxes of metal ions is shown in Fig. 4. As seen, the initial fluxes of all investigated metal cations decrease with

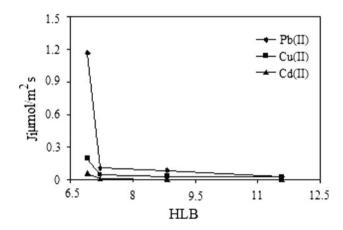


Fig. 4 Initial metal ions transport fluxes across BLM versus HLB. Source phase: 15 mL of Pb(II) 1.0×10^{-4} mol L⁻¹ and 1.5×10^{-2} mol L⁻¹ of ClO₄⁻; membrane phase, 25 ml of 0.03 mol L⁻¹ OA and 5.0×10^{-4} mol L⁻¹ of L1 in chloroform, receiving phase, 15 mL of 0.4 mol L⁻¹ HCl, time of transport, 120 min

increasing HLB value in the order L1 > L2 > L3 > L4; the observed sequence is indicative of the character of the heteroatom in the macrocyclic rings. In addition, the highest values of removal of Pb(II) in the presence of Cd(II) and Cu(II) in equimolar concentration after 2 h were obtained for L1 (i.e., some 91 % removal of Pb(II)).

In order to examine the influence of the metal ions concentration in the source phase on the transport selectivity, the transport of metal ions from equimolar mixture of three ions was performed. As can be expected, flux through the interfaces depends also on the initial metal ion concentration (Table 2). Figure 5 shows that, in the case of low metal ion concentrations $(10^{-5}-10^{-4} \text{ mol L}^{-1})$, the flux is a function of the source initial concentration. However, at higher concentrations than 10^{-4} mol L⁻¹, the flux tends to a maximal value and becomes independent of the metal ions concentration. This is due to the saturation

Table 2 Kinetics parameters: rate constants (K) and initial fluxes (J_i) , for competitive transport of metal ions across BLM with L1 (Condition same as Fig. 5)

Metal ion concentration mol L ⁻¹	Metal ion	Rate constants (min ⁻¹)	Initial fluxes (μmol/m²s)
1.0×10^{-4}	Pb(II)	0.0230	1.1680
	Cu(II)	0.0039	0.1984
	Cd(II)	0.0012	0.0611
1.0×10^{-5}	Pb(II)	0.0130	0.06618
	Cu(II)	0.0019	0.00967
	Cd(II)	0.0006	0.00305

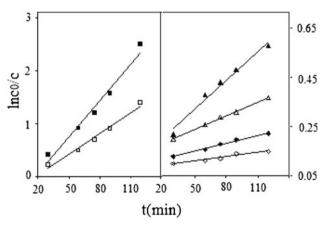


Fig. 5 Relation of $\ln(C_0/C)$ versus time for $[1.0 \times 10^{-4} \text{ mol L}^{-1}$ of (Pb(II), Cu(II), Cd(II)) and $1.0 \times 10^{-5} \text{ mol L}^{-1}$ of Pb(II), Cu(II), Cd(II))] transport across BLMs with L1 from source phase of different metal ions concentration and $1.5 \times 10^{-2} \text{ mol L}^{-1}$ ClO₄⁻, membrane phase, 25 ml of 0.03 mol L⁻¹ OA and A₄14C4 (5.0 \times 10⁻⁴ mol L⁻¹) in chloroform, receiving phase, 15 mL of 0.4 mol L⁻¹ HCl, time of transport, 120 min



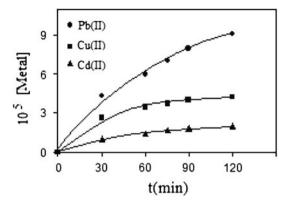


Fig. 6 Concentration of Pb(II), Cu(II) and Cadmium ions in the strip phase versus time. Conditions: source phase: 15 mL aqueous solution of Pb(II), Cu(II) and Cd(II), 1.5×10^{-2} mol L⁻¹ and 1.5×10^{-2} mol L⁻¹ ClO₄⁻, Membrane phase, 25 ml of 0.03 mol L⁻¹ OA and A₄14C4 (5 × 10⁻⁴ mol L⁻¹) in chloroform, receiving phase, 15 mL of 0.4 mol L⁻¹ HCl; time of transport, 120 min

of the membrane by the metal-carrier complex molecules, as the decomplexation at the strip interface is presumably the rate limiting step. It is evident that, at higher concentrations, the metal ions possess a better transport across the BLMs.

The separation factor was calculated by:

$$SF_{\frac{M_1}{M_2}} = \frac{[M1]_s}{[M2]_s} \tag{4}$$

where M_1 and M_2 is the concentration of two metals in the strip phase. Figure 6 shows that working with a high concentration factor will result in an even higher concentration of the ion of interest in the strip phase.

In Table 3 the Permeability coefficient, $P(\mu m/s)$, initial flux, $J_i(\mu mol/m^2 s)$, time of recovery (h) and recovery factor RF% for lead ion are compared with the corresponding values reported for the recovery of lead ions

based on different carriers and different methods, so far reported in the literature [24, 28, 31–34]. In terms of shorter time of recovery, higher J and P, and higher recovery percent, it is apparent that this work is sometimes superior and in some cases similar to the recovery of lead reported previously.

The separation factor of a BLM is a parameter that allows evaluating the degree of purification of one species with respect to others. The results obtained at pseudosteady-state showed that the lead ion has higher mobility than copper and cadmium ions (SF_{Pb-Cu} = 2.15, SF_{Cu-Cd} = 2.10, SF_{Pb-Cd} = 4.52); furthermore, by stopping the separation after 2 h, a higher SF is obtained with respect to the steady state. In an industrial separation, by multiplying the number of strip stages, it is possible to separate Pb(II) from Cu(II) and Cd(II).

Conclusion

A highly selective and efficient transport of Pb(II) through a chloroform BLM was designed. In this system, tetraaza-14-crown- 4 accompanied with OA was used as a suitable carrier for ion-transport of Pb(II). Optimum transport conditions were found to be 1.0×10^{-4} mol L^{-1} of Pb(II) ion and 1.5×10^{-2} mol L^{-1} of ClO_4^- , in the source phase, 0.03 mol L^{-1} OA and 4.0×10^{-4} mol L^{-1} L1, in the membrane phase, and 0.30 mol L^{-1} of HCl, in the receiving phase.

The kinetic parameters for the transport of Pb(II) in the presence of Cu(II) and Cd(II) were calculated. Correlation between the initial fluxes of transported metal ions as well as the molar intrinsic volumes and HLB values of studied azocrown ethers was found. The initial fluxes of Pb(II), Cu(II), and Cd(II) decrease with the increase of crown ethers HLB, i.e., L1 > L2 > L3 > L4.

Table 3 The comparison between the methods for recovery of Pb²⁺

Recovery methods	Solution mixture	Carrier	$J (\mu mol/s m^2)$	P (µm/s)	Time (h)	Recovery (%)	References
PIM	Pb^{2+} , Zn^{2+} , Cd^2	Calix[4]crown-6 with- OCH ₂ CONHCH ₂ C ₅ H ₆	5.56	-	72	75.8	[25]
BLM	Pb^{2+}	DA18C6	0.185	-	24	_	[32]
PIM	Pb^{2+} , Zn^{2+} , Cd^{2+}	PNP-16C6 lariat ethers	$0.1 - 9 \times 10^{-6}$	-	_	25-90	[33]
PIM	Pb^{2+}, Zn^{2+}, Cd^2	1[34]	0.623	623	48	67.7	[34]
PIM	Pb^{2+}, Zn^{2+}, Cd^2	2[34]	0.191	191	48	30.1	[34]
PIM	Pb^{2+}, Zn^{2+}, Cd^2	3[34]	1.265	1265	48	90.4	[34]
BLM	Pb^{2+} , Cu^{2+} , Cd^{2+}	A ₄ 14C4	1.168	11.68	2	91	This work



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