Competitive Removal of Lead(II), Copper(II), and Cadmium(II) Ions through a Bulk Liquid Membrane Containing Macrocyclic Crown Ethers and Oleic Acid as Ion Carriers

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The competitive transport in equimolar mixtures of Cu(II), Cd(II), and Pb(II) ions from an aqueous source phase ($C_M = 0.0001\ \mathrm{mol \cdot L^{-1}}$) through bulk liquid membranes (BLMs) using tetra aza-14-crown-4 ($A_4$14C4) and oleic acid (OA) as a cooperative ion carrier has been investigated. The BLMs were used to experimentally determine the transport behavior of Cu(II), Cd(II), and Pb(II). So, the influence of chemical parameters (i.e., macrocycle molecular structure, macrocyclic and fatty acid concentrations in the membrane phase, perchlorate concentration in the source phase, and the concentration of HCl in the stripping phase) was assessed for each metal ion. Among the examined ligands, $A_4$14C4 had the best transport efficiency. The initial fluxes and transport selectivity of the BLMs with $A_4$14C4 and OA were: Pb(II) > Cu(II) > Cd(II). Moreover, the influence of Zn(II), Co(II), and Ni(II) ions on the initial fluxes, selectivity coefficient, and removal percentage of Pb(II), Cu(II), and Cd(II) ions in the BLMs was investigated. The sequences of ion initial fluxes and transport selectivity have negligible changes as: Pb(II) > Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II).

1. Introduction

Attempts to remove toxic heavy metal ions (e.g., Cd(II), Hg(II), and Pb(II)) from the environment and from biological systems have utilized a variety of separation methods such as adsorption, precipitation, solvent extraction, and liquid membrane transport.[1,2] Large-scale solvent extraction has been successfully utilized, but the use of a high volume of volatile organic diluents risks people's health and the environment. An alternative approach for metal separation and concentration, which offers significant advantages over conventional solvent extraction methods and alleviates the problems mentioned above, is based on the use of liquid membranes (LMs).[3] In recent years, LMs have widely been used to study ion transport with a concentration gradient.[4] The use of LMs in metal ion transport and removal processes with a mobile carrier has been proposed as a promising technology. Ion transport through the LM plays an important role in simulating biological membrane functions and separation technologies because of the high transport efficiency, excellent selectivity, and economic advantages of the LM.[5]

Regardless of the type of LM, the transfer of a chemical solute between the aqueous phases can be considered as a simultaneous extraction and stripping process. A hydrophobic organic phase contains a carrier which acts as a barrier between two aqueous phases.[6] Recently, transport studies using the azacrown ethers have been reported. Cho et al. claimed that a single transport of Cd(II) across emulsion LMs mediated by diaza-18-crown-6 (DA18C6) from 0.4 $\mathrm{mol \cdot L^{-1}}$ SCN^- aqueous solutions is much more effective in comparison with Zn(II).[7] On the other hand, we found the quantitative transport of Ag(I) in the presence of Zn(II), Cd(II), Pb(II), Co(II), Ni(II), Tl(I), K(I), Ca(II), Sr(II), Hg(II), and Cu(II) ions through bulk liquid membranes (BLMs) using azacrown ether.[8]

A comparison of carrier-facilitated transport of lead(II) across supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) has been studied by Aguilar et al.[9] It was shown that ligands like diazadibenzo-18-crown-6 had a high selectivity for lead(II) over cadmium(II) and zinc(II) ions using a cellulose triacetate/2-nitrophenyl octyl ether (CTA/2-NPOE). Shamsipur et al. investigated selective transport of Ag(I) over Mg(II), Ca(II), Sr(II), Ba(II), Co(II), Ni(II), Zn(II), Cu(II), Pb(II), and Cd(II) through SLM using a series of 2-NPOE solutions containing some mixed aza thio ether.[10]

Ulewicz et al. investigated competitive transport of Zn(II), Cd(II), and Cu(II) ions from an aqueous chloride source phase through PIMs containing side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 as an ion carrier. It was found that the initial fluxes of all investigated cations increase when the feed phase acidity increases, and the selectivity order was Cd(II) > Zn(II) > Cu(II).[11]

A comparison of BLM transport and extraction of Cu(II), Ni(II), Zn(II), and Mn(II) cations has been studied by Nejadali et al.[5] It was shown that, although the extraction and transport behavior of Cu(II) and Zn(II) with both examined ligands is fundamentally similar, the transport efficiency for Cu(II) is much better than Zn(II).

In our previous papers it was shown that azacrown ethers and fatty acids are both surface active and interact with each other.[12−14] Now this study is going to elucidate the influence of carrier concentration and structural features of macrocyclic crown ether derivatives and other factors on the efficiency and selectivity of ion removal in a competitive transport of lead(II), copper(II), and cadmium(II). The selectivity of metal ion separation as a function of hydrochloric acid concentration in the stripping solution was studied.

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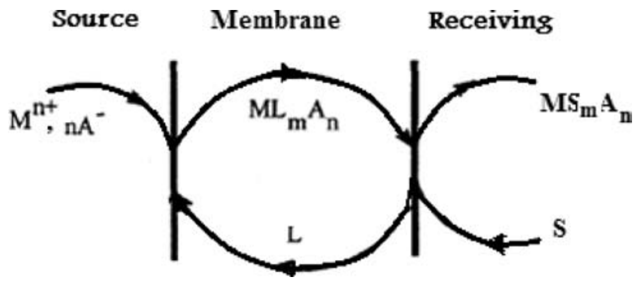

Figure 1. Scheme of the facilitated cotransport.

1.1. Theory. The competitive removal of lead, copper, and cadmium ions by using A_414C4 obeys facilitated cotransport. To suggest a mechanism for the transport of the metal ion, the pH values of the source and receiving phase were measured before and after metal ion transport. Since there were no considerable changes in pH, it proves that the mechanism is not H^+-driven. The transport mechanism is represented in Figure 1.

The metal ion is complexed at the interface of the source/membrane-phase, and the formed complex diffuses through the membrane phase to the interface of the membrane/strip-phase where the decomplexation of the metal ion is carried out. The equilibrium of reaction can be represented as:

$$\begin{aligned} M^{n+} + mL + nA^- &\rightarrow ML_mA_n \\ ML_mA_n + mS &\rightarrow MS_mA_n + mL \end{aligned} \tag{1}$$

where M^{n+} is the metal ion, L the ligand, S the stripping agent (HCl in this work), and A^- the co-ion (ClO_4^- in this work).

1.1.1. Membrane Transport Experiments. The effects of A_414C4 and OA concentration in the membrane phase, HCl concentration in the receiving phase, and sodium perchlorate concentration in the source phase on the kinetic behavior of competitive removal of Pb(II), Cd(II), and Cu(II) cations in the BLM have been investigated. These parameters were varied systematically in order to determine their particular influences on the metal ion transport.

The variation of metal ion concentrations at different times were calculated for both the source (C_s) and receiving phases (C_r). The metal ion concentrations in the membrane phase (C_m) were calculated from the material balance between the phases. For practical reasons, dimensionless metal ion concentrations in the three phases were used:

$$R_s = \frac{C_s}{C_{s0}} \qquad R_m = \frac{C_m}{C_{s0}} \qquad R_r = \frac{C_r}{C_{s0}} \tag{2}$$

where C_{s0} is the initial M^{n+} concentration in the source phase, while C_s, C_m, and C_r represent the metal ion concentration in the source, membrane, and receiving phases after t (min), respectively. From these expressions, the kinetic behavior of the consecutive irreversible first-order reactions can be described by eqs 3 and 4:

$$C_s \xrightarrow{k_1} C_m \xrightarrow{k_2} C_r \tag{3}$$

$$\ln \frac{C_0}{C} = k_1 t \tag{4}$$

where k_1 and k_2 are the membrane entrance and exit rate constants (min^{-1}), respectively, and t is the time of transport (min). To calculate the k_1 value, $\ln(C_{s0}/C_s)$ versus time was plotted. The correlation between $\ln(C_{s0}/C_s)$ and time was linear, which was confirmed by high coefficient of determination (R^2) values.

The k_2 value can be calculated as follows:

$$C_M = \frac{k_1 C_{s0}}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{5}$$

k_1 and k_2 were calculated from eqs 4 and 5. Since k_1 and k_2 are nearly equal, the overall rate constant can be considered equal to the first step. Then, k_1 can be applied instead of the overall rate constant k. The permeability coefficient P (cm·min^{-1}) can be evaluated as:[15]

$$P = -\frac{V}{A} \cdot k_1 \tag{6}$$

where V (mL) is the volume of the aqueous source phase, and A (cm^2) is an effective area of the membrane.

The initial flux (J_i) is equal to:

$$J_i = P \cdot C_{s0} \tag{7}$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for M_1 and M_2 metal ions, respectively:

$$S = \frac{J_{i,M_1}}{J_{i,M_2}} \tag{8}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (R_F %) was calculated:

$$R_F\,\% = \frac{C_r}{C_{s0}} \cdot 100 \tag{9}$$

2. Experimental Section

2.1. Reagents. The tetraaza-14-crown-4 (A_414C4, **L1**), dibenzyldiaza-18-crown-6 (DBzDA18C6, **L2**), benzo-15-crown-5 (B15C5, **L3**), 4′-aminobenzo-15-crown-5 (Am15C5, **L4**), nitrobenzo-15-crown-5 (NB15C5, **L5**) ethers, oleic acid (OA), and HCl were purchased from Merck or Fluka. Reagent grade chloroform (Merck) was used as the membrane organic solvent. $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Co(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, and $NaClO_4$ used in this study were of the highest purity from Merck and were used without further purification except for vacuum drying over P_2O_5. Doubly distilled, deionized water was used.

2.2. Apparatus. A bulk type LM 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

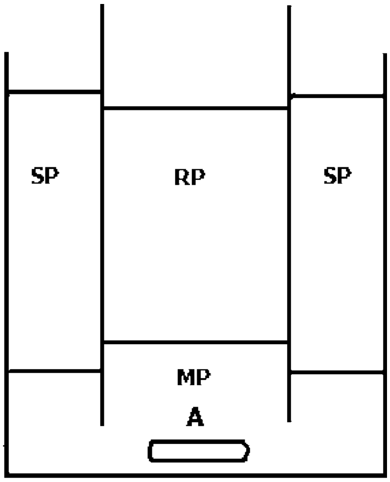

Figure 2. Representation of the bulk type LM cell: SP, source phase; RP, receiving phase; MP, membrane phase; A, magnetic stirrer.

at recommended wavelengths of $\lambda = (213.9, 217, 228.8, 232, 240.4, \text{ and } 324.7)$ nm for zinc, lead, cadmium, nickel, cobalt, and copper, respectively.

2.3. Procedure. All transport experiments were done as reported earlier using a BLM apparatus at ambient temperature.[12−14]

A cylindrical glass cell (inside diameter 5.0 cm) which holds a glass tube (inside diameter 2.5 cm) and separates the two aqueous phases was used (Figure 2). The source phase contained a mixture of metal nitrates (15 mL, $1.0 \cdot 10^{-4}$ mol$\cdot$L^{-1}) and sodium perchlorate ($1.5 \cdot 10^{-2}$ mol$\cdot$L^{-1}). The stripping phase included HCl as a metal ion receptor, (15 mL, 0.4 mol$\cdot$L^{-1}). A chloroform phase (25 mL) containing $A_4$14C4 ($5.0 \cdot 10^{-4}$ mol$\cdot$L^{-1}) and OA (0.03 mol$\cdot$L^{-1}) lay below these aqueous phases and bridged them. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (2 cm × 5 mm diameter). The source and stripping phases were sampled and analyzed for the corresponding metal ion concentration by atomic absorption spectrophotometry.

3. Result and Discussion

The kinetic parameters that affect the transport efficiency are usually rate constant values (k), the permeability coefficient (P), the initial flux (J_i), and the selectivity coefficient (S). In our preliminary experiment k_1 and k_2 were calculated via first-order consecutive kinetics eqs 3 to 5. The results are shown in Tables 1 to 4. To quantitatively describe factors which influence cation transport, we examined the effect of carrier structure and concentration in the membrane phase and counterion concentration in the source phase as well as HCl concentration in the stripping phase on the kinetic parameters affecting the competitive transport of lead(II), copper(II), and cadmium(II) cations.

3.1. Influence of the Carrier Structure. Among the ion carriers used for the transport experiments, the strong binding of the cyclic and bicyclic polyether macrocyclic ligands with alkali and alkaline earth metal ions have been well-documented.[16] However, such ligands generally hold very weak complexes with transition metal ions. Nevertheless, the incorporation of donor atoms other than oxygen in the backbone of polyether ligands tends to improve the complexing ability toward transition and heavy metal ions.[17−19] A major problem associated with the use of aza-substituted crown ethers as metal ion carriers is their substantial bleeding from the membrane phase into the aqueous phase.[12] However, it has been shown that the addition of fatty acids to the organic membrane phase dramatically reduces the degree of macrocyclic loss from the membrane.[13,14,20] The synergistic effects of the mixture of azacrown ether and fatty acid on the selectivity of Cu(II) transport have been reported earlier.[21,22]

It is well-known that the flux and transport selectivity of mixture ions are significantly dependent on the nature of the macrocyclic ligand and OA which are used as binary carriers.[14] As can be expected, an efficient and suitable carrier in the separation technology is needed to remove the desired ions selectively on the source phase and to release them readily on the stripping phase side. To investigate the suitable macrocyclic ligand as an ion carrier for transport, five different macrocyclic ligands were tried (Figure 3). The kinetic parameters were obtained, and then the results are summarized in Table 1. It was revealed that in all cases the initial fluxes of metal ion transport across BLMs increase in the sequence: Cd(II) < Cu(II) ≪ Pb(II). Under similar experimental conditions, the efficiency of the ligand as an ion carrier on kinetic parameters decreases in this way: **L1** > **L2** > **L3** > **L4** > **L5**. It is clear that both types of donor groups and the cavity size influence considerably the complexing ability of the ligands toward metal ions and

Table 1. Effect of Carrier Structure on Initial Flux Value J_i, Permeability Coefficient p, Selectivity Order, and Selectivity Ratio S for the Competitive Transport of Pb(II), Cu(II), and Cd(II)[a]

crown ether	metal ion	k_1 min^{-1}	k_2 min^{-1}	permeability coefficient, p μm$\cdot$s^{-1}	initial flux, J_i μmol$\cdot$m$^{-2}\cdot$s^{-1}	selectivity order and selectivity ratio S
$A_4$14C4	Pb(II)	0.0230	0.0230	11.680	1.168	Pb(II) > Cu(II) > Cd(II)
L1	Cu(II)	0.0039	0.0039	1.980	0.198	5.90 19.14
	Cd(II)	0.0012	0.0012	0.610	0.061	
DBzDA18C6	Pb(II)	0.0170	0.0160	8.737	0.874	Pb(II) > Cu(II) > Cd(II)
L2	Cu(II)	0.0050	0.0035	2.540	0.254	3.43 87.75
	Cd(II)	0.0002	0.0002	0.127	0.013	
B15C5	Pb(II)	0.0021	0.0010	1.066	0.107	Pb(II) > Cu(II) > Cd(II)
L3	Cu(II)	0.0010	0.0009	0.507	0.051	2.12 9.63
	Cd(II)	0.0002	0.00025	0.110	0.011	
4′-aminobenzo-15C5	Pb(II)	0.0018	0.0010	0.914	0.091	Pb(II) > Cu(II) > Cd(II)
L4	Cu(II)	0.00068	0.0008	0.350	0.035	2.60 9.1
	Cd(II)	0.00021	0.0003	0.106	0.011	
NB15C5	Pb(II)	0.0006	0.00065	0.304	0.030	Pb(II) > Cu(II) > Cd(II)
L5	Cu(II)	0.0005	0.0004	0.254	0.025	1.20 3.33
	Cd(II)	0.00019	0.00016	0.096	0.009	

[a] Conditions: source phase: 15 mL of aqueous solution of Pb(II), Cu(II), and Cd(II), each metal 0.0001 mol$\cdot$L^{-1} and $1.5 \cdot 10^{-2}$ mol$\cdot$L^{-1} $NaClO_4$; membrane phase: 25 mL of 0.03 mol$\cdot$L^{-1} OA and crown ether ($4.0 \cdot 10^{-4}$ mol$\cdot$L^{-1}) in chloroform; stripping phase: 15 mL of 0.4 mol$\cdot$L^{-1} HCl; time of transport, 120 min.

Table 2. Effect of $A_4$14C4 Concentration on Kinetic Parameters p and J_i, Selectivity Order, and Selectivity Ratio S for the Competitive Transport of Pb(II), Cu(II), and Cd(II)[a]

$A_4$14C4 concentration mol·L^{-1}	metal ion	k_1 min^{-1}	k_2 min^{-1}	permeability coefficient, p μm·s^{-1}	initial flux, J_i μmol·m^{-2}·s^{-1}	selectivity order and selectivity ratio S
0	Pb(II)	0.0012	0.00091	0.610	0.061	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.00066	0.0004	0.340	0.034	1.80 6.1
	Cd(II)	0.0002	0.00017	0.101	0.010	
0.0002	Pb(II)	0.0070	0.0050	3.657	0.366	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.0020	0.0012	1.016	0.102	3.61 18.25
	Cd(II)	0.0004	0.00041	0.203	0.020	
0.0003	Pb(II)	0.0128	0.0130	6.590	0.659	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.0026	0.0020	1.320	0.132	4.99 19.10
	Cd(II)	0.00068	0.00088	0.345	0.0345	
0.0004	Pb(II)	0.0230	0.0230	11.680	1.168	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.0039	0.00389	1.980	0.198	5.90 19.14
	Cd(II)	0.0012	0.0012	0.610	0.061	

[a] Conditions: source phase: 15 mL of Pb(II), Cu(II), and Cd(II), each metal 0.0001 mol·L^{-1} and $1.5 \cdot 10^{-2}$ mol·L^{-1} $NaClO_4$; membrane phase: 25 mL of 0.03 mol·L^{-1} OA and varying amounts of $A_4$14C4 in chloroform; stripping phase: 15 mL of 0.4 mol·L^{-1} HCl; time of transport, 120 min.

Table 3. Effect of OA Concentration on Kinetic Parameters p and J_i, Selectivity Order, and Selectivity Ratio S for the Competitive Transport of Pb(II), Cu(II), and Cd(II)[a]

OA concentration mol·L^{-1}	metal ion	k_1 min^{-1}	k_2 min^{-1}	permeability coefficient, p μm·s^{-1}	initial flux, J_i μmol·m^{-2}·s^{-1}	selectivity order and selectivity ratio S
0	Pb(II)	0.000697	0.00067	0.355	0.035	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.000198	0.00033	0.101	0.010	3.50
	Cd(II)					
0.01	Pb(II)	0.0023	0.0021	1.170	0.117	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.0013	0.0011	0.660	0.066	1.75 7.73
	Cd(II)	0.0003	0.00026	0.152	0.015	
0.03	Pb(II)	0.0230	0.0230	11.680	1.168	Pb(II) > Cu(II) > Cd(II)
	Cu(II)	0.0039	0.00389	1.980	0.198	5.90 19.14
	Cd(II)	0.0012	0.0012	0.610	0.061	

[a] Conditions: source phase: 15 mL of Pb(II), Cu(II), and Cd(II), each metal 0.0001 mol·L^{-1} and $1.5 \cdot 10^{-2}$ mol·L^{-1} $NaClO_4$; membrane phase: 25 mL of $A_4$14C4 ($4.0 \cdot 10^{-4}$ mol·L^{-1}) and varying amounts of OA in chloroform; stripping phase: 15 mL of 0.4 mol·L^{-1} HCl; time of transport, 120 min.

Table 4. Effect of Perchlorate Ion Concentration on Kinetic Parameters p and J_i, Selectivity Order, and Selectivity Ratio S for the Competitive Transport of Pb(II), Cu(II), and Cd(II)[a]

$NaClO_4$ concentration mol·L^{-1}	metal ion	k_1 min^{-1}	k_2 min^{-1}	permeability coefficient, p μm·s^{-1}	initial flux, J_i μmol·m^{-2}·s^{-1}	selectivity order and selectivity ratio S
	Pb(II)	0.0173	0.0182	8.838	0.884	Pb(II) > Cu(II) > Cd(II)
0	Cu(II)	0.0028	0.0030	1.420	0.142	6.20 16.05
	Cd(II)	0.0011	0.0012	0.558	0.056	
	Pb(II)	0.0230	0.0230	11.680	1.168	Pb(II) > Cu(II) > Cd(II)
0.015	Cu(II)	0.0039	0.00389	1.980	0.198	5.90 19.14
	Cd(II)	0.0012	0.0012	0.610	0.061	
	Pb(II)	0.0232	0.0230	12.080	1.208	Pb(II) > Cu(II) > Cd(II)
0.03	Cu(II)	0.0048	0.0050	2.450	0.245	4.93 19.80
	Cd(II)	0.0012	0.0011	0.615	0.062	

[a] Conditions: source phase: 15 mL of aqueous solution of Pb(II), Cu(II), and Cd(II), each at 0.0001 mol·L^{-1} and varying amounts of $NaClO_4$; membrane phase: 25 mL of 0.03 mol·L^{-1} OA and $A_4$14C4 ($4.0 \cdot 10^{-4}$ mol·L^{-1}) in chloroform; stripping phase: 15 mL of 0.4 mol·L^{-1} HCl; time of transport, 120 min.

consequently transport effeciency. As Lamb et al. outlined in their previous studies, the maximum cation transport occurs when the cation−carrier complex stability constant is in the range of the optimum value. The rate of cation transport decreases rapidly at stability constant values higher or lower than this range.[23]

It is obvious that the maximum of initial fluxes of Pb(II) and Cd (II) ions were for **L1**, while the maximum of initial fluxes of Cu(II) was for **L2**. The best selectivity of Pb(II)/Cu(II) and Pb(II)/Cd(II) coefficients are equal to 5.90 and 19.14, respectively. The maximum values of the initial flux and permeability coefficient for **L1** seem to be mainly due to the existence of four nitrogen atoms in the macrocyclic ring which can considerably influence the stability constant. As can be noted from Table 1, the membranes with carriers **L3** to **L5** have a lower initial flux and permeability coefficient than **L1** and **L2**. The largely decreased efficiency of macrocycles **L3** to **L5** compared with **L1** and **L2** seems to be due to the existence of benzo groups on the macrocyclic rings, which results in the enhanced configuration rigidity of the ligand.[23−25] According to Pearson's hard soft acid base theory,[26] because of the softer character of nitrogen atoms in the framework of the azacrown ether, **L1** and **L2** they show higher sensitivity toward transition metal ions in comparison with their fully oxygenated analogues of comparable cavity size, **L3** to **L5**. Thus, **L1** with the best transport efficiency was chosen as the most suitable ion carrier in this study.

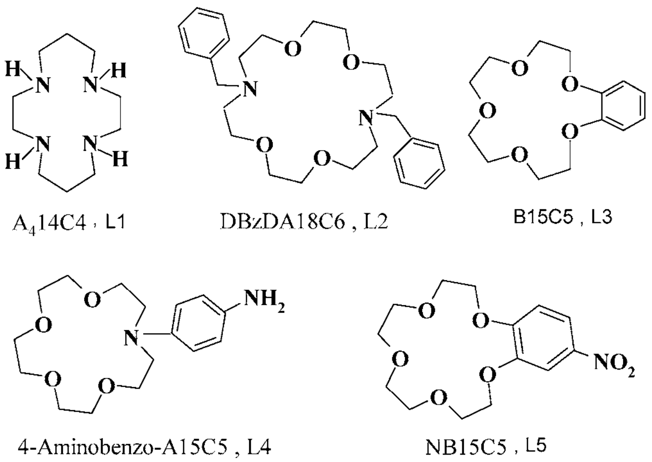

Figure 3. Structures of ligands.

Selectivity was one of the parameters that evaluated the efficiency of separation. In fact, the greater the selectivity from unity, the better the separation. Table 1 shows the selectivity of transport across the BLMs with carriers **L1** to **L5** were Pb(II) ≫ Cu(II) > Cd(II). The selective separation of metal ions has received considerable attention particularly with regards to host−guest complexation. As mentioned earlier, these complexes are formed by noncovalent binding forces such as electrostatic attraction between electron donors and acceptors as well as the shape and size complementation between the host molecule and the metal ion as the guest.[27] The high response toward lead ions may be explained by the cation−carrier complex stability constant of **L1** and Pb(II).

3.2. Influence of Membrane Composition on Competitive Transport. The membrane system was studied with respect to the relative concentrations of A$_4$14C4/OA by making the amount of one of the constituents constant and varying the concentration of the other. The relationship between $\ln(C_{s0}/C_s)$ and time for Pb(II), Cu(II), and Cd(II) transport across BLMs is shown in Figure 4, and the calculated kinetic parameters are summarized in Tables 2 and 3. It was found that in the presence of A$_4$14C4 as the only carrier, the permeability coefficient and initial flux of the metal ion is very low (Table 3). It is interesting to note that, in the presence of OA as the only carrier, the permeability coefficient and initial flux of metal is very low too (Table 2). Guyon et al. reported on the basis of proton NMR studies in chloroform that the interaction between azacrown ether and lauric acid is mainly caused by the presence of basic nitrogen atoms in the former and the acidic protons in the latter molecule.[28] The proton shared by the azacrown ethers and fatty acid delocalizes its positive charge between the amine part of the azacrown ether and carboxylic part of the fatty acid. Thus, the interactions between OA and A$_4$14C4 can impart a greater degree of lipophilicity to the carrier system, facilitating the cation transport through the LM. In addition, a synergistic effect of the mixture of azacrown ether and fatty acid on the selectivity of Cu(II) transport has been observed.[28,29] As could be expected, the carboxylate group tends to dimerize in the presence of Cu(II) ions and form stable complexes as:

$$2\mathrm{Cu(LA)_2(LAH)_2} \leftrightarrow \mathrm{(CuLA_2{\cdot}LAH)_2} + \mathrm{(LAH)_2} \tag{10}$$

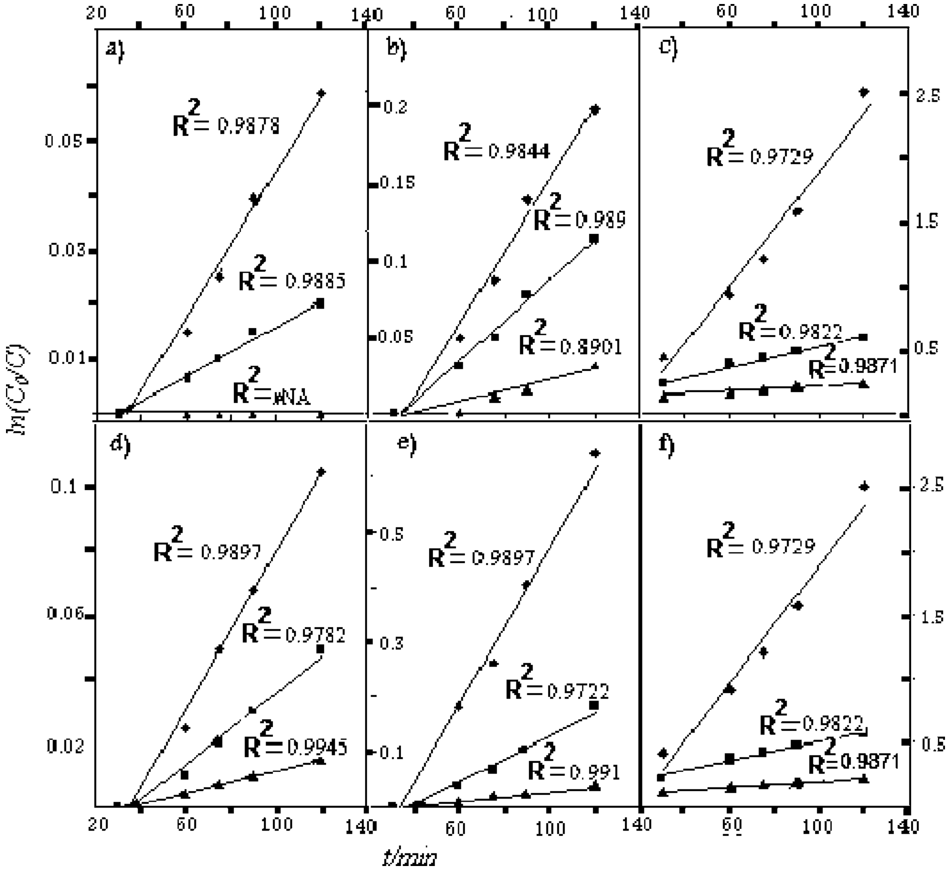

Figure 4. Kinetics of ◆, Pb(II); ■, Cu(II); and ▲, Cd(II) transport across BLMs containing of varying amounts of OA and A$_4$14C4: 3 (a), 3 (b), 3 (c). 0.03 mol·L^{-1} OA and A$_4$14C4: (a) 0 mol·L^{-1}, (b) 0.015 mol·L^{-1}, (c) 0.03 mol·L^{-1}. 3 (d), 3 (e), 3 (f). 4.0·10^{-4} mol·L^{-1} of A$_4$14C4 and OA: (d) 0 mol·L^{-1}, (e) 2.0·10^{-4} mol·L^{-1}, (f) 4.0·10^{-4} mol·L^{-1}.

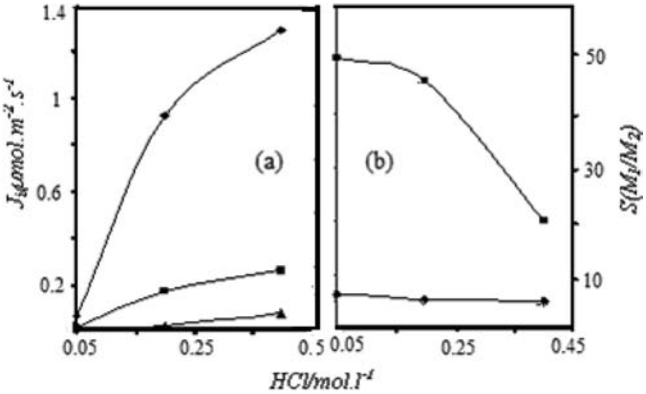

Figure 5. Relationship between initial fluxes values and (a) selectivity coefficient, [◆, Pb(II); ■, Cu(II); and ▲, Cd(II)], and (b) concentration of HCl for competitive transport of Pb(II), Cu(II), and Cd(II) ions), [◆, Pb(II)/Cu(II); ■, Pb(II)/Cd(II)] with 5. Conditions: source phase: 15 mL of aqueous solution of Pb(II), Cu(II), and Cd(II), each metal 0.0001 mol·L^{-1} and 1.5·10^{-2} mol·L^{-1} ClO_4^-; membrane phase: 25 mL of 0.03 mol·L^{-1} OA and $A_4$14C4 (5.0·10^{-4} mol·L^{-1}) in chloroform; stripping phase: 10 mL of varying amounts of HCl; time of transport, 120 min.

where LA and LAH are the lauric anion and lauric acid, respectively.

Therefore, both azacrown ether and fatty acid could serve as carrier, since both are known to complex the metal in bulk and that both are expected to have surfactant properties.[22] This confirms the cooperative behavior of the two components as carriers. A possible reason for this behavior would be the existence of some proton- donor, proton- acceptor interactions between OA and crown ether which can impart a greater degree of lipophilicity to the carrier system facilitating the cation transport through the LM. [20]

In Figure 5, the transport of Cu(II), Cd(II) and Pb(II) ions with $A_4$14C4 and OA according to the mathematical model proposed by Danesi can be described by first-order kinetics relatively to transported ions.[30] The increase of the fluxes can be seen with the concentration of $A_4$14C4 and OA. It was revealed that in all cases, the lead(II) ion gave selective transport over the other metal ions. In Tables 2 and 3 the initial fluxes and selectivity of transport of metal ions across the BLMs with $A_4$14C4 and OA increase as: Cd(II) < Cu(II) < Pb(II).

In addition, Kirch and Lehn demonstrated that there is a relationship between thermodynamic and transport selectivities by relating the thermodynamic stability constants for cation−macrocycle complexation and the rates of individual cation transport through LMs containing macrocyclic carriers.[31] Also a theoretical basis for relating J_M to the stability constant (K) has been proposed by Reusch and Cussler.[32]

3.3. Influence of the $NaClO_4$ Concentration. In preliminary experiments, it was found that the nitrate ion is not a suitable counterion to accompany the M(II)−$A_4$14C4 complex into the membrane phase. As shown earlier, the metal ion transfer efficiency from aqueous solution 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.[10,33] However, the addition of sodium perchlorate to the source phase increased the extent of metal ion transport significantly.

A similar influence of the perchlorate ion on the solvent extraction of the metal−macrocyclic ligand complex has been reported in the literature.[32,33] It has been suggested that the crown ether places M^{n+} in its cavity and the counteranion is coordinated in the axial position forming a lipophilic neutral complex. This complex is suitable for transferring M^{n+} to the organic phase. Thus, the degree of extraction increases as the hydrophobicity of the anion increases.

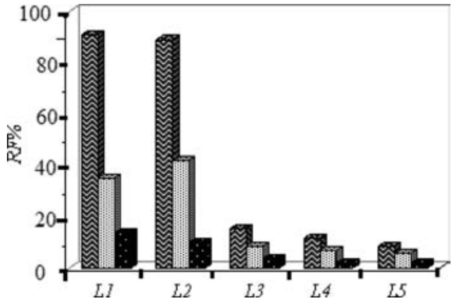

Figure 6. Effect of crown ethers structure on the recovery factors. Conditions: source phase: 15 mL aqueous solution of ■, Pb(II); □, Cu(II); and ■, Cd(II), each metal 0.0001 mol·L^{-1} and 1.5·10^{-2} mol·L^{-1} ClO_4^-; membrane phase: 25 mL of 0.03 mol·L^{-1} OA and crown ether (4.0·10^{-4} mol·L^{-1}) in chloroform; stripping phase: 15 mL of 0.4 mol·L^{-1} HCl; time of transport, 120 min.

The influence of the concentration of the perchlorate ion in the source phase on the initial fluxes, selectivity order, and selectivity ratio for competitive transport of Pb(II), Cu(II), and Cd(II) across BLMs with $A_4$14C4 and OA was investigated, and the results are shown in Table 4. It is obvious that the maximum of initial fluxes of Pb(II), Cu(II), and Cd(II) ions was obtained for 0.015 mol·L^{-1} $NaClO_4$ in the source phase. The best selectivity coefficients of Pb(II)/Cu(II) and Pb(II)/Cd(II) are equal to 5.90 and 19.14, respectively.

3.4. Influence of the HCl Concentration in Receiving Phase. As expected, the permeability of the membrane system for metal ion transport was found to be largely dependent on the nature and concentration of the stripping ligand used in the stripping phase.

Metal ion extraction mechanisms from the source phase using acidic carriers at the stripping solutions can be written as:[34]

$$M^{n+}_{(SP,MP)} + nHA_{(RP,MP)} \leftrightarrow MA_{n(SP,MP)} + nH^{+}_{(RP,MP)} \tag{8a}$$

where SP, MP, and RP are the source, membrane, and stripping phases, respectively. It is evident that metal extraction occurs when the equilibrium is shifted to the right, whereas in an excess of acid in the aqueous stripping phase, metal stripping occurs, and the equilibrium is shifted to the left. The relation between initial fluxes, selectivity ratio, and HCl concentration of the stripping phase for competitive transport of Pb(II), Cu(II), and Cd(II) with **L1** at 0.4 mmol·L^{-1} and 0.03 mol·L^{-1} of OA in the membrane are shown in Figure 4. It is interesting to note that initial fluxes of all investigated metal cations increase with an acidity increase of the stripping phase. On the other hand, the selectivity coefficients of Pb(II)/Cu(II) and Pb(II)/Cd(II) for BLMs decrease with a HCl concentration increase in the stripping phase. The same tendency was reported in the literature.[27]

3.5. Recovery Factors. The recovery factors of metal ions under optimized experimental conditions are as follows: Source phase: 15 mL, containing a mixture of metal nitrate, 1.0·10^{-4} mol·L^{-1} and $NaClO_4$, 1.5·10^{-2} mol·L^{-1}. Receiving phase: 15 mL, containing HCl (0.4 mol·L^{-1}). Membrane phase: 25 mL, containing a mixture of $A_4$14C4, 5.0·10^{-4} mol·L^{-1} and OA, 0.03 mol·L^{-1}. These factors were calculated by eq 9. The removal percentage of divalent metal ions from the source phase after 2 h in transport across the BLM with **L1** to **L5** carriers is

Table 5. Kinetics Parameters, Selectivity Order, and Selectivity Ratio for the Competitive Transport of Pb(II), Cu(II), Cd(II), Zn(II), Co(II), and Ni(II)[a]

metal ion	permeability coefficient μmol·s^{-1}	initial flux, J_i μmol·m^{-2}·s^{-1}	selectivity order and selectivity ratio
Pb(II)	10.413	1.041	
Cu(II)	1.320	0.132	
Cd(II)	0.660	0.066	Pb(II) > Zn(II) > Cu(II) > Cd(II) > Co(II) > Ni(II)
Zn(II)	1.820	0.182	
Co(II)	0.690	0.069	5.72 7.88 15.77 15.08 69.40
Ni(II)	0.152	0.015	

[a] Conditions: source phase: 15 mL of aqueous solution of Pb(II), Cu(II), Ni(II) Zn(II), Co(II), and Cd(II), each metal 0.0001 mol·L^{-1} and 1.5·10^{-2} mol·L^{-1} $NaClO_4$; and all other conditions same as mentioned in Table 4.

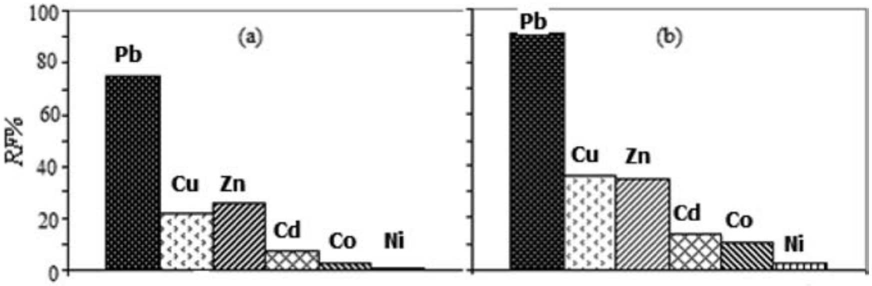

Figure 7. Recovery factor of Pb(II), Cu(II), Cd(II), Zn(II), Co(II), and Ni(II) ion transport from the source phase across BLM after (a) 60 and (b) 120 min; conditions as mentioned in Table 5.

shown in Figure 6. The high removal toward lead ions might be due to the complementary size between the cavity of the **L2** [(1.34 to 1.43) Å] and Pb(II) ion radius (1.18 Å).[23] On the other hand, it is clear that both **L1** and **L2** have a stronger affinity for the Pb(II) ion. This can be related to the nature and the number of heteroatoms forming the carriers too. The recovery factors for **L1** in optimized conditions after 2 h was (94.0, 44.0, and 20.0) %, for Pb(II), Cu(II), and Cd(II), respectively.

3.6. Effect of Zn(II), Co(II), and Ni(II) Salts on Cu(II), Cd(II), and Pb(II) Ion Transport Across the Membrane. In another experiment we were interested in studying the effect of Zn(II), Co(II), and Ni(II) cations on the kinetic behavior of Cu(II), Cd(II), and Pb(II) ion transport. The values of permeability coefficients, initial fluxes, selectivity order, and selectivity ratio for competitive transport of six divalent metal ions across BLMs with $A_4$14C4 and OA are summarized in Table 5. The highest initial fluxes were obtained for Pb(II). The selectivity order was: Pb(II) > Zn(II) > Cu(II) > Cd(II) > Co(II) > Ni(II). As is shown, there was no significant change in the kinetic behavior. The removal percentage of divalent metal ions from the source phase after (1 and 2) h of ion transport across the BLM with $A_4$14C4 and OA are shown in Figure 7. The highest removal percentages from source phase containing an equimolar mixture of six metal ions were obtained for Pb(II), with a recovery factor of 91 % (after 2 h).

4. Conclusion

The optimum value and behavior of the main parameters influencing the removal of lead, copper, and cadmium ions through BLMs containing $A_4$14C4 and OA as carriers were determined. The types of attached groups, ring size, and the type and the number of hetroatoms in ligand carriers affect the selectivity and efficiency of metal ion transport through the BLMs.

Competitive transport tests showed a maximum permeability coefficient value, initial flux selectivity ratio, and recovery factors using $A_4$14C4 and OA as carriers. In transport experiments the transmembrane flux increased with increasing carrier concentration in the membrane phase, perclorate concentration in the source phase, and concentration of HCl in the receiving phase. The selectivity coefficients Pb(II)/Cu(II) and Pb(II)/Cd(II) decrease with an increase of HCl concentration in the stripping phase. The selectivity order of metal ion fluxes for the studied crown ethers **L1** to **L5** is: Pb(II) ≫ Cu(II) > Cd(II). **L1** with the most efficiency was selected for this study. **L1** and **L2** can be used for the quantitative removal of Pb(II) and Cu(II) cations.

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