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STUDIES ON REMOVAL OF Zn(II), Cd(II) AND Pb(II) IONS IN POLYMER INCLUSION MEMBRANE TRANSPORT WITH CALIX[4]-CROWN-6 DERIVATIVES

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Competitive transport of Zn(II), Cd(II), and Pb(II) ions from aqueous nitrate source phase ($c_{Me} = 0.01$ M) through polymer inclusion membranes (PIMs) containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and calix[4]crown-6 derivatives (as ion carriers) has been investigated. The influence of the group, i.e. –OH, –OMe attached type to the calix[4]-crown-6 molecule on the selectivity and efficiency of Zn(II), Cd(II), and Pb(II) transport through polymer inclusion membranes is studied. The removal of metal ions by transport through PIM's from acid nitrate aqueous solutions is presented. The selectivity coefficients of Pb/Zn and Cd/Zn decrease with acid concentration increase in receiving phase. On the other hand, the initial fluxes of investigated ions decrease using the same membrane for the second and third time.

Key words: polymer inclusion membrane, zinc(II), cadmium(II), lead(II), calix[4]crown-6 derivatives

INTRODUCTION

Selective separation of metal ions from industrial and waste aqueous solutions is frequently required in hydrometallurgical processing. The transport through liquid membranes containing ion carriers is an alternative to solvent extraction for selective separation and concentration of metal ions from source aqueous phase, in which the concentration of metal ionic species is $> 1 \cdot 10^{-4}$ M (Bartsch and Way, 1996). A new

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type of membrane system, called polymer inclusion membrane (PIM), has been developed which provides metal ion transport with high selectivity, as well as easy setup and operation (Bond et al., 1999).

Macrocycles as ion carriers were successfully used for metal ions separation in solvent extraction, transport through liquid membranes and in ion exchange systems. Along with the crown ethers and cryptands, the calixarenes are a major class of ion carriers. The calixarenes can recognize cationic and anionic species, as well as neutral molecule. Several calixarenes with different donor atoms have been applied as heavy metal extractants. Arnaud-Neu et al. (Arnaud-Neu et al., 1997) used of ionophores for complexation of Pb(II), Hg(II) and Cd(II) cations by replacing hard oxygen-based binding group with softer sulfur based binders. Calixarenes with thioamide functions in lower rim have demonstrated good efficiency in the selective extraction of Cd(II) and Pb(II) ions. Solvent extraction of heavy metals with macrocyclic ligands based on calix[4]arenes was also studied by Dung and Ludwig (Dung and Ludwig, 1999).

Arena et al. (Arena et al., 2001) have proposed a new allyl functionalized thioamide calix[4]arene in 1,3-alternate conformation for complexation of Pb(II) and Hg(II) ions. This new ligand is able to discriminate mercury(II) and lead(II) ions from cadmium(II) and sodium mixture. Otho and coworkers (Otho et al., 1999) have been reported the possibility to bound two lead(II) ions with a single molecule of calix[4]arene tetracarboxylic acid. The order of extraction selectivity to metal ions was as follows: Pb(II) >> Fe(III) > Al(III) > Cu(II) > Zn(II).

Calixarenes and their derivatives are a new generation of such highly selective carrier for cesium ions across liquid membrane (Levitskaia et al., 2002; Kim et al., 2001). Levitskaia et al. (Levitskaia et al., 2002) studied competitive Cs⁺ ion transport through polymer inclusion membranes with bis(dodecyloxy)calix[4]arene-crown-6 or calix[4]arene-biscrown-6 as ion carriers. The PIM matrix consisted of cellulose triacetate, *o*-nitrophenyloctyl ether and ion carrier. Membranes containing calix-monocrown carrier exhibited slightly less efficient but more selective Cs⁺ transport than those with calix-biscrown carrier. Selective extraction of cesium cation with 1,3-propyloxycalix[4]arene crown ether (CCE1) and 1,3-dipropyloxycalix[4]arene dibenzo crown ether (CCE2) through thin sheet supported liquid membranes was found. Permeation coefficients of cesium ion with CCE1 as extractant was higher than with CCE2 (Kim et al., 2001).

A few papers deal with the selective removal of heavy metal ions with calixarenes. Alpoguz et al. (Alpoguz et al., 2002) studied co-transport of metals (Hg²⁺, Pb²⁺, Na⁺) from an aqueous solution into an aqueous receiving solution through the bulk liquid membrane containing calix[4]arene nitrile derivatives as ion carriers. Kinetic parameters were analyzed with consecutive irreversible first-order reactions and the effect of solvents such as CH₂Cl₂, CHCl₃, and CCl₄ was observed. The transport rates show that both nitrile derivatives are efficient and selective for Hg(II) ions with respect to Na⁺ and Pb²⁺ ions and the dinitrile derivatives is found to be a better carrier than the tetranitrile one. The membrane entrance and exit rate constant depend on the

solvent type and are found to be in the order $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$. Hui-Min et al. (Hui-Min et al., 2001) studied the selective transport of Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Zn^{2+} across liquid membrane with new calix[4]crowns. It was found that one of these calix crowns, 25,27-dihydroxy-26,28-(3',6'-dioxo-2',7'-dioxooctylene)dioxy-calix[4]arene, transported efficiently Cu^{2+} .

During last years several neutral crown ethers and lariat ethers were successfully used for separation transport of heavy metal ions. In competitive transport of Zn(II) and Cd(II) through emulsion liquid membrane containing dicyclohexane-18-crown-6, near quantitative selectivity for Cd(II) over Zn(II) and Hg(II) has been achieved (Izatt et al., 1987). This can be explained by the preferential transport of neutral cation-anion moieties of CdA_2 from Zn^{2+} and $[\text{HgA}_2]^{2-}$, where A = SCN^- , I^- , Br^- or Cl^- (Izatt et al., 1986). Cho et al. (Cho et al., 1991, 1995) found out that a single transport of Cd^{2+} across emulsion liquid membranes by diazo-18-crown-6 (DA18C6) from 0.4 M SCN^- aqueous solutions is much more effective in comparison with Zn^{2+} . On the other hand, Dadfarnia and Shamsipur (Dadfarnia and Shamsipur, 1992) discovered quantitatively transport of zinc(II) and only 1 % of cadmium(II) across bulk liquid membrane with DA18C6 and palmitic acid. Ulewicz et al. (Ulewicz et al., 2004) investigated competitive transport of Zn(II), Cd(II), and Cu(II) ions from aqueous chloride source phase through polymer inclusion membranes containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 (ion carrier). It was found, that the initial fluxes of all investigated cations increase with acidity of the feed phase increase and the selectivity order was as follows: $\text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)}$.

We now present results for competitive transport of zinc(II), cadmium(II), and lead(II) ions from dilute aqueous solutions with calix[4]crown-6 derivatives. The compounds studied here are *t-butyl*-calix[4]-crowns-6 with two distal unsubstituted phenolic OH groups (compound **1**) or methylated compound **2**. Both are in *cone* conformation. Calix[4]crowns were found to be good complexants for the alkali metal ions, showing selectivity for Na^+ , K^+ or Cs^+ ions according to the size of the polyether loops attached. These compounds can find application as sensing materials. Bochenska et al. (Bocheńska et al., 2003) Compound **2** in ion-selective membrane electrodes shows high selectivity for cesium ions. Calix[4]-crown-6 are known as selective cesium extractants for radioactive water treatments (Calixarenes, 2001). The selectivity of metal ions separation as a function of nitric acid concentration in receiving aqueous solution is studied. Also effects of structural modification of calixarene derivatives upon the efficiency and selectivity of ions transport is now reported.

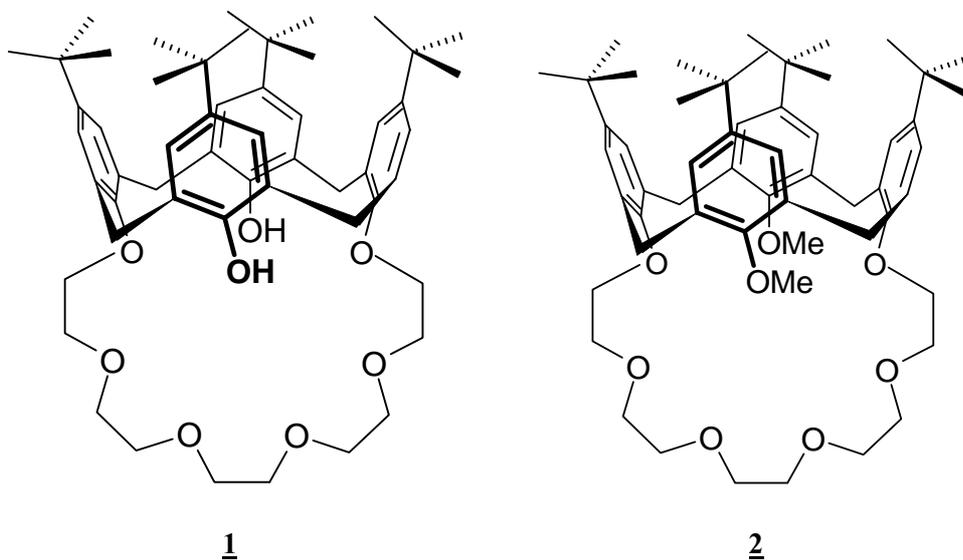
EXPERIMENTAL

REAGENTS

The inorganic chemicals, i.e. zinc(II), cadmium(II), and lead(II) nitrates as well as nitric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (ONPPE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. The density of plasticizer, i.e. *o*-nitrophenyl pentyl ether was 1.085 g/cm³. The aqueous solutions were prepared with double distilled water, which conductivity was 0.1 μS/m. Tert-butyl-calix[4]-crown-6, the compounds 1 and 2 were synthesized by Bochenka et al. (Bochenka et al., 2005).

POLYMER INCLUSION MEMBRANE PREPARATION

A solution of cellulose triacetate as the support, *o*-nitrophenyl pentyl ether as the plasticizer, and calix[4]-crown-6 1 and 2 as the ion carriers in dichloromethane as the organic solvent were prepared. A specified portion of this organic solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a plate glass with cellulose triacetate - dichloromethane glue. The dichloromethane was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water. Next, the membrane was soaked in water for 12 hours. Two samples of membrane were cut from the same membrane film for duplicate transport experiments. The membrane contained 2.6 cm³ ONPPE /1g CTA, and 0.1 M calix[4]-crown-6 based on plasticizer.



TRANSPORT STUDIES

Transport experiments were conducted in a permeation cell in which the membrane film (at surface area of 4.9 cm^2) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm^3 each) were mechanically stirred at 600 rpm. The receiving phase was 0.01-1.0 M HNO_3 . The PIM transport experiments were carried out at the temperature of $20 \pm 0.2 \text{ }^\circ\text{C}$. Small samples (0.1 cm^3 each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc, cadmium and lead concentrations by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant and controlled by pH meter (pH meter, CX-731 Elmetron, with combine pH electrode, ERH-126, Hydromet, Poland).

The kinetics of PIM transport can be described by a first-order reaction in metal ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (1)$$

where c is the metal ions concentration (M) in the source aqueous phase at some given time, c_i is the initial metal ions concentration in the source phase, k is the rate constant (s^{-1}), and t is the time of transport (s).

To calculate the k value, a plot of $\ln(c/c_i)$ versus time was prepared. The rate constant value for the duplicate transport experiment was averaged and standard deviation was calculated. The relationship of $\ln(c/c_i)$ vs. time was linear, which was confirmed by high values of determination coefficient (r^2), i.e., which were mostly from 0.9835 to 0.9982. The permeability coefficient (P) was calculated as follows:

$$P = -\frac{V}{A}k, \quad (2)$$

where V is volume of the aqueous source phase, and A is an effective area of membrane.

The initial flux (J_i) was determined as equal to:

$$J_i = P \cdot c_i. \quad (3)$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for $M1$ and $M2$ metal ions, respectively:

$$S = J_{i,M1} / J_{i,M2} \quad (4)$$

RESULTS AND DISCUSSION

Previously was found (Ulewicz et al., 2004) that competitive transport of zinc(II), cadmium(II) and copper(II) ions through PIM with diphosphaza-16-crown-6 derivatives as the ion carrier allows to remove metal ions from acidic chloride aqueous solutions. Now we applied the lipophilic calix[4]-crown-6 derivatives for zinc(II), cadmium(II), and lead(II) removal from nitrate aqueous solutions.

The transport kinetics of metal ions is presented in Fig.1. The recovery factors and selectivity of metal ions transport through PIM from aqueous source phase containing equimolar mixture of all metals is shown in Table 1. The selectivity order for both ion carriers is as follows: Pb(II) > Cd(II) > Zn(II). Pb^{2+}/Cd^{2+} , Pb^{2+}/Zn^{2+} and Cd^{2+}/Zn^{2+} selectivity coefficients for 1 and 2 were 2.8, 9.9, 3.5 and 3.1, 12.7, 4.1, respectively.

The initial fluxes factor of all investigated metals with calixarene 2 was higher than for 1. This suggests that metal ions transport is influenced by the group attached to the crown.

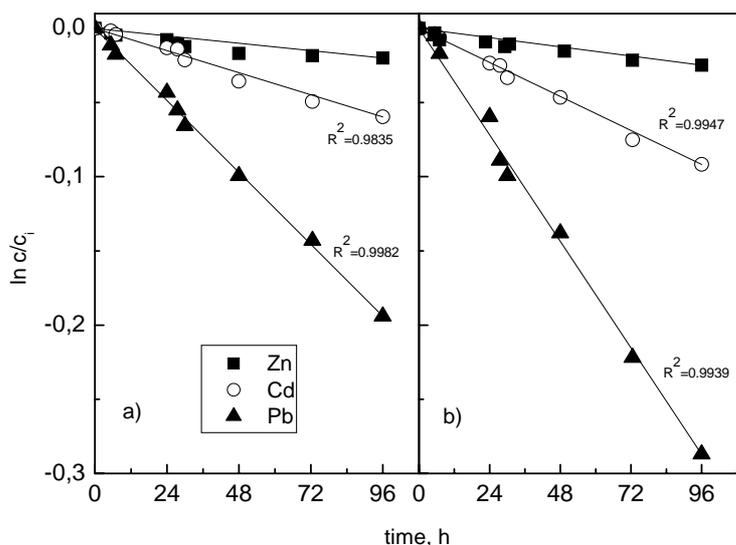


Fig. 1. Kinetics of Zn(II), Cd(II), and Pb(II) transport through PIMs containing 0.1 M calix[4]-crown-6 1 (a) and 2 (b). Source phase: $c_{Me} = 0.01$ M, pH = 6.0; receiving phase: 1.0 M HNO_3 ; membrane: 2.50 cm^3 ONPPE / 1.0 g CTA, 0.10 M calix[4]-crown-6 based on plastizer

The influence of nitric acid concentration in receiving phase on the initial fluxes of investigated ions is shown in Fig.2. As can be seen from this figure, the initial fluxes of all investigated metal cations increase with acidity of the feed phase increase. On the other hand, the selectivity coefficients of Pb(II)/Cd(II) and Pb(II)/Zn(II) for PIM decreases with HNO_3 concentration increase in receiving phase. For compound 1 the

selectivity coefficients of Pb(II)/Cd(II) were 6.8; 3.2; 2.8 for 0.01; 0.1 and 1.0 M HNO₃, respectively. The selectivity coefficients of Pb(II)/Zn(II) were 16.8; 9.9 for 0.01 and 1.0 M HNO₃, respectively.

Table 1. The values of initial fluxes, selectivity coefficients and selectivity orders for competitive transport of Zn(II), Cd(II), and Pb(II) through PIM.
Source phase: aqueous solution of Cd(II), Zn(II), Pb(II) at 0.01M concentration; Receiving phase: 1.0 M HNO₃; Membrane: 2.6 cm³ ONPPE / 1g CTA, 0.1 M calix[4]crown-6

Metal ions		Initial flux, J _i (μmol/m ² s)	Selectivity order and selectivity ratios
1	Zn(II)	0.0530	Pb(II) > Cd(II) > Zn(II) 2.8 9.9
	Cd(II)	0.1837	
	Pb(II)	0.5228	
2	Zn(II)	0.0730	Pb(II) > Cd(II) > Zn(II) 3.1 12.7
	Cd(II)	0.2982	
	Pb(II)	0.9257	

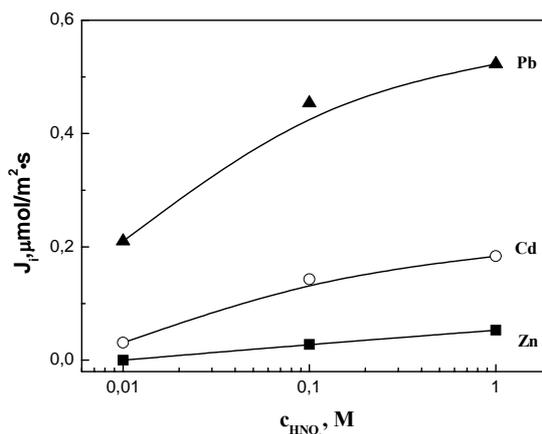


Fig. 2. Initial Zn(II), Cd(II) and Pb(II) transport fluxes through PIM vs. concentration of acid in receiving phase. Source aqueous phase: solution of Cd(II), Zn(II), Pb(II) at 0.01 M concentration, Membrane: 2.6 cm³ ONPPE / 1g CTA, 0.1 M calixarene 1.

In competitive transport of Zn(II), Cd (II) and Pb(II) through the PIM membrane with compounds **1** or **2** as ionophore the selectivity order was following: Pb(II) > Cd (II) > Zn(II). As might be expected the size of the cation plays a role. The larger Pb(II) ion is most suitable to match the loop of the calix-crown-6. Cadmium(II) and specially zinc(II) ions are too small ions to be bind by these ligands.

Transport of lead(II) with the use of unsubstituted ligand **1** is less efficient and less selective than with bis-methylated ligand **2**. The reason for such results might be explained in the following way: in unsubstituted ligand there is possibility of hydrogen bond formation between OH groups and ethereal oxygen atoms and it may affect the

shape of the loop. In compound **2** there is no possibility of hydrogen bond formation and both methoxy groups oxygen atoms can take part in complexation of lead(II) cation together with six oxygen atoms from the crown loop.

The initial fluxes of Pb(II), Cd(II) and Zn(II) from aqueous solutions using three times of the same membrane is shown in Fig 3. As it comes from this figure the initial fluxes of metal ions transport decreases with use of the same membrane two- or three times. After 2·96 hours the initial fluxes of metal ions drastically decreases.

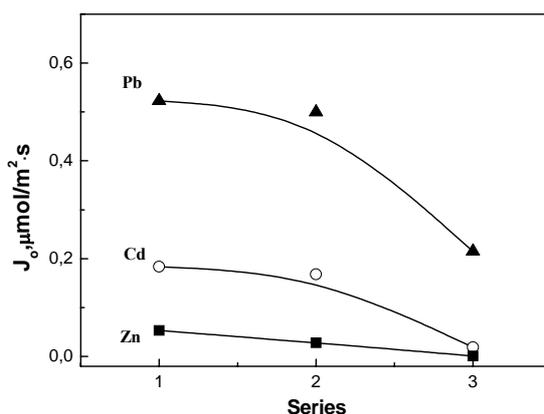


Fig. 3. Initial Zn(II), Cd(II) and Pb(II) transport fluxes through PIM after one-, twice, and three times membrane with **1**; Source phase: Cd(II), Zn(II), Pb(II) at concentration 0.01M; receiving phase: 0.1 M HNO₃

CONCLUSION

Lead(II) cations can be effectively removed from aqueous nitrate solutions in hydrometallurgical process of polymer inclusion membrane transport with derivatives of calix[4]crown-6 as ion carriers. The type of group (-OH, -OMe) attached to the calix[4]-crown-6 molecule has the influence on selectivity and efficiency of Zn(II), Cd(II), and Pb(II) transport through polymer inclusion membranes. The selectivity coefficient of Pb/Zn and Cd/Zn decreases with nitric acid concentration increase in receiving phase. Initial fluxes of investigated metal ions decrease when three times of membrane was used.

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Zbadano selektywność procesu wydzielania jonów cynku(II), kadmu(II) i ołowiu(II) z wodnych roztworów azotanowych zawierających równomolową mieszaninę tych trzech metali ($c_{Me} = 0,01$ M) w procesie transportu przez polimerowe membrany inkluzyjne (PIM) przy użyciu w roli przenośników jonów pochodnych kaliks[4]-korony-6. Membrany typu PIM syntezowano z trójoctanu celulozy (nośnik), eteru *o*-nitrofenylopentyłowego (pastyfikator) i pochodnych kaliks[4]-korony-6 (przenośnik jonów); stężenie przenośnika jonów w przeliczeniu na plastyfikator wynosiło 0,1 M. Współczynniki separacji Pb/Cd i Pb/Zn przez PIM przy użyciu kalixkorony **2** były nieznacznie wyższe niż przy użyciu kalixarenu **1**. Współczynniki separacji Pb(II)/Cd(II) i Pb(II)/Zn(II) wynosiły odpowiednio 2,8;9,9 i 3,1; 12,7 dla **1** i **2**, natomiast współczynniki separacji Cd(II)/Zn(II) wynosiły odpowiednio 3,5 i 4,1. Wykazano, że początkowe wartości strumienia transportu badanych jonów maleją ze wzrostem stężenia kwasu azotowego w fazie odbierającej. Maleją również wartości współczynników selektywności Pb(II)/Cd(II) i Pb(II)/Zn(II). Ponadto w pracy zaprezentowano wyniki wydzielania jonów badanych metali przy kilkakrotnym użyciu tej samej membrany. Badania pokazały, że wartości strumienia transportu badanych jonów metali przy dwukrotnym użyciu polimerowej membrany były porównywalne. Natomiast praca membrany przez 192 h i 288 h, powoduje zmniejszenie efektywności transportu jonów przez membranę.