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REMOVAL OF Zn(II), Cd(II) AND Pb(II) USING POLYMER INCLUSION MEMBRANE TRANSPORT WITH PROTON IONIZABLE DB-16-C-5 CROWN ETHERS

Received March 15, 2006; reviewed; accepted May 15, 2006

Competitive transport of Zn(II), Cd(II), and Pb(II) ions from aqueous nitrate source phase ($c_{Me} = 0.001$ M) through polymer inclusion membranes (PIMs) containing cellulose triacetate (as support), *o*-nitrophenyl pentyl ether (as plasticizer) and proton ionizable lariat ether derivatives (as ion carriers) has been investigated. The influence of varying the lipophilicity of *sym*(R)(hydroxy)dibenzo-16-crown-5 macrocycles with R groups such as hydrogen (in 1), decyl (in 2) and phenyl (in 3) on the selectivity and efficiency of Zn(II), Cd(II), and Pb(II) transport through polymer inclusion membranes is studied. The influence of HLB (hydrophile-lipophile balance) and V_x (molecular volumes) on the transport selectivity of metal ions was investigated. Relationship between the cation size and initial fluxes transport of metal cation was shown. The selectivity coefficients of Pb(II)/Zn(II) and Cd(II)/Zn(II) decrease with increase of carrier concentration in inclusion membrane.

Key words: polymer inclusion membrane, zinc(II), cadmium(II), lead(II), proton ionizable ethers

INTRODUCTION

Selective removal of metal ions from industrial and waste aqueous solutions is very important for the hydrometallurgical processing. Among the different methods used for removal and separations of the metal ions, such as solvent extraction, ion exchange, the transport across liquid membranes is very attractive. The transport through liquid membrane is used for selective separation and concentration of metal ions from source aqueous phase, in which the concentration of metal ionic species is above $1 \cdot 10^{-4}$ M. A variety of types of liquid membranes exists, i.e. bulk (BLMs),

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emulsion (ELMs), supported (SLMs) and polymer inclusion membranes (PIMs). A new 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).

Macrocyclic compounds such as crown ethers were successfully used for metal ions separation in solvent extraction, transport through liquid membranes and in ion exchange systems. During last years several neutral crown ethers and lariat ethers were successfully used for separation transport of heavy metal ions. In competitive transport of zinc(II) and cadmium(II) across emulsion liquid membrane with 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., (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 (1992) discovered quantitatively transport of zinc(II) and only 1 % of cadmium(II) across bulk liquid membrane with DA18C6 and palmitic acid.

The transport studies through cellulose triacetate membrane have been reported recently. Polymer inclusion membranes containing CTA and macrocyclic compounds such as dibenzo-18-crown-6, hexathia-18-crown-6, diaza-18-crown-6 and hexaaza-18-crown-6 were investigated by Gherrou et al., (2001, 2004, 2005). Comparison of carrier-facilitated transport of lead(II) across SLM and PIM has been reported by Aguilar et al., (2001). It was shown that ligands like 18-crown-6 provide high selectivity for lead(II) over cadmium(II) and zinc(II) ions. Competitive transport of trace radionuclide ions, i.e. Cs-137, Sr-90 and Co-60 from aqueous solutions through PIM's using dibenzo-21-crown-7 and dinonylnaphtalenesulfonic acid was studied by Kozłowski et al., (2000). Competitive alkali metal cation transport through PIM's containing alkyldibenzo-16-crown-5-oxyacetic acid carriers shown the excellent selectivity for sodium(I) transport with fluxes being strongly influenced by the length of the alkyl chain geminally attached to the functional side arm in the lariat ether molecule.

Hayashi et al., (2003) reported on the selective proton-driven transport of lead(II) ions across polymer inclusion membranes with proton diionizable polyethers bearing different alkyl chain lengths (from $-\text{C}_7\text{H}_{15}$ to $-\text{C}_{16}\text{H}_{33}$). The transport selectivity of PIM with polyether bearing $-\text{C}_8\text{H}_{17}$ alkyl chain was as follows $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. However 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 side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 as 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: $\text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)}$.

A few papers deal with the selective removal of metal ions with calix-crown ethers. Kim et al., (2001) studied calixcrown ethers for transport of alkali metal cations through PIM and SLM. The calix-crown-6 exhibited the best selectivity toward cesium cation over other alkali metal cations. The PIM's exhibited faster transport as well as higher durability than the SLM's. Also Levitskaia et al., (2002) studied competitive cesium(I) ions transport with calix[4]arene-crown-6 or calix[4]arene-biscrown-6 as ion carriers. Membrane containing calix-*monocrown* carriers exhibited less efficient but more selective cesium(I) transport than those with calyx-*biscrown* carriers. Ulewicz et al., (2005) also investigated competitive transport of Zn(II), Cd(II), and Pb(II) ions from aqueous nitrate source phase through polymer inclusion membranes with derivatives of calix[4]crown-6 as ion carriers. It was found, that type of groups (-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(II)/Zn(II) and Cd(II)/Zn(II) decreases with nitric acid concentration increase in receiving phase.

We now present the competitive transport of zinc(II), cadmium(II), and lead(II) ions from dilute aqueous solutions with lipophilic proton-ionizable lariat ethers. The selectivity of metal ions transport as a function of carrier concentration in membrane is studied. Also effects of structural modification of ionizable ethers derivatives upon the efficiency and selectivity of ions transport is now reported.

EXPERIMENTAL

REAGENTS

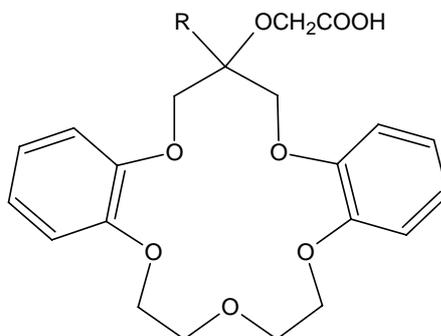
The inorganic chemicals, i.e. zinc(II), cadmium(II), lead(II) nitrates and hydrochloric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). The aqueous solutions were prepared with double distilled water, which conductivity was 0.1 $\mu\text{S}/\text{m}$. The organic reagents, 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/cm^3 . Derivatives of proton-ionizable crown ethers 1 ÷ 3 were synthesized by Bartsch et al., (2000) and Brown et al., (1991).

POLYMER INCLUSION MEMBRANE PREPARATION

A solution of cellulose triacetate as the support, *o*-nitrophenyl pentyl ether as the plasticizer, and proton-ionizable crown ether 1 or 2 as the ion carrier 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 0.3 ÷ 1.0 M lariat ether based on plasticizer. The average PIM membrane thickness was 35 μm.

Crown ether -R:
 $\frac{1}{2}$ -H
 $\frac{2}{2}$ -C₁₀H₂₁
 $\frac{3}{2}$ -C₆H₅



TRANSPORT STUDIES

Transport experiments were conducted in a permeation cell in which the membrane film (at surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm³ each), were mechanically stirred at 600 rpm. The receiving phase was 1.0 M HCl. The PIM transport experiments were carried out at the temperature of 20 ± 0.2 °C. Small samples of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc(II), cadmium(II) and lead(II) 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 was 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 0.980 to 0.998. 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

It was previously found (Ulewicz et al., 2005) that competitive transport of Zn(II), Cd(II) and Pb(II) ions through PIM with calix[4]crown-6 derivatives as the ion carriers allow for removal of metal ions from acidic nitrate aqueous solutions. Now we applied ionizable lariat ether derivatives for zinc(II), cadmium(II), and lead(II) removal from nitrate aqueous solutions.

Table 1. The values of initial fluxes, selectivity orders and selectivity coefficients for competitive transport of Zn(II), Cd(II), and Pb(II) across PIM with ether **2** in membrane. Source phase: aqueous solution of Cd(II), Zn(II), Pb(II) at 0.001M concentration, pH = 7.0. Receiving phase: 1.0 M HCl. Membrane: 2.6 cm³ ONPPE / 1g CTA

| Ether, M | Metal ions | Initial flux, J_i ($\mu\text{mol}/\text{m}^2\text{s}$) | Selectivity order and selectivity ratios |
|----------|------------|---|--|
| 0.3 | Zn(II) | 0.47 | Pb(II) > Cd(II) > Zn(II) 1.67 3.23 |
| | Cd(II) | 0.91 | |
| | Pb(II) | 1.52 | |
| 0.5 | Zn(II) | 0.68 | Pb(II) > Cd(II) > Zn(II) 1.53 3.09 |
| | Cd(II) | 1.37 | |
| | Pb(II) | 2.10 | |
| 1.0 | Zn(II) | 1.68 | Pb(II) > Cd(II) > Zn(II) 1.40 2.11 |
| | Cd(II) | 2.54 | |
| | Pb(II) | 3.55 | |

The transport kinetics of metal ions with **1** or **2** is presented in Fig. 1. As can be seen from this figure crown ether **1** is transported metal ions much slower than crown ether **2**. The initial fluxes and selectivity of metal ions transport through PIM with crown ether **2** from aqueous source phase containing equimolar mixture of all metals

is shown in Table 1. The selectivity order of metal ions fluxes transported with 2 is as follows: Pb(II) > Cd(II) > Zn(II). At pH equal 7.0 the percent molar contributions of uncomplexed cations (i.e. Zn²⁺, Cd²⁺ or Pb²⁺) of complex species for those metals with OH⁻ are over 99,5 % (Stability Constants of Metal-Ion Complexes, 1982).

As can be seen from this table, the initial fluxes of all investigated metal cations increase with concentration of crown ether 2 in membrane increase. On the other hand, the selectivity coefficients of Pb(II)/Cd(II) and Pb(II)/Zn(II) for PIM slightly decrease with crown ether 2 concentration increase in membrane.

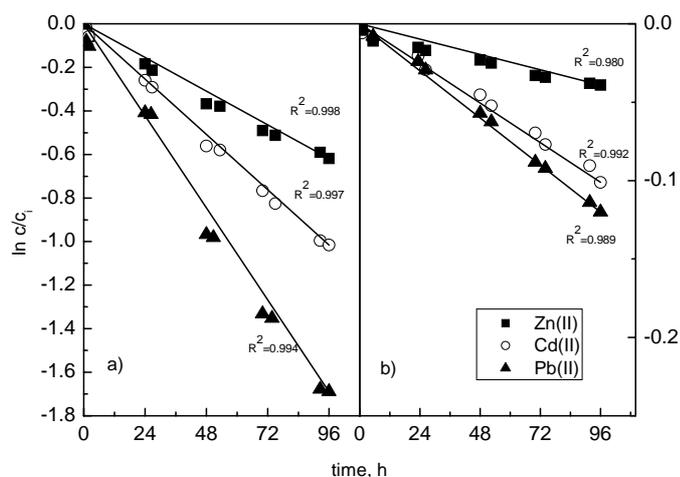


Fig. 1. Kinetics of Zn(II), Cd(II), and Pb(II) transport through PIMs containing 1.0 M ether 2 (a) and 0.5 M ether 1 (b). Source phase: $c_{Me} = 0.001$ M, pH = 7.0; receiving phase: 1.0 M HCl; membrane: 2.50 cm^3 ONPPE / 1.0 g CTA

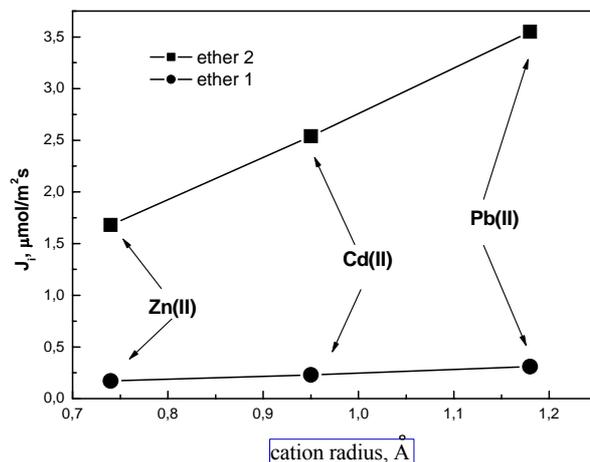


Fig. 2. Relationship of initial metal ions fluxes obtained from transport through PIM with ether 1 and 2 vs. metal cation radius. Experimental conditions as in Fig.1

Diameter of DB-16-crown-5 is estimated as $2.0 \div 2.4 \text{ \AA}$ (Vögtle and Weber, 1989). On the other hand, all metal cations studied processes diameters lower than crown ether cavity diameter (Matrel and Hancock, 1996). As can be seen from Fig. 2, the best transport cation is lead(II), which possess the highest diameter values.

The obtained results prove that the selectivity of zinc(II), cadmium(II) and lead(II) ions separation with the ionizable lariat ethers 1 \div 3 depends upon the nature of the substituents attached at the ring. The chemical behaviour of these lariat ethers with the same internal crown cavity size involving five oxygen atoms is affected by the external substituents (side arms). Therefore, the considered lariat ethers could be specifically characterized by means of their molar intrinsic volume, V_x (cm^3/mol), and hydrophile-lipophile balance (HLB), both calculated according to McGowan et al., (1990) and McGowan and Sowada (1993).

$$V_x = \sum n_i V_{x,i} - 6.56 \cdot B \quad (5)$$

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

$$B = N - 1 + R \quad (6)$$

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

The HLB value was calculated as:

$$HLB = 7 - 0.337 \cdot V_x + 1.5 \cdot n \quad (7)$$

where n denotes the total number of oxygen and nitrogen atoms in the molecule. Calculated values of V_x and HLB are show in Table 2.

Table 2. Value of V_x and HLB for lariat ethers studied

| Compounds | V_x , mol/cm^3 | HLB |
|-----------|----------------------------------|-----|
| <u>1</u> | 291.0 | 9.2 |
| <u>2</u> | 431.9 | 4.4 |
| <u>3</u> | 351.8 | 7.1 |

In Fig. 3 the relationship of hydrophile-lipophile balance (HLB) and molecular volumes (V_x) vs. the flux transport of metal ions is shown. As can be seen from this figure, the initial fluxes of all investigated metal cations increase with molecular volumes of lariat ether increase and decrease with hydrophile-lipophile balance value

increase. For compound 3, at the concentration of 0.5 M in membrane, the selectivity coefficients of Pb(II)/Cd(II) and Pb(II)/Zn(II) were 1.6 and 3.4, respectively. However, the selectivity coefficients of Pb(II)/Cd(II) and Pb(II)/Zn(II) for crown ether 1 at the concentration of 0.5 M were 1.4 and 1.8, respectively.

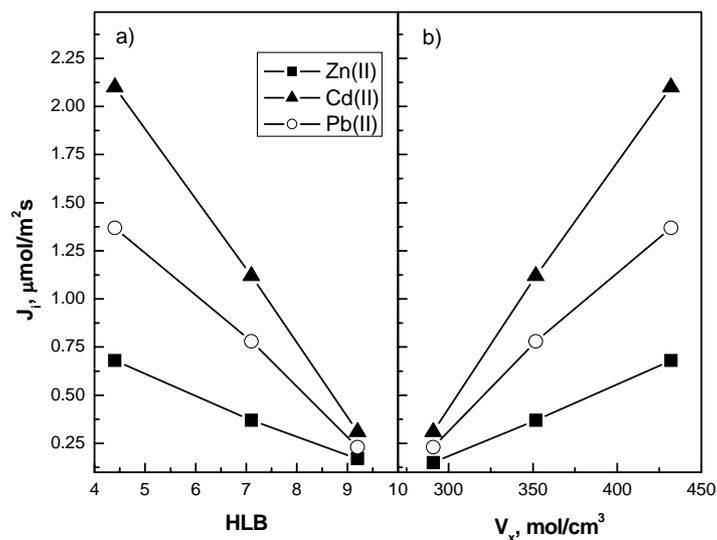


Fig. 3. Initial Zn(II), Cd(II) and Pb(II) transport fluxes through PIM vs. HLB and V_x . Source aqueous phase: solution of Cd(II), Zn(II), Pb(II) at 0.001 M concentration, pH = 7.0 Membrane: 2.6 cm³ ONPPE / 1g CTA, 0.5 M crown ethers 1, 2 and 3.

CONCLUSIONS

Lead(II), cadmium(II) and zinc(II) cations can be effectively removed from aqueous nitrate solutions in polymer inclusion membrane transport with derivatives of ionizable crown ethers as an carriers. The type of group attached (-H, -C₁₀H₂₁, and -C₆H₅) to the DB-16-crown-5 molecule has the influence on selectivity and efficiency of Zn(II), Cd(II), and Pb(II) transport through polymer inclusion membranes. The selectivity order of metal ions fluxes for crown ether 2 is as follows: Pb(II) > Cd(II) > Zn(II). The selectivity coefficients of Pb(II)/Cd(II) and Pb(II)/Zn(II) slightly decreases with lariat ether concentration increase in membrane. It was shown that the hydrophile-lipophile balance and molecular volumes of crown ethers influence on transport of metal ions. On the other hand, the relationship between the cavity diameter of ethers and initial fluxes was shown.

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Zbadano selektywność wydzielania jonów cynku(II), kadmu(II) i ołowiu(II) z wodnych roztworów azotanowych zawierających równomolową mieszaninę metali ($c_{Me} = 0,001$ M) w procesie transportu przez polimerowe membrany inkluzyjne (PIM) przy użyciu w roli przenośników jonów jonizowalnych eterów koronowych o koronie DB-16-C-5. Badane etery różniły się rodzajem grupy dołączanej do korony (-H, -C₁₀H₂₁, -C₆H₅). Polimerowe membrany inkluzyjne syntezowano z trójoctanu celulozy (nośnik), eteru *o*-nitrofenylopentylowego (pastyfikator) i jednego z eterów koronowych 1 ÷ 3 (przenośnik jonów); stężenie przenośnika jonów w przeliczeniu na plastyfikator zmieniano w granicach 0,3 - 1,0 M. Współczynniki separacji Pb(II)/Cd(II) i Pb(II)/Zn(II) przez PIM przy użyciu eteru 2 były nieznacznie wyższe niż przy użyciu eteru 3 i 1. Dla badanych eterów o stężeniu 0,5 M w membranie współczynniki separacji Pb(II)/Cd(II) i Pb(II)/Zn(II) wynosiły odpowiednio 1,4 i 1,8; 1,5 i 3,1 oraz 1,6 i 3,4 dla eterów 1, 2, i 3. Wykazano, że początkowe wartości strumienia transportu badanych jonów rosną ze wzrostem objętości molowej eteru koronowego, natomiast maleją ze wzrostem bilansu hydrofilowo-hydrofobowego (HLB) eteru koronowego. Ponadto stwierdzono, że niezależnie od zastosowanego eteru lariatowego o koronie DB-16-C-5 najlepiej transportowane są kationy o największej średnicy.