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SELECTIVE TRANSPORT OF Pb(II) ACROSS POLYMER INCLUSION MEMBRANE USING IMIDAZOLE AZOCROWN ETHERS AS CARRIERS

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Transport of Pb(II) ions from equimolar aqueous solutions of Zn(II), Cd(II), and Pb(II) as well as from solutions containing only Pb(II) ions source phase ($c_{Me} = 0.001$ M) through polymer inclusion membranes (PIMs) containing imidazole azocrown ethers as carriers has been investigated. The polymer membranes consisting of cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and imidazole crown ether derivatives (as ion carriers) were investigated. The influence of lipophilicity of macrocycles on the selectivity and efficiency of Pb(II) transport with azocrown **3** are higher than **1**, accordingly with the hydrophile-lipophile balance of imidazole azocrown ethers. The highest transport recovery for Pb(II) ions was observed for **3** (91.6%). The transport selectivity of the polymer inclusion membrane with **3** was: Pb(II) > Zn(II) > Cd(II) and the selectivity coefficient Pb(II)/Cd(II) and Pb(II)/Zn(II) equals 40.1 and 13.4, respectively. The stability of PIM with imidazole azocrown derivatives was confirmed by replicate experiments.

Keywords: polymer inclusion membrane, lead(II), zinc(II), cadmium(II), azocrown ethers

INTRODUCTION

The purifying of waste waters by removing transition/heavy metal ions is one of the major objectives of research in the hydrometallurgical processing. Liquid membranes (emulsion - ELMs or supported - SLMs), and recently, polymer inclusion membranes (PIMs) represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions such as Zn(II), Cd(II), and Pb(II) from aqueous solutions. The transport across liquid membrane is used for selective

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separation and concentration of metal ions from source aqueous phase, in which the concentration of metal ionic species is above $1\cdot10^{-4}$ M (Bond et al., 1999).

During last years several neutral crown ethers and lariat ethers were successfully used for metal ions separation in solvent extraction, in ion exchange systems and transport across liquid membranes. Unfortunately, only few papers refer to heavy metals (Nghiem et al., 2006). In competitive transport of Zn(II) and Cd(II) ions across emulsion liquid membrane with dicyclohexane-18-crown-6, near quantitative selectivity for Cd(II) over Zn(II) and Hg(II) was achieved (Izatt et al., 1987). Hayashi et al. (2003) reported the selective proton-driven transport of lead(II) ions across polymer inclusion membranes with proton diionizable polyethers bearing alkyl chains of different length (from -C_7H_{15} to -$C_{16}H_{33}$). The transport selectivity of PIM with polyether bearing -C_8H_{17} alkyl chain was $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$. Lead(II), cadmium(II) and zinc(II) cations can be effectively removed from aqueous nitrate solutions by polymer inclusion membrane transport with derivatives of ionizable dibenzo-16-crown-5 (DB-16C5) ethers as carriers. The type of group attached (-H, -$C_{10}H_{21}$, and -C_6H_5) to the DB-16C5 molecule has the influence on selectivity and efficiency of Zn(II), Cd(II), and Pb(II) transport through polymer inclusion membranes (Ulewicz at al., 2006).

Recently, the transport studies using the azacrown ethers have been reported. Cho et al. (1995) found that a single transport of Cd^{2+} across emulsion liquid membranes mediated by diaza-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 quantitative transport of zinc(II) and only 1 % of cadmium(II) across bulk liquid membrane with DA18C6 and palmitic acid. Polymer inclusion membranes containing CTA and macrocyclic compounds such as DA18C6, dibenzo-18-crown-6 (DB18C6), hexathia-18-crown-6 and hexaaza-18-crown-6 were investigated by Gherrou et al. (2001, 2004, 2005). Pyrrole azocrown ethers in ordinary bulk membrane system were also found to preferentially transport lead(II) from equimolar mixture of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} ions (Luboch et al., 2007). 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 diazadibenzo18-crown-6 had high selectivity for lead(II) over cadmium(II) and zinc(II) ions using a CTA/2-NPOE membrane of composition (w/w) 22 % CTA, 71,6 % 2-NPOE and 6,4 % carrier. On the other hand, Kim et al. (2001) observed selective transport of Ag(I) over Pb(II) and Cd(II) for a series of calix[4]azacrown ether derivatives immobilized in a CTA-based PIM plasticized with 2-NPOE and TBEP. Similarly, high transport selectivity for Ag(I) in the presence of Zn(II), Cd(II), Pb(II), Co(II), Ni(II) and Cu(II) ions was observed for transport across SLMs and PIMs using acyclic polyether ligands with diamide and diamine end-groups (Kim et al., 2001a).

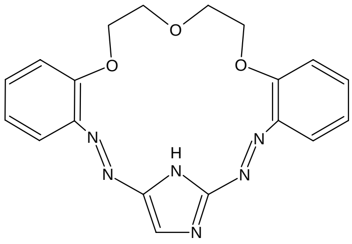
Ulewicz et al. (2004) investigated competitive transport of Zn(II), Cd(II), and Cu(II) ions from aqueous chloride source phase across polymer inclusion membranes containing side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 as ion carrier. It was found, that the initial fluxes of all investigated cations increase with increase of the feed phase acidity and the selectivity order was Cd(II) > Zn(II) > Cu(II).

The present article deals with a competitive transport of lead(II) ions from a dilute aqueous solutions using PIM doped with imidazole azocrowns. The effects of structural modification of imidazole azocrown ether derivatives upon the efficiency and selectivity Pb(II) ions transport is reported. Also, the stability of PIMs with imidazole azocrown derivatives was confirmed by replication of experiments using the same membranes.

EXPERIMENTAL

REAGENTS

The inorganic chemicals, i.e. lead(II), zinc(II) and cadmium(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 µS/m. The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (*o*-NPPE) 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. Azocrown ethers **1** ÷ **3** (Fig.1) were synthesized as described by Wagner-Wysiecka et al (Wagner-Wysiecka et al., 2003; Luboch et al., 2007).



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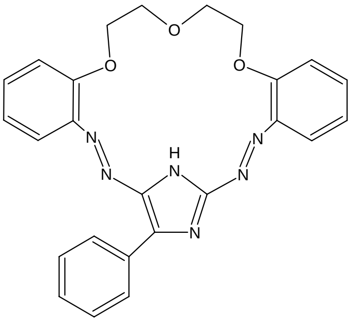

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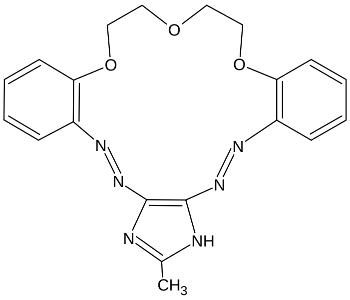

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Fig. 1. Formulas of imidazole azocrown ethers

POLYMER INCLUSION MEMBRANE PREPARATION

A dichloromethane solution of cellulose triacetate, plasticizer (for example *o*-NPPE), and azocrown (**1** ÷ **3**) as the ion carrier was prepared. A specified portion of this solution was poured into a membrane mold comprised of a 9.0 cm diameter glass ring placed on a glass plate with cellulose triacetate - dichloromethane glue. After evaporation of the solvent overnight the resulting membrane was peeled off from the glass plate by immersion in cold water. Then the membrane was soaked for 12 hours in water. Two membrane samples were cut out from the same preparation for duplicate transport experiments. The membrane contained 2.6 cm^3 *o*-NPPE /1g CTA, and 0.05 M azocrown based on plasticizer. The average PIM thickness was 30-35μm.

TRANSPORT STUDIES

Transport experiments were performed in a permeation cell in which the membrane film (surface area 4.9 cm^2) was tightly clamped between two cell compartments. Both, source and receiving aqueous phases (50 cm^3 each) were mechanically stirred at 600 rpm. 1.0 M HCl was used as a receiving phase. The PIM transport experiments were carried out at 20 ± 0.2°C. Small samples of the aqueous receiving phase were taken periodically *via* a sampling port equipped with a syringe and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam) to determine lead(II), zinc(II), and cadmium(II) concentration. The source phase pH (equal 5.0) was kept constant and controlled by pH meter (CX-731 Elmetron, with combined pH electrode, ERH-126, Hydromet, Poland).

The transport across PIMs fits the first-order kinetics in relation to the metal-ion concentration (Danesi, 1984-85), which can be described by Equation 1:

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

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 permeability coefficient (P) was calculated as follows:

$$P = -\frac{V}{A}k, \qquad [\mathrm{m/s}] \tag{2}$$

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:

$$J_i = P \cdot c_i \qquad [\text{mol/m}^2\cdot\text{s}] \tag{3}$$

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

$$S = J_{i,M1} / J_{i,M2} \tag{4}$$

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

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \qquad [\%] \tag{5}.$$

RESULTS AND DISCUSSION

In the first series of experiments, the transport of lead(II) from nitrate aqueous solutions containing metal ions at 0.001 M concentration through PIM with imidazole azocrown and *o*-NPPE as plasticizer into 1.0 M hydrochloric acid aqueous solutions was investigated. For blank experiment no transport was detected for more than 48 h of continuous running. The relationship between ln(c/c_i) and time for Pb(II) transport across PIM containing **1** or **3** azocrown is shown in Fig. 2. The kinetics parameters are summarized in Table 1. As shown in Fig. 2, the transport of Pb(II) ions across PIM with azocrowns can be described by first order kinetics in metal ion concentration changes. It is in accordance to the mathematical model proposed by Danesi (1984-85).

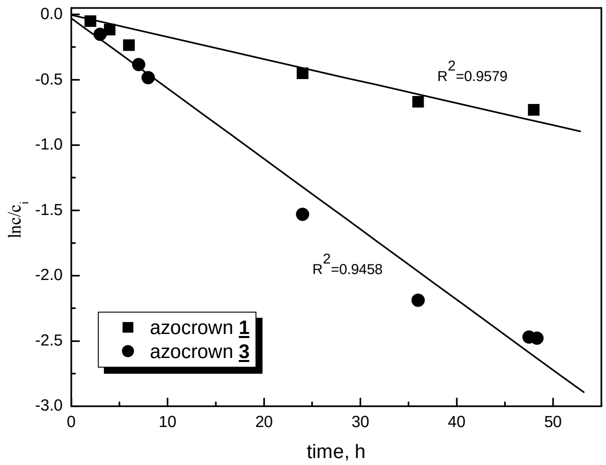

Fig. 2. Kinetics of Pb(II) ions transport across PIMs containing 0.05 M of azocrown ethers **1** or **3** from aqueous solutions. Source phase: $c_{Pb(II)}$ = 0.001 M; pH = 5.0; receiving phase: 1.0 M HCl; membrane: 2.60 cm^3 *o*-NPPE /1 g CTA, 0.05 M of azocrown (based on plasticizer volume)

Table 1. Kinetics parameters, selectivity order and selectivity coefficients for competitive transport of metal ions across PIM with carriers **1** or **3**. Conditions as in Fig. 2

Azocrown	Metal ions	Permeability coefficient, J_i (μm/s)	Initial flux, J_i (μmol/m^{2}s)	RF, %
1	Pb(II)	46.30	0.397	51.8
3	Pb(II)	160.6	1.375	91.6

As can be seen from this table, higher value of permeability coefficient and initial fluxes for Pb(II) ions were obtained for compound **3**. Previously it was found (Ulewicz et al., 2007) that the initial fluxes of transported metal ions under competitive conditions depend on the hydrophile-lipophile balance (HLB) of azocrown ethers. At present, the similar dependence was obtained for solutions containing only Pb(II) ions. The initial fluxes of Pb(II) from aqueous solutions decrease with increase of hydrophile-lipophile balance value (HLB) for azocrown, i.e. **3** > **1**; HLB for these azocrowns are 10.9 and 11.4, respectively. In addition, the highest values of recovery factor of Pb(II) ions after 48 hours were obtained for compound **3**.

The transport of lead(II) from equimolar nitrate mixture of three metal ions, each at 0.001 M concentration through PIM with imidazole azocrown **3** was also investigated. The kinetics parameters and selectivity order are summarized in Table 2; the recovery factors of all investigated ions are shown in Fig. 3.

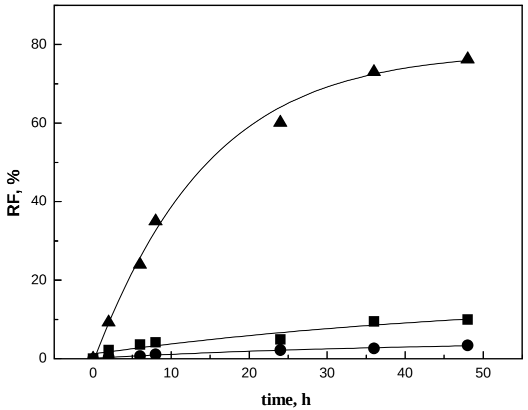

Fig. 3. Recovery of Zn(II), Cd(II), and Pb(II) ions from source phase from aqueous solutions in transport across PIM with azocrown ethers **3**. Source phase: $c_{Me(II)}$ = 0.001 M each; pH = 5.0; receiving phase: 1.0 M HCl; membrane: 2.60 cm^3 *o*-NPPE /1 g CTA, 0.05 M of azocrown (based on plasticizer volume)

As seen from this figure, the recovery factors of all investigated ions increase with time. The highest recovery factors 76.24 % (after 48 h) were obtained for Pb(II) ions, whereas for Zn(II) and Cd(II) the factors were 10.0 and 3.4 %, respectively. The transport selectivity of the polymer inclusion membranes with **3** were: Pb(II) > Zn(II) > Cd(II).

Table 2. Kinetics parameters, selectivity order and selectivity coefficients for competitive transport of metal ions across PIM with carriers **3**. Conditions as in Fig. 3

Metal ions	Permeability coefficient, J_i (µm/s)	Initial flux, J_i (µmol/m^{2}s)	Selectivity order and selectivity ratios
Zn(II)	6.02	0.060	Pb(II) > Zn(II) > Cd(II) 13.4 40.1
Cd(II)	2.08	0.020	
Pb(II)	93.40	0.801	

In order to examine the influence of the metal ions concentration in the source phase, the transport of metal ions from equimolar mixture of three ions was performed. The relationship between ln*(c/c$_i$)* and time for Pb(II), Cd(II) and Zn(II) transport across PIM is shown in Fig. 4, whereas the found kinetic parameters are summarized in Table 3. It is evident that metal ions are transported across PIMs with higher rate from solutions of lower concentration but initial fluxes are higher for solutions of higher metal concentration. For 0.01M concentration the selectivity coefficients Pb(II)/Zn(II) and Pb(II)/Cd(II) equal 11.3 and 53.6, respectively. For 0.001 M solutions the same parameters are 16.3 and 46.0, respectively. For both concentrations, the transport selectivity across the polymer inclusion membranes with **2** are: Pb(II) > Zn(II) > Cd(II) (Figure 4).

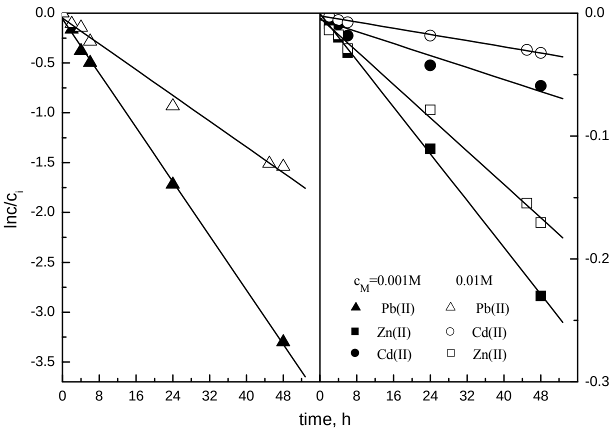

Fig. 4. Relationship of lnc/c$_i$ vs. time for Pb(II), Cd(II) and Zn(II) transport across PIMs with **2** from source phase of different metal ions concentration; receiving phase: 1.0 M HCl; membrane: 2.60 cm^3 *o*-NPPE /1 g CTA, 0.05 M of azocrown (based on plasticizer volume)

Recently, many papers deal with the membrane stability and lifetime. These factors determine the usefulness of membrane on large industrial scale. Kim et al. (2000, 2001) investigated the stability of SLMs and PIMs under similar experimental conditions. They reported small flux decline after 15 days of continuous transport across PIMs containing CTA/2-NPOE and acyclic polyether carriers, and after 20 days using calix[4]arene derivatives as carrier. Ulewicz et al. (2005) also shown flux stability of Pb(II), Zn(II), and Cd(II) ions across PIMs with calix[4]-crown-6 derivative for 12 days. The higher stability of PIMs over SLMs was reported for membranes with Aliquat 336 as a carrier (Scindia et al., 2006).

Table 3**.** Kinetics parameters for competitive transport of metal ions across PIM with carrier **2**. Conditions as in Fig. 4

Metal concentration	Metal ions	Rate constants, k (h^{-1})	Initial flux, J_i ($\mu mol/m^2s$)
0.001 M	Zn(II)	0.0048	0.1376
	Cd(II)	0.0012	0.0486
	Pb(II)	0.0681	2.2380
0.01 M	Zn(II)	0.0033	0.9400
	Cd(II)	0.0005	0.1986
	Pb(II)	0.0324	10.650

Stable performance of PIMs for 30 days was evidenced, while SLMs membrane worked well only for 7 days. Alguacil et al. (2005) showed that the percent extraction of Zn(II) in experiments with SLM with re-impregnated membrane decreased from 93.2 to 56.2 % after 12 h work (4 runs for 3 h). It demonstrates that the process with use of PIM type membranes show higher stability than with the use of SLM, although in both casus leaching of the carrier is observed.

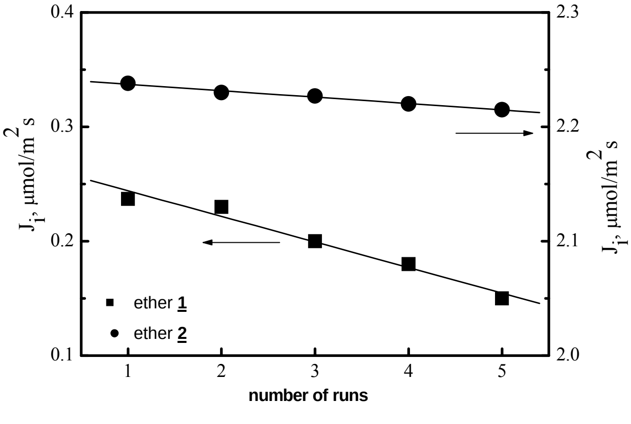

Fig. 5. Initial flux *vs.* number of run in repeated transport of Pb(II) ions across PIM with carriers **1** or **2**; source phase: [Pb(II)]=[Cd(II)]=[Zn(II)] =0.001M each, receiving phase: 1.0 M HCl; membrane: 2.60 cm^3 *o*-NPPE /1 g CTA, 0.05 M of azocrown (based on plasticizer volume)

To examine the long-term stability of the PIMs with imidazole azocrown ethers, we reused the same membranes with azocrown **1** or **2** as ion carriers in successive metal ions transport experiments (48 h duration) from aqueous solutions at the same concentration. Fig. 5 shows that the initial flux of Pb(II) ions decrease with the number of runs of repeated transport across PIM. For azocrown **1** we observed that the initial flux decrease more than using azocrown **2**. The carrier leaching from membrane is associated with their hydrophilicity and water solubility. As can be seen from Fig. 6, the azocrown **1** is slightly soluble in water. Therefore, leaking of the ionophore **1** from the membrane is not the only reason of the initial fluxes decrease. It is considered, that it stays in connection with complex formation rate in the source phase (Wagner-Wysiecka et al., 2007, cf. Luboch et al., 2006).

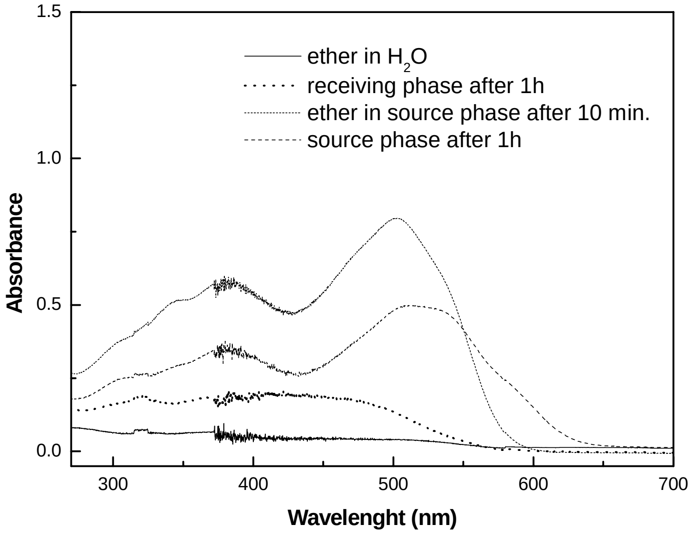

Fig.6. Changes of absorbance for ether **1** in source and receiving phase

CONCLUSIONS

Lead(II) ions can be effectively removed from aqueous nitrate solutions using polymer inclusion membrane transport with derivatives of imidazole azocrown ethers as carriers. The initial fluxes of Pb(II) ions decrease with the increase of azocrown ethers hydrophile-lipophile balance, i.e. **3** > **1**. The selectivity order of metal ions fluxes for azocrown ether **3** is as follows: Pb(II) > Zn(II) > Cd(II), whereas the selectivity coefficients Pb(II)/Cd(II) and Pb(II)/Zn(II) equal 40.1 and 13.4, respectively. The selectivity coefficients of Pb(II)/Cd(II) decrease with increase of metal ions concentration in the source phase. The type of group attached to the imidazole azocrown molecule has the influence on long-term stability of the PIMs.

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Zbadano selektywność transportu jonów ołowiu(II) z równomolowych roztworów jonów Zn(II), Cd(II) i Pb(II) oraz z roztworów zawierających jony Pb(II) przez polimerowe membrany inkluzyjne (PIM) zawierające imidazolowe etery azokoronowe. Badania prowadzono dla azotanowych roztworów Pb(II) o stężeniu 0,001 M oraz dla roztworów zawierających równomolową mieszaninę jonów Pb(II), Cd(II) i Zn(II) (c_{Me}= 0,001 M każdego). Badane azokorony różniły się miejscem podstawienia imidazolu i rodzajem dołączonej do niego grupy (-H, $-CH_3$, $-C_6H_5$). Polimerowe membrany inkluzyjne otrzymywano z trójoctanu celulozy (nośnik), eteru *o*-nitrofenylopentylowego (pastyfikator) i jednego z eterów koronowych **1** ÷ **3** (przenośnik jonów); stężenie przenośnika jonów w przeliczeniu na objętość plastyfikatora wynosiło 0,05 M. Wykazano, że początkowe wartości strumienia transportu jonów ołowiu(II) maleją ze wzrostem balansu hydrofilowo-hydrofobowego (HLB) eteru koronowego, tj. **3** > **1**. Ponadto stwierdzono, że strumienie początkowe transportu jonów przy użyciu eterów **2** i **3** maleją w szeregu: Pb(II) > Zn(II) > Cd(II). Współczynniki separacji Pb(II)/Cd(II) i Pb(II)/Zn(II) przez PIM przy użyciu eteru **2** z 0,01M roztworu mieszaniny jonów wynosiły 11,3 i 53,6 natomiast z roztworów o stężeniu 0,001 M odpowiednio 16,3 i 46,0. Ponadto wykazano, że polimerowe membrany inkluzyjne z imidazolowymi azokoronami wykazują dużą stabilność, zależną w dużym stopniu od rodzaju jonoforu.