

Małgorzata ULEWICZ*, Cezary Kozłowski**, Władysław WALKOWIAK***

REMOVAL OF Zn(II), Cd(II) AND Cu(II) IONS BY POLYMER INCLUSION MEMBRANE WITH SIDE-ARMED DIPHOSHAZA-16-CROWN-6 ETHERS

Received March 15, 2004; reviewed; accepted May 27, 2004

Competitive transport of Zn(II), Cd(II), and Cu(II) ions from aqueous chloride source phase ($c_{Me} = 0.01$ M) through polymer inclusion membranes (PIMs) containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and side-armed lariat ether-type derivative of diphosphaza-16-crown-6 (ion carrier) has been investigated. The influence of the group attached type to the PNP-lariat ether molecule on the selectivity and efficiency of Zn(II), Cd(II), and Cu(II) transport through polymer inclusion membranes is studied. The removal of metal ions by transport through PIM's from acid aqueous phase into 0.1 M CH_3COONH_4 , NH_4OH or EDTA aqueous solution (receiving phase) is presented. The selectivity coefficient of Cd/Zn and Cd/Cu decreases with Cl^- concentration increase in source phase for transport with bis-lariat ether, whereas for mono-lariat ether the selectivity coefficients are not changed.

Key words: polymer inclusion membrane, zinc(II), cadmium(II), copper(II), PNP-crown ethers

INTRODUCTION

Recently a remarkable increase in the applications of liquid membranes for separation processes was found. The use of 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 type of membrane system, called polymer inclusion membrane (PIM), has been developed which provides metal

*Department of Chemistry, Czestochowa University of Technology, 42-200 Czestochowa, Armii Krajowej 19 Street, e-mail: ulewicz@mim.pcz.czest.pl.

**Institute of Chemistry and Environment Protection, Pedagogical University of Czestochowa, 42-200 Czestochowa, Armii Krajowej 13.

***Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27.

ion transport with high selectivity, as well as easy setup and operation (Bond et al., 1999).

Crown ethers as ion carriers were successfully used for metal ions separation in solvent extraction, transport through liquid membranes and ion exchange systems. A few papers deal with the selective removal of Zn(II) and Cd(II) ions with neutral crown ethers. Katsuta et al. (Katsuta et al., 2000) has studied the extraction of Zn^{2+} and Cd^{2+} cations with benzo-18-crown-6 (B18C6) into benzene organic phase in the presence of picric acid. Compared with Cd^{2+} , B18C6 extracts Zn^{2+} more effectively although the size of Zn^{2+} cation is less suited for the cavity of crown ether. Billah and Hohjo (Billah and Hohjo, 1997) extracted the mixture of cadmium(II) and zinc(II) from aqueous solutions as their thenyltrifluoroacetone (TTA) complexes with dibenzo-18-crown-6 (DB18C6) into *o*-dichlorobenzene. At pH 4.9 only Zn(II) was extracted quantitatively, whereas Cd(II) remained in the aqueous solution.

A reverse selectivity in Zn^{2+} and Cd^{2+} separation was obtained in transport across liquid membranes containing 18-membered crown ethers. 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 HgA_2^{2-} , where A = SCN^- , I^- , Br^- or Cl^- (Izatt et al., 1986). Cho et al. (Cho et al., 1988, 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 by DA18C6 and hexadecanoic.

We now present results for competitive transport of zinc(II), cadmium(II), and copper(II) ions from dilute aqueous solutions by side-armed PNP 16-crown-6 derivatives. PNP-lariat ether were used for separation of zinc(II) and cadmium(II) ions by ion flotation (Ulewicz et al., 2003). We have shown that the selectivity of cadmium(II) and zinc(II) separation with use of the PNP-lariat ethers depends upon pH of aqueous solution and the nature of the substituents at the N_3P_3 ring, playing part of the side arms. Present work deals with the separation of zinc(II), cadmium(II) and copper(II) metal ionic species ($c_{Me} = 0.01M$) from chloric aqueous solutions containing equimolar mixture of these metals by polymer inclusion membranes. Effects of structural modification of crown ethers upon the efficiency and selectivity of ions transport is now reported.

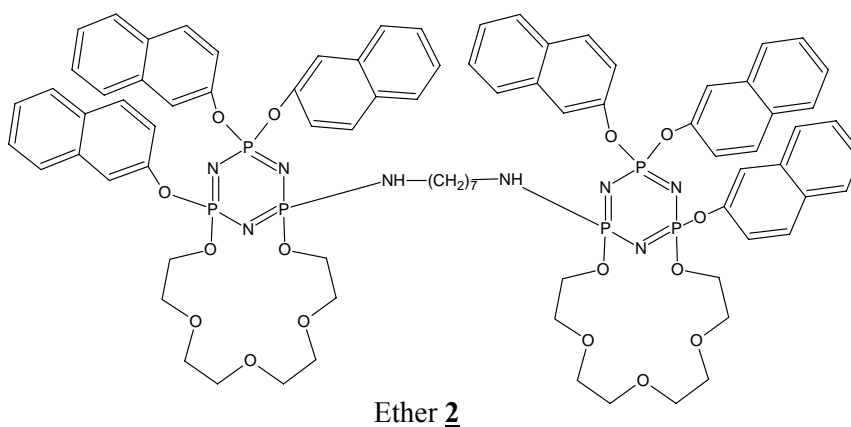
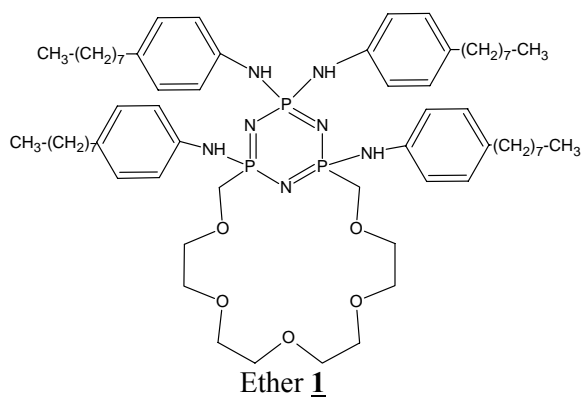
EXPERIMENTAL

POLYMER INCLUSION MEMBRANE PREPARATION

A solution of cellulose triacetate as the support, *o*-nitrophenyl pentyl ether as the plasticizer, and crown ethers **1** and **2** as the ion carriers in dichloromethane as the organic solution was 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 0.1 M aqueous solution of hydrochloric acid for 12 hours. Two samples of membrane were cut from the same membrane for duplicate transport experiments. The membrane contained 2.6 cm³ ONPPE / 1g CTA, and 0.1M crown ether based on plasticizer.

The inorganic chemicals, i.e. zinc(II), cadmium(II), copper(II) chlorides and hydrochloric 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 distillation water, which conductivity was 0.1 μS/m. Crown ethers **1** and **2** were synthesized in Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze (Poland).



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 0.1 - 0.5 M aqueous solution of ammonium acetate, EDTA or ammonium hydroxide. The PIM transport experiments were carried out at the temperature of 20 ± 0.2 °C. Small samples (0.1 cm³ each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc and cadmium concentrations by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase acidity was controlled by pH meter (pH meter, CX-731 Elmetron, with combine pH electrode, ERH-136, Hydromet, Poland) and pH was kept constant by adding periodically small amounts of 1.0 M HCl aqueous solution.

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., from 0.9974 to 0.9912.

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

$$J_i = -\frac{V}{A}k \cdot c_i \quad (2)$$

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

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

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \quad (3)$$

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 it was found that competitive transport of zinc(II) and cadmium(II) ions through PIM with tri-*n*-octyl amine (TOA) as the anionic carrier (Kozłowski et al., 2000), allows to remove both metals from acidic chloride aqueous solutions. Now we applied lariat ethers with cyclophosphazene subunits for zinc(II), cadmium(II), and copper(II) removal from chloride aqueous solutions. The mono- and bis-lariat ethers (**1**, **2**) were synthesized for the purpose of this study with diphosphaza-16-crown-6 rings and different sets of substituents.

The kinetic parameters and selectivity orders of metal ions transport through PIM from aqueous source phase containing equimolar mixture of all metal ions are shown in Table 1. The initial fluxes of all investigated cations increase with acidity of the feed phase increase. The selectivity order was as follows: Cd(II) \geq Zn(II) $>$ Cu(II). The selectivity coefficients of Cd/Cu and Zn/Cu for PIM decreases with HCl concentration increase in source phase. The highest values of $S_{Cd(II)/Cu(II)}$ and $S_{Zn(II)/Cu(II)}$ was observed for lariat ethers **2** – the selectivity coefficients of Cd(II)/Cu(II) were 8.7, 6.6 and 5.4 for 0.1, 0.3 and 0.5M HCl, respectively.

Table 1. The values of initial fluxes, selectivity coefficients and selectivity orders for competitive transport of Zn(II), Cd(II), and Cu(II) through PIM

Source phase: solution of Cd(II), Zn(II), Cu(II) at concentration 0.01M in 0.1÷0.5 M HCl;

Receiving phase: 0.1 M CH₃COONH₄; Membrane: 2.6 cm³ ONPPE / 1g CTA, 0.1 M crown ether

Crown ether	[HCl], M	Cation	Initial flux, (μmol/m ² s)	Selectivity orders and selectivity coefficient of Cd to other metals
1	0.1	Cd(II)	3.52	Cd \geq Zn , Cu 1.8
		Zn(II)	1.97	
		Cu(II)	1.92	
	0.3	Cd(II)	5.75	Cd \geq Zn \geq Cu 1.1 1.9
		Zn(II)	5.25	
		Cu(II)	3.04	
	0.5	Cd(II)	48.1	Cd \geq Zn \geq Cu 1.8 1.9
		Zn(II)	26.9	
		Cu(II)	24.3	
2	0.1	Cd(II)	17.4	Cd \geq Zn $>$ Cu 1.2 8.7
		Zn(II)	14.1	
		Cu(II)	2.01	
	0.3	Cd(II)	39.5	Cd \geq Zn $>$ Cu 1.0 6.6
		Zn(II)	38.1	
		Cu(II)	6.02	
	0.5	Cd(II)	76.7	Cd \geq Zn $>$ Cu 5.4
		Zn(II)	73.8	
		Cu(II)	14.3	

The results of metal ions removal, i.e. zinc(II), cadmium(II), and copper(II) from aqueous solutions containing equimolar mixture of metals ($c_{Me} = 0.01M$) with lariat ethers **1** and **2**, are shown in Fig.1. As it comes from Fig.1a using mono lariat ether **1** all metal ions are removed from aqueous solutions in the comparable percent. Removal of metal ions increased with the increase of acidic solutions. Using bis-lariat ether **2** Cd(II) and Zn(II) ions are removed better than Cu(II) from 0.1 and 0.3M HCl solutions, but from 0.5M HCl solutions cadmium, zinc and copper ions are removed comparable. In the presence of chlorides at concentration $> 0.3 M$ all metals studied are in the form of chloride complex anions (Stability constants, 1982), which are attached to donor nitrogen atoms of ether **2**. As the effect of ion pairs formation zinc(II), cadmium(II) and copper(II) are transported across polymer inclusion membranes with **2** (Fig.1b). The recovery factor of all investigated metals with ether **2** was higher than for ether **1**. This suggests that formed ion pair between metal ion and ligand is determined by number of nitrogen atoms in the ring and sidearm of ligand (Bartsch et al., 2002).

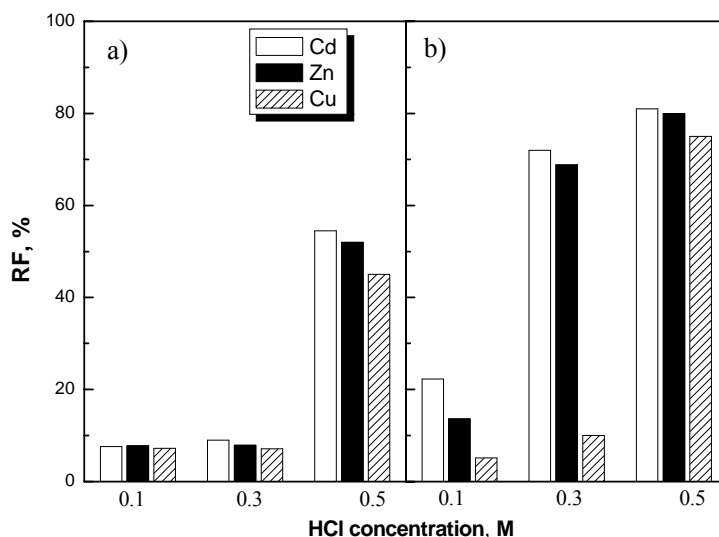


Fig. 1. Recovery factor (%) after 8 hours of transport for Zn(II), Cd(II), and Cu(II) ions from chloride aqueous solutions through polymer inclusion membrane with **1** (a) and **2** (b).

Source phase: solution of Cd(II), Zn(II), Cu(II) at concentration 0.01M in 0.1-0.5 M HCl; Receiving phase: 0.1 M CH_3COONH_4 ; Membrane: 2.6 cm³ ONPPE / 1g CTA, 0.1 M crown ether

Type of receiving aqueous phase also influences on the process transport of metal ions through PIM's. The maximal percent metal removal from chloride aqueous solutions into different receiving phases is shown in Fig.2. As it comes from this figure removal of metal ions increased in the sequence: $CH_3COONH_4 > EDTA > NH_4OH$.

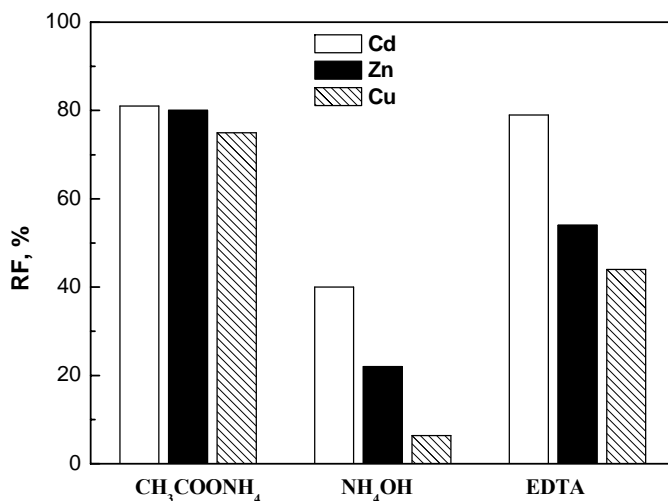


Fig. 2. Recovery factor (%) after 8 hours of transport through PIM with **2** of Zn(II), Cd(II), and Cu(II) ions from chloride aqueous solutions; Source phase: Cd(II), Zn(II), Cu(II) at concentration 0.01M in 0.5 M HCl; receiving phase: 0.1 M solution of CH₃COONH₄, NH₄OH or EDTA

CONCLUSION

Zinc(II), cadmium(II), and copper(II) ions can be effectively removed from aqueous chloride solutions in hydrometallurgical processes of polymer inclusion membranes. Competitive transport of zinc(II), cadmium(II) and copper(II) ($c_{Me} = 0.01$ M) from an aqueous chloride source phase through polymer inclusion membranes containing derivatives of PNP-crown ethers as ion carriers into aqueous ammonium acetate solutions allows removal of zinc(II), cadmium(II) and copper(II). The selectivity coefficients of Cd/Cu and Zn/Cu for PIM decreases with HCl concentration increase in source phase.

ACKNOWLEDGMENT

The authors would like to thank the Polish Science Foundation for financial support of this research (grant 4 T09B 107 22). We would also like to thank dr Iwona Porwolik-Czomperlik from Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze for synthesis of PNP-crown ethers.

REFERENCES

- BARTSCH R. A., WAY J., Eds. (1996), *Chemical Separation with Liquid Membranes*, ACS Symposium Series 642, Amer. Chem. Soc., Washington, DC
 BOND H., DIETZ M. L., ROGERS R.D., Eds. (1999), *ASC Symposium Series 716*, Washington, DC.
 KATSUTA S., TSUCHIYA F., TAKEDA Y. (2000), *Equilibrium studies on complexation in water and solvent extraction of zinc(II) and cadmium(II) with benzo-18-crown-6*, *Talanta*, 51, 637 - 644.

- BILLAH M., HONJO T. (1997), *Separation and determination of cadmium and zinc as their thenoyltrifluoroacetone complexes with dibenzo-18-crown-6 by means of synergistic extraction and atomic absorption spectrometry*, J. Fresenius, Anal. Chem., 357, 61 - 64.
- IZATT R. M., BONALD R. L., GENG W., CHO M. H., CHRISTENSEN J. J. (1987), *Separation of bivalent cadmium, mercury and zinc in a natural macrocyclic-mediated emulsion liquid membrane*, Anal. Chem., 59, 2405 - 2409.
- IZATT R. M., LINDCH G. C., BRUENING R. L., BRADSHAW J. S., LAMM J. D., CHRISTENSEN J. J. (1986), *Design of cation selectivity into liquid membrane systems using macrocyclic carriers*, Pure Appl. Chem., 58, 1453 - 1460.
- CHO M. H., SEON-WOO K. H., HEO M. Y., LEE I. C., YOON C. J., KIM S. J. (1988), *Studies on the macrocycles mediated transport in bulk liquid membrane system of transport metal ions*, Bull. Korean Chem. Soc., 9, 292 - 295.
- CHO M. H., CHUN H. S., KIM J. H., RHEE Ch. H., KIM S. J. (1991), *Study on separation of heavy metal ions in a natural macrocycle-mediated emulsion liquid membrane system*, Bull. Korean Chem. Soc., 12, 474 - 477.
- CHO M. H., SHIN S. Ch. (1995), *Studies on the macrocycle-mediated transport of divalent metals ions in a supported liquid membrane system*, Bull. Korean Chem. Soc., 16, 33 - 36.
- DADFARNIA S., SHAMSIPUR M. (1992), *Highly selective membrane transport of zinc(2+) ion by a cooperative carrier composed of 1,10-diaza-18-crown-6 and palmitic acid*, Bull. Chem. Soc. Jpn., 65, 2779 - 2783.
- ULEWICZ M., WALKOWIAK W., BRANDT K., PORWOLIK-CZOMBERLIK I. (2003), *Ion flotation of zinc(II) and cadmium(II) in the presence of side-armed diphosphaza-16-crown-6-ethers*, Sep. Sci. Technol., 38, 633 - 645.
- KOZŁOWSKI C., ULEWICZ M., WALKOWIAK W. (2000), *Separation of zinc and cadmium ions from aqueous chloride solutions by ion flotation and liquid membranes*, Physicochemical Problems of Mineral Processing, 34, 141-151.
- BARTSCH R. A., LEE E. K., CHUN S., ELKARIM N., BRANDT K., PORWOLIK-CZOMPERLIK I., SIWY D., LACH D., SILBERRING J. (2002), *Structure –alcalimetal cation complexation relationships for macrocyclic PNP-lariat ether ligands*, J. Chem. Soc., Perkin Trans, 2, 442 - 448.
- STABILITY CONSTANTS OF METAL-ION COMPLEX; Part A: Inorganic Ligands, Pergamon Press, New York, 1982.

Ulewicz M., Kozłowski C., Walkowiak W., *Wydzielanie jonów Zn(II), Cd(II) i Cu(II) przez polimerowe membrany inkluzyjne przy użyciu pochodnych PNP-dipozphaza-16-korony-6*, Physicochemical Problems of Mineral Processing, 38, (2004) 131-138 (w jęz. ang.).

Zbadano selektywność procesu wydzielania jonów cynku(II), kadmu(II) i miedzi(II) z wodnych roztworów chlorkowych zawierających równomolową mieszaninę tych trzech metali ($c_{Me}=1,0 \cdot 10^{-2}$ M) w procesie transportu przez polimerowe membrany inkluzyjne (PIM) przy użyciu w roli przenośników jonów eterów PNP-difosfazakoronowych. Membrany typu PIM zbudowano z trójocianu celulozy (nośnik), eteru *o*-nitrofenylopentylowego (pastyfikator) i eteru koronowego (przenośnik jonów); stężenie eteru w przeliczeniu na plastyfikator wynosiło 0,1 M. Współczynniki separacji Cd/Cu i Zn/Cu przez PIM przy użyciu mono-lariat eteru były porównywalne, podczas gdy przy użyciu bis-lariat eteru malały wraz ze wzrostem stężenia jonów Cl⁻ w fazie zasilającej. Współczynniki separacji Cd/Cu wynosiły odpowiednio 8,7; 6,6 i 5,4 dla roztworu 0.1; 0.3 i 0.5 M HCl, natomiast współczynniki separacji Zn/Cu dla tych roztworów wynosiły odpowiednio 7.0; 6.3 i 1.2. Tak więc współczynniki separacji jonów kadmu do miedzi były wyższe niż jonów cynku do miedzi. Separacja jonów Cd/Zn nie zachodzi. W pracy przedstawiono ponadto wyniki transportu badanych jonów przy zastosowaniu różnych faz odbierających, tj., roztworu octanu amonu, wodorotlenku amonu i EDTA. Najwyższy procent wydzielania jonów badanych metali uzyskano przy zastosowaniu CH₃COONH₄ (RF ≈ 80 %).