



**N-(DIETHYLTHIOPHOSPHORYL)-AZA[18]CROWN-6:
SYNTHESIS AND ABILITY OF SOLVENT EXTRACTION
TOWARDS LEAD(II), ZINC(II) AND CADMIUM(II)
METAL CATIONS**

Jolanta KOZLOWSKA¹, Stanislaw MIROSHNYCHENKO²

¹Institute of Chemistry, Environmental Protection, and Biotechnology
Jan Dlugosz University of Czestochowa
Armii Krajowej 13, 42-200 Czestochowa, Poland

²Institute of Organic Chemistry, NASU, Kiev, Ukraine

ABSTRACT

This work presents the synthesis of a strongly hydrophobic, functionalized monaza crown ether, i.e., lariat ether, namely *N*-(diethylthiophosphoryl)-aza[18]crown-6 and its application as ion extractant in solvent extraction systems. The synthesis of thiophosphorylated aza[18]crown-6 was performed with good yield. Separation systems have been successfully developed to extract Pb(II), Cd(II) and Zn(II) into organic phase, i.e., chloroform with the crown ethers: aza[18]crown-6 and *N*-(diethylthiophosphoryl)-aza[18]crown-6 as extractants. The selectivity order in both crown ethers was Pb(II) >> Cd(II) > Zn(II). The obtained results suggest that *N*-(diethylthiophosphoryl)-aza[18]crown-6 can be used for the selective removal of Pb(II) at lower pH values than aza[18]crown-6.

Keywords: crown ethers, solvent extraction, lead(II), zinc(II), cadmium(II)

1. INTRODUCTION

Lariat crown ethers have acceptable complexation-decomplexation dynamics, connected with the possibility of three-dimensional cation encapsulation by the crown ether unit and the side arm. In order to achieve an effective transfer of the metal ion in the separation process, the system must have a counter-anion that is soluble in both the aqueous and organic phases. However, the distribution coefficients of complexes formed with common anions, such as chlorides, sulfates or nitrates, between an aqueous phase and organic

phase are too low to be useful. Attaching a proton-ionizable sidearm to the crown ethers can eliminate the need to transfer aqueous phase anions into the organic phase. Another advantage of proton-ionizable crown ethers as ion carriers in liquid membrane transport processes is the coupling of metal ion transport from the aqueous source phase into the aqueous receiving phase with the back-transport of a proton. Thus a pH gradient is the driving force for metal ion transport.

A variety of proton ionizable crown ethers were synthesized and studied by Bartsch *et al.* [1]. The transport of Pb(II) was studied by Aguilar *et al.* [2]. They synthesized a series of diazadibenzocrown ethers and found two of them showing high selectivities for lead(II) over cadmium(II) and zinc(II) when using a polymer inclusion membrane (PIM). Hydrophilic diazadibenzocrown ethers were reported to have higher selectivities for Pb(II) over Zn(II) and Cd(II), compared with more hydrophobic derivatives. Moreover, the high selectivity transport of silver ions over other metals was maintained when the above tribenzylated ligand (O₂N₃-ring) was incorporated as the ionophore in a polymer inclusion membrane system [3].

Cho *et al.* [4, 5] proved that the transport of Cu²⁺ from a 0.4 M SCN⁻ aqueous solution across emulsion liquid membranes doped with tetrathia-18-crown-6 reached 73.0%; an increase to 89.1% was found by applying an analogous hexathia-18-crown-6 (HT18C6). They also noticed that dithia-18-crown-6 much more effectively transported Cu(II) ions (68.2%), compared with Pb(II) (57.7%), Cd(II) (15.2%), and Zn(II) (13.3%). Shamsipur *et al.* [6] showed that the transport of mercury(II) ions into the 0.05M ethylenediaminetetraacetic acid (EDTA) receiving phase at pH 6.0 through chloroform-tetrathia-12-crown-4 bulk liquid membrane runs with efficiencies as high as 98%. They also disclosed that, among a wide variety of tested cations, the transport of Hg(II) ions from a mixture of Hg(II), Cd(II), and Ag(I) ions was affected, a little, only by Ag(I) ions. In recent years, the transport across plasticized cellulose triacetate membranes doped with dibenzo-18-crown-6, hexathia-18-crown-6, diaza-18-crown-6 and hexaaza-18-crown-6 was investigated by Gherrou *et al.* [7], indicating that the dibenzo-18-crown-6 carrier showed its highest selectivity for silver(I), copper(II) and gold(III).

Moreover, the competitive transport of zinc(II), cadmium(II), and lead(II) ions from dilute aqueous solutions across PIMs containing an imidazole azacrown ether derivative and an ionizable crown ether was studied by Ulewicz *et al.* [8-11]. The kind of carriers had an influence on the rate of constant transport of Pb(II), as well as Zn(II) and Cd(II). The selectivity order of metal ion fluxes for the azacrown ether and the ionizable lariat ether was: Pb(II) > Cd(II) > Zn(II). Also, using azacrown ethers in the presence of other metal ions, the highest initial fluxes were obtained for Pb(II) ions. Moreover, acidity and HCl concentration in the source phase had an influence on the value of the selectivity coefficient. A relationship was found to exist also between the initial fluxes of transported ions and the hydrophile-lipophile balance of the crown ethers

used. The initial fluxes of Zn(II), Cd(II), and Pb(II) ions decrease with an increase in the azacrown ethers hydrophile-lipophile balance. Pyrrole azacrown ethers in an ordinary bulk membrane system were also found to preferentially transport lead(II) from an equimolar mixture of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ and Pb^{2+} ions [12]. A considerable number of studies on PIMs to-date have used polyethers. The sizes of the polyether pseudo cavities and of the inserted ions are fundamental parameters that make polyethers effective in the selective transport of metal ions across a liquid membrane. A series of polyesters were examined for the transport abilities toward the mixture of Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) ions by Hayashi *et al.* [13]. They used ionizable polyethers with different alkyl chain lengths (from $-\text{C}_7\text{H}_{15}$ to $-\text{C}_{16}\text{H}_{33}$) and found that one of them had a high selectivity for Pb(II). The metal ions were transported across the polymer inclusion membranes (PIMs) in the following sequence: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. On the other hand, Lee *et al.* [14], using lipophilic acyclic polyether dicarboxylic acid, studied the transport of Pb(II), Cu(II), Co(II), Zn(II), and Ni(II) ions across PIMs. That PIM system exhibited a selective transport of Pb^{2+} over other transition metal ions. Kim *et al.* [15] also found a highly selective transport of Ag(I) in the presence of Cd(II), Pb(II), Zn(II), Co(II), and Ni(II).

The competitive solvent extraction of equimolar mixtures of Zn^{2+} , Cd^{2+} , and Pb^{2+} ions from an aqueous source phase into chloroform solution containing aza[18]crown-6 or N-(diethylthiophosphoryl)-aza[18]crown-6 as an ion extractant has been studied. In the present experiments, the influence of substituents attached to the simple aza[18]crown-6 molecule on selectivity and efficiency has been investigated.

2. EXPERIMENTAL PART

Synthesis

The general procedure for the phosphorylation of the aza[18]crown-6 (obtained from Fluka) according to [16] leading to N-(diethylthiophosphoryl)-aza[18]crown-6 was as follows: the starting aza[18]crown-6 1 (0.01 mol) was dissolved in absolute chloroform (25 ml) and dry triethylamine (0.05 mol) was added. The resulting mixture was cooled on an ice bath and the solution of the appropriate diethyl chlorothiophosphate (0.01 mol) in the dry chloroform (10 ml) was added drop wise within 30 minutes. The reaction mixture was stirred on the ice bath for 1 hour and at a room temperature overnight. The precipitate was filtered off and washed with dry chloroform. Then the filtrate was evaporated and dried under high vacuum conditions for 8 hrs at 40°C. The obtained N-(diethylthiophosphoryl)-aza[18]crown-6 was a colorless viscous liquid.

3. RESULTS AND DISCUSSION

The effect of pH on the competitive solvent extraction of Pb(II), Cd(II) and Zn(II) using aza[18]crown-6 was studied in the range from 5.0 to 7.6, adjusted with an acetic acid/sodium acetate buffer solution. The results shown in Fig. 1 suggest that the percentage recovery of Pb(II) increased as the pH of the feed solution increased from 5.5 to 6.5, and the maximum percentage was observed at a pH of 6.2. Above a pH of 6.5 in the aqueous solution, the percentage of Cd(II) and Zn(II) increased.

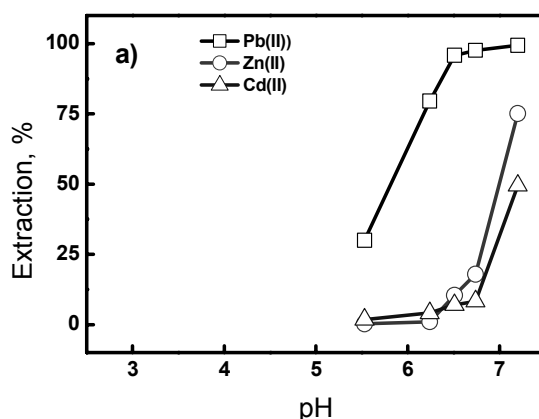


Fig.1. Effect of pH values in aqueous phase on lead(II), cadmium(II) and zinc(II) extraction percentage with aza[18]crown-6

Next, the solvent extractions of metal ions from aqueous solutions into chloroform by N-(diethylthiophosphoryl)-aza[18]crown-6 were performed. Results of competitive extractions of aqueous solutions, each containing 1.0 mM of Pb(II), Cd(II) and Zn(II) cations with 5.0 mM chloroform solutions of N-(diethylthiophosphoryl)-aza[18]crown-6 are presented in Fig. 1.

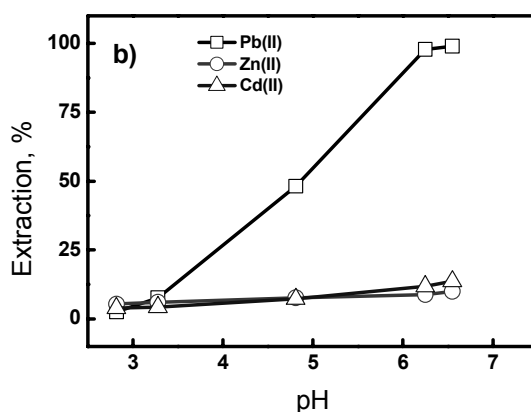


Fig. 2. Effect of pH values in aqueous phase on lead(II), cadmium(II) and zinc(II) extraction percentage with N-(diethylthiophosphoryl)-aza[18]crown-6

The lariat ether N-(diethylthiophosphoryl)-aza[18]crown-6 containing a thiophosphate ionizable group was found to be an efficient extractant with a very high selectivity for Pb(II). The maximum extraction percentage is 98%, as calculated for the formation of 1 : 1 ionized lariat ether–metal ion complexes. At pH 6.2, only Pb(II) are detectably extracted into the chloroform phase and selectivity for Pb(II)/Cd(II) is 49 under high loading conditions. A similarity of extraction selectivity of Pb(II)/Zn(II) for the extractant N-(diethylthiophosphoryl)-aza[18]crown-6 with an aza[18]crown-6 indicates that the attached lariat group does not exert any appreciable steric hindrance.

The extraction ability of neither extractant is reflected as expected by the values of pKa. Phosphate lariat ethers have two different donor sites which provide weak complementarity and a rugged coordination site. Furthermore, since the P=S group in N-(diethylthiophosphoryl)-aza[18]crown-6 is located at the side arm, if a metal ion complex is formed with the phosphorylated aza[18]crown-6, its complexation is apparently preferred due to the presence of the oxygen atoms.

Stripping experiment

The stripping agent in the reextraction has an important role in the removal of metal ions from the organic phase to the stripping phase. Therefore, the influence of different stripping agents in the stripping phase on the reextraction of lead(II) using N-(diethylthiophosphoryl)-aza[18]crown-6 was studied. The experiments were performed with the use of different types of stripping agents, i.e., nitric acid (HNO₃) or hydrochloric acid (HCl) in the concentration range 0.01-1.0 mol/L. The percentage of stripping by various concentrations of stripping agents was illustrated in Fig. 3.

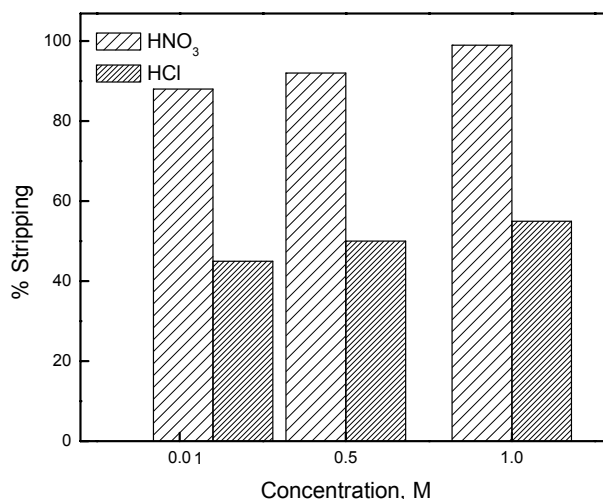


Fig. 3. Percentage of lead(II) stripping against concentration of stripping agents

The experimental results indicate that the stripping efficiency of lead decreased in the following order: $\text{HNO}_3 > \text{HCl}$. Nitric acid provided the highest stripping efficiency and obtained the maximum yield at a concentration 1.0 mol/L.

4. CONCLUSION

Both crown ethers, *i.e.*, aza[18]crown-6 and N-(diethylthiophosphoryl)-aza[18]crown-6 used as extractants for the competitive extraction of lead(II), cadmium(II) and zinc(II) give a preferential selectivity order: $\text{Pb(II)} \gg \text{Cd(II)} > \text{Zn(II)}$, though with low recovery for aza[18]crown-6 at lower pH values of aqueous solution. The N-(diethylthiophosphoryl)-aza[18]crown-6 applied as the ionic extractant gave a very high removal for Pb(II) cations with good selectivity and the entire amount of Pb(II) was removed from the aqueous phase for pH values above 6.2. On the other hand, for N-(diethylthiophosphoryl)-aza[18]crown-6 as the ionic extractant, the removal of a practically entire Pb(II) using 1.0 M nitric acid was observed in the stripping process.

Acknowledgments

This work is part of the project No. 2011/01/D/ST5/05781. The authors acknowledge the NCN (National Science Centre, Poland) for its financial support of this project.

REFERENCES

- [1] Sgarlata C., Arena G., Longo E., Zhang D.M., Yang Y.F., Bartsch R.A., 2008. Heavy metal separation with polymer inclusion membranes. *J. Membr. Sci.* 323, 444-451.
- [2] Aguilar J.C., Miguel E.R.D.S., Gyves J.D., Bartsch R.A., Kim M., 2001. Design, synthesis and evaluation of diazadibenzocrown ethers as Pb^{2+} extractants and carriers in plasticized cellulose triacetate membranes. *Talanta* 54, 1195-1209.
- [3] Kim J., Ahn T.H., Lee M., Leong A.J., Lindoy L.F., Rumbel B.W., Skelton B.W., Strixner T., Wei G., White A.H., 2002. Metal ion recognition. The interaction of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) with N-benzylated macrocycles incorporating O_2N_2 -, O_3N_2 - and O_2N_3 -donor sets. *J. Chem. Soc. Dalton Trans.* 21, 3993-3998.
- [4] Cho M.H., Chun H.S., Kim J.H., Rhee C.H., Kim S.J., 1991. Study on Separation of Heavy Metal Ions in A Neutral Macrocyclic-Mediated Emulsion Liquid Membrane System. *Bull. Korean Chem. Soc.* 12, 474-477.
- [5] 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.
- [6] Shamsipur M., Mashhadizadeh M.H., Azimi A., 2002. Highly selective and efficient transport of mercury(II) ions across a bulk liquid membrane containing tetrathia-12-crown-4 as a specific ion carrier. *Sep. Purif. Technol.* 27, 155-161.

- [7] Gherrou A., Kerdjoudj H., Molinari R., Seta P., Drioli E., 2004. Fixed sites plasticized cellulose triacetate membranes containing crown ethers for silver(I), copper(II) and gold(III) ions transport. *J. Membr. Sci.* 228, 149-157.
- [8] Ulewicz M., Kozłowski C., Walkowiak W., 2004. Removal of Zn(II), Cd(II) and Cu(II) ions by polymer inclusion membrane with side-armed diphosphaza-16-crown-6-ethers. *Physicochem. Probl. Miner. Process.* 38, 131-138.
- [9] Ulewicz M., Sadowska K., Biernat J.F., Szczygelska-Tao J., 2009. Selectivity of Pb(II) transport across polymer inclusion membranes doped with imidazole azothiacrown ethers. *J. Membr. Sci.* 344, 32-38.
- [10] Ulewicz M., Sadowska K., Biernat J.F., 2007. Selective transport of Pb(II) across polymer inclusion membrane using imidazole azocrown ethers as carriers. *Physicochem. Probl. Miner. Process.* 41, 133-143.
- [11] Ulewicz M., Walkowiak W., 2006. Removal of Zn(II), Cd(II) and Pb(II) using polymer inclusion membrane transport with proton ionizable DB-16-C-5 crown ethers. *Physicochem. Probl. Miner. Process.* 40, 185-194.
- [12] Luboch E., Wagner-Wysiecka E., Fainerman-Melnikova M., Lindoy L.F., Biernat J.F., 2006. Pyrrole azocrown ethers. Synthesis, complexation, selective lead transport and ion-selective membrane electrode studies. *Supramol. Chem.* 18, 593-601.
- [13] Hayashi R., Hayashita T., Yoshikawa T., Hiratani K., Bartsch R.A., 2003. Design of a polymer inclusion membrane having proton-ionizable polyether carriers and their separation function for lead ion. *Bunseki Kagaku* 52, 755-762.
- [14] Lee S.Ch., Lamb J.D., Cho M.H., Rhee Ch.H., Kim J.S., 2000. A lipophilic acyclic polyether dicarboxylic acid as Pb^{2+} carrier in polymer inclusion and bulk liquid membranes. *Sep. Sci. Technol.*, 35, 767-778.
- [15] Kim J.S., Kim S.K., Cho M.H., Lee S.H., Kim J.Y., Kwon S.-G., Lee E.-H., 2001. Permeation of Silver Ion through Polymeric CTA Membrane Containing Acyclic Polyether Bearing Amide and Amine Eng-Group. *Bull. Korean Chem. Soc.* 22, 1076-1080.
- [16] Maeda H., Furuyoshi S., Nakatsuji Y., Okahara M., 1983. Synthesis of Monoaza Crown Ethers from N,N-Di[oligo(oxyalkylene)]amines and Oligoethylene Glycol Di(p-toluenesulfonates) or Corresponding Dichlorides. *Bull. Chem. Soc. Jpn.* 56, 212-218.