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SELECTIVE REMOVAL OF Ag(I) AND Cu(II) BY PLASTICIZER MEMBRANES WITH *N*-(DIETHYLTHIOPHOSPHORYL)- AZA[18]CROWN-6 AS A CARRIER

Marta KOŁODZIEJSKA^{*}, Cezary KOZŁOWSKI^{**}, Jolanta KOZŁOWSKA^{**},
Malgorzata ULEWICZ^{***}

^{*} Department of Metal Extraction and Recirculation, Czestochowa University of Technology, 42-200 Czestochowa, Armii Krajowej 19, Poland

^{**} Institute of Chemistry and Environment Protection, Jan Dlugosz University of Czestochowa, 42-201 Czestochowa, Armii Krajowej 13/15, Poland, e-mail: c.kozlowski@ajd.czyst.pl

^{***} Department General Building Engineering and Building Physics, Faculty of Civil Engineering, Czestochowa University of Technology, Akademicka 3, 42-200, Czestochowa, Poland

Abstract: The competitive transport of equimolar mixtures of Ag(I) and Cu(II) ions from aqueous source phase ($c_{Me} = 0.001 \text{ mol/dm}^3$) across polymer inclusion membranes PIMs with *N*-(diethylthiophosphoryl)-aza[18]crown-6 as ion carriers, was studied. The influence of pH of source phase and metal concentration on an efficiency of silver(I) transport through polymer inclusion membranes containing cellulose triacetate as the support and *o*-nitrophenyl pentyl ether as the plasticizer was studied. The transport selectivity order for the PIM with *N*-(diethylthiophosphoryl)-aza[18]crown-6 was: Ag(I) \gg Cu(II). The metal cations transport rate can be explained by size and nature of substituent in lariat ether molecule, which prefer formation of Ag(I) complex in the membrane phase.

Keywords: *plasticizer membranes, lariat ether, separation, silver(I), copper(II)*

Introduction

Transport of metal ions across liquid membranes (LMs) is a powerful tool, which combines extraction and stripping into one step process. LMs play important role in science and technology, and many efforts were made for development of these kind of membranes (Kislik, 2010). Liquid membrane systems include bulk liquid (BLMs), emulsion liquid (ELMs) and supported liquid membranes (SLMs) (de Gyves and de Miguel, 1999). Polymer inclusion membranes (PIMs) were developed as an alternative of SLMs. This kind of liquid membranes was reviewed recently by Nghiem et al.

(2006). PIMs are formed by casting cellulose triacetate (CTA) or polyvinyl chloride (PCV) from an organic solvent solution to form a thin stable film. The organic solution also contains an ion carrier and a plasticizer (usually *o*-nitrophenyl alkyl ethers). The prepared membrane is used to separate source and receiving aqueous phases, but it does not contain an organic solvent to allow the transport of ions or molecules through PIMs.

The most common group of macrocyclic compounds constitute crown ethers, which contain oxygen, sulfur and nitrogen atoms as donor sites. The first crown ether was synthesized by Pedersen (1967). He obtained dibenzo-18-crown-6, which gained attention for its ability to form stable complexes with metal ions within its central cavity. The stability of the crown ether-metal ion complex is dependent on the number of ethers donor atoms. Of particular importance is the size and shape of the cavity relative to the cation size. Due to differences in polarizability, the nitrogen-containing crown ethers (azacrowns) and sulfur-containing crown ethers (thiacrowns) display different ionic selectivities than oxygen-containing crown ethers.

The introduction of one or more side arms into monocyclic crown ethers gives the lariat ethers and may enhance the metal ion binding strength and selectivity over monocyclic crown ethers by providing donor sites in addition to those found in the macro ring. The modified crown ethers, i.e. lariat 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 effective transfer of the metal ion in a separation process, the system must have a counter anion that is soluble in both 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 an organic phase are too low to be useful. The attachment of a proton-ionizable sidearm to the crown ether ring can eliminate the need to transfer aqueous phase anions into the organic phase. Another advantage of proton-ionizable lariat ethers as ion carriers in the liquid membranes transport processes is coupling of metal ions transport from the aqueous source phase into the aqueous receiving phase with back-transport of a proton. Thus, pH gradient provides the potential for metal ions transport. A variety of proton ionizable lariat ethers were synthesized and investigated by Bartsch and his coworkers (1992).

The transport of Pb(II) was studied by Aguilar et al. (2001). They synthesized a series of diazadibenzocrown ethers and found that two of them possessed a high selectivity for lead(II) over cadmium(II) and zinc(II), when using the polymer inclusion membrane (PIM). Hydrophilic diazadibenzocrown ethers were reported to have higher selectivity for Pb(II) over Zn(II) and Cd(II) than the more hydrophobic derivatives. Moreover, the high selectivity transport of silver ions over other metals was maintained when the above tribenzylated ligand (O_2N_3 -ring) was incorporated as the ionophore in the polymer inclusion membrane system (Kim et al., 2001).

Cho et al. (1996) proved that transport of Cu^{2+} from 0.4 mol/dm^3 SCN^- aqueous solution across the emulsion liquid membranes doped with tetrathia-18-crown-6

reaches 73.0%; increase to 89.1% was found by applying analogous hexathia-18-crown-6 (HT18C6). They also noticed that dithia-18-crown-6 much more effectively transported Cu(II) ions (68.2%) compared to Pb(II) (57.7%), Cd(II) (15.2%), and Zn(II) (13.3%). Shamsipur et al. (2002) showed that transport of mercury(II) ions into 0.05 M ethylenediaminetetraacetic acid (EDTA) receiving phase at pH 6.0 through a chloroform-tetrathia-12-crown-4 bulk liquid membrane runs with efficiency equal to 98%. They also revealed that among a wide variety of tested cations, only Ag(I) ions affect a little the transport of Hg(II) ions from mixture of Hg(II), Cd(II), and 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 were investigated by Gherrou et al. (2002). They showed that dibenzo-18-crown-6 carrier was the most selective for silver(I), copper(II) and gold(III).

The competitive transport of zinc(II), cadmium(II), and lead(II) ions from dilute aqueous solutions across PIMs containing imidazole azacrown ether derivative and ionizable crown ether was studied by Ulewicz et al. (2007a, b). 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 azacrown ether and 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, the acidity and HCl concentration in the source phase had the influence on the selectivity coefficient value. A relationship was found to exist also between the initial fluxes of transported ions and the hydrophile-lipophile balance of crown ethers used. The initial fluxes of Zn(II), Cd(II), and Pb(II) ions decrease with the increase in azacrown ethers hydrophile-lipophile balance. Pyrrole azacrown 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., 2006).

A considerable number of studies on PIMs to date used polyethers. The sizes of the polyether cavities and of the inserted ions are fundamental parameters that make polyethers effective in the selective transport of metal ions across the 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. (2003). 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 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. (2000), using lipophilic acyclic polyether dicarboxylic acid, studied the transport of Pb(II), Cu(II), Co(II), Zn(II), and Ni(II) ions across PIMs. This PIM system exhibited a selective transport of Pb^{2+} over other transition metal ions. Kim et al. (2001) also found a highly selective transport of Ag(I) in the presence of Cd(II), Pb(II), Zn(II), Co(II), and Ni(II).

In this work, the competitive transport of equimolar mixtures of Ag(I) and Cu(II) ions from aqueous source phase across PIM containing aza[18]crown-6 or *N*-(diethylthiophosphoryl)-aza[18]crown-6 as an ion carrier was studied. The influence of carrier concentration on the selectivity and efficiency was investigated.

Experimental part

Reagents

The inorganic chemicals, i.e. silver(II) and copper(II) nitrates were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e. cellulose triacetate (CTA, $M_n = 72,000\text{--}74,000$), *o*-nitrophenyloctyl ether (*o*-NPOE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification.

The general procedure to phosphorylation of the aza[18]crown-6 according to (Maeda et al., 1983) leading to *N*-(diethylthiophosphoryl)-aza[18]crown-6 is as follows: the starting aza[18]crown-6 1 (0.01 mol/dm^3) was dissolved in absolute chloroform (25 dm^3), and dry triethylamine (0.05 mol/dm^3) was added (Fig 1). This mixture was cooled in the ice bath and the solution of the appropriate diethyl chlorothiophosphate (0.01 mol/dm^3) in the dry chloroform (10 dm^3) was added dropwise in 30 minutes. The reaction mixture was stirred for 1 hour in the ice bath for overnight at room temperature. The precipitate was filtered off and washed with dry chloroform. Then, the filtrate was evaporated and dried in high vacuum for 8 h at $40\text{ }^\circ\text{C}$. The obtained *N*-(diethylthiophosphoryl)-aza[18]crown-6 was a colorless viscous liquid.

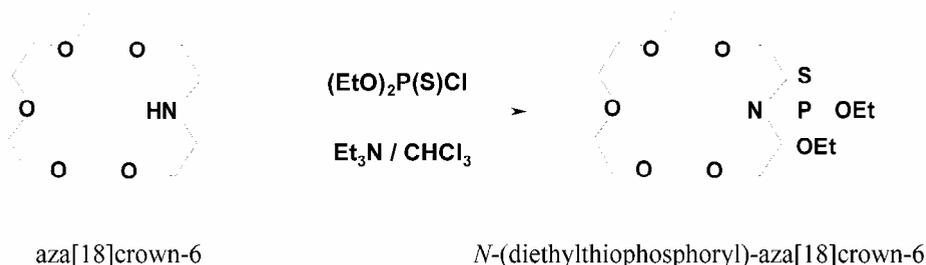


Fig. 1. The diagram of phosphorylation of the aza[18]crown-6. ^1H NMR of *N*-(diethylthiophosphoryl)-aza[18]crown-6: (ppm; CDCl_3): 1.32 (t, 6 H, CH_3), 3.4 (m, 4 H, NCH_2), 3.65 (m, 20 H, $\text{CH}_2\text{CH}_2\text{O}$), 3.96 (m, 4 H, CH_3CH_2). ^{31}P (ppm; CDCl_3): 10.49. Yield 82 %.

Polymer membrane preparation and characterization

The polymer membranes were prepared according to the procedure reported in the previous paper (Kozłowski, 2007). The organic solutions of support (CTA), the ion carrier (lariat ether), and the plasticizer (*o*-nitrophenyl octyl ether) in dichloromethane

were prepared. A portion of this solution was poured into a membrane mold comprised of a 6.0 cm glass ring attached to a glass plate with CTA - dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

The thickness of the PIM samples was measured using a digital micrometer (Mitutoyo) with an accuracy of 0.0001 mm. The thickness of membrane was measured 10 times for each case and shown as average value of these measurements with the standard deviation below 1%. The thickness of membrane before and after the transport was the same. The prepared membranes had thickness equal to 27 μm .

The each experiential point was repeated 4 times, *i.e.* formed membrane by immobilization, thickness measured and transport parameters calculated. Experimental reproducibility was high with standard deviation below 1% measured values.

Transport studies

Transport experiments were carried out in a permeation module cell described in our previous paper (Ulewicz et al., 2007b). 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. As the receiving phase the deionized water was used. The transport experiments were carried out at temperature of 20 ± 0.2 $^\circ\text{C}$. Metal concentration was determined by withdrawing small samples (0.1 cm^3 each) of the aqueous receiving phase at different time intervals and analyzing by an atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant (pH = 5.0) and controlled by a pH meter (pH meter, CX-731 Elmetron, with combine pH electrode, ERH-126, Hydromet, Poland). The permeability coefficient (P , m/s) of metal ions across membranes was described by the following equation (Danesi, 1984):

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

where c is the metal ions concentration (mol/dm^3) in the source aqueous phase at some given time, c_i initial metal ions concentration in the source phase, t time of transport (s), V volume of the aqueous source phase (m^3), and A is an effective area of membrane (m^2).

A linear dependence of $\ln(c/c_i)$ in the source phase versus time was obtained and the permeability coefficient was calculated from the slope of the straight line that fits the experimental data. The initial flux (J_i) was determined as equal to:

$$J_i = P \cdot c_i \quad (2)$$

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

$$S = \frac{J_{i,M1}}{J_{i,m2}} \quad (3)$$

The reported values correspond to the average values of three replicates, with the standard deviation within 5%.

Results and discussion

Permeation of Ag(I) influenced by *N*-(diethylthiophosphoryl)-aza[18]crown-6 in the CTA-based polymer inclusion membrane system

The flux (J) of ions transported in the liquid membrane systems is defined as follows

$$J_M = \frac{c_{(receiving)} \cdot V}{(A \cdot t)} \quad (5)$$

where A and V stand for the effective surface area of the membrane and volume of the source phase, respectively. dc/dt denotes a derivative of the concentration (c) of ions in the source phase versus time (t). The derivatives of the concentration (c) of ions in the source phase versus time (t) $d(\ln c)/dt$ for Ag(I) transported in the considered membrane system depended upon the initial total concentration of silver(I) in the source phase ranging from 0.0002 to 0.010 mol/dm³, but in every case constant values were found irrespective of the elapsed time. The results of Ag(I) transport experiments were interpreted in terms of changes of the initial flux. According to (Danesi, 1984) the permeation coefficient (P) was computed from the changes of the total silver concentration in the source phase at time 0 and elapsed time t , respectively. The effect of pH values in the source phase, ranging from 1 to 7, was studied for 0.25 mol/dm³ *N*-(diethylthiophosphoryl)-aza[18]crown-6 in the membrane phase based on the plasticizer. The initial concentration of Ag(I) in the source phase was 0.001 mol/dm³. The initial flux reaches maximum at pH 2.8 and then decreases with further increase of nitric acid concentration in the source phase (Fig. 2). It is obvious that this effect is parallel to that observed for metal ion extraction with lariat ethers and can be discussed from a similar point of view, namely, taking into account the effective concentration of protonated ion carrier in the membrane phase, and the influence of strong hydrolysis form of metal species.

At constant pH 3.0 in the source phase, the linear dependence $\log J_i$ versus \log of the initial concentration of Ag(I) was found (Fig. 3). The initial Ag(I) concentrations (0.002–0.01 mol/dm³) in the source phase were small in comparison to the concentration (0.25 mol/dm³) of *N*-(diethylthiophosphoryl)-aza[18]crown-6 in the membrane phase. Therefore, the linear dependence of slope 1 indicates that metal-extracted complexes in the membrane phase at stoichiometry 1:1 was formation

resulting from the better fitting of silver(I) diameter (0.22 nm) to the diameter of the crown cavity (0.24 nm).

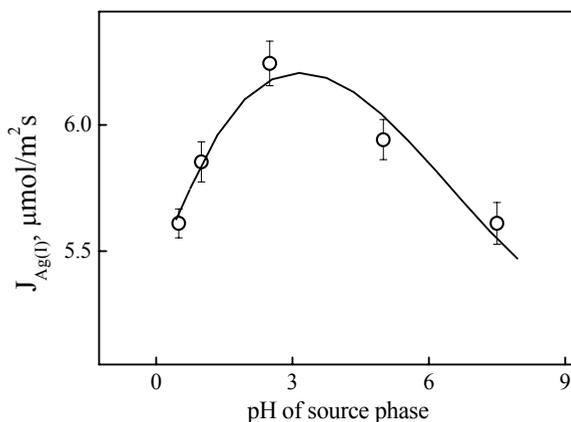


Fig. 2. Dependence of initial flux on pH values in source phase at constant concentration ($2.0 \text{ mmol}/\text{dm}^3$) of Ag(I). Concentration of *N*-(diethylthiophosphoryl)-aza[18]crown-6 in the CTA-membrane phase, $0.25 \text{ mol}/\text{dm}^3$ (based on the plasticiser); the receiving phase: $0.10 \text{ mol}/\text{dm}^3 \text{ Na}_2\text{S}_2\text{O}_3$

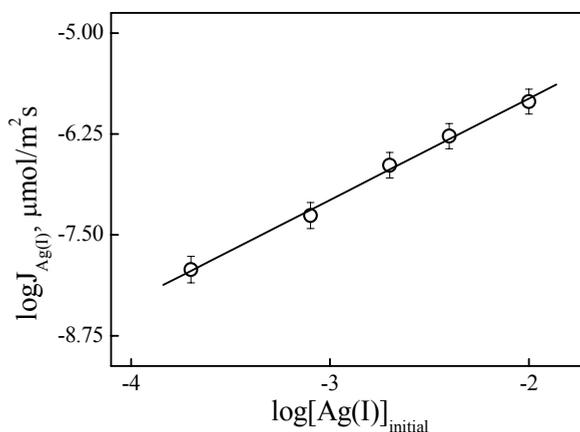


Fig. 3. The log-log plot of initial flux vs. the initial concentration of Ag(I) at 3.0 pH value in source phase; $0.25 \text{ mol}/\text{dm}^3$ (based on plasticizer) and $0.10 \text{ mol}/\text{dm}^3 \text{ Na}_2\text{S}_2\text{O}_3$ in the receiving phase

Competitive separation of Ag(I) and Cu(II) using lariat ether

In the study of Ag(I), and Cu(II) ions transport across PIMs containing *N*-(diethylthiophosphoryl)-aza[18]crown-6 lariat ether as the ion carrier were conducted. The kinetic parameters of this process were determined in the aspect of its effectiveness and selectivity. The extraction ability of ion carrier is not reflected as

expected by the pKa values. Phosphate lariat ethers have two different donor sites, which provide weak complementarily 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.

The membranes containing 0.25 mol/dm³ solution of *N*-(diethylthiophosphoryl)-aza[18]crown-6 lariat ether in the plasticizer, *i.e.* in ONPPE were used for investigations. The aqueous solutions containing equimolar mixture of metal ions of 1.0·10⁻⁴ mol/dm³ concentration served as a source aqueous phases and 0.10 mol/dm³ Na₂S₂O₃ were received as the aqueous phase. Table 1 shows the selectivity order and selectivity coefficients of the above metal ions removed by the transport across PIMs. The transport of Ag(I) is faster due to its larger ionic radius. In the case of Cu(II) much lower transport rate is probably determined by the formation of “sandwich” complexes for lariat ethers (Shampsipur et al., 2003). The selectivity of the metal ion transport for *N*-(diethylthiophosphoryl)-aza[18]crown-6 lariat decreases in the order: Ag(I) >> Cu(II), with the Ag(I)/Cu(II) selectivity coefficient equal to 180 for membrane containing 0.3 mol/dm³ of ion carrier. The large separation factors among divalent heavy metal cations rival those reported by Hayashi et al. (2003) for separation of lead from copper in a PIM transport system with proton-ionizable polyether as a carrier, as well as those reported by Sgarlata et al. (2008). Although these papers deal with the separation of some transition metal ions, only Ulewicz et al. (Ulewicz et al., 2007a, b) report on the selective separation of Zn(II), Cd(II) and Pb(II) from mixtures using macrocyclic carriers. However these results show lower selectivity and efficiency. To our knowledge, this is the first report of successful separation with a PIM system of Ag(I) from the source phase solutions containing Cu(II) ions.

Table 1. Results of measurements of Ag(I), and Cu(II) transport across PIMs containing 0.30 mol/dm³ of *N*-(diethylthiophosphoryl)-aza[18]crown-6 lariat ether. Source phase: 1.0·10⁻³ mol/dm³ metal ions (pH=3.0). Receiving phase: 0.10 mol/dm³ Na₂S₂O₃. PIM: 0.30 mol/dm³ lariat ether and *o*-NPPE (4.0 cm³ *o*-NPOE per 1.0 g CTA)

Concentration of lariat ether, mol/dm ³	Metal ion	Flux, μmole/m ² ·s	Selectivity order and coefficient
0.2	Ag(I)	4.0	Ag(I) >> Cu(II) 60
	Cu(II)	0.07	
0.1	Ag(I)	2.4	Ag(I) >> Cu(II) 40
	Cu(II)	0.06	
0.3	Ag(I)	6.8	Ag(I) >> Cu(II) 180
	Cu(II)	0.04	
0.5	Ag(I)	5.0	Ag(I) >> Cu(II) 70
	Cu(II)	0.07	

Conclusions

In this paper it was demonstrated that *N*-(diethylthiophosphoryl)-aza[18]crown-6 could be regarded as an effective agent used for separation of Ag(I) from aqueous solutions of nitric acid. The crown ether, *i.e.* *N*-(diethylthiophosphoryl)-aza[18]crown-6 used as an ion carrier for competitive transport of Ag(I), and Cu(II) give preferential selectivity order: Ag(II) >> Cu(II). The *N*-(diethylthiophosphoryl)-aza[18]crown-6 applied as ionic extractant gives very high removal for silver cations with good selectivity and the entire amount of Ag(I) can be removed from source aqueous phase under pH 3.0.

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