SEPARATION OF LEAD(II) AND COPPER(II) BY PLASTICIZER MEMBRANES WITH SULPHUR ANA-LOGUS OF PHOSPHINIC ACIDS AS CARRIERS

Marta KOLODZIEJSKA[1], Cezary KOZLOWSKI[2], Malgorzata ULEWICZ[1]

[1] Department of Metal Extraction and Recirculation, Czestochowa University of Technology, 42-200 Czestochowa, Armii Krajowej 19 Street, Poland

[2] Institute of Chemistry and Environment Protection, Jan Dlugosz University of Czestochowa, 42-201 Czestochowa, Armii Krajowej 13/15, Poland, e-mail: c.kozlowski@ajd.czest.pl

Abstract: Investigation of selective removal of Pb(II) and Cu(II) from acidic nitrate aqueous solutions using transport across polymer inclusion membranes PIMs was performed. The sulphur analogus of phosphinic acids, *i.e.* bis(2,4,4-trimethylpentyl)monothiophosphinic acid (**1**) and *tert*-butyl(phenyl)-phosphinothioic acid (**2**) as well as their mixture were incorporated into polymer inclusion membranes composed of cellulose triacetate as a support and *o*-nitrophenyl octyl ether as a plasticizer. In the experiments the transport of Cu(II) across PIM with **1** was rapid and complete, however the lead(II) removal increased with increased membrane saturation. Selective transport of Cu(II) over Pb(II) through PIMs with binary carrier system (**1** + **2**) was observed; the selectivity order was: Cu(II) >> Pb(II). At temperature of 50°C the selectivity coefficient Cu(II)/Pb(II) for membrane with binary carriers was the highest and was equal to 758.

Introduction

Recently polymer inclusion membranes (PIMs) represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of divalent metals ions from aqueous solutions. Transport of metal ions across PIM can be described as simultaneous extraction and back-extraction operations combined in a single stage. PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin, stable film. The casting solution also contains an ion exchange carrier and a membrane plasticizer (Kislik, 2010, Nghiem et al., 2006).

As metal ion carriers in the liquid membrane processes very often the phosphoroorganic compounds are used. The separation of Co(II) and Ni(II) by sup-

ported and hybrid liquid membranes with Cyanex 301, Cyanex 302, Cyanex 272, and D2EHPA, was presented by Gega et al. (2001), whereas Ulewicz and Walkowiak (Ulewicz, 2004, 2007; Ulewicz and Walkowiak, 2003) studied separation of Zn(II), Cd(II), Cu(II), Co(II), and Ni(II) by polymer liquid membranes with D2EHPA, Cyanex 301 and Cyanex 272. Zinc(II) ions can be effectively separated from aqueous chloride solutions containing another metal ions, *i.e.* Cd(II), Cu(II), Co(II), and Ni(II), due to the transport across polymer inclusion membrane with D2EHPA or Cyanex 272 as the ion carrier, whereas Cyanex 301 used as ion carrier allowed much further transport of Cu(II) ions from mixture of metal ions solutions. Although the extraction of lead(II) using PIMs with tailor made carriers (Kozlowski et al., 2008) and commercial carriers (Salazar-Alvarez et al., 2005) has been reported previously, to our knowledge there are no experimental reports on the selective transport of Pb(II) with organophosphorous acids using PIMs.

The influence of natural extractants on cation transport selectivity and efficiency has been also explored by Kozlowski (2006) as well as Kozlowska at al. (2007). Cyanex 301 and 302 used as ionic carriers for competitive transport of Zn(II), Cd(II), and Pb(II) gave preferential selectivity order: Pb(II) > Cd(II) > Zn(II). They also proved that the addition of 3,7–dinonylnaphthalenene-1-sulfonic acid into PIM with Cyanex 302 causes a synergetic effect on separation of Pb(II) and Cd(II) ions from Zn(II). From transport across PIM with mixture of carriers, the selectivity coefficient Pb(II)/Zn(II) and Cd(II)/Zn(II) was 3.5 whereas from transport across PIM containing only Cyanex 302 the selectivity coefficients Pb(II)/Cd(II) and Pb(II)/Zn(II) were 1.3 and 2.2, respectively. The synergistic membrane transport of Pb(II) across PIMs containing different crown ethers in the presence of dialkylnaphthalenesulphonic acids was also reported by Nazarenko and Lamb (1997). A synergistic effect between the calixarenes and dinonylnaphthalenesulfonic acids, used as the counter-ions, was observed in transport of Cs(I) and Sr(II) ions across PIMs by Arena et al. (1998).

In this work the authors present the results for competitive transport of copper(II) and lead(II) ions from dilute aqueous solutions across polymer inclusion membranes with sulphur analogus of phosphinic acids. Also effects of temperature upon the efficiency and selectivity of ions transport with binary carriers is now reported.

Experimental part

Reagents

The inorganic chemicals, i.e. copper(II) and lead(II) nitrates were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyloctyl ether (*o*-NPOE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. The ion carrier, *i.e.* bis(2,4,4-trimethylpentyl)monothiophosphinic acid (**1**) was obtained from Fluka. The sample of optically active *tert*-butyl(phenyl)phosphinothioic acid (**2**) having $[\alpha]_{589} = +5.3$ (MeOH) was prepared in the Centre of Molecular and

Macromolecular Studies in Lodz by the addition of elemental sulfur to secondary *t*-butylphenylphosphine oxide; unpublished results (Wang et al., 2001 cited in literature data). It should be noted here that both thiophosphinic acids exist as tautomeric mixtures (**1**a and **1**b or **2**a and **2**b respectively). For *tert*-butyl(phenyl)phosphinothioic acid the tautomeric form **2**b was found to predominate – Fig. 1. Extraction of Pb(II) and Cu(II) by phosphinothioic acid tautomeric form used in this study depends not only on the acidity strength, but also on the ion–dipole interaction between the hydroxyl and sulfur groups and the cations, steric (depth) effect of the substituent.
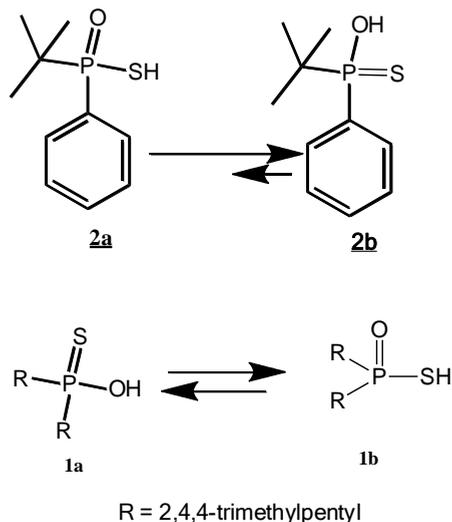

R = 2,4,4-trimethylpentyl

Fig. 1. Tautomeric structures of sulphur analogus of phosphinic acids

Polymer membrane preparation and characterization

The polymer membranes were prepared according to the procedure reported in the previous paper (Kozlowski, 2007). A solution of cellulose triacetate as the support, plasticizer and sulfur analogues of phosphinic acid as ion carrier in dichloromethane was prepared. A specified portion of this solution was poured into a membrane mould comprised of a 9.0 cm diameter glass ring placed on a glass plate with cellulose triacetate - dichloromethane glue. After slow solvent evaporation 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 distilled water to achieve their homogeneity.

The thickness of the PIM samples was measured using a digital micrometer (Mitutoy) 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 earlier paper (Ulewicz et al., 2007). The membrane film (at surface area of 4.9 cm^3) 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 the temperature of $20 \pm 0.2°C$. 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 atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant (pH = 5.0) and controlled by 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, 1984-85):

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

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, t is the time of transport (s), V is 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:

$$J_i = P c_i . \tag{2}$$

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

$$S = \frac{J_{i,M1}}{J_{i,M2}} . \tag{3}$$

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

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \cdot \tag{4}$$

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

Results and discussion

The most important factors influencing the transport of metal ions through polymer inclusion membranes are the acidity of the ion carrier, kind of solvent (plasticizer) as well as the maximal concentration of carrier playing also an important role in saturation of membranes. In the first series of experiments, competitive transport of Cu(II) and Pb(II) from aqueous nitrate solutions containing the metal ion species at concentrations of 0.0010 M through PIM with organophosphorous acid (**1**) as the ionic carrier and *o*-NPOE as the plasticizer into 0.50 M HNO_3 aqueous solution was investigated. Membrane composition was: 80% *o*-NPPE, 15% CTA, and 5% ion carrier. The blanc experiments for the transport when the ion carrier was absent, i.e. with membranes containing the support (CTA) and plasticizer (*o*-NPPE) only, show no significant flux across PIM.

Effect of carrier **1** concentration

The effect of the concentration of ion carrier **1** in the organic membrane phase on the copper(II) and lead(II) transport is given in Fig. 2. Showing the removal curves of metal ions transport through PIM with **1** at concentrations range from 0.10 to 1.0 M. The copper(II) ions were transported with a very high rate, and the selectivity order was as follows: Cu(II) > Pb(II). The process efficiency increased with the ionic carrier saturation of liquid phase membrane, especially for copper ions.
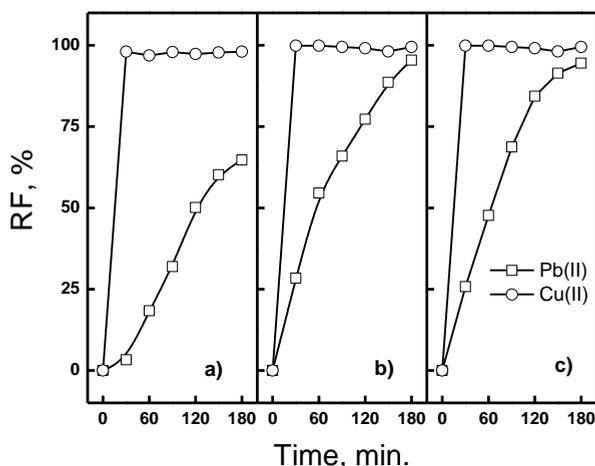

Fig. 2. The recovery factors of lead(II) and copper(II) vs. time of competitive transport across PIM with carrier **1**. Source phase: 0.0010 M for Pb(II) and Cu(II); receiving phase: 0.50 M HNO_3; membrane: 4.0 cm^3 *o*-NPOE/1.0 g CTA, a) 0.10 M, b) 0.50 M, c) 1.0 M carrier **1** (based on plasticizer)

The aqueous source phase acidity constantly increases by protons and metal ions exchange during counter-transport in the membrane system, and is a significant factor determining the selectivity transport. We found that the source phase pH value in the process of transport through PIM containing **1** became stable on the level of 3.5 after 30 min of transport.

For copper(II) removal the optimum concentration range of the carrier was 0.1–1.0 M; in the experiments the transport of Cu(II) was rapid and complete. However the lead(II) removal increased with increase of membrane saturation. When the concentration of ion carrier **1** was 0.1 M, the best recovery factors for copper(II) and lead(II) were 99% and 65%, respectively. The examined cation permeation of PIM with **1** was found to be very efficient, also the permeation selectivity for this membrane was very poor. For this reason for next experiments the phosphinothioic acid derivative as a carrier of a lower acidity was applied.

Effect of binary carriers

The next series of experiments dealt with competitive transport of Pb^{2+} and Cu^{2+} cations from aqueous solutions containing the metal ions at concentrations of $1.0-10^{-3}$ M through PIM with organophosphoric acids **1** and **2** as well as the binary mixture as the ion carriers, and *o*-NPOE as the plasticizer into 0.5 M HNO_3. Figure 3 presents the recovery factor values of investigated metal ions from the source phase, determined after 2 hours of transport through PIM with carriers **1** and **2** and binary carrier system at the concentration of 0.10 M. The Cu(II) and Pb(II) ions were extracted more efficiently, since their RF values for the transport through PIM containing **1** were 98% and 55%.
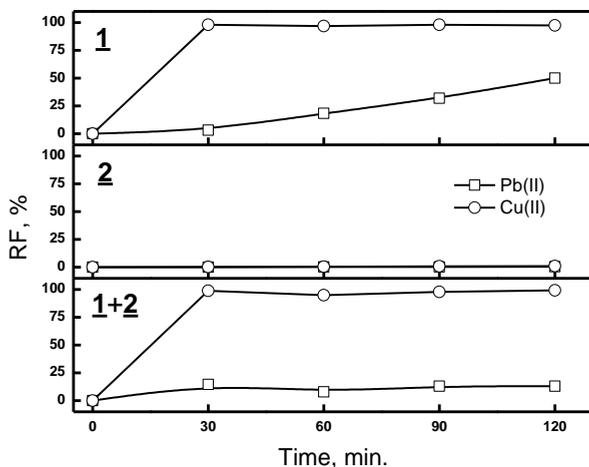

Fig. 3. The recovery factors of lead(II) and copper(II) vs. time of competitive transport across PIM with carriers **1**, **2**, and binary carrier **1** + **2**. Source phase: 0.0010 M for Pb(II) and Cu(II); receiving phase: 0.50 M HNO_3; membrane: 0.40 cm^3 *o*-NPOE/1.0 g CTA, 0.10 M each carrier (based on plasticizer)

However carrier **2**, used for the Cu(II) and Pb(II) ions transport is a less acidic organic acid. The both metal ions were transported with a small rate and the selectivity order was as follows: Cu(II) > Pb(II); the process efficiency was determined by tendency to tautomeric reagouping ionic carrier **2** in liquid phase membrane as well as namely spherical hindrance *t*-butyl group. These factors interfere with ion exchange (deprotonation), resulting in a low affinity to form metal complexes.

After that time, metal ions were still transported due to the protonation and deprotonation reactions of the carrier which occurred because of the difference between the source phase pH and the receiving phase pH and because of the low protonation constant of the acidic carrier.

For membranes with 0.10 M of **2** the maximum value of the RF for Cu(II) ions was equal to 1.46% which practically suggests that carrier structure is not able to metal ion complexation.

In the case of transport by PIM with binary mixture of carriers **1** + **2** the separation of Cu(II) over Pb(II) was higher, compared to the membranes with alone **1** or **2**, the recovery factor values of investigated metal ions from the source phase determined after 2 hours transport through PIM with **1** + **2** were more efficient only for copper(II), since their RF values for Cu(II) and Pb(II) were 98% and 11%, respectively. Under conditions, the transport through the membrane with binary carrier shows a relatively high selectivity of Cu(II) over Pb(II) ions for 0.10 M **1** + **2**; the $S_{Cu/Pb}$ value was 11.4. The use of a mixture of carriers does not favor lead(II) complexation due to tendency of thiophosphinic acid and phosphinothioic acid to form hydrogen bonds, and the presence of the sterically hindered structures, *i.e. tert*-butyl group.

These large separation factors among Cu(II) over Pb(II) cations rival those reported by Hiratani et al. (1997). The separation of Pb(II) from Cu(II) in a liquid membrane transport system, as well as those reported by Molinari et al. (2005) and Sabry et al. (2007). Although these papers deal with the separation of some metal ions, they do not report on the selective separation of Cu(II) over Pb(II) from mixtures using organophosphoric acid as ion carriers.

The RF values recorded in this paper agree well with those reported by us for the removal of Pb(II), Zn(II) and Cu(II) (Ranpreet. et. al., 2011) and are lower than those reported by Salazar-Alvarez et al. (2005).

Effect of temperature on transport with binary carriers

The complexing behavior towards copper and lead of binary organophosphorus acid was examined at temperature of 50°C. The influence of temperature on the selective transport of metal ions across PIM with **1**+**2** were determined. The competitive transport of copper(II) and lead(II) through PIM containing binary carriers showed higher selectivity than membranes with single carrier. Combination of **1** with **2** in the membrane also significantly improved selective removal of copper(II) when the PIM system at temperature 50°C was used. Initial fluxes, selectivity orders for PIM with carriers **1** and **2** and mixture **1**+**2** are shown in Table 1.

Table 1. Kinetics and selectivity parameters for competitive transport of copper(II) and lead(II) through PIM with organophosphorous acids as the ion carriers. Source phase: $1.0 \cdot 10^{-3}$ M Cu^{2+} and 0.10 M Pb^{2+}, pH = 3.0; Receiving phase: 0.5 M $NaNO_3$; Membrane: 75% o-NPPE, 15% CTA, and 10% carrier (4.0 cm^3 o-NPOE/1.0 g CTA, 0.10 M carrier based on plasticizer volume)

Ion carriers	Metal ions	Initial fluxes $\mu mol/m^2 \cdot s$	Selectivity orders and selectivity coefficients
1	Cu(II)	85.2 ± 0.05*	Cu(II) > Pb(II)
	Pb(II)	2.4 ± 0.03	36
2	Cu(II)	8.1 ± 0.04	Cu(II) > Pb(II)
	Pb(II)	0.80 ± 0.06	10
1+**2**	Cu(II)	83.4 ± 0.07	Cu(II) >> Pb(II)
	Pb(II)	0.11 ± 0.02	758

* Standard deviation values for 4 experiments

The initial fluxes for copper(II) are much higher for PIM with **1** and PIM with **1** + **2** than for membranes with **2**, but the selectivity of binary carriers is very high. Selectivity coefficients Cu(II)/Pb(II) for membrane with binary carriers was the highest and was equal to 758. On the other hand the highest value separation coefficient was found in the case in which practically negligible removal of Pb(II) was observed. In both experiments under temperatures 25 and 50°C the controllable factor of selectivity for binary carrier system was proton migration in each of tautomeric forms; as a consequence the best selectivity of copper(II) ions removal. High recoveries of copper(II) from dilute aqueous solution containing lead(II) were obtained by applying thiophosphinic and phosphinothioic acids as carriers in transport across polymer inclusion membranes at relatively shorter times when comparing to other separation methods.

Conclusion

Polymer inclusion membranes containing organophosphorous acid, i.e. bis(2,4,4-trimethylpentyl)monothiophosphinic acid transfer Cu(II) and Pb(II) ions efficiently, at concentration of ion carrier in membrane equal to 0.5 M. With the use of the bis(2,4,4-trimethylpentyl)monothiophosphinic acid and *tert*-butyl(phenyl)phosphinothioic acid as an mixture of ionic carriers, the competitive transport of metal ions shows the preferential selectivity order: Cu(II) >> Pb(II).

The addition of *tert*-butyl(phenyl)phosphinothioic acid into PIM with bis(2,4,4-trimethylpentyl)monothiophosphinic acid plays a role of the factor which increases the selectivity in the membrane process. Competitive transport through polymer inclusion membranes containing above mixture of carriers was found to be an effective method for separation and recovery of copper(II) from solutions containing lead(II) ion, the selectivity factor Cu(II)/Pb(II) being over 750. The application of the proposed methods for the selective removal of ions from spent solutions, generated after the galvanizing process or hydrometallurgical ore process, has also been examined.

Acknowledgments

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