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

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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), \( \alpha \)-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\(_3\)COONH\(_4\), NH\(_4\)OH 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 > 1·10⁻⁷ M (Bartsch and Way 1996). A new type of membrane system, called polymer inclusion membrane (PIM), has been developed which provides metal...
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$, where A = SCN$^-$, I$^-$ 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$_3$P$_3$ 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), $\alpha$-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. $\alpha$-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 experiments were conducted in a permeation cell in which 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. 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 cm\(^3\) 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:

\[\ln\left(\frac{c}{c_i}\right) = -kt\]  

(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:

\[J_i = \frac{V}{A} k \cdot c_i\]  

(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:

\[RF = \frac{c_i - c}{c_i} \cdot 100\%\]  

(3)

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

\[S = \frac{J_{i,M1}}{J_{i,M2}}\]  

(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) ≥ 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 0.5 M 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

<table>
<thead>
<tr>
<th>Crown ether</th>
<th>[HCl], M</th>
<th>Cation</th>
<th>Initial flux, (µmol/m²s)</th>
<th>Selectivity orders and selectivity coefficient of Cd to other metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>Cd(II)</td>
<td>3.52</td>
<td>Cd ≥ Zn, Cu</td>
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<tr>
<td></td>
<td></td>
<td>Zn(II)</td>
<td>1.97</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>Cd(II)</td>
<td>5.75</td>
<td>Cd ≥ Zn ≥ Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn(II)</td>
<td>5.25</td>
<td>1.1</td>
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<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
<td>3.04</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Cd(II)</td>
<td>48.1</td>
<td>Cd ≥ Zn ≥ Cu</td>
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<tr>
<td></td>
<td></td>
<td>Zn(II)</td>
<td>26.9</td>
<td>1.8</td>
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<td></td>
<td></td>
<td>Cu(II)</td>
<td>24.3</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>Cd(II)</td>
<td>17.4</td>
<td>Cd ≥ Zn &gt; Cu</td>
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<tr>
<td></td>
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<td>Zn(II)</td>
<td>14.1</td>
<td>1.2</td>
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<td></td>
<td></td>
<td>Cu(II)</td>
<td>2.01</td>
<td>8.7</td>
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<td>0.3</td>
<td>Cd(II)</td>
<td>39.5</td>
<td>Cd ≥ Zn &gt; Cu</td>
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<td></td>
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<td></td>
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<td>Cu(II)</td>
<td>6.02</td>
<td>6.6</td>
</tr>
<tr>
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<td>76.7</td>
<td>Cd ≥ Zn &gt; Cu</td>
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<tr>
<td></td>
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<td>Zn(II)</td>
<td>73.8</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
<td>14.3</td>
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</table>
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 ethers 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 removal 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).](image)

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

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: CH₃COONH₄ > EDTA > NH₃OH.
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) ($c_{Me} = 0.01 \text{ M}$) 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.

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REFERENCES

