PREPARATION AND APPLICATION OF POLYMER INCLUSION MEMBRANES (PIMs) INCLUDING ALAMINE 336 FOR THE EXTRACTION OF METALS FROM AN AQUEOUS SOLUTION

PRIPRAVA IN UPORABA MEMBRANE IZ POLIMERA (PIM) IN ALAMINA 336 ZA LOČENJE KOVIN IZ VODNIH RAZTOPIN

Yasemin Yildiz¹, Aynur Manzak¹, Büşra Aydın¹, Osman Tutkun²

¹Department of Chemistry, Sakarya University, Sakarya, Turkey
²Beykent University, Department of Chemical Engineering, Engineering and Architecture Faculty, Istanbul, Turkey

manzak@sakarya.edu.tr

Prejem rokopisa – received: 2013-10-12; sprejem za objavo – accepted for publication: 2013-11-12

Polymer inclusion membranes (PIMs) present an attractive approach for the separation of metals from an aqueous solution. The present study is about the application of Alamine 336 as an ion carrier in PIMs. The separation of copper (II), cobalt (II), nickel (II) and cadmium (II) from aqueous solutions with polymer inclusion membranes was investigated. PIMs are formed by casting a solution containing a carrier (extractant), a plasticizer and a base polymer, such as cellulose tri-acetate (CTA) or poly(vinyl chloride) (PVC), to form a thin, flexible and stable film. Several important transport parameters such as the type and amount of the plasticizer, the type of the stripping solution, the thickness of the membrane, the pH of the acid in the donor phase and the concentration of the base in the acceptor phase are discussed. The membrane was characterized to obtain information regarding its composition using AFM, FT-IR and SEM.

Keywords: polymer inclusion membranes, plasticizer, extractant, thickness of membrane

1 INTRODUCTION

The separation of metals from sulphate and chloride media has been of practical interest to the researchers. Solvent extraction is a well-established technology used for the production of metals from a relatively concentrated feed. However, industrial diluent effluents pose an important challenge as the solvent-extraction technique is not cost effective for the separation of metals from a dilute solution¹.

Recently, the supported liquid membrane (SLM) extraction has been emerging as an alternative to the conventional solvent extraction due to its advantages such as high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent discharge, and a combination of extraction and stripping in a single unit². Currently, considerable attention is focused upon polymer inclusion membranes (PIMs)³. Their specific advantages are an effective carrier immobilization, easy preparation, versatility, stability, good chemical resistance and better mechanical properties than in the case of SLM³. The large surface-area-to-volume ratio exhibited by PIMs gives them the potential to be used in nuclear and harmful-metal waste remediation on an industrial scale. They consist of a polymer providing the mechanical strength, a carrier molecule that effectively binds and transports the ions across the membrane, and a plasticizer that provides elasticity and acts as the solvent, in which the carrier molecule can diffuse. PIMs are formed by casting a solution containing a carrier (extractant), a plasticizer and a base polymer, such as cellulose tri-acetate (CTA) or poly(vinyl chloride) (PVC), to form a thin, flexible and stable film⁴.

The choice of different constituents of the membrane is crucial to ensure its separation efficiency, so it is important to investigate the effect of different components on the extraction and transport of the target species. Among the polymers used to form a gel-like network that entraps the carrier and plasticizer/modifier, poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are most frequently encountered⁵.

Examples of such membranes are those containing only PVC and Aliquate 336 that have been used successfully for the transport of both metallic (e.g., Cd (II) and Cu (II)⁶ and non-metallic (e.g., thiocyanate)⁷ ionic species. Moreover, Konczyk et al.⁸ have used Aliquate 336
as a plasticizer in a PIM system containing D2EHPA as the carrier for the removal of Cr (III).

The present study focuses on the application of Alamine 336 as an ion carrier in PIMs and deals with the selective separation of Co, Cd, Ni and Cu ions from an acidic media into an NH$_4$SCN aqueous solution. Amines were used to extract the metal ions. The amine extraction chemistry of thiocyanate complexes was investigated by Sanuki et al.$^{11}$

2 EXPERIMENTAL WORK

2.1 Materials

All the reagents used were of analytical grade. Cellulose triacetate (CTA), 2-nitrophenyl pentyl ether (NPPE) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Tributyl phosphate (TBP), dichloromethane, CoCl$_2$ · 6H$_2$O, NiSO$_4$ · 6H$_2$O, 3CdSO$_4$ · 8H$_2$O, CuSO$_4$ · 5H$_2$O, acetic acid, NaOH, ammonium, triethanolamine, NH$_4$SCN and Alamine 336 were of analytical grade (Merck) and all the stock solutions were prepared by dissolving the salts in distilled water.

2.2 Preparation of PIMs

PIMs were prepared in accordance with the casting solution. CTA (480 mg) was dissolved in 70 mL of dichloromethane at room temperature. In the following step 0.1–0.5 mL of 2-NPPE was added into the solution. After stirring, the carrier (Alamine 336 and TBP) was added and the solution was stirred for 6 h to obtain a homogenous solution. The solvent of this mixed solution was allowed to slowly evaporate in a square glass container (24 cm × 24 cm). The organic solvent was allowed to evaporate overnight at room temperature. After the evaporation of the solvent, a few drops of cold and distilled water swirled on the top of the polymer film. Afterwards, the membrane was peeled out of the container. The average thickness of the membrane was determined as 25 μm with a digital micrometer (Salutron Combi-D3).

2.3 PIM transport experiment

The prepared polymeric film was sandwiched between two glass cells. The transport of metal ions across the PIM from the aqueous solutions was studied by using a two-compartment permeation cell made from Pyrex glass, having flat-sheet membranes with the 12.56 cm$^2$ area (A), as shown schematically in Figure 1.

The volumes of both the aqueous feed and the strip phases were 250 mL. The feed solutions were prepared by adding cobalt, nickel, cadmium and copper salts to study the effect of the feed composition. Ammonium thiocyanate (NH$_4$SCN) was added into the feed mixture to increase the selectivity of cobalt against nickel. 1 M acetic acid/1 M sodium acetate buffer was used to maintain the desired feed pH. A stripping solution containing 1 M NH$_3$ + 1 M TEA was selected as the stripping-phase mixture. The feed and stripping phases were mechanically stirred at the desired mixing speed of (20 ± 1) °C to avoid the concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. During the PIM-transport experiments, the samples of the feed and strip phases (about 1 mL) were periodically removed for a determination of the metal concentration with ICP-OES.

3 RESULTS AND DISCUSSION

3.1 Plasticizer type and concentration

The nature of the plasticizer used to form the membrane is also a key parameter to consider. Plasticizers are organic compounds incorporating a hydrophobic alkyl backbone and one or several highly solvating polar groups. They are added to hard, stiff plastics to make them softer and more flexible. The softening action of the plasticizers, plasticization, is usually attributed to their ability to reduce the intermolecular attractive forces between the polymer chains. For this reason, it is anticipated that in PIMs the presence of these compounds may also influence the mobility of membrane components, the degree of interaction between different constituents of the membrane and the characteristics of the polymeric medium.$^7$ A low plasticizer concentration may cause more rigid and brittle membranes. So, it is not preferred.$^4$ The minimum plasticizer concentration varies widely depending on both the plasticizer and the base polymer. The influence of the plasticizer nature on the Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Cu$^{2+}$ transport through PIMs with different plasticizers, i.e., 2-Nitrophenyl octyl ether (NPOE) and 2-nitrophenyl pentyl ether (NPPE) was tested. Copper was precipitated in the feed phase. Nickel was not transferred to the stripping solution. The cobalt and cadmium ions in the acidic feed solutions reacted with the excess NH$_4$SCN, whereas in the case of nickel ions, they hardly formed a thiocyanate complex.$^{12,13}$

The results obtained for the Cd$^{2+}$ and Co$^{2+}$ ion transport with different concentrations of the plasticizers...
in the PIMs are shown in Figures 2 and 3. For NPPE, this concentration can be in the range of up to 0.2 mL (w = 27 %) (Figure 2). Above this upper limit the mass transport diminishes.

The results obtained for the Cd\textsuperscript{2+} and Co\textsuperscript{2+} ion transport with different types of plasticizers in the PIMs are shown in Figures 4 and 5. 2-Nitrophenyl pentyl ether (NPPE) is the most frequently used plasticizer in PIMs due to its high dielectric constant that enhances the membrane permeability. A decrease in the permeability, together with an increase in the plasticizer content, is probably related to a reduction in the viscosity of the medium\textsuperscript{4}.

The recovery factor (RF) of the metal ions from the feed phase into the stripping phase is given by:

$$RF = \frac{C_f - C_i}{C_i} \times 100\%$$  \hspace{1cm} (1)

where \( C \) is the metal-ion concentration in the feed phase at some given time and \( C_i \) is the initial metal-ion concentration in the feed phase. Recovery factors (RF) for different plasticizers are shown in Table 1.

<table>
<thead>
<tr>
<th>Plasticizer type</th>
<th>RF (Co)</th>
<th>RF (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPOE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPOE (stripping)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPE (stripping)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The recovery factor (RF) of the metal ions from the feed phase into the stripping phase is given by:

where \( C \) is the metal-ion concentration in the feed phase at some given time and \( C_i \) is the initial metal-ion concentration in the feed phase. Recovery factors (RF) for different plasticizers are shown in Table 1.

Table 1: Effect of the plasticizer type on the cobalt and cadmium transport

<table>
<thead>
<tr>
<th>Plasticizer type</th>
<th>RF (Co)</th>
<th>RF (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPOE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPOE (stripping)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPPE (stripping)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2 Effect of the stripping-solution type

In general, metallic ions extracted by amines can be stripped from the protonated amine with the removal of a proton using neutral or alkaline solutions. 1 M ammonia and 1 M triethanol amine solution mixtures were used as the reagents to strip and separate the cobalt and cadmium from the membrane phase to the aqueous phase.

3.3 Membrane characteristics

One important aspect of PIMs is the microstructure of the membrane materials, which determines the distribution of the carriers in the polymer matrix and ultimately affects the membrane transport efficiency. Consequently, a considerable research effort was devoted to clarifying this issue. While a variety of surface-characterization techniques were employed in these studies, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were most frequently used. The results obtained from the SEM and AFM studies consistently indicate a remarkable influence of the polymeric composition on the membrane morphology.

The membrane was characterized to obtain information regarding its composition using AFM (Figure 6), SEM (Figure 7) and FT-IR (Figure 8).

The AFM technique was used to characterize the surface morphology of the prepared membranes. The AFM picture of the PIM formed with CTA + NPPE + TBP + Alamine 336 is shown in Figure 6. The surface morphology of the membrane shows a rough surface. These regions may have occurred because of either a different speed of the solvent vaporization or the membrane having a porous structure where the pores were filled by NPPE or NPPE + Alamine 336 + TBP.

Although both SEM and AFM techniques are versatile and can provide a good image of the membrane surface and, to some degree, of the membrane interior structure, to date, the studies employing these techniques have not been able to clearly elucidate the distribution of the carrier and the plasticizer within the membrane. Consequently, more advanced material-characterization techniques have been attempted.

In order to investigate the absorption bands of the constituents of the membranes containing CTA + NPPE + Alamine 336 + TBP, FTIR was performed as shown in Figure 8. The bands at 2986 cm⁻¹ and 2936 cm⁻¹ were attributed to the stretching vibration of C–H in -CH₂ and -CH₃. The absorption at 1750 cm⁻¹ was assigned to the stretching vibration of C=O in CTA.

The fingerprint region of the spectra becomes complicated because of the P–O, C–O and C–N vibrations. These three vibrations are absorbed in the same region. For example, the peaks in the 1250 cm⁻¹ and 1100 cm⁻¹ region appear in both CTA and TBP and they overlap completely. The expected peaks in the spectra appear in almost the same region as in the case of pure components like CTA, Alamine 336 and TBP. This indicates that these four compounds do not form any new covalent interactions, but only secondary interactions like hydrogen bonding or electrostatic interactions.

Consequently, the analysis and comparison of the obtained spectra revealed that all the membrane constituents remained as pure components inside the membrane. The surface of the films shows a good uniformity and the absence of cracks indicates a good regularity of the membranes as shown in Figure 7.

3.4 Membrane thickness

The investigated membrane thickness was 20 μm to 45 μm, shown in Figures 9 and 10. The best recovery factor (RF) was obtained with a thickness of 25 μm, with 81% in the feed phase over 5 h as shown in Table 2.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NPOE</td>
<td>59</td>
<td>25</td>
</tr>
<tr>
<td>NPPE</td>
<td>81</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 2: Recovery factor (RF) for different membrane thicknesses.
optimum membrane thickness was 25 μm. As the membrane thickness increased, the extraction would decrease. As shown in 19 thinner membranes exhibiting high permeability are formed. However, the thinnest membranes only partly allow high permeability due to a decrease in the extractant content limiting the transport efficiency.

As shown in reference 20 the flux decreased linearly with the membrane thickness. This is unambiguous evidence that the slow step in the transport process represents the migration through the membrane and not a decoupling from the carrier.

4 CONCLUSIONS

With the use of Alamine 336 and TBP as the carriers, the competitive transport of metal ions shows the preferential selectivity order: Co (II) > Cd (II). The transport facilitated through the polymer inclusion membranes containing Alamine 336 and TBP was found to be an effective method for separation and recovery of cobalt (II) and cadmium (II) from aqueous solutions. Copper was precipitated in the feed phase. Nickel was not transferred to the stripping solution. The recovery factor for the cobalt ions was over 87 % over a period 6 h.

Table 2: Effect of the membrane thickness on the cobalt and cadmium transport

<table>
<thead>
<tr>
<th>Membrane thickness (μm)</th>
<th>RF (Co)</th>
<th>RF (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>39</td>
<td>15</td>
</tr>
<tr>
<td>25</td>
<td>81</td>
<td>46</td>
</tr>
<tr>
<td>45</td>
<td>54</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 9: Effect of the membrane thickness on the cadmium transport (feed phase: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH₃ + 1 M TEA; complex reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; feed-solution pH: 4)

Slika 9: Vpliv debeline membrane na prenos kadmija (raztopina: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH₃ + 1 M TEA; kompleksni reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; raztopina pH: 4)

Table 2: Vpliv debeline membrane na prenos kobalta in kadmija na kadmijski transport

Table 2: Effect of the membrane thickness on the cobalt and cadmium transport

Acknowledgement

The financial support of this work, provided by the scientific research commission of Sakarya University (BAPK), Project No: 2010-02-04-025, is gratefully acknowledged.

5 REFERENCES

7. O. Kebiche-Senhadji, S. Tingry, P. Seta, M. Benamor, Selective extraction of Cr(VI) over metallic species by polymer inclusion membrane (PIM) using anion (Aliquat 336) as carrier, Desalination, 258 (2010), 59–65
10 J. Konczyk, C. Kozlowski, W. Walkowiak, Removal of chromium (III) from acidic aqueous solution by polymer inclusion membranes with D2EHPA and Aliquat 336, Desalination, 263 (2010), 211–216
11 S. Sanuki, M. Yata, H. Majima, Stripping of silver from Primene JMT loaded with silver thio cyanate complexes, Hydrometallurgy, 52 (1999), 123–135
14 C. A. Kozlowski, W. Walkowiak, Applicability of liquid membranes in chromium (VI) transport with amines as ion carriers, Journal of Membrane Science, 266 (2005), 143–150
17 N. Bayou, O. Arous, M. Amara, H. Kerdjoudj, Elaboration and characterization of a plasticized cellulose triacetate membrane containing trioctylphosphine oxide (TOPO): Application to the transport of uranium and molybdenum ions, C. R. Chim., 13 (2010), 1370–1376
18 O. Kebiche-Senhadji, L. Mansouri, S. Tingry, P. Seta, M. Benamor, Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion (Aliquat336) and cation (D2EHPA) metal carriers, Journal of Membrane Science, 310 (2008), 438–445
20 A. Gherrou, H. Kerdjoudj, R. Molinari, P. Seta, Preparation and characterization of polymeric plasticized membranes (PPM) embedding a crown ether carrier application to copper ions transport, Materials Science and Engineering C, 25 (2005), 436–443