Efficient Facilitated Transport of Lead and Cadmium across a Plasticized Triacetate Membrane Mediated by D2EHPA and TOPO

Omar Arous1,2*, Fairouz Saad Saoud1, Mourad Amara1,2, Hacène Kerdjoudj1

1Laboratory of Hydrometallurgy and Inorganic Molecular Chemistry, Faculty of Chemistry, University of Sciences and Technology Houari Boumediene, Bab Ezzouar, Algeria; 2Center of Research in Physical and Chemical Analysis, Algiers, Algeria.

Email: omararous@yahoo.fr

Received February 9th, 2011; revised March 11th, 2011; accepted April 21st, 2011.

ABSTRACT

Cellulose triacetate membranes doped with organo-phosphoric carriers (2-ethylhexyl) phosphoric acid noted (D2EHPA) or trioctyl phosphine oxide noted (TOPO) as fixed carriers and 2-nitro phenyl octyl ether noted (NPOE) or tris ethylhexyl phosphate noted (TEHP) as a plasticizers have been prepared and applied for investigation to the facilitated transport of Pb(II) and Cd(II) ions from aqueous nitrate source phase. The membranes Polymer - Plasticizer - Carrier were characterised using chemical techniques as well as Fourier Transform Infra-Red (FTIR), X-ray Diffraction and Scanning electron microscopy (SEM). A study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using D2EHPA as carrier at pH 1-2.

Keywords: Cellulose Triacetate, NPOE, TEHP, D2EHPA, TOPO, Membrane

1. Introduction

Liquid membranes have received considerable attention by many researchers because of their high selectivity accomplished by carriers incorporated in the membranes. Many efforts have been done to investigate the use of liquid membranes for various separation and purification processes such as separation of isomers [1,2], gases [3-5], metal ions [6,7], etc.

The separation and removal of toxic metal cations and neutral chemicals from water has frequently been addressed in membrane separation systems. Environmentally damaging and toxic anions have received significantly less attention primarily due to the challenging nature of selectively binding anions. Recently, a novel type of liquid membrane called polymer inclusion membrane (PIM) has been developed which provides metal ion transport with high selectivity, as well as easy setup and operation [8]. Polymer inclusion membranes (PIM) show great potential for industrial separations over other membrane types. Bulk liquid membranes (BLM) are not economically scalable to industrial levels, while the more practical supported liquid membranes (SLM) tend to lose solvent to the water phases. PIM consist of a polymer support, which is commonly cellulose triacetate (CTA), a plasticizer (solvent) and carrier molecules. The plasticizer is an integral part of the membrane, acting as the solvent in which the carrier diffuses. This makes the membrane easy to handle and promotes membrane durability. In fact, the common plasticizer α-nitrophenyl octyl ether (NPOE) suffers virtually no loss from the membrane into adjacent water phases [9]. Also, PIM demonstrate permeability of ionic and neutral species comparable to SLM [10]. Any loss of transport in PIM in comparison to SLM is due to slower diffusion across the membrane, however, the higher carrier capacity of CTA membranes helps increase transport to counteract this effect [11,12]. The PIM plasticizer can be changed to optimize transport. NPOE, TEHP are common plasticizers in CTA-based PIM. The durability and relatively high polarity of NPOE allow counter ions to be dissolved in the membrane as free ions. NPOE has the further advantages that it is non-volatile, high boiling and insoluble in water. CTA-based PIM using NPOE as the plasticizer retain macrocyclic carriers, such as calixarenes and provide a stable, durable membrane [13-17]. The fabrication and characterization of new membranes is reported recently [18,19].

Facilitated transport of metal ions through PIM carrier
membranes has resulted in good selectivity in ions separa-
tions with real improvements of the membrane stability as
defined in liquid membranes as well as polymer -
stabilized liquid membranes. This is reflected by an
increasing number of PIM investigations reported in the
literature over the last two decades [20,21]. Transport
studies through cellulose triacetate membranes as poly-
meric matrix with showing high flux and good stability
have been recently reported [22-34].

In this work, we have developed a novel class of plastic-
tized cellulose triacetate membrane modified by or-
gano-phosphoric carrier’s incorporation that are selec-
tively permeable to lead and cadmium cations. The mem-
brane CTA - Plasticizer - Carrier was characterised using
technical techniques as well as Fourier Transform Infra-
Red (FTIR), X-Ray Diffraction, and Scanning electron
microscopy (SEM). We compared the behaviour of a Di
(2-ethylhexyl) Phosphoric acid noted D_{2}EHPA (Ac-
id-type carrier) and a Trioctylphosphine oxide noted
TOPO (solvating-type carrier) towards a facilitated tran-
port of lead and cadmium through a synthesized mem-
bane.

2. Experimental

2.1. Reagents

Analytical-grade inorganic chemicals: Pb(NO₃)₂, Cd(NO₃)₂,
were obtained from CARLO ERBA. Organic reagents:
cellulose triacetate (CTA), o-nitrophenyl octyl ether
(NPOE), chloroform were purchased from Fluka. Tris
ethylhexyl phosphate (TEHP) was purchased from Merck. The ion carriers (2-ethylhexyl) phosphoric acid
(D_{2}EHPA) and trioctyl phosphine oxide (TOPO) were
obtained from Aldrich. Doubly distilled water was used
for preparing all aqueous solutions.

2.2. Membrane Preparation

Polymer Inclusion Membranes were prepared using the
same procedure described by Sugiuara et al. [34]. The
solution of cellulose triacetate (0.2 g) (Figure 1), ion
carrier (D_{2}EHPA or TOPO) (Figure 2), and plasticizer
(o-nitrophenyl octyl ether) or tris ethylhexyl phosphate
(0.2 mL) (Figure 3) in chloroform (20 mL) was poured
into a Petri glass of 9.0 cm diameter. The solvent was
allowed to evaporate overnight and the resulting mem-
bane was separated from the Petri glass by immersion in
cold water.

2.3. Transport Studies

Transport experiments were carried out in a permeation
cell in which the membrane film was tightly clamped
between two cell compartments. Both the source and
receiving aqueous phases (50 mL each) were stirred at
800 rpm. Samples of the aqueous receiving phase were
removed periodically via a sampling port with a syringe
and after appropriate dilution with deionized water were
analyzed to determine the metal ion concentrations by the
Atomic Absorption Spectroscopy technique (AAS). Three
independent experiments were realized to determine the
lead and cadmium concentration. The experimental
standard deviation was determined to be ± 5%.

Transport of lead and cadmium ions obeys to a facili-
tated co-transport in the case of TOPO (solvating-type
carrier) and counter-transport in the case of D_{2}EHPA
(Acid-type carrier).

The mechanism transport is represented in Figures 4(a)
and 4(b). The metal ion is complexed at the interface
feed-phase/membrane and the complex formed diffuses
through the membrane phase to the interface membrane/strip-phase where the decomplexation of the metal ion is
realized [35]. The mass flux can be calculated by the

Copyright © 2011 SciRes.
Efficient Facilitated Transport of Lead and Cadmium Across a Plasticized Triacetate Membrane Mediated by D2EHPA and TOPO

2.4. Analyses

The metal concentrations were determined by samplings at different time intervals aliquots of 0.5 ml each from the feed and strip solutions and analysed with an atomic absorption spectrophotometer (Perkin Elmer 2380). Mass flux \( J = \frac{\Delta n}{S\Delta t} \), where \( \Delta n \) is the variation of the number of moles in the feed phase during the interval time \( \Delta t \) (s) and \( S \) is the membrane area (cm²).

2.4. Analyses

The metal concentrations were determined by samplings at different time intervals aliquots of 0.5 ml each from the feed and strip solutions and analysed with an atomic absorption spectrophotometer (Perkin Elmer 2380). Mass flux \( J = \frac{\Delta n}{S\Delta t} \), where \( \Delta n \) is the variation of the number of moles in the feed phase during the interval time \( \Delta t \) (s) and \( S \) is the membrane area (cm²).

2.4. Analyses

The metal concentrations were determined by samplings at different time intervals aliquots of 0.5 ml each from the feed and strip solutions and analysed with an atomic absorption spectrophotometer (Perkin Elmer 2380). Mass flux \( J = \frac{\Delta n}{S\Delta t} \), where \( \Delta n \) is the variation of the number of moles in the feed phase during the interval time \( \Delta t \) (s) and \( S \) is the membrane area (cm²).

3. Results and Discussion

3.1. Physical and Chemical Characteristics of Cellulose Triacetate Membranes

In Table 1, some of the characteristics of the membrane made with the carriers have been listed in comparison with those of the reference CTA membrane. As the carrier molecules (TOPO and D2EHPA) and plasticizers (NPOE and TEHP) are hydrophobic, the location of carrier molecules at the surface of the CTA modified membranes should modify the contact angle which is a parameter indicative of the wetting character of a material.

3.2. X-Ray Diffraction

Based on this figure, we can observe the following:

- The CTA membrane presents a single maximum located at approximately 20° found in all polymers and corresponds to the Van der Waals halo [36,37]. Thus, this material presents basically amorphous characteristics.

- The systems constituted by the mixture of CTA + NPOE + carrier and CTA + TEHP + carrier do not give any diffraction. It can be due to the absence of crystallisation within the membrane which permits us to eliminate the mechanism of transfer of the ions by successive jumps between carrier complexing sites in a 3D assembled state.

3.3. Characterization by FTIR

The membranes CTA + Plasticizer + Carrier were characterized using chemical techniques as well as Fourier Transform Infra-Red (FTIR). IR spectra were recorded on with Perkin-Elmer (Spectrum One) spectrophotometer.

Table 2 collects the peak values and the corresponding radical of the reference CTA, TEHP, NPOE, CTA + TEHP and CTA + NPOE membranes.

The obtained results showed that all the maximum values extracted from the spectrum of the CTA reference membrane, i.e. without plasticizer and carrier, are present.

<table>
<thead>
<tr>
<th>membrane</th>
<th>thickness (µm)</th>
<th>density (mg/cm²)</th>
<th>contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>10</td>
<td>4.88</td>
<td>46.4</td>
</tr>
<tr>
<td>CTA-NPOE</td>
<td>15</td>
<td>6.12</td>
<td>80.5</td>
</tr>
<tr>
<td>CTA-TEHP</td>
<td>12</td>
<td>5.84</td>
<td>75.8</td>
</tr>
<tr>
<td>CTA-NPOE-TOPO</td>
<td>32</td>
<td>7.42</td>
<td>79.2</td>
</tr>
<tr>
<td>CTA-TEHP-TOPO</td>
<td>28</td>
<td>6.91</td>
<td>76.3</td>
</tr>
<tr>
<td>CTA-NPOE-D2EHPA</td>
<td>27</td>
<td>6.87</td>
<td>78.8</td>
</tr>
<tr>
<td>CTA-TEHP-D2EHPA</td>
<td>25</td>
<td>6.33</td>
<td>76.1</td>
</tr>
</tbody>
</table>
Efficient Facilitated Transport of Lead and Cadmium Across a Plasticized Triacetate Membrane Mediated by D2EHPA and TOPO

in the modified membranes spectra in addition to those of the carrier molecules. This result confirms the presence of plasticizer and carrier in the polymer matrix.

3.4. Characterisation by Scanning Electron Microscopy (SEM)

The morphologies of the CTA + Plasticizer + carrier membranes (cross section) (Figure 8) show that the CTA-plasticizer (NPOE or TEHP) and carrier (TOPO or D2EHPA) membranes present a dense structure where the pores of membrane have been filled by the NPOE, TEHP TOPO and D2EHPA molecules yielding a thick and less porous membrane.

3.5. Influence of the Plasticizer Nature

We examined the effect of a plasticizer nature. We used two plasticizers (NPOE and TEHP).

Figure 9 shows the concentrations of lead in a strip phase using TOPO as carrier and two plasticizers. It can be perceived that tris (2-ethyhexyl) phosphate (TEHP, viscosity, \(\eta = 10.2\) cP, dielectric constant, \(\varepsilon_r = 4.8\)) and 2-nitrophenyl octyl ether (NPOE, \(\eta = 12.8\) cP, \(\varepsilon_r = 23.1\)) produces the highest PIM transport of ions.

3.6. Influence of the Carrier Nature

The transport has been achieved with two carriers (TOPO and D2EHPA) using a same polymer and a same plasticizer (NPOE).

Figure 10 represents the variation of the concentration of lead ions in the strip phase versus time using TOPO and D2EHPA carriers. The results show that the concentration of lead in the strip phase obtained with D2EHPA...
Efficient Facilitated Transport of Lead and Cadmium Across a Plasticized Triacetate Membrane Mediated by D2EHPA and TOPO

Figure 6. FTIR spectrums of the CTA + TEHP + carriers membranes.

Figure 7. FTIR spectrums of the CTA + NPOE + carriers membranes.
Efficient Facilitated Transport of Lead and Cadmium Across a Plasticized Triaacetate Membrane Mediated by D2EHPA and TOPO

is slightly lower than that of TOPO. This can be also related to the difference in viscosity between the two organic phases of D2EHPA and TOPO, and probably, to the formation of emulsions in the organic phase of TOPO that would block the active surface of the membrane and prevent the metallic ions to react with TOPO molecules present in the membrane.

3.7. Influence of the pH of the Strip Phase

Extraction and transport of a metal cation by an acidic carrier is governed by the exchange of the metal ion for protons of the carrier. Consequently, counter-transport of protons is the driving force and is achieved by maintaining a suitable pH difference between the strip and feed solutions. In addition, careful pH control in the source solution can result in good selectivity as in the case of solvent extraction systems using acidic reagents.

Figure 11 represents the variation of the concentration of lead and cadmium ions in the strip phase versus pH using D2EHPA carrier. We demonstrate that a maximum permeability for Pb(II) and Cd(II) across a CTA + TEHP + D2EHPA membrane from a source phase to a receiving phase was obtained at pH 1 - 2.

4. Conclusions

A cellulose triacetate (CTA) membrane containing organophosphoric carriers (2-ethylhexyl) phosphoric acid noted (D2EHPA) or trioctyl phosphate oxide noted (TOPO) and 2 - nitrophenyloctyl ether noted (NPOE) or Tris ethylhexyl phosphate (TEHP) noted (TEHP) as a plasticizer has been synthesized. These CTA - plasticizer - Carrier membranes were characterised using chemical techniques as well as Fourier Transform Infra-Red (FTIR), X-ray diffraction (DRX) and SEM analysis. The systems constituted by the mixture of CTA + plasticizers + carriers do not give any diffraction. The morphologies of the CTA + Plasticizer + Carrier membranes (view of Cross-section) show that these membranes present a dense structure. A
Table 2. peak values and the corresponding radicals in different membranes. $m$ (CTA) = 0.2 g, $v$ (TEHP) = $v$ (NPOE) = 0.2 mL.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Peak value (cm$^{-1}$)</th>
<th>Corresponding radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>3480 - 3550</td>
<td>O–H</td>
</tr>
<tr>
<td></td>
<td>2935</td>
<td>C–H</td>
</tr>
<tr>
<td></td>
<td>1755</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>1526</td>
<td>COO$^-$</td>
</tr>
<tr>
<td></td>
<td>1246</td>
<td>C–O–C asym</td>
</tr>
<tr>
<td></td>
<td>1054</td>
<td>C–O–C sym</td>
</tr>
<tr>
<td>TEHP</td>
<td>2960</td>
<td>C–H</td>
</tr>
<tr>
<td></td>
<td>1464</td>
<td>CH$_2$</td>
</tr>
<tr>
<td></td>
<td>1381</td>
<td>CH$_3$</td>
</tr>
<tr>
<td></td>
<td>1285</td>
<td>P=O</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>P–O–C</td>
</tr>
<tr>
<td></td>
<td>1534</td>
<td>NO$_2$ (NPOE)</td>
</tr>
<tr>
<td>NPOE</td>
<td>1488</td>
<td>–CH$_3$ (NPOE)</td>
</tr>
<tr>
<td></td>
<td>1325</td>
<td>C–N (NPOE)</td>
</tr>
<tr>
<td></td>
<td>3477</td>
<td>O–H (TAC)</td>
</tr>
<tr>
<td></td>
<td>2913</td>
<td>C–H</td>
</tr>
<tr>
<td></td>
<td>1767</td>
<td>C=O (TAC)</td>
</tr>
<tr>
<td>TAC + TEHP</td>
<td>1370</td>
<td>–CH$_3$ (TAC)</td>
</tr>
<tr>
<td></td>
<td>1241</td>
<td>C–O–C asym</td>
</tr>
<tr>
<td></td>
<td>1054</td>
<td>C–O–C sym</td>
</tr>
<tr>
<td></td>
<td>1034</td>
<td>P – O – C</td>
</tr>
<tr>
<td></td>
<td>3481</td>
<td>O–H (TAC)</td>
</tr>
<tr>
<td></td>
<td>1755</td>
<td>C=O (TAC)</td>
</tr>
<tr>
<td></td>
<td>1534</td>
<td>NO$_2$ (NPOE)</td>
</tr>
<tr>
<td>TAC + NPOE</td>
<td>1488</td>
<td>–CH$_3$ (NPOE)</td>
</tr>
<tr>
<td></td>
<td>1325</td>
<td>C–N (NPOE)</td>
</tr>
<tr>
<td></td>
<td>1169</td>
<td>C–O–C (NPOE)</td>
</tr>
<tr>
<td></td>
<td>1096</td>
<td>C–O–C (TAC)</td>
</tr>
</tbody>
</table>

Figure 9. Evolution of the concentration of lead in a strip phase versus time using two plasticizer (NPOE) and (TEHP).

Figure 10. Evolution of the concentration of lead in a strip phase versus time using (CTA + TOPO + NPOE) and (CTA + D2EHPA + NPOE) membranes.

Figure 11. Evolution of the concentration of lead and cadmium in a strip phase versus the pH of a strip phase using (CTA + D2EHPA + TEHP) membrane.
study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using D2EHPA as carrier at pH 1 - 2. The inclusion of a selective TOPO or D2EHPA in the matrix of a polymer CTA gives rise to stable membranes able to transport ions and to work for a long time. Our results indicate that facilitated transport through plasticized membranes is an attractive and effective way to solve the enduring problem of membrane stability whilst improving the permeability to metal ions.

Further efforts will be directed to the determination of the nature of interactions between polymer and carrier by use of other materials and analysis as well.

REFERENCES


