SYNTHESIS OF POLYMER INCLUSION MEMBRANES BASED ON CELLULOSE TRIACETATE FOR RECOVERY OF LANTHANUM(III) FROM AQUEOUS SOLUTIONS

Adam Makowka, Beata Pospiech

Department of Chemistry, Czestochowa University of Technology, Armii Krajowej 19, 42-200 Czestochowa, Poland

Corresponding author email: b.pospiech@wip.pcz.pl

Abstract:

Polymer inclusion membrane (PIM) containing cellulose triacetate (CTA) as a polymer matrix and 2-nitrophenyl octyl ether (NPOE) as a plasticizer was developed. This membrane also contained di(2-ethylhexyl)phosphoric acid (D2EHPA) and tributyl phosphate (TBP) as the carriers of metal ions. The facilitated transport of lanthanum(III) from aqueous nitrate(V) solutions across PIM was studied. It was observed that metal ions were transported from the source phase into 2M H₂SO₄ as the receiving phase. The transport through PIM with D2EHPA as the ion carrier was found as the more effective method of lanthanum(III) removal from the aqueous solution than transport through PIM with TBP as the ion carrier.

Keywords:

polymer inclusion membrane (PIM), lanthanum(III), cerium(III), rare earth elements (REEs), di(2-ethylhexyl) phosphoric acid (D2EHPA), tributyl phosphate (TBP)

1. Introduction

Rare earth elements (REEs) due to their unique physicochemical properties, many applications and increasing demand in green technologies and material industries have been designated as critical materials [1-3]. Lister et al. [1] reported that many of the critical REEs have low concentration in the ores. For instance, the concentration of rare earths varies from 10 to 300 ppm in the most of rare earth minerals [2]. On the other hand, recycling methods for REEs from spent electronic materials (pre-consumer scrap, industrial residues, end-of-life products, etc.) are not as well developed compared to the other value metals. Hydrometallurgical technologies are very often used for the recovery of rare earths from secondary sources. The principle processes in the hydrometallurgical treatment are the following: (1) leaching of REEs from processed materials (primary/secondary) and (2) separation of metal ions from leach liquors [2, 3].

The separation of REEs from different leached solutions (i.e. nitrate, chloride, sulfate, thiocyanate, etc.) is a difficult challenge due to the similarity in their ionic radii [2, 4]. A survey of literature indicates that separation of REEs from aqueous solutions can be achieved by liquid-liquid extraction [2, 3]. Cationic, solvating and anionic extractants have been proposed for extraction of REEs, i.e. di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), (2-ethylhexyl) phosphonic acid, mono 2-ethylhexyl ester (PC 88A), tributyl phosphate (TBP), trioctylphosphine oxide (TOPO) as well as quaternary ammonium salt (trioctylmethylammonium chloride, Aliquat 336 – anion exchanger) [2, 3, 5-9]. However, application of this technique requires large amounts of extractants and volatile, flammable, toxic solvents [10, 11]. On the other hand, transport across polymer inclusion membranes (PIMs)

is suggested as an attractive green alternative method to classical solvent extraction [12, 13]. The membrane transport is a promising separation technique because it combines the extraction and stripping at the same time as well as because of low consumption of reagents [10, 11]. Polymer membrane separates source and stripping (receiving) phases. Metal ions from the aqueous source phase are selectively transported through PIM into the receiving phase. The most important advantage is possibility of the design of the membrane composition according to the required conditions [14, 15]. PIM is formed by casting polymer (i.e. cellulose triacetate [CTA]) from an organic solvent (i.e. dichloromethane) containing a plasticizer and an ion carrier to form a stable film. The polymer is very important component of membrane because it provides PIM with mechanical strength [10-12]. The second important component is plasticizer that provides elasticity and flexibility as well as improves the compatibility of the membrane components [10]. The characteristics of PIMs are long-term use, stability, high selectivity and quick transport [14].

A survey of literature indicates that very little is research done on extraction of REEs with PIMs. For instance, Kusumocahyo et al. [13] reported transport of cerium(III) across PIM based on CTA with octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) or *N,N,N',N'*-tetraoctyl-3-oxapentanediamide (TODGA) as the carriers. However, neither CMPO nor TODGA is commercially available.

The organophosphorus compounds such as D2EHPA and TBP were used successfully as the extractants in the conventional solvent extraction process. Therefore, the aim of the present work was to study the facilitated transport of La(III) ions from the aqueous nitrate solution across PIMs with D2EHPA and TBP as the ion carriers. Moreover, the mentioned compounds

were selected as the ion carriers for synthesis of polymer membranes due to the fact that they are available commercially.

2. Experimental

2.1. Reagents

Inorganic chemicals, i.e. lanthanum(III) nitrate(V) ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cerium(III) nitrate(V) ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and nitric acid (HNO_3), were of analytical grade and were purchased from POCH (Gliwice, Poland). Aqueous solutions were prepared with deionized water.

Organic reagents, i.e. CTA ($\text{C}_{40}\text{H}_{54}\text{O}_{27}$, molecular weight: 966.845 g/mol; catalog number: 22199, Sigma-Aldrich, CAS 9012-09-3), dichloromethane, 2-nitrophenyl octyl ether (NPOE), D2EHPA and TBP, were supplied as reagent grade products by Sigma-Aldrich and used without further purification.

2.2. Polymer inclusion membrane

The membranes were prepared as described in detail elsewhere [14, 15]. Solutions of CTA (1.25 g/100 ml of dichloromethane), ion carrier (D2EHPA, TBP) and plasticizer (NPOE) in dichloromethane were prepared. A portion of this solution was poured on a flat-bottom glass Petri dish that was kept on a leveled surface. Organic solvent was allowed to evaporate over a period of 12 h. The obtained membrane was peeled off of the Petri dish and subsequently it was washed with water and conditioned in distilled water before use.

2.3. Transport experiments

Transport measurements were carried out in the experimental rig described and presented in detail elsewhere [14, 15]. The volumes of source and receiving phases were both equal to 100 cm³. During experiments, membrane samples with the effective membrane area of 12.56 cm² were used. The source and receiving aqueous phases were stirred by using magnetic stirrers. Aqueous phases were pumped through the membrane module using a multichannel peristaltic pump (PP1B-05A type; Zalimp, Poland). The permeation rate of La(III) and Ce(III) ions was determined by sampling of the source phase. Samples were subsequently analyzed using a plasma emission spectrometer MP-AES 4200 (Agilent). The source phase contained 0.01M $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ in distilled water. Time of the transport process was 8 hours.

The kinetics of La(III) and Ce(III) ions transport through the PIM membrane follows the kinetics of the first-order reaction:

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

where c is the metal ion concentration (M) in the source phase at a given time, c_i is the initial metal ion concentration in the source phase, k is the rate constant (s⁻¹) and t is the time of transport (s).

The value of rate constant (k) was calculated from the plot of $\ln(c/c_i)$ vs. time – Eq. (1). Experiments were run in duplicates, and

the rate constant value is an average from both experiments. The value of the permeability coefficient (P) was subsequently calculated using the following equation:

$$P = \frac{V}{A}k \quad (2)$$

where V is volume of the aqueous source phase and A is the effective area of the membrane.

The initial flux value (J_i) was then obtained from the following equation:

$$J_i = P \cdot c_i \quad (3)$$

Additionally, the recovery factor (RF) was determined using the following equation:

$$\text{RF} = \frac{c_i - c}{c_i} \cdot 100\% \quad (4)$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for M_1 and M_2 metal ions, respectively:

$$S = \frac{J_{i,M_1}}{J_{i,M_2}} \quad (5)$$

3. Results and discussion

3.1. Effect of carrier kind in polymer membrane on the transport of La(III)

The facilitated transport of La(III) from nitrate(V) solutions across PIMs containing CTA as the polymer support, NPOE as the plasticizer and various carriers was studied. As rare earths form soluble complex in nitrate(V) solutions, different extractants can be used as the effective carriers from aqueous solutions. It is well known that D2EHPA and TBP are used as the extractants of metals in conventional solvent extraction because these extractants have good extracting properties and separate lanthanides efficiently [2, 3, 8, 9]. Therefore, D2EHPA as the cationic extractant and TBP as the solvating extractant were used as the ion carriers for synthesis of PIMs. The membrane composition was 30.0 wt.% CTA, 40.0 wt.% NPOE and 30.0 wt.% ion carriers. The ion carriers differed in chemical structure and mechanism of transport. The cationic extractant (i.e. organophosphorus acid) was employed for the extraction of REEs as they form cationic species in the aqueous solutions. The chemical reaction can be expressed as [2] follows:

where RE stands for any rare earth metal.

The subscripts aq and org denote species in the aqueous and organic phases, respectively.

In the preliminary experiments, PIM containing CTA as the polymer support, NPOE as the plasticizer and D2EHPA as the cationic carrier was used for La(III) transport from the aqueous nitrate solution into 2M H_2SO_4 . D2EHPA exists as a dimmer in the membrane. Therefore, the mechanism of reaction with La^{3+}

can be represented as follows [9]:

where $(\text{HA})_2$ represents the dimmer D2EHPA.

As can be seen from Eqs. (6) and (7), La^{3+} extraction with cationic extractants (cation exchangers) increases by increasing the pH of aqueous phase, while the re-extraction (the stripping from organic phase) increases with the acidity of the stripping phase (i.e. inorganic acid) [2, 9].

In the next experiments, the transport of metal ions across PIM with TBP as the ion carrier was performed. This is a neutral extractant that was used as the extractant of Th(III), La(III), Ce(III), Y(III) and Fe(III) from synthetic solution [6]. Solvating agents such as TBP complexed metal ions from aqueous solutions according to the following reaction:

where S is the solvating extractant (TBP).

Fig. 1 shows the kinetics dependence of $\ln(c/c_i)$ versus time for the transport of La(III) through the studied membranes PIM1 and PIM2. As can be seen from Fig. 1, in the case of PIM containing D2EHPA, this relation is linear. The linear relation of $\ln(c/c_i)$ versus time of the transport shows the facilitated mechanism of La(III) transport through PIM with organophosphorous compounds as the ion carriers. The results show that the transport rate of La(III) is the highest for PIM1 containing 30.0 wt.% CTA, 30.0 wt.% D2EHPA and 40.0 wt.% NPOE.

Fig. 2 shows the RF values of La(III) versus time transport for the respective experiments conducted with different membranes containing various ion carriers (PIM1 and PIM2). The highest RF was 38.5% for PIM1 with D2EHPA after 8 hours.

The kinetic parameters such as the rate constant (k) and the initial flux (J_i) for the transport of La(III) are shown in Table 1. The initial flux of La(III) is much higher for PIM1 with D2EHPA than for PIM2 with TBP. Therefore, D2EHPA can be recommended as the effective ion carrier for synthesis of PIM in order to separate La(III) and Ce(III).

3.2. Selectivity studies

The competitive transport of La(III) and Ce(III) from aqueous nitrate(V) solution across polymer membranes containing various ion carriers was studied. Figs. 3 and 4 show the relationship of $\ln(c/c_i)$ vs. time for La(III) and Ce(III) across PIM1 with D2EHPA and PIM2 with TBP, respectively.

Table 1. Kinetic parameters for competitive transport of La(III). Conditions as Fig. 1.

Membrane	Rate constant, k , h^{-1}	r^2	Initial flux, J_i , $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
PIM1 with D2EHPA	0.055	0.9820	12.2
PIM2 with TBP	0.029	0.9927	6.47

Figure 1. Relationship of $\ln(c/c_i)$ vs. time for La(III) transport across PIM1 with D2EHPA and PIM2 with TBP. Source phase: 0.01M La(III); receiving phase: 2M H_2SO_4 .

Figure 2. Effect of membrane composition on the recovery factor of La(III). Conditions as Fig. 1.

From the separation point of view, the most important is the effective and selective removal of metal ions from the source phase, described by the RF (%) and selectivity coefficient (S). Figs. 5 and 6 show the RF (%) versus time for the studied metal ions obtained during the experiments. The highest RF was obtained for Ce(III) across PIM1 (Fig. 5). The recovery of Ce(III) after 8 hours was 66.8%. As can be seen from Table 2, the selectivity coefficient for Ce(III) over La(III) was 2.6 for PIM with D2EHPA. In the case of PIM with TBP, the selectivity coefficient ($S_{\text{Ce/La}}$) was equal to only 1.4.

The kinetic parameters such as rate constant (k) and the initial flux (J_i) for transport of metal ions are shown in Table 2. The initial flux of Ce(III) was much higher than that of La(III) across PIM1 with D2EHPA. In the case of transport across PIM2,

Figure 3. Relationship of $\ln(c/c_i)$ vs. time for La(III) and Ce(III). PIM: 30.0 wt.% CTA, 30.0 wt.% D2EHPA and 40.0 wt.% NPOE. Source phase: $[Me] = 0.001M$ metal ions; receiving phase: $2M H_2SO_4$.

Figure 4. Relationship of $\ln(c/c_i)$ vs. time for La(III) and Ce(III). PIM: 30.0 wt.% CTA, 30.0 wt.% TBP and 40.0 wt.% NPOE. Source phase: $[Me] = 0.001M$ metal ions; receiving phase: $2M H_2SO_4$.

Table 2. Kinetic parameters for competitive transport of metal ions. Conditions as Fig. 3.

Membrane	Metal ions	Rate constant k, h^{-1}	Initial flux, $J_i, \mu mol \times m^{-2} \times s^{-1}$	Selectivity order
PIM with D2EHPA	La(III)	0.050	11.1	Ce(III)>La(III), 2.8
	Ce(III)	0.139	30.7	
PIM with TBP	La(III)	0.029	6.5	Ce(III)>La(III), 1.4
	Ce(III)	0.041	9.2	

the kinetic parameters for the studied metal ions were very similar and not so high. As can be observed from Table 2, the initial fluxes of La^{3+} and Ce^{3+} increase in the following order of carriers: D2EHPA>TBP.

4. Conclusions

La(III) ions were transported from the source phase into $2M H_2SO_4$ as the receiving phase. The transport of metal ions across PIM with D2EHPA was more effective than the transport of metal ions across PIM with TBP. PIM including

Figure 5. Recovery factor of La(III) and Ce(III) in the transport across PIM1 with D2EHPA. Conditions as Fig. 3.

Figure 6. Recovery factor of La(III) and Ce(III) in the transport across PIM2 with TBP. Conditions as Fig. 4.

organophosphorus acid D2EHPA as the ion carrier can be also used for the effective and selective transport of La(III) and Ce(III) from the aqueous nitrate solutions. With the use of D2EHPA and TBP as the ion carriers, the competitive transport of metal ions shows the preferential selectivity order: Ce(III)>La(III). It was found that the RF of La(III) and Ce(III) and transport rate were strongly dependent on the kind of the ion carrier in membrane. PIM containing 30.0 wt.% CTA, 40.0 wt.% NPOE and 30.0 wt.% D2EHPA was successfully used for the transport of Ce(III) over La(III) ions from the studied aqueous solution.

References

- [1] Lister, T. E., Wang, P., Anderko, A. (2014). Recovery of critical and value metals from mobile electronic enabled by electrochemical processing. *Hydrometallurgy* 149, 228-237.
- [2] Jha, M. K., Kumari, A., Panda, R., Kumar J. R., Yoo, K., Lee, J. Y. (2016). Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* 165, 2-26.
- [3] Xie, F., Zhang, T. A., Dreisinger, D., Doyle, F. (2014). A critical review on solvent extraction of rare earths from aqueous solutions. *Mineral Engineering*, 56, 10-28.
- [4] Kujawski, W., Pospiech, B. (2014). Process and technologies for the recycling of spent fluorescent lamps. *Polish Journal of Chemical Technology*, 16, 3, 80-85.
- [5] Mishra, S., Sahu, S. K. (2016). Solvent extraction of Ce(III) from nitric acid medium using binary mixture of PC 88A and Cyanex 921. *Hydrometallurgy* 166, 252-259.
- [6] Nasab, M. E., Sam, A., Milani, S. A. (2011). Determination of optimum process conditions for the separation of thorium and rare earth elements by solvent extraction. *Hydrometallurgy* 106, 141-147.
- [7] Kumbasar, R. A., Tutkun, O. (2004). Separation and concentration of gallium from acidic leach solutions containing various metal ions by emulsion type of liquid membranes using TOPO as mobile carrier. *Hydrometallurgy*, 75, 111-121.
- [8] Zhang, F., Wu, W., Bian, X., Zeng, W. (2014). Synergistic extraction and separation of lanthanum(III) and cerium(III) using a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid in the presence of two complexing agents containing lactic acid and citric acid. *Hydrometallurgy*, 149, 238-24.
- [9] Zhao, Z., Qiu, Z., Yang, J., Lu, S., Cao, L., Zhang, W., Xu, Y. (2017). Recovery of rare earth elements from spent fluid catalytic cracking catalysts using leaching and solvent extraction techniques. *Hydrometallurgy* 167, 183-188.
- [10] Ines, M., Almeida, G. S., Cattrall, R. W., Kolev, S. D. (2012). Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs). *Journal of Membrane Science*, 415-416, 9-23.
- [11] Kaya, A., Onac, C., Surucu, A., Karapinar, E., Alpoguz, H. K., Tabaki, E. (2014). Preparation of CTA-based polymer inclusion membrane using calix[4]arene derivative as a carrier for Cr(VI) transport. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 79, 103-111.
- [12] Pospiech, B., Kujawski, W. (2015). Ionic liquids as selective extractants and ion carriers of heavy metal ions from aqueous solutions utilized in extraction and membrane separation. *Reviews in Chemical Engineering* 31, 179-191.
- [13] Kusumocahyo, S. P., Kanamori, T., Sumaru, K., Aomatsu, S., Matsuyama, H., Teramoto, M., Shinbo, T. (2004). Development of polymer inclusion membranes based on cellulose triacetate: carrier-mediated transport of cerium(III). *Journal of Membrane Science* 244, 251-257.
- [14] Pospiech, B. (2015). Studies on extraction and permeation of cadmium(II) using Cyphos IL 104 as selective extractant and ion carrier. *Hydrometallurgy*, 154, 88-94.
- [15] Pospiech, B. (2018). Facilitated transport of palladium(II) across polymer inclusion membranes with ammonium ionic liquid as effective carrier. *Chemical Papers*, 72(2), 301-308.