

Extraction-separation of Eu(III)/Th(IV) Ions with a Phosphorylated Ligand in an Ionic Liquid

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ABSTRACT: Extraction-separation of Eu(III) and Th(IV) ions from nitrate media into the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate by a phosphorylated salen extractant, bis(chlorophosphoryl)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (DPO), is investigated. It is found that Eu(III) ions are extracted via a solvation mechanism, and the extraction of Th(IV) ions proceeds through an ion exchange mechanism. The analysis of the experimental data reveals that the extraction of Eu(III) and Th(IV) ions is taken place by formation of $\text{Eu}(\text{DPO})(\text{NO}_3)_3$ and $\text{Th}(\text{DPO})_2(\text{PF}_6)_4$ complexes. A significant selectivity towards thorium ions with respect to trivalent lanthanides (lanthanum, europium, and erbium) was observed. Thorium(IV) can be efficiently extracted from nitric acid solutions into the studied ionic liquid in the presence of DPO.

KEYWORDS: Phosphorylated ligand; Ionic liquid; Europium; Thorium; Extraction; Separation.

INTRODUCTION

One of the main processes in nuclear wastes management is the intra- and inter-group separation of lanthanides and actinides [1,2]. To fulfill this need, several separation strategies have been studied and developed [3]. Liquid-liquid extraction is among the known efficient techniques for separation and concentration of these metal ions. Selection of the extractant and organic solvent used in such process play a key role for achieving to an efficient separation design.

In many cases these technique involves the use of toxic and hazardous organic solvents.

Room-Temperature Ionic Liquids (RTILs) are non-volatile, nonflammable, thermally stable solvents. These characteristics allow they play important role in green chemistry [4]. RTILs are widely used as replacements for traditional organic solvents in separation processes [5]. They have been used for the extraction and separation of a variety of organic species [6] and metal ions [7-11].

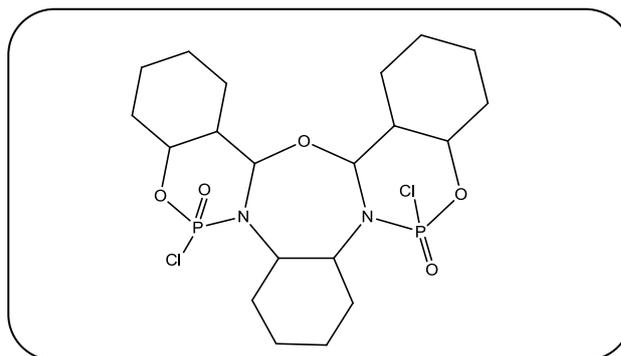
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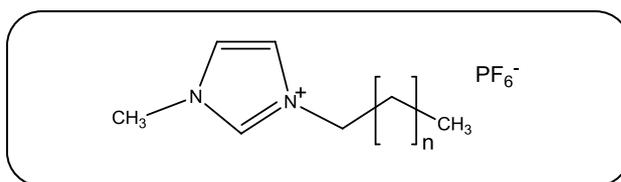
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Knowing the dissimilarities in the behaviour of ionic liquids with conventional organic solvents [12] and by considering the potential of phosphorus bearing molecules [1-3], few studies have recently been concerned on the extraction of lanthanides and actinides by phosphorylated ligands into ionic liquids. For example, *Visser et al.* [13] have studied the extraction of uranyl ions with *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tri-*n*-butylphosphate (TBP) into 1-butyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide from aqueous acidic media. This study showed an enhancement of UO_2^{2+} extraction when RTILs are used in comparison with the results obtained by using conventional diluents. The analysis of the extraction data reveals that, the extraction of uranyl ions into ionic liquids are occurred via the formation of cationic species $\text{UO}_2(\text{NO}_3)(\text{CMPO})^+$, while the extracted species in dodecane were neutral complexes $\text{UO}_2(\text{NO}_3)_2(\text{CMPO})_2$. The employment of ionic liquids has also been reported for the extraction of Am(III), Pu(IV), U(VI) and Th(IV) ions from nitric acid [14]. A cation exchange mechanism for the extraction of trivalent lanthanides by dissolving CMPO in 1-butyl-3-methylimidazolium hexafluorophosphate is reported by *Nakashima et al.* [15]. *Srinivasan et al.* [16] have studied the extraction of Am(III) ions from nitric acid medium by the extractants applied in TRUEX process into 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[\text{C}_4\text{mim}][\text{NTf}_2]$). The stoichiometry of the extracted complexes was determined $\text{CMPO-TBP}/[\text{C}_4\text{mim}][\text{NTf}_2]$ which was similar with that found in conventional TRUEX process. Recently, *Srinivasan et al.* [17] have also shown the extraction behavior of a mixture of CMPO and TBP in the room temperature ionic liquid $[\text{C}_4\text{mim}][\text{NTf}_2]$ for the extraction of europium(III) ions from nitric acid medium. The distribution ratio of Eu(III) in $\text{CMPO-TBP}/[\text{C}_4\text{mim}][\text{NTf}_2]$ was measured as a function of various parameters such as the concentration of nitric acid, europium ions, CMPO, and TBP, as well as temperature.

In continuation of our studies concerning on the extraction-separation of europium(III) and thorium(IV) ions by a variety of ionophores including phosphorylated extractants [18-24], we have recently reported the application of a room-temperature ionic liquid for such



Bis(chlorophosphoryle)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (DPO)



1-Hexyl-3-methylimidazolium hexafluorophosphate (IL, n=4)

goal [10]. It is noteworthy that in many investigations Eu(III) and Th(IV) ions have been selected because they are used as models for trivalent and tetravalent actinides, respectively [25]. In the present paper, the extraction of Eu(III) and Th(IV) ions by using a new phosphorylated ligand, bis(chlorophosphoryle)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (DPO), dissolved in an ionic liquid (**IL**) named 1-hexyl-3-methylimidazolium hexafluoro phosphate is reported.

EXPERIMENTAL SECTION

Chemicals

1-Hexyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_6\text{mim}^+][\text{PF}_6^-]$), abbreviated as **IL** was from Kimia Exir Chemical Company (Iran). Bis(chlorophosphoryle)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (DPO) has been prepared and characterized according to the procedure reported by *Hosseini Monfared et al.* [26]. Nitric acid and sodium nitrate (Merck) were the highest purity available grade. Stock solution of thorium (0.01 mol/L) was prepared by dissolving a proper quantity of tetrahydrated thorium nitrate (Fluka) in distilled water. For preparing the stock solution of lanthanides (0.01 mol/L), a weighed quantity of the corresponding oxide (Fluka) was dissolved in nitric acid and then diluted appropriately with distilled water. As the nitrate salts

Table 1: Extraction percentage of Eu(III) and Th(IV) ions from sodium nitrate aqueous solution (1 mol / L) adjusted at pH 2.5, into the studied ionic liquid (IL) and some conventional solvents, after 60 min magnetically stirring at 20°C.

Solvent	Eu(III) %		Th(IV) %	
	Without DPO	With DPO ^a	Without DPO	With DPO ^b
IL	C	25	37	100
Carbon tetrachloride	C	7	8	71
Chloroform	C	4	8	54
Dichloromethane	C	c	9	60
1,2-Dichloroethane	C	5	7	63

a) 0.01 mol/L; b) 0.001 mol/L; c) non-detectable

used for preparation of thorium and lanthanides solutions were not primary standard materials, the stock solutions were standardized. The standardization of the stock solutions was performed by complex formation titration using EDTA (Merck) at pH 2 in the presence of Pyrocatechol violet (Fluka) for thorium and at pH 7 in the presence of Eriochrome black T (Merck) for lanthanides [27]. A 6.4×10^{-4} mol/L solution of ArsenazoIII (Fluka) was used for spectrophotometric determination of thorium and europium ions [28].

Apparatus

A HACH spectrophotometer (DR 5000, Canada) was used for uv-vis spectrometric measurements. The pH adjustments were performed by a Metrohm digital pH meter (model 780, Switzerland) equipped with a combined glass electrode. Temperature of the extraction vessels was controlled using a Julabo MP5 thermostate water circulator. An inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro-Genesis, Germany) was used for the determination of Th(IV), La(III), Eu(III) and Er(III) ions in their mixtures in competitive extraction experiment.

Extraction procedure

The solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath ($20 \pm 1^\circ\text{C}$) using 5 mL aqueous phase in contact with 1 mL of organic phase including **IL**. It is confirmed that the extraction equilibrium was reached after 35 min magnetically stirring. After separation of the two phases, by centrifugation, the concentration of cation

remaining in the aqueous phase was measured spectrophotometrically using ArsenazoIII as indicator. In the selectivity investigation the concentration of Th(IV), La(III), Eu(III) and Er(III) ions in their mixture was determined by ICP.

RESULTS AND DISCUSSION

Extraction of Eu(III) and Th(IV) ions by DPO in IL and conventional solvents

Extraction of europium and thorium ions in the presence of DPO into the Ionic Liquid **IL**, and into the conventional organic solvents including carbon tetrachloride, chloroform, dichloromethane and 1,2-dichloroethane has been investigated (Table 1). Because of the lower efficiency of DPO towards europium ions with respect to thorium ions, the concentration of DPO used for the europium ions was higher than that used for thorium ions.

The results demonstrate the importance of the studied ionic liquid in the extraction of both ions. In addition the presence of DPO enhances markedly the extraction percentage of thorium ions in all solvents, and increases the extraction of europium ions in **IL**. It is also seen that the extraction process into the studied solvents shows a significant selectivity towards thorium ions.

Effect of aqueous phase pH

The possible protonation of DPO has enforced to study the effect of aqueous phase pH on the extraction efficiency. To this end, the extraction of Eu(III) and Th(IV) ions from aqueous nitrate media as a function of aqueous phase pH into the studied ionic liquid

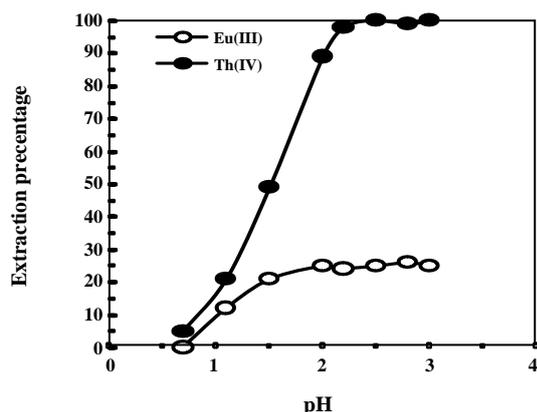


Fig. 1: Variation of extraction percentage vs. pH for extraction of Eu(III) and Th(IV) ions (1×10^{-4} mol/L) from sodium nitrate solution (1 mol/L) into IL in the presence DPO (0.01 and 0.001 mol/L for the extraction of Eu(III) and Th(IV) ions, respectively) after 60 min magnetically stirring, at 20°C.

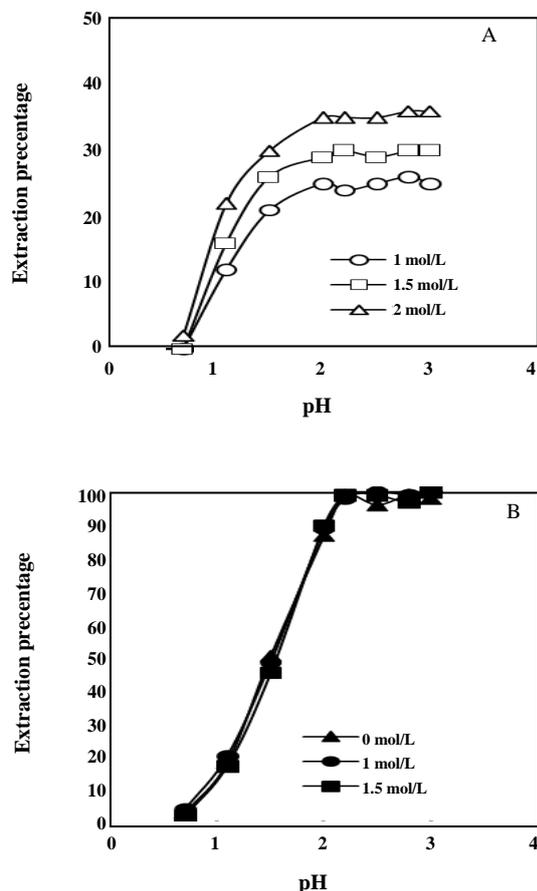


Fig. 2: Variation of extraction percentage versus pH for the extraction of Eu(III) (A) and Th(IV) (B) ions (1×10^{-4} mol/L) at different sodium nitrate concentration into IL, stirring time 60 min, at 20°C.

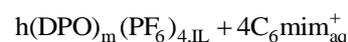
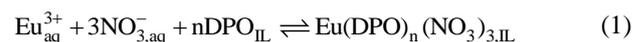
in the presence of DPO has been investigated (Fig. 1). A significant pH dependency at pH values < 2 was observed for the extraction of europium and thorium ions into the studied ionic liquid. This behavior can be attributed to the protonation of DPO molecules at the lower pH values inferior to 2. This pH was used for continuing the experiments. This selection was done because the maximum extraction percentage of both thorium and europium ions can be achieved at this pH. In addition nuclear wastes, as many other industrial effluents, are usually acidic and it is important to examine an extraction procedure in acidic conditions.

Effect of nitrate concentration

Extraction via solvation is the mechanism assumed for the extraction of Eu(III) and Th(IV) ions by the neutral ligand DPO in IL. In this case the anion accompanying the complexed cation plays a decisive role for enhancing the extraction efficiency. In order to verify this effect, the extraction of the studied ions from sodium nitrate solution with different concentrations into DPO in IL has been performed. The results (Fig. 2) show that, although the extraction of europium ions is influenced by the nitrate concentration, the extraction of thorium ions does not depend on this parameter. As the nuclear waste solutions contain nitrate ion, a concentration of 1 mol/L was selected for performing the experiments.

Characterization of the extracted species

The results in previous section allow considering a mechanism via solvation for the extraction of europium ions by DPO dissolved in IL. In fact, in this case the ionic liquid plays a role as a polar diluent and it is not participated in the extracted species of europium ions. In contrast, the independency on the nitrate ion concentration permits to propose an ion exchange process for the extraction of thorium ions. These conclusions conduct to suggest the following extraction reactions for the extraction of the studied ions:



where the subscribers "aq" and "IL" denote the phase, aqueous or ionic liquid, in which the species are presented.

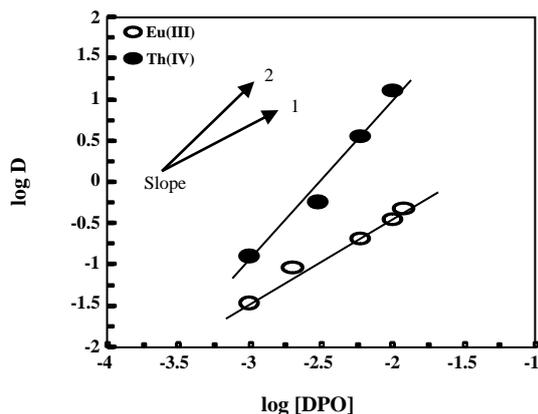


Fig. 3: Variation of $\log D$ vs. $\log [DPO]$ for the extraction of Eu(III) and Th(IV) ions (1×10^{-4} mol/L) from sodium nitrate aqueous phase (1 mol/L), at pH 1.5, stirring time 60 min, at 20°C .

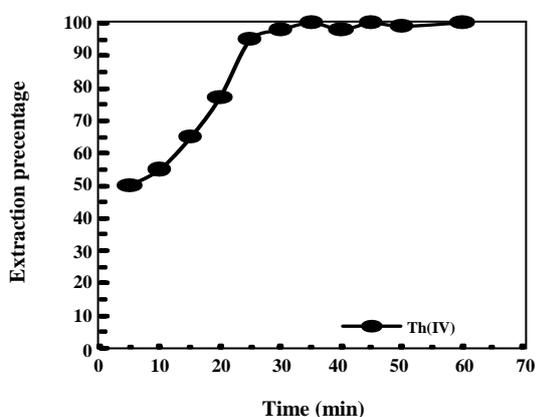


Fig. 4: Variation of the extraction percentage of Th(IV) ions from aqueous sodium nitrate solutions (1 mol/L) into IL containing DPO (0.001 mol/L) at pH 2, at 20°C .

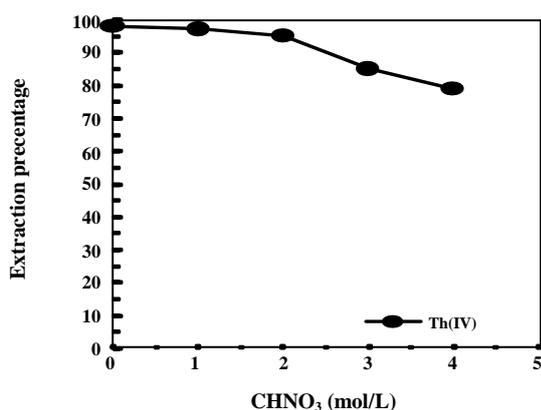


Fig. 5: Effect of nitric acid concentration on the extraction of Th(IV) ions into IL containing DPO (0.01 mol/L), stirring time 35 min, at 20°C .

In order to determine the number of molecules of DPO in the extracted Eu(III) and Th(IV) complexes the conventional log-log analysis was used [10]. Based on these results (Fig. 3) the values of “n” and “m” in the above mentioned equations was found to be 1 and 2, respectively.

Time dependency of the process

Time dependency of the extraction of thorium ions into ionic liquid **IL** in the presence of DPO from sodium nitrate solution (1 mol/L) was verified (Fig. 4). It is found that the extraction equilibrium of thorium ions is achieved after 35 minutes. This relatively long time requirement for the extraction into **IL** is already encountered for the extraction of metal ions into the ionic liquids [10]. Thus 35 min was selected as the time required for achieving to an equilibrium condition.

Extraction² of Eu(III) and Th(IV) ions from nitric acid solutions

One requirement for an extraction process employed in waste management is its ability in acidic media. In order to investigate this potential of the proposed processes, the extraction of Th(IV) and Eu(III) ions from nitric acid solutions was performed. The obtained results (Fig. 5) show, although the extraction percentage of Th(IV) ions by the studied ionic liquids was not altered by the presence of NaNO_3 , the extraction of these ions from nitric acid solutions decreases by the acid concentration. This is a consequence of the enhancement of the competition between hydrogen and thorium ions. These results present the ability of the proposed extraction procedure for extraction thorium ions from high nitric acid concentration. Due to the very weak extraction of Eu(III) ions into **IL**, the results do not reported.

Selectivity

Although individual single ion extraction experiments allow estimating the extraction performance of an extractant, a real evaluation of the extraction efficiency and selectivity of a ligand can be provided by performing competitive extraction experiments. The results of the extraction of lanthanum, europium, erbium and thorium ions (each 1×10^{-4} mol/L) from sodium nitrate solution (1 mol L^{-1}) into **IL** solution of DPO (0.01 mol/L)

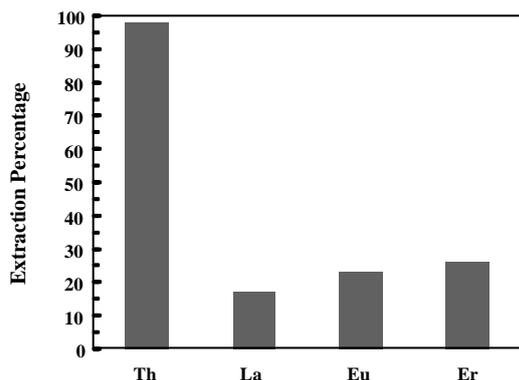


Fig. 6: Results of a competitive extraction of lanthanum, europium, erbium and thorium ions (1×10^{-4} mol/L) from sodium nitrate solution (1 mol/L) by DPO (0.01 mol/L) in IL, stirring time 35 minutes.

adjusted at pH 2 are presented in Fig. 6. The order of the extraction selectivity was found to be Th(IV) \gg Er(III) > Eu(III) \approx La(III). A significant selectivity towards thorium ions with respect to the investigated lanthanides was demonstrated by the solution of DPO dissolved in IL.

CONCLUSIONS

A solution formed by dissolving bis(chlorophosphoryle) decahydro-2,4-di(2-hydroxyphenyl) benzo[d] [1,3,6] oxadiazepine (DPO) into ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate can be used for extraction-separation of thorium and europium ions from nitrate media. A neutral extraction (extraction via solvation) was suggested for the europium ions, whereas thorium ions have been extracted with an ion exchange mechanism. An excellent selectivity for the extraction of thorium with respect to some lanthanides has been found. The extraction of thorium and europium ions from nitric acid solutions shows the ability of DPO/IL mixture for removal of thorium ions from such solutions.

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