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Extraction and coordination behavior of diphenyl hydrogen phosphine oxide towards actinides

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Extraction behavior of some selected actinides like U(VI), Th(IV) and Am(III) was investigated with three different H-phosphine oxides, *viz.* diphenyl hydrogen phosphine oxide (DPhPO), dihexyl hydrogen phosphine oxide (DHePO) and diphenyl phosphite (DPP). The H-phosphine oxides exhibited a dual nature towards the extraction of actinides where the ligand not only extracts the metals by cation exchange but also by coordination with the phosphoryl group at lower and higher acidic concentrations, respectively. Among all ligands employed, DPhPO showed highest extraction with actinides with a substituent dependent trend as follows: DPhPO > DHePO > DPP. This trend emphasizes the importance of substituents around the phosphine oxide towards their extraction of actinides. The coordination behavior of DPhPO was studied by investigating its corresponding complexes with Th(NO₃)₄ and UO₂(NO₃)₂. The metal complexes of these actinides were characterized using FT-IR, ¹H and ³¹P NMR spectroscopic techniques. Density Functional Theory (DFT) calculations were also performed to understand the electronic and geometric structure of the ligand and the corresponding metal complexes.

Keywords: Diphenyl hydrogen phosphine oxide; Coordination behavior; Solvent extraction; Uranium; Actinides

1. Introduction

Chemical separations play an important role in nuclear fuel cycle. The reprocessing of the spent

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fuel and individual separation of metal ions from spent nuclear waste and high-level liquid waste (HLLW) has attracted significant global attention towards the development of better, cheaper, and radiation-resistant ligands. Various methods such as precipitation, ion exchange, and liquid-liquid extraction (solvent extraction) have been developed and successfully employed for the separation of actinides and other metal ions in nuclear waste management, amongst which solvent extraction has been the most convenient method for the separation of actinides on a bulk scale [1-3]. On the other hand, tributyl phosphate (TBP) is widely employed not only for the extraction and separation of actinides from the dissolver solution in PUREX [4] and TRUEX process (based on octyl, phenyl-N, N-diisobutyl carbamoylmethyl phosphine oxide) [5] but also for the co-extraction of lanthanides and actinides from the HLLW. Apart from the above mentioned processes, TRPO [6] (trialkyl phosphine oxides), DIDPA [7] (diisodecyl phosphoric acid) and DIAMEX [8, 9] (diamide extraction) are also used for the co-extraction of actinides.

Numerous ligands with varying substituents and donor atoms like S, O, and N have been reported towards the separation of actinides from lanthanides and comprehensively discussed in some excellent reviews [10-13]. Additionally, phosphonate, phosphonothioate and amide-based ligands are also reported for the extraction of actinides and lanthanides [14]. The extraction behavior of actinides is governed by the basicity on phosphoryl oxygen [15] which is as follows: phosphates < phosphonates < phosphinates < phosphine oxides [16, 17]. Consequently, the extraction ability of organophosphorus extractant depends on the substituents attached to the phosphorus atom. Higher analogs of TBP and H-phosphonates were also synthesized and studied previously [18-21]. The extraction behavior of dialkyl phosphine oxides (DAPOs) with various alkyl substituents from hexyl to decyl side chains and also dicyclohexyl phosphinic acid towards U(VI) and Am(III) was investigated to understand the influence of alkyl substituents on the distribution values [22, 23].

To the best of our knowledge, the extraction behavior of phosphine oxides with aromatic substituents for actinides has not been investigated. In this contribution, we attempt to demonstrate a comparative study on the extraction behavior of phosphine oxides tagged with aromatic substituents and alkyl and alkoxy groups towards actinides. In this regard, we present the extraction studies of actinides with diphenyl hydrogen phosphine oxide (DPhPO) and compared the same with that of diphenyl phosphite (DPP) and dihexyl hydrogen phosphine oxide (DHePO). The present study involves synthesis, characterization and extraction behavior

of diphenyl hydrogen phosphine oxide (DPhPO) towards actinides like U(VI), Th(IV) and Am(III) and its comparison on extraction behavior of same metals with diphenyl phosphite (DPP, also known as diphenyl hydrogen phosphonate) and dihexyl hydrogen phosphine oxide (DHePO). The coordination behavior of DPhPO was also evaluated towards uranium and thorium by synthesizing the corresponding metal complexes. Additionally, we have performed Density Functional Theory (DFT) calculations to probe the electronic structure and geometries of the ligands and the corresponding metal complexes employed in this study.

2. Experimental

2.1. Materials and Instrumentation

Chlorodiphenyl phosphine, diphenyl phosphite (DPP), diethyl phosphite and CDCl₃ (Sigma-Aldrich) were used as received. Hexyl bromide, magnesium turnings and solvents like diethyl ether, dichloromethane (DCM) (SD Fine chemicals) were distilled prior to use. Th(NO₃)₄·5H₂O (Sigma-Aldrich) was used as received. UO₂(NO₃)₂·6H₂O metal salt and ²³³U tracers were used from laboratory stock and their radiochemical purity was checked prior to use.

¹H, ¹³C and ³¹P NMR spectra were recorded by a BRUKER DMX-400 and ¹H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 298 K, CDCl₃). H₃PO₄ was used as an external standard for ³¹P NMR. FT-IR spectra were recorded on a SHIMADZU Affinity 1 FT-IR spectrometer using KBr pellets. UV-vis absorption spectra were recorded with a UNICAM UV4-100 type double-beam spectrophotometer (ATI UNICAM, Cambridge, UK).

2.2. General procedure for preparation of dihexyl hydrogen phosphine oxide (DHePO)

Dihexyl hydrogen phosphine oxide was synthesized by a modified literature procedure [24] as shown in equation 2. 9.5 g (397.05 mmol) of activated magnesium turnings in 200 mL of dry THF were taken in a two-necked, round-bottomed flask and to it 65.5 g (397.05 mmol) of 1-bromohexane diluted with 50 mL of dry THF were added dropwise with continuous stirring at 65 °C for 6 h. When the reaction mixture turned dark grey, 18 g (132.35 mmol) of diethyl phosphite were added dropwise at ice-cooled temperature and the mixture was allowed to stir at room temperature for 1 h. Excess amount of Grignard reagent was quenched with 1 N HCl solution. The reaction mixture was subjected under reduced pressure to remove the volatile

impurity including the solvent and the residue material was purified by recrystallization using *n*-hexane to give a colorless amorphous solid in 19.6 g (68.8% as isolated yield). M.P: 75-77 °C, IR (cm⁻¹): (P=O) 1159.22. ¹H NMR (δ /ppm, 400 MHz, CDCl₃): 0.89-0.92 (t, *CH*₃CH₂, 6H), 1.81-1.88 (m, P-*CH*₂, 4H), 1.32-1.79 (m, CH₃*CH*₂, 16H), 6.8 (d, ¹J_{P-H}: 448.8 Hz, 1H). ³¹P NMR (δ /ppm, 162 MHz, CDCl₃): 36.14 (d, ¹J_{P-H}: 458.46 Hz). ¹³C NMR (δ /ppm, 100 MHz, CDCl₃): 31.30, 30.43, 28.24 (d), 22.38, 21.74 (d), 13.98.

2.3. Synthesis of actinide complexes

2.3.1. [Th(NO₃)₄(DPhPO)₂] (1). All complexes were synthesized using the following procedure [25, 26]. Solution of DPhPO (0.154 g, 0.7 mmol) in 5 mL of methanol was added dropwise to the stirred solution of Th(NO₃)₄·5H₂O (0.2 g, 0.35 mmol) in 10 mL of methanol. The reaction mixture was allowed to stir overnight and subjected to high vacuum to remove solvent and other volatile impurities. The residue was washed with diethyl ether (2×5 mL) which gave a yellow viscous liquid (0.31 g). The purity and the composition of all complexes were confirmed by analytical and spectroscopic techniques. Yield: 91% (isolated yield), IR (cm⁻¹): 1278.81 (P=O), ³¹P NMR (δ /ppm, 162 MHz, CDCl₃): 30.27 (d, ¹J_{P-H}: 571.62 Hz). ¹H NMR (δ /ppm, 400 MHz, CDCl₃): 7.37-7.44 (m, Ar-*p*, 4H), 7.55-7.60 (m, Ar-*o* and Ar-*m*, 6H), 8.67 (s, P-H, 1H). Anal. Calcd. for C₂₄H₂₂N₄O₁₄P₂Th: C, 32.59; H, 2.51; N, 6.33. Observed: C, 31.39; H, 2.21; N, 6.05.

2.3.2. $[UO_2(NO_3)_2(DPhPO)_2]$ (2). $[UO_2(NO_3)_2 \cdot 6H_2O$ (0.2 g, 0.39 mmol) and DPhPO (0.175 g, 0.79 mmol)], Product: 0.325 g, Yield: 92% (isolated yield), IR (cm⁻¹): 1149.57 (P=O), ³¹P NMR (δ /ppm, 162 MHz, CDCl₃): 25.67 (d, ¹J_{P-H}: 486 Hz). ¹H NMR (δ /ppm, 400 MHz, CDCl₃): δ = 7.54-7.87 (m, Ar, 10H), 9.31 (s, P-H, 1H). Anal. Calcd. for C₂₄H₂₂N₂O₁₀P₂U: C, 36.11; H, 2.78; N, 3.51. Observed; C, 35.27; H, 2.51; N, 3.14.

2.4. Computational methodologies

We applied DFT calculations to study the electronic structure and geometries of diphenyl hydrogen phosphine oxide (DPhPO), dihexyl hydrogen phosphine oxide (DHePO) and diphenyl phosphate (DPP). Geometry optimizations were performed at DFT level employing B3LYP functional [27, 28] in conjunction with def2-TZVP basis set. The B3LYP functional is expected to provide better description for organic molecules [29, 30]. The located stationary points are

characterized as energy minima by evaluating real harmonic vibrational frequencies at the same level. The resolution-of-identity (RI) approximation was applied in conjunction with the appropriate auxiliary basis sets to speed up the computations [31-33]. In order to account for dispersion effects, empirical Grimme-type dispersion corrections were incorporated during this step using the latest atom-pairwise dispersion correction with Becke-Johnson damping (D3BJ) [34, 35]. Increased integration grids (Grid 6 in ORCA convention) and tight SCF convergence criteria were used throughout the calculations. For the calculation of metal complexes, the hybrid density functional PBE0 [36], with 20% HF exchange, was employed and tight SCF convergence criteria was used throughout the calculations. For thorium atom, 60 inner-shell core electrons were replaced by an effective core potential (ECP) generated for the neutral atom using quasi-relativistic methods [37-39] and explicitly treated electrons were described by the standard def2-TZVP basis sets. This basis set combination referred to hereafter as def2-TZVP-ECP was adopted for previous theoretical calculations of actinide metal complexes [40, 41]. All calculations were performed with ORCA version 3.0.3 program package [42].

2.5. Batch studies of uranium and thorium by solvent extraction

Uranium and americium: All extractants were pre-equilibrated with appropriate nitric acid concentration prior to performing the extraction studies. Equal amounts of H-phosphine oxide solutions in xylene (0.01 M for U(VI) and 0.3 M for Am(III)) and appropriate nitric acid were taken in an equilibration tube, spiked with $^{233}U/^{241}Am$ tracer and equilibrated in a constant temperature bath at 303 K for 2 h. After attainment of equilibrium, suitable aliquots from both phases were taken for radiometric assay of actinides. ^{233}U α -activity was obtained from the liquid scintillation counting using dioxane based cocktail and from that the equilibrium concentration of Am(III) in the aqueous and organic phases was computed by measuring the activities of the 60 keVy photons of the respective phases using NaI(TI) counter. The precision in the counting by detectors is ±5%. The distribution ratio (D_M) was calculated as the ratio of concentration of the metal ion in organic phase to that in aqueous phase,

$$\mathbf{D}_{\mathbf{M}} = \frac{[\mathbf{M}]_{\mathrm{org}}}{[\mathbf{M}]_{\mathrm{aq}}} \tag{1}$$

where [M]_{org} and [M]_{aq} are the concentrations of metal ion in organic and aqueous phases, respectively.

Thorium: The extraction of Th(IV) was performed by following the similar experimental procedure mentioned for uranium using 0.01 M solutions of extractant in xylene. Thorium amount was calculated spectrophotometrically using arsenazo-III as the chromogenic agent [43] in the initial and at equilibrium aqueous phase; subsequently the organic samples were estimated by subtracting the equilibrium aqueous concentration from the initial feed concentration. The distribution ratio can be defined as:

$$D_{M} = \frac{[M]_{aq(i)} - [M]_{aq(f)}}{[M]_{aq(f)}}$$

where $[M]_{aq(i)}$ and $[M]_{aq(f)}$ concentration of metal ions before and after contact with organic phase. All experiments were carried out at least in triplicate. Batch sorption studies were performed in nitric acid media ranging from 0.01 M - 6 M.

3. Results and discussion

3.1. Synthesis and characterization of DHePO

The effect on distribution values of some selected actinides like U(VI), Th(IV) and Am(III) by di-*n*-alkyl phosphine oxides and H-phosphonates as a function of alkyl chain length were studied previously [20, 21]. But the effect on distribution values of actinides with the change in substitution from acyclic to cyclic groups in H-phosphine oxides will be interesting to investigate. On that note, we have chosen three different H-phosphine oxides, *viz.* diphenyl hydrogen phosphine oxide (DPhPO), dihexyl hydrogen phosphine oxide (DHePO) and diphenyl hydrogen phosphonate or diphenyl phosphite (DPP), having a different substitution on phosphine oxide moiety. DHePO was prepared by the reported literature (chart 1). Structural confirmation and the purity of DHePO were established by different spectral characterization techniques like FT-IR, ³¹P, ¹H and ¹³C NMR spectroscopy (see Supporting Information for spectral data). DHePO showed strong infrared absorptions at 1159.22 cm⁻¹ for the presence of the phosphoryl group. Both compounds showed a substantial downfield shift in ³¹P NMR chemical shifts (DHePO: $\delta = 36.14$ {d} ppm) compared to the precursor, diethyl phosphite ($\delta = 7.45$ {d} ppm),

confirming the complete formation of the compounds. The structural confirmation was further carried out by ¹H and ¹³C NMR. The -CH₂ groups of alkyl chains from DHePO resonate between $\delta = 1.2$ -1.9 ppm, confirming the presence of alkyl and the aromatic substitutions in the respective compounds.

3.2. Synthesis, characterization and coordination chemistry of metal complexes

To understand the coordination behavior of the DPhPO for actinides solid state complexes of DPhPO with UO₂(NO₃)₂ and Th(NO₃)₄ were synthesized and characterized by various spectroscopic techniques. DPhPO complex with UO2(NO3)2 and Th(NO3)4 was synthesized by taking stoichiometric amounts of the ligand and the corresponding metal salt (2:1 ratio) using methanol as solvent. The volatile compounds including solvent were removed under high vacuum. The final product was washed with 2×5 mL (diethyl ether (3:1)) to remove slight excess of ligand, if any. The obtained product was dried under reduced pressure and characterized by FT-IR, ¹H, ³¹P NMR spectra and elemental analysis. The IR spectra of [UO₂(NO₃)₂(DPhPO)₂] and [Th(NO₃)₄(DPhPO)₂] show that there is a large shift in P=O stretching towards near- and far-IR regions, respectively, in comparison with the free ligand, indicating coordination to the metal center through the phosphoryl oxygen (figure 1). The proton coupled ³¹P NMR spectra of complexes 1 and 2 were significantly deshielded with respect to the free ligands, which further confirmed the complete formation of complexes. Ligand shows a doublet at 21.65 ppm but the corresponding Th(NO₃)₄ and UO₂(NO₃)₂ complexes resonate at 30.27 {d} ppm and 25.67 {d} ppm, respectively (figure 2). The purity of the synthesized complexes was also confirmed by the elemental analysis. This further confirms the metal-to-ligand ratio as 1:2 in uranium and thorium complexes (Supporting Information, table S1).

3.3. Distribution studies

Substitutions on the phosphine oxide moiety play a very important role in distribution of actinides. The extraction efficiency of a ligand is dependent on the nature of substituents, which also greatly influence the performance of the extractants. Previously, authors have studied the effect of alkyl chain length in distribution values of actinides in various di-*n*-alkyl phosphine oxides or H-phosphine oxides. Subsequently, we wanted to study the effect of aromatic substitutions on H-phosphine oxides. In that connection, we have planned to study and compare

the extraction behavior of three different H-phosphine oxides, *viz*. DPhPO, DHePO and DPP with some selected actinides, like U(VI), Th(IV) and Am(III).

3.3.1. Extraction mechanism in H-phosphine oxides. Phosphine oxide-based neutral ligands extract the actinides by solvation mechanism which is through phosphoryl group coordination. The tautomeric form diesters of H-phosphonic acid is well known in literature [44]. Equation 3 shows the tautomeric form of the H-phosphine oxide where phosphorus atom is trivalent (II) in nature and exists in equilibrium with its tetracoordinate pentavalent form of phosphorus (I).



The expression for cation-exchange reaction is shown in equation 3.

$$nR_2P-OH_{org} + M_{aq}^{n+} \longrightarrow R_2P-OM_{org} + nH_{aq}^{+}$$
 (4)

where R_2P -OH is the trivalent form II (equation 3) in which H-phosphine oxide exist in the OH form and where in H⁺ is exchangeable there by making it acidic extractant in nature. Giving the equilibrium constant K_{eq} for the reaction

 $K_{eq} = [R_2 P-OM]_{org} [H^+]^n / [R_2 P-OH][M]_{aq}^{n+}$ (5)

Rearranging equation 5.

$$D = K_{eq} [R_2 P-OH]/[H^+]^n$$
(6)

The above equation shows that distribution ratio D is inversely proportional to [H⁺] concentration.

3.3.2. Extraction of actinides. $D_{U(VI)}$ values for 0.01 M DPhPO, DPP and DHePO in xylene as a function of nitric acid are given in figure 3 where it was observed that at lower acidities the $D_{U(VI)}$ values of H-phosphine oxides are higher and a prominent decrease in D value was

followed with increasing nitric acid concentration *i.e.* 0.01 to 0.1 M. The *D* values decrease as the aqueous phase acidity was enhanced to 2 M nitric acid and a slight increase at 4 M. H-phosphine oxides behave like acidic extractants. Tautomeric equilibrium occurs between P=O and P-OH (equation 3) at lower acidities and hence the extraction of the metals is through cation-exchange mechanism. With the increase of the acidity, the distribution ratios fall gradually. The equilibrium between P=O and P-OH drives towards the left (equation 3) at higher nitric acid concentration, reducing the extraction of metal. At higher acidity the extraction is through the P=O group which is through solvation mechanism (equation 7). At higher concentration of nitric acid, the uranyl ion forms a series of complex species: $[UO_2NO_3]^+$, $[UO_2(NO_3)_2]$, $[UO_2(NO_3)_3]^-$. The extraction behavior of H-phosphine oxides is similar to neutral extractants at higher nitric acid concentration, a copious amount of the anionic nitrate complex $[UO_2(NO_3)_3]^-$ is formed which is not extracted by H-phosphine oxides and hence there is a reduction in *D* values.

$$UO_2^{++}(aq) + 2NO_3^{-}(aq) + 2H-PO_{(org)} \longrightarrow UO_2(NO_3)_2 \cdot 2H-PO_{(org)}$$
 (7)

Figure 4 gives the variation of D values for Th(IV) using 0.01 M solutions of H-phosphine oxides in xylene (diluent) where Th(IV) shows a similar trend as that of U(VI) which confirms the dual nature of extraction of H-phosphine oxides, *i.e.* at lower acidity it behaves as an acidic extractant while at higher acidity as a neutral extractant.

The lower distribution ratios observed for U(VI) with DPhPO, DPP and DHePO compared to phosphate system are due to the use of lower extractant concentration employed in the present study, 0.01 M extractant/xylene, whereas in the case of phosphate-based systems *e.g.* TBP, typically 1.1 M solutions are used, where distribution ratio as high as 28 [19] was observed at 4 M HNO₃ medium. The extractants (DPhPO, DPP, DHePO) are stronger compared to phosphate systems and hence the amount of these molecules used is in the range of 0.01 M in order to get appreciable amount of metal in the aqueous phase which can be analyzed.

Distribution of americium by 0.3 M solutions in xylene of H-phosphine oxides is given in figure 5. The distribution trend of Am(III) is also similar to Th(IV) and U(VI) distribution for all three ligands and suggests that the mechanism of extraction is identical in both. The higher distribution ratio for Am(III) at lower acidity compared to U(VI) and Th(VI) is due to the use of

higher concentration of the extractant. The higher concentration of the extractant was employed to obtain sufficient activity of americium in the organic phase as the distribution ratio is expected to be lower in this system. Distributions of Am(III) at higher acidities are very low as P=O group is not strong enough to extract Am(III).

Among these three H-phosphine oxides, DPhPO shows a better extraction towards the actinides in comparison with DPP and DHePO. The extraction behavior of these H-phosphine oxides towards U(VI) and Th(IV) is in the following order: DPhPO > DHePO > DPP. This phosphoryl group in phosphine oxide is more basic than phosphonate and hence in H-phosphine oxides have higher distribution ratios than DPP. This is reflected in the higher D where the phosphoryl group of the extractant participates through solvation in the higher nitric acid region. Among the H-phosphine oxides, the substitution of phenyl groups around phosphoryl molecule show higher distribution ratios than linear hexyl groups. One possible reason for higher D in the phenyl system is the compact nature of the molecule, thereby making the metal complex less bulky and hence requiring less energy to transfer the complex from the aqueous phase to organic phase as compared to linear alkyl hexyl group. The explanation of the reason for the differences in the extraction behavior at lower acidity by cation-exchange mechanism is not clear. The cation-exchange mechanism depends on the number of hydrogen atoms replaced for each metal ion depending on the charge of the metal. In the case of uranium extraction, each uranyl ion requires two molecules of the extractants to satisfy the charge and in the case of thorium and americium the requirement is four and three molecule of ligands, respectively. The spatial requirement dictates the ease of formation of the metal complex. The trend observed is not in line with the number of molecule required to satisfy the charge of the metal. If we take DPhPO at 0.01 M nitric acid concentration, the expected trend would have been U>Am>Th, whereas the observed trend is Am>U>Th. So there are more than one factor that is operational at lower acidity and thereby deciding the value of D.

3.4. DFT Studies

In an attempt to understand the electronic structure and geometries of the ligands, a systematic geometry optimization procedure was adopted. Ten starting geometric configurations were considered for each ligand. Each of these structures was optimized at B3LYP/def2-TZVP level and the energetically lowest-lying conformer was considered for further studies. These stationary

points were characterized as energy minima by evaluating real harmonic vibrational frequencies at the same level. The lowest-energy conformer for DHePO is already reported [21]. The energetically lowest-lying conformers for DPhPO, DHePO and DPP are illustrated in figure 6. In all three structures, the phosphorus atom is positively charged with considerable amount of electron density localized on the phosphoryl oxygen atom. Mulliken charges for oxygen and phosphorus atoms are -0.55 e and 0.59 e for DHePO, -0.55 e and 0.58 e for DPhPO, and -0.49 e and 0.72 e for DPP, respectively. The comparatively large positive charge on phosphorus atom in DPP is due to the presence of two additional oxygen atoms that are directly coordinated to phosphorus atom.

After establishing the geometries of the ligands, we turned our interest towards the corresponding metal complexes with thorium atom. For the calculations, we have considered 1:2 stoichiometry as the same stoichiometric amounts were considered for the synthesis of corresponding metal complexes. Ten starting geometric configurations were generated for each metal complex by distributing four nitrate groups and two ligands around thorium atom. These starting structures were subjected to geometry optimization at PBE0/def2-TZVP-ECP level. For Th(NO₃)₄·2DHePO, the lowest-energy structure is reported already and therefore is taken from reference 21. The optimized geometries of the three thorium metal complexes are shown in figure 7. The coordination geometry of all three metal complexes is similar. In all complexes, the ligands are oriented in the opposite phases of the metal nitrate unit and all the nitrate groups are bidentate in nature.

4. Conclusion

Extraction behavior of U(VI), Th(IV) and Am(III) was studied by three homologues of H-phosphine oxide having three different substituents around the phosphoryl group. Studies reveal that DPhPO shows better extractability than DHePO and DPP for these three actinides. Distribution values for actinides of these H-phosphine oxides are in the following order: DPhPO > DHePO > DPP. These extractants also showed a dual nature of extraction behavior, *i.e.* at lower acidity they behave as acidic extractants and extract the metal ions through cationexchange mechanism, while at higher acidity the mode of extraction is through solvation mechanism. Based on the DFT calculations we were able to establish lowest energy structures for DHePO, DPhPO, DPP and their corresponding metal complexes, Th(NO₃)₄·2DHePO, Th(NO₃)₄·2DPhPO and Th(NO₃)₄·2DPP. The Mullikan population analysis shows considerable amount of positive charge on phosphorus atom and charge concentration on phosphoryl oxygen.

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Chart 1. Ligands used in present study a. Diphenyl Phosphite (DPP), b. Diphenyl hydrogen phosphine oxide (DPhPO), c. Dihexyl hydrogen phosphine oxide (DHePO).

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Scheme 3. Formation of uranium and thorium complex with DPhPO.

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Figure 1. Overlay of FT-IR spectra of free DPhPO and its U(VI) and Th(IV) complexes.



Figure 2. Overlay of ³¹P NMR spectra of free DPhPO and its U(VI) and Th(IV) complexes.





Figure 3. Variation of $D_{U(VI)}$ with equilibrium aqueous phase nitric acid concentration for DPhPO, DPP and DHePO at 303 K.



Figure 4. Variation of $D_{\text{Th}(IV)}$ with equilibrium aqueous phase nitric acid concentration for DPhPO, DPP and DHePO at 303 K.



Figure 5. Variation of $D_{Am(III)}$ with equilibrium aqueous phase nitric acid concentration for DPhPO, DPP and DHePO at 303 K.



Figure 6. Optimized geometries of the ligands (a) DHePO (b) DPhPO and (c) DPP at B3LYP/def2-TZVP level. (Color code: orange ball is phosphorus, red balls are oxygen, grey balls are carbon and white balls are hydrogen atoms).



Figure 7. Optimized geometries of (a) $Th(NO_3)_4$ ·2DHePO (b) $Th(NO_3)_4$ ·2DPhPO and (c) $Th(NO_3)_4$ ·2DPP at PBE0/def2-TZVP-ECP level. Bottom: color code for the elements used in this figure.



