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Experimental and Theoretical Studies on Extraction behavior of Di-*n*-Alkyl Phosphine Oxides towards Actinides

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Abstract

Di-*n*-alkyl phosphine oxides (DAPOs) with different alkyl chain length viz. C₆, C₇, C₈ and C₁₀ and their corresponding Th(IV) and La(III) complexes were synthesized and characterized using FT-IR, ¹H, ³¹P{¹H}, and ¹³C NMR. The extraction behavior of U(VI) and Am(III) with DAPOs was investigated and it largely depends on nitric acid concentration. These DAPOs showed highest distribution coefficients with U(VI) among U(VI) and Am(III). The D_{U(VI)} values of DAPOs are higher at lower acidities i.e. 0.1M nitric acid concentration. Among four tested DAPOs for the extraction of Uranium with a molar concentration of 0.025 M, DDPO that bearing longest alkyl chains showed highest D_{U(VI)} values 84.6 and their distribution coefficient increased with increase in alkyl chain length in the tested DAPOs. Here we have proposed a mechanism for the extraction of actinides using di-*n*-alkyl phosphine oxides, which was further supported by theoretical calculations. At lower acidity, DAPO behaves like an acidic extractant and extracts the metal ion via cation exchange mechanism. On the contrary, at higher acidity, the metal ions are extracted via solvation mechanism through phosphoryl group coordination. Density functional theory (DFT) calculations support a bimolecular mechanism for the tautomerism reaction in DHePO (di-*n*-hexyl phosphine oxide) ligand, where both pentavalent (tetracoordinate) and trivalent phosphorus are in equilibrium. An activation barrier of ~27.3 kcal/mol is estimated with respect to the reactant complex at B3LYP/def2-TZVP level. The length of the alkyl chain in di-*n*-alkyl phosphine oxides (DAPO) also plays a significant role in actinide extraction at lower acidity.

Keywords:

Di-*n*-alkyl phosphine oxide, Uranium, Thorium, DFT, distribution coefficient, bimolecular mechanism

1. Introduction

The selective separation of actinides from other metal ions plays an important role in various stages of nuclear fuel cycle.¹ In general, the separation of actinides has been carried out using precipitation, ion exchange and liquid-liquid extraction (solvent extraction) processes.²⁻⁴ One of the most convenient modes of separation on a bulk scale for actinides is using solvent extraction method, which uses a specific ligand/extractant in the organic phase with a suitable diluent. Most popular processes used throughout the world for separation of actinides are PUREX⁵, TRUEX⁶ and DIAMEX.^{7,8} In the nuclear reprocessing industry, tri-*n*-butyl phosphate (TBP) has been used for the past six decades for the recovery of Pu from irradiated spent fuel by PUREX process using TBP⁹ as the extractant. TBP is widely used since it is a mild extractant and can extract uranium and plutonium at higher acidity and the metal can be stripped at lower acidity. In the past few years, various types of ligands bearing S, O and N-donor atoms have been developed for the separation of actinides from lanthanides.¹⁰⁻¹² Among the ligands reported, mixed amides, phosphonate and phosphonothioate ligands are known for the extraction of actinides and lanthanides.¹³ Actinides are hard in nature and prefer ligands with oxygen for coordination and complexation.¹⁴ Organophosphorus esters are the preferred class of compounds for the extraction and separation of actinides. The extraction of actinides is due to the basicity of phosphoryl oxygen, which exhibits higher coordinating ability with the actinides.¹⁵ Thus the extraction ability of the organophosphorus extractant depends on the basicity of the phosphoryl oxygen and nature of the substituents attached to the phosphorus atom. This basic nature of phosphoryl group can be enhanced by replacing the C-O-P group in the extractant by a C-P group. The basicity on the phosphoryl oxygen in the neutral organophosphorus extractant series increases in the order: phosphates < phosphonates < phosphinates < phosphine oxides.^{16,17} The higher homologues of

TBP were synthesized and the extraction behavior of actinides was reported.¹⁸ Families of dialkylalkylphosphonates and H-phosphonates were also synthesized and studied in one of our laboratories.¹⁹⁻²¹ As phosphine oxides are strong ligands among the other organophosphorus extractants, stripping of the metal ions from the phosphine oxide complexes (organic phase) requires an external complexing agent. There is a need for the specific extractants for the actinide extraction and separation. In this regard, it is proposed to investigate the extraction behavior of di-*n*-alkyl phosphine oxides (DAPOs) or H-phosphine oxides towards actinides, which were not explored in detail.

The present study involves synthesis, characterization, complexation and extraction behavior of di-*n*-alkyl phosphine oxides (DAPOs) with some actinides. The electronic structure and geometries of these ligands are further explored using density functional theory (DFT) calculations.

2. Experimental

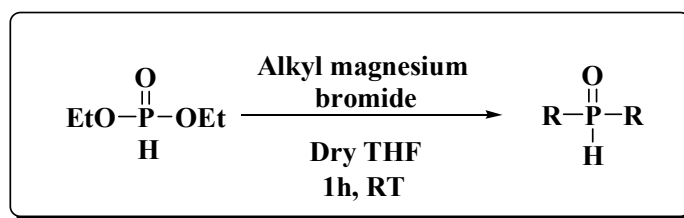
2.1. Materials and Instrumentation

Diethyl phosphite and CDCl_3 (Sigma-Aldrich) were used as received. The solvents used were 1-bromohexane, 1-bromoheptane, 1-bromooctane, 1-bromodecane, tetrahydrofuran (THF), dichloromethane (DCM), chloroform and hexane (SD Fine chemicals). Solvents were distilled and dried over Na/benzophenone prior to usage. Magnesium turnings were activated by washing with dilute HCl and dried at 110°C overnight before use. Hydrated metal salts $[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}]$ and $[\text{LaCl}_3 \cdot 7\text{H}_2\text{O}]$ (Aldrich and Loba) were used as received. The actinides,

^{241}Am and ^{233}U tracers were used from laboratory stock solutions and their radiochemical purity was checked prior to their use.

^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded by BRUKER DMX-400 and all ^1H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 25°C , CDCl_3). H_3PO_4 was used as an external standard for $^{31}\text{P}\{^1\text{H}\}$ -NMR. FT-IR spectra were recorded on SHIMADZU Affinity1 FT-IR spectrometer using KBr pellet. UV-vis absorption spectra were recorded with a UNICAM UV4-100 type double-beam spectrophotometer (ATI UNICAM, Cambridge, UK).

2.2. General procedure for the preparation of di-*n*-alkylphosphineoxide (DAPO)



Eq 1. Synthesis of di-*n*-alkyl phosphine oxides

All di-*n*-alkylphosphineoxides were synthesized by a modified literature procedure as shown in Eq.1.²² A general procedure for synthesis of di-*n*-octyl phosphineoxide (DOPO) is as follows: 7.8 g (326.09mmol) of activated magnesium turnings in 150 mL of dry THF was taken in a round bottomed flask and to it 62.9g (326.09mmol) of 1-bromooctane (in THF) was added drop-wise with continuous stirring at 60°C for 5 h. To this, 15g (108.69mmol) diethyl phosphite was added drop-wise at 0°C and allowed to stir at room temperature for 1h. The excess Grignard reagent was quenched with 1N HCl solution and the compound was extracted in dichloromethane (3 x 25 mL). The volatile impurity including the solvent was removed under reduced pressure and the

residue material was purified by recrystallization using *n*-hexane to give a colorless solid in 25.65 g (86% as isolated yield). A similar procedure was used for the preparation of di-*n*-hexylphosphine oxide (DHePO), di-*n*-heptylphosphine oxide (DHpPO), and di-*n*-decylphosphine oxide (DDPO) (for spectral details, please see SI).

2.3. Synthesis of various metal complexes

2.3.1. [Th(NO₃)₄(DHePO)₂] (1): The following procedure was used for the preparation of [Th(NO₃)₄(DHePO)₂] as per the literature reports.^{23,24} A finely powdered solid of Th(NO₃)₄·5H₂O (0.2 g, 0.35 mmol) was added to a stirred solution of DHePO (0.153 g, 0.7 mmol) in DCM mixture and was stirred for 24 h to get yellow colored solution. The solvent was removed completely under reduced pressure and the residue was washed with diethyl ether (2x5 mL) which gave a viscous yellow color liquid (0.29 g). The purity and the composition of all the complexes were confirmed by analytical and spectroscopic techniques. Yield: 83%, IR (cm⁻¹): (P=O) 1072.42, ³¹P{¹H}-NMR (̈, 162 MHz, CDCl₃): 47.59 (d, ¹J_{P-H}: 484.38 Hz). ¹H-NMR (̈, 400 MHz, CDCl₃): 0.85-0.89 (t, CH₃CH₂, 6 H), 1.96 (m, P-CH₂, 4 H), 1.27-1.88 (m, CH₃CH₂, 16 H), 6.91 (d, ¹J_{P-H}: 484 Hz, 1 H). A similar procedure was followed for the synthesis of other metal complexes (for spectral details, please see SI).

2.4. Batch studies of uranium and americium by solvent extraction

Uranium: The distribution studies of uranium with extractants were carried out as follows: initially the ligand of interest was pre-equilibrated with appropriate nitric acid concentration; subsequently, 2 mL of the extractant (0.025M) in xylene and 2 mL of nitric acid were taken in an equilibration tube and was spiked with ²³³U tracer. The samples were equilibrated by stirring in a constant temperature bath at 30°C for 90 min. The equilibrium concentrations of U(VI) in both

the phases were measured by sampling a known quantity of the aqueous and organic phases and the ^{233}U α -activity was obtained from the liquid scintillation counting using dioxane based cocktail.

Americium: After pre-equilibration with required acid, 2 mL of the extractant (0.1M and 0.3M) in xylene was further equilibrated by stirring with 2 mL of nitric acid, spiked with ^{241}Am tracer in a constant temperature bath at 30°C for 90 min. The equilibrium concentrations of Am (III) in the aqueous and organic phases were determined by measuring the activities of the 60 keV γ photons of the respective phases using NaI (TI) counter. The experiment was carried out at various nitric acid concentrations.

3. Computational methods

Density functional theory (DFT) was applied to study the electronic structure and geometries of di-*n*-alkyl phosphine oxides (DAPOs). All geometry optimizations were performed at density functional theory (DFT) level employing B3LYP functional²⁵ in conjunction with triple- ζ def2-TZVP basis sets.²⁶ The stationary points were characterized as minima by performing vibrational frequency calculations at the same level. The resolution-of-identity (RI) approximation was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations. Empirical Grimme-type dispersion corrections were incorporated during this step using the latest atom-pairwise dispersion correction with Becke-Johnson damping (D3BJ).²⁷ Increased integration grids (Grid6 in ORCA convention) and tight SCF convergence criteria were used throughout the calculations. For the calculation of metal complexes (Th), the hybrid density functional PBE0,²⁸ with 25% HF exchange, was employed. In the case of Thorium, 60 inner-shell core electrons were replaced by an effective core potential (ECP) generated for the neutral

atom using quasi-relativistic methods²⁹ and the explicitly treated electrons were described by the standard def2-TZVP basis sets, denoted hereafter as def2-TZVP-ECP. All quantum chemical calculations were performed with ORCA version 3.0.3 program package.³⁰

4. Results and discussion

4.1. Synthesis and characterization of DAPOs:

Four different di-*n*-alkyl phosphineoxides, namely, di-*n*-hexyl phosphine oxide (DHePO), di-*n*-heptyl phosphine oxide (DHpPO), di-*n*-octyl phosphine oxide (DOPO) and di-*n*-decyl phosphine oxide (DDPO) were prepared from diethyl phosphite (Chart 1). The purity and structural confirmation of all phosphineoxides were established by different spectroscopic techniques (see supporting information for spectra data). It is also significant to note that all the DAPOs showed substantial downfield shift in ³¹P{¹H}-NMR chemical shifts i.e. DHePO = δ 36.14 {d}, DHpPO = δ 35.69 {d}, DOPO = δ 35.56 {d}, and DDPO = δ 35.56 {d} compared to the precursor, diethyl phosphite which resonates at δ 7.45 {d}. The existence of P-H group in all the DAPOs is realized by the presence of a doublet in ³¹P NMR with coupling constants around 450 Hz. The structural confirmation was further carried out by ¹H-NMR and mass spectral analysis. The -CH₂ groups of alkyl chains from di-*n*-alkyl phosphine oxide resonated between δ 1.2-1.9 and the mass spectra of all the ligands matches well with the calculated masses.

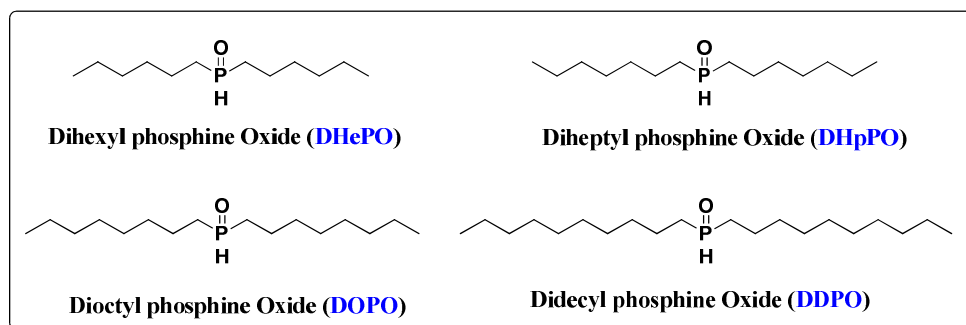
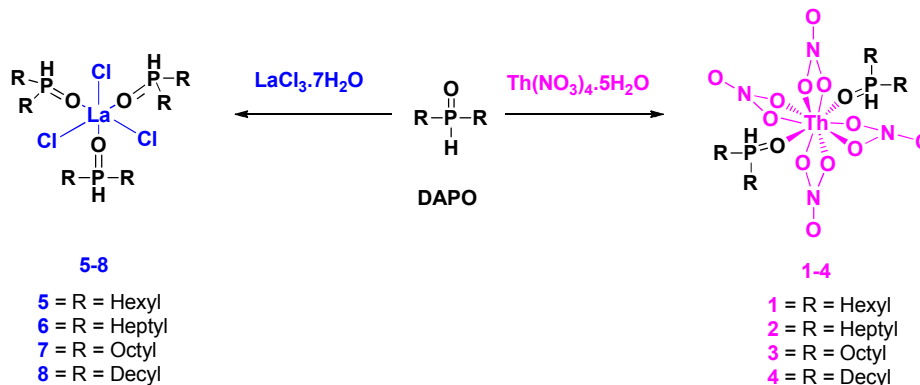


Chart 1. Various di-*n*-alkylphosphineoxides considered in the present study

4.2. Synthesis, characterization and coordination chemistry of metal complexes:



Scheme 1. Schematic representation of the formation of metal complexes with various ligands

The phosphine oxide ligands form complexes with lanthanides and actinides through the P=O group coordination. The complexes of di-*n*-alkylphosphineoxides with $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**1-4**) and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (**5-8**) in dichloromethane (Scheme 1) were obtained in good yields. In comparison with free ligands, the characteristic P=O stretching (in IR spectra) of complexes (both thorium (**1-4**) and lanthanum (**5-8**)) showed momentous shift towards near IR region indicating the coordination to the metal centre through the phosphoryl oxygen (Figure 1). It is noteworthy to mention that the shift of P=O stretching frequency is more prominent in thorium complexes compared to lanthanum complexes.

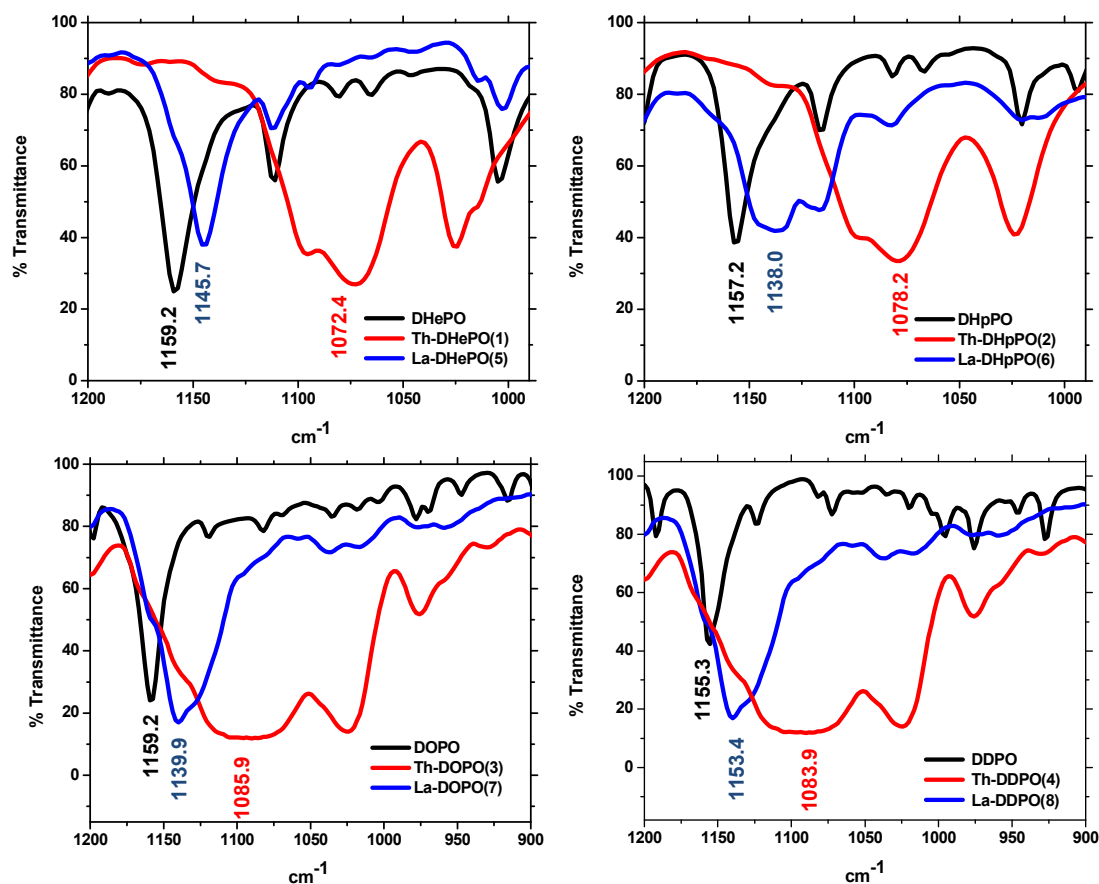


Figure 1. Overlay of FT-IR spectra of free ligands and their La(III) and Th(IV) complexes

As shown in Figure 2, the proton coupled ^{31}P -NMR spectra of complexes **1-8** were significantly deshielded with respect to the free ligands, which further confirmed the formation of complexes. For example, the free DOPO ligand shows a doublet at 35.56 ppm but the corresponding Th(IV) and La(III) complexes give two signals at 49.73 ppm and 37.6 ppm, respectively. In case of ^1H -NMR spectra, a significant downfield shift was observed for P- CH_2 group in all the metal complexes derived from the ligands. For example, the methylene protons of P- CH_2 of DHePO resonates at 1.88 ppm and that of Th(IV) complex (**2**) resonated at 1.96 ppm.

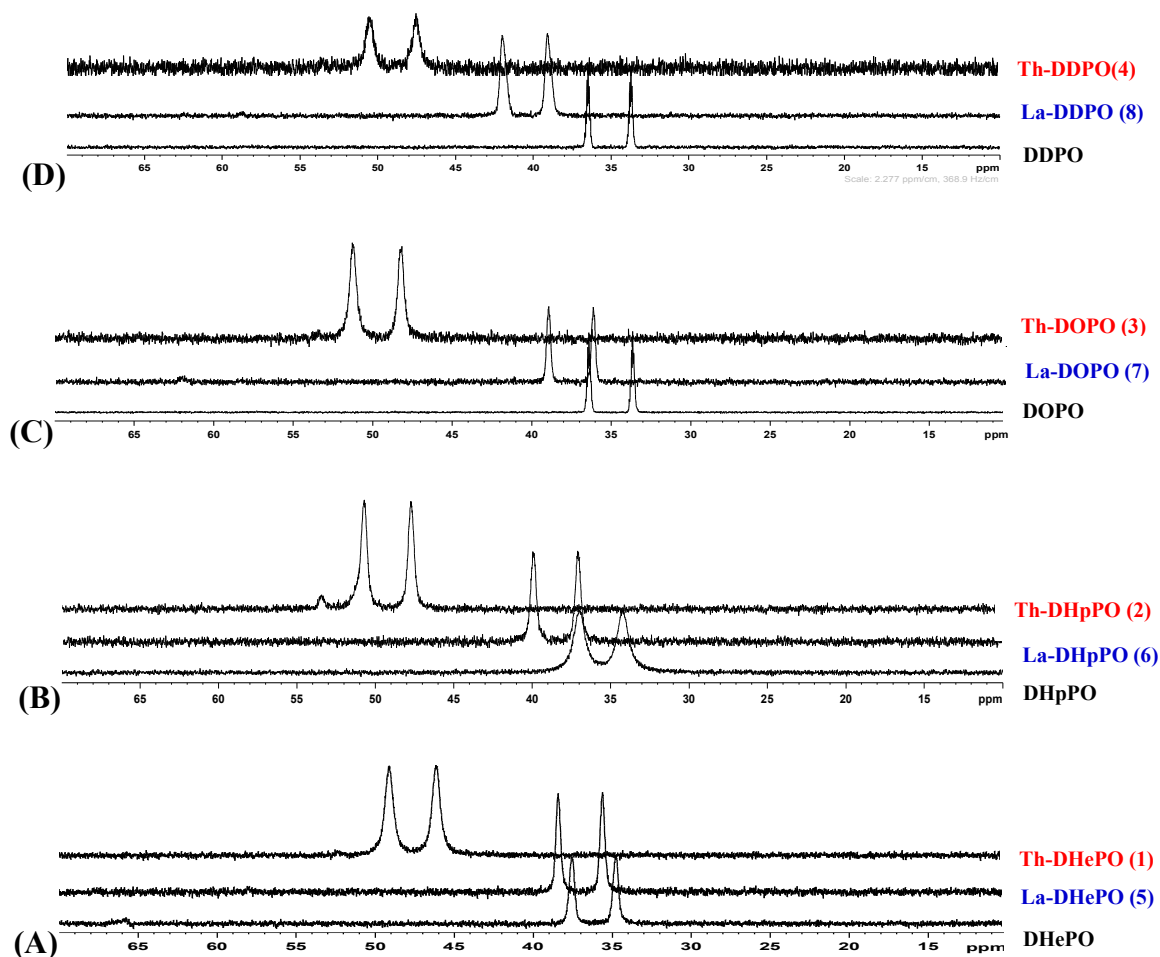
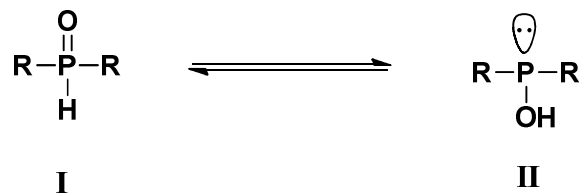


Figure 2. Overlay of ^{31}P NMR spectra of free ligands and their La(III) and Th(IV) complexes

4.3. Distribution studies

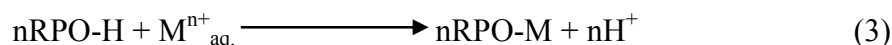
Generally the phosphine oxide based ligands extract actinides and lanthanides by solvation mechanism.¹¹ It is known that the diesters of H-phosphonic acid exist primarily in tautomeric form^{31,32} (Eq 2) in which the phosphorus atom is trivalent (**II**) and exists in equilibrium with its tetracoordinate pentavalent form of phosphorus(**I**).



Eq 2. Tautomeric equilibrium in H-phosphine oxide derivatives

In this connection, we have carried out the extraction studies of U(VI) and Am(III) with four different di-*n*-alkyl phosphine oxides (DAPO) to understand the extraction behavior. From our results, we are proposing the following mechanism for the extraction of actinides using di-*n*-alkyl phosphine oxides.

The cation exchange involves the following reaction:



Where RPOH is in form **II** (Eq 2), in which DAPO exists in the OH form and this makes H exchangeable similar to acidic extractants.

The equilibrium constant K_{eq} , for the reaction is given by

$$K_{\text{eq}} = [\text{RPO-M}]^n_{\text{org}} [\text{H}^+]^n / [\text{RPO-H}]^n [\text{M}]^{n+}_{\text{aq}} \quad (4)$$

Rearranging equation 4,

$$D = K_{\text{eq}} [\text{RPOH}]^n / [\text{H}^+]^n \quad (5)$$

From this equation it can be observed that distribution coefficient “D” is inversely proportional to $[\text{H}^+]$, when the extraction takes place by cation exchange mechanism as observed in acidic extractants.

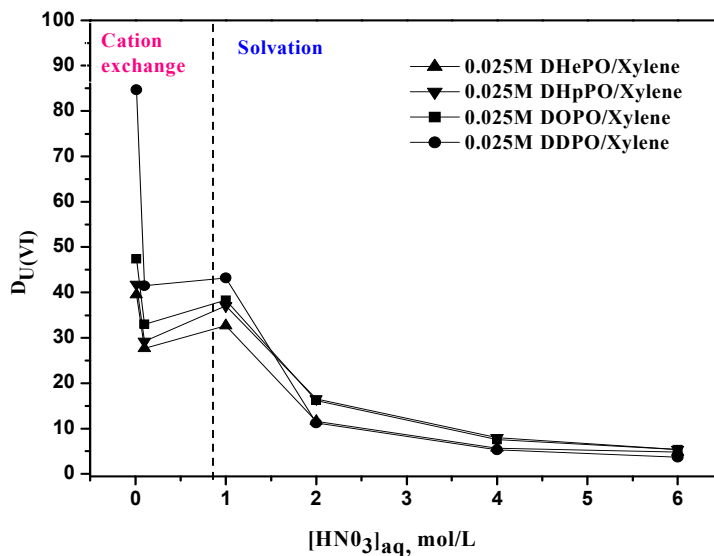


Figure 3. Variation of $D_{U(VI)}$ as a function of nitric acid concentration for DAPOs at 30°C

Figure 3 gives the variation of distribution coefficients of uranium as a function of nitric acid concentration for 0.025M DAPOs in xylene. The $D_{U(VI)}$ values of DAPOs are higher at lower acidities followed by a decrease with increasing nitric acid concentration i.e. 0.01 to 0.1M. The D values increase with nitric acid concentration from 0.1M to 1M. This was followed by a decrease in D values as the acidity of the aqueous phase was enhanced to 6M nitric acid concentration. These extractants behave like acidic extractants at lower acidities because of the tautomeric equilibrium between P=O and P-OH (Eq 2). The D values fall down as the nitric acid concentration is increased. At higher nitric acid concentration, the acid drives the equilibrium towards the left reducing the extraction of metal. The extraction at 1M nitric acid is by direct coordination of the phosphoryl group present in the molecule and proceeds via the solvation mechanism. In all the cases of U(VI) extraction by DAPO systems, maximum D at higher acidity is seen around 1M, with a subsequent fall in the extraction behavior. As the concentration of

nitric acid is further increased, the uranyl ion forms a series of complex species: $[\text{UO}_2\text{NO}_3]^+$, $[\text{UO}_2(\text{NO}_3)_2]$, $[\text{UO}_2(\text{NO}_3)_3]^-$. DAPO's behave like neutral extractants at higher acidity and hence extracts neutral species. When the concentration of nitric acid is $>4\text{M}$, a significant amount of the anionic nitrate complex, $[\text{UO}_2(\text{NO}_3)_3]^-$ is formed. Since the species are charged, they are not extracted by DAPOs and hence there is a fall in D values at higher nitric acid concentrations. DDPO shows higher extraction at lower acidity in comparison with other extractants.

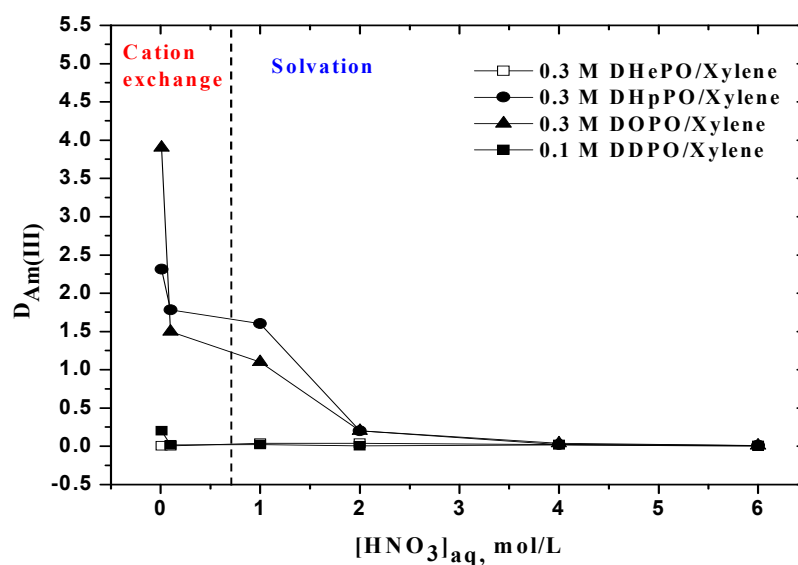


Figure 4. Variation of $D_{\text{Am(III)}}$ as a function of nitric acid concentration for DAPOs at 30°C

Figure 4 gives the variation of distribution ratios of Am(III) by 0.3 M DAPO/xylene except for DDPO, which was at 0.1M concentration (303 K). The reason for the usage of 0.1M concentration of DDPO is because of its limited solubility in xylene. The D values are maximum at 0.01M HNO_3 concentration followed by a gradual decrease with the increase in nitric acid concentration. This clearly suggests that the mechanism of extraction of Am(III) at lower acidities is through P-OH group. At higher acidities the extraction is by solvation through P=O

group. The P=O group is not strong enough to extract Am(III) which requires ligands like octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) or *N,N,N',N'* tetraoctyldiglycolamide (TODGA).⁴ The extraction values of Am(III) by DAPOs suggest that these ligands cannot be used for practical application in solvent extraction mode. Recently the use of the more unusual hexavalent oxidation state of americium has been receiving increased attention for the purpose of developing an efficient Am/Cm or Am/Ln separation system. Martin *et al.*³³ demonstrated the feasibility of performing this separation using 30% TBP in *n*-dodecane. In this regard, the authors tried dibutylbutylphosphonate (DBBP)³⁴ for higher D values for Am(VI). They oxidized Am(III) to Am(VI) by sodium bismuthate and studied the extraction with 0.1 M DBBP/*n*-DD (dodecane) from 0.1M to 6M nitric acid concentration. DAPOs can be used in a similar mode and hence can have potential application after conversion of Am(III) to Am(VI).

4.4. Density Function Theory Studies

In order to understand the electronic structure of the ligands, a systematic geometry optimization procedure was adopted. Eleven starting geometric configurations were generated for each ligand by C-C single bond rotation and the resulting structures were subjected to geometry optimization at B3LYP/def2-TZVP level. For each ligand, we were able to identify a set of energetically lower-lying conformers within 5 kcal/mol energy window. This suggests that the system is in conformational equilibrium, as C-C bond rotation is an energetically favorable process. The lowest energy conformers for DHePO, DHpPO, DOPO, and DDPO are given as Figure 5a, 5b, 5c and 5d, respectively. The P=O bond length (~ 1.48 Å) and IR stretching frequencies (~ 1242 cm⁻¹) are almost identical for all the four ligands (cf. Table 1). The Löwdin population analysis

suggests a partial positive charge on phosphorus ($\sim 0.50 e$) and negative charge on oxygen ($\sim 0.30 e$) atoms. The Mayer bond order analysis predicted single bond character for C-P and P-H bonds while the large bond order value 1.9 suggested a double bond character for the P=O bond. The highest occupied molecular orbital (HOMO) shows similar shape for all ligands (cf. supporting information Figure S41 and Figure S42) and therefore suggest similar coordination behavior when complexed with metal atoms. The electronic similarity of all four metal complexes correlates well with their similarity in experimentally observed extraction behavior.

Table 1. Calculated Löwdin charges, selected Mayer bond orders and calculated P=O stretching frequencies for DHePO, DHpPO, DOPO, and DDPO at B3LYP/def2-TZVP level.

Molecule	Selected Bonds	Mayer Bond Orders	Atoms	Löwdin Charges	P=O bond length in angstrom units and ν (P=O) in cm^{-1} is given in parenthesis
DHePO	C1-P	0.9217	P	0.50	1.48 (1247)
	C2-P	0.9274			
	O-P	1.9495	O	-0.30	
	H-P	0.8785			
DHpPO	C1-P	0.9332	P	0.50	1.48 (1242)
	C2-P	0.9350			
	O-P	1.9458	O	-0.30	
	H-P	0.8795			
DOPO	C1-P	0.9205	P	0.50	1.48 (1240)
	C2-P	0.9326			
	O-P	1.9743	O	-0.30	
	H-P	0.8816			
DDPO	C1-P	0.9319	P	0.50	1.48 (1242)
	C2-P	0.9219			
	O-P	1.9323	O	-0.30	
	H-P	0.8780			

After establishing the electronic similarity of ligands, we have applied DFT calculations to understand the coordination geometry of metal complexes formed during extraction. In the

present study we have considered DHePO-Thorium complex. For the metal complex, seven starting geometric configurations were considered by distributing two DHePO ligands and four nitrate groups around the metal atom. These starting configurations were subsequently subjected to geometry optimization at PBE0/def2-TZVP-ECP level. The lowest energy structure for $\text{Th}(\text{NO}_3)_4 \cdot 2\text{DHePO}$ is illustrated in Figure 6. The two DHePO ligands are in the *trans*-orientation and the bidentate nitrate groups are unsymmetrically distributed around the metal atom in the equatorial plane (cf. Figure 6).

Our experimental results also indicate that under low acidic conditions, the extraction is governed by ion exchange mechanism because of the tautomeric equilibrium²¹ between P=O and P-OH (Eq 2). In this regard, we have also investigated the mechanism of *tautomerism* (Eq 2) at density functional theory level, by considering DHePO ligand as an example. All possible mechanistic pathways were explored during this step. Previous calculations on “hydrophosphoryl (HPC) compounds” indicated that both unimolecular and bimolecular mechanisms are possible, with the latter being energetically favorable.³⁵ The results of our calculations also support the fact that the unimolecular mechanism proceeds via a high free energy barrier (~60.2 kcal/mol). The calculated free energy barrier for the bimolecular mechanism is ~27.3 kcal/mol and can be regarded as a possible mechanism for the *tautomerism*. The geometries of the transition state structures for both unimolecular and bimolecular mechanisms are represented in Figure 7.

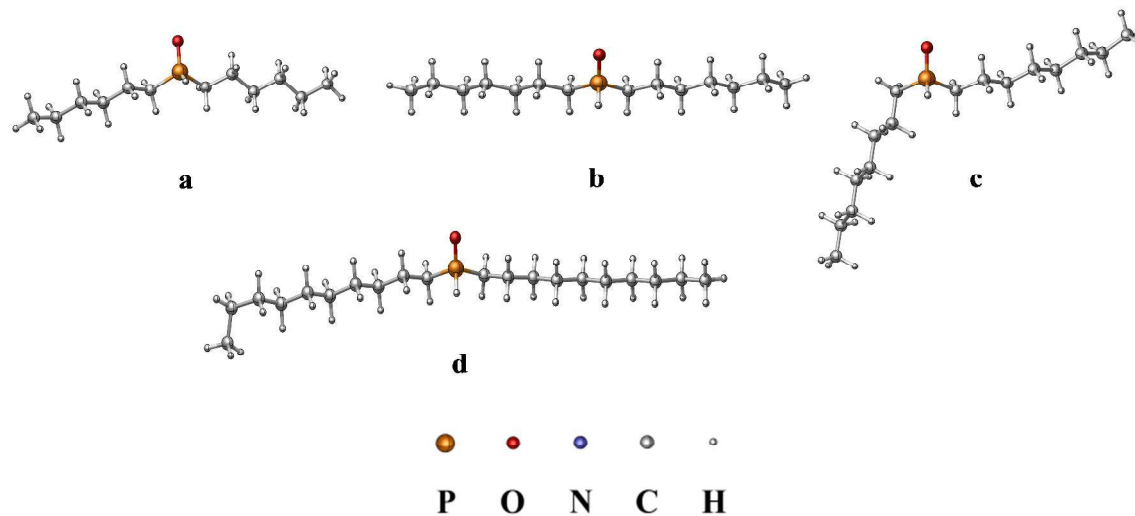


Figure 5. Optimized geometries of the ligands (a) DHePO (b) DHpPO (c) DOPO and (d) DDPO at B3LYP/def2-TZVP level

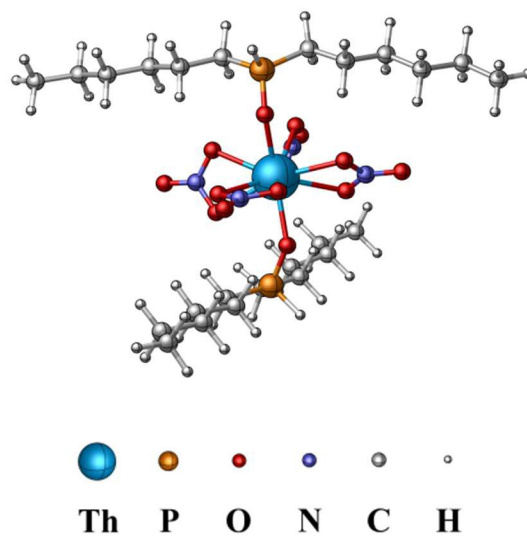
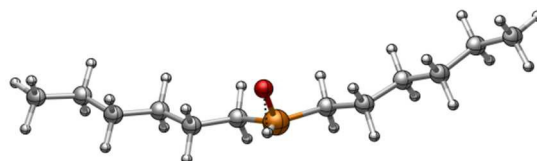


Figure 6. Optimized geometries of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{DHePO}$ at PBE0/def2-TZVP-ECP level. Bottom: Color code for the elements used in this figure



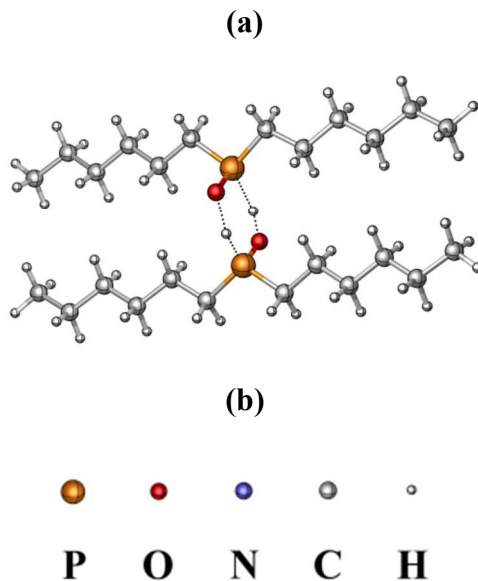


Figure 7. Optimized geometries of transition state structures for unimolecular (a) and bimolecular (b) mechanism for the *tautomerisation* reaction in DHePO.

5. Conclusions

A series of di-*n*-alkylphosphine oxides (alkyl = hexyl, heptyl, octyl and decyl) and their corresponding Th(IV) and La(III) complexes were synthesized and characterized by spectroscopic and analytical methods. These DAPOs showed relatively good extractability of U(VI) at lower nitric acid concentration. At 0.01M HNO₃ concentration, the $D_{U(VI)}$ for different di-*n*-alkyl phosphine oxides increased with increase in the alkyl chain length and the values are as follows 39.4 (DHePO) < 41.8 (DHpPO) < 47.4 (DOPO) < 84.6 (DDPO). The extraction of actinides (uranium and americium) is through cation exchange mechanism at lower acidity and by solvation at higher nitric acid concentration. This implies that both P=O and P-OH forms exists in tautomeric equilibrium, controlled by the acidity of the medium. We have applied DFT

calculations to investigate the mechanism of tautomerism reaction in DHePO ligand. Our calculations support a bimolecular mechanism (with an activation barrier of ~ 27.3 kcal/mol with respect to the reactant complex), where tetracoordinate pentavalent and trivalent phosphorus are in equilibrium. The unimolecular mechanism was energetically less favorable due to the high free energy barrier (~ 60.2 kcal/mol). Additionally, we have also investigated the electronic structure of various ligands considered in the present study. In order to understand the coordination geometry of metal complexes formed during extraction, we have explored Th(NO₃)₄.2DHePO complex at density functional theory level. The two DHePO ligands are in the *trans*- orientation and the bidentate nitrate groups are unsymmetrically distributed around the metal atom.

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Graphical Abstract

Experimental and Theoretical Studies on Extraction behavior of Di-*n*-Alkyl Phosphine Oxides towards Actinides

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