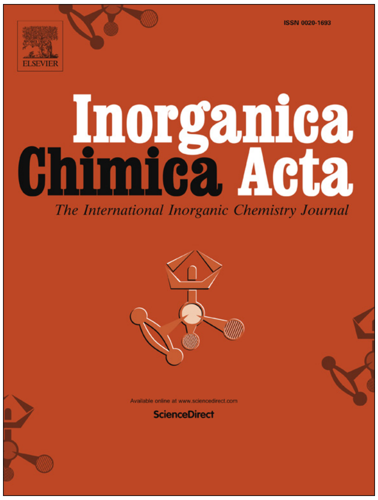

Research paper

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Suresh Annam, Gopinadhanpillai Gopakumar, C.V.S. Brahmmananda Rao, N. Sivaraman, Akella Sivaramakrishna, Kari Vijayakrishna

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Extraction of Actinides by Tri-n-butyl Phosphate Derivatives: Effect of Substituents

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Abstract

Tri-*n*-butyl phosphate (TBP) is most extensively used extractant in the nuclear fuel cycle. The present work investigates the effect of substituents and their role in the basicity of organophosphorus extractant on the uptake of actinides. In this connection, we have synthesized six different analogues of TBP by altering one of its butoxy group. The synthesized TBP derivatives were well characterized and evaluated for their solvent extraction behavior towards U(VI), Th(IV), Pu(IV) and Am(III), as well as acid uptake as a function of nitric acid ranging from 0.01–6 M and the data provides the comparison of their extraction behavior with that of 30% (1.1 M) tri-n-butyl phosphate under identical conditions. It was observed that distribution coefficient values strongly depend on the nature and size of the substituents. The presence of electron donating groups enhances the uptake of the actinides and the distribution coefficient values were significantly larger as compared to that of TBP. In addition, the effect of sodium nitrate on the extraction of uranium and enthalpy of extraction were also studied and revealed that the extraction process was exothermic.

Keywords: Tri-n-butyl Phosphate; Phosphonates; Solvent extraction; Actinides; Density functional theory.

1. Introduction

Tri-n-butyl phosphate (TBP) is one of the commonly used extractant in PUREX process since last six decades and has been the workhorse for the recovery and purification of uranium and plutonium from the irradiated nuclear fuels [1]. The process employs 30% (1.1M) solution of TBP diluted with suitable diluents [2]. TBP has been the unanimous choice for the reprocessing industry due to its optimum physical properties and its selectivity for uranium and plutonium over the fission products. TBP has also been employed in various separation processes such as separation of ^{233}U from irradiated thorium by THOREX/Interim-23 process [3]. However, TBP has some limitations such as undesirable aqueous solubility, radiation degradation and susceptibility to third-phase formation under high loading of tetravalent actinides [4]. To overcome these properties various higher homologous of TBP such as tri-n-amyl phosphate, tri-n-hexyl phosphate (THP) [5], tri-iso-amyl phosphate (TAP) [6] etc., were studied and found to have a lesser tendency towards third phase formation coupled with lower aqueous solubility. Dialkyl amides are another class of extractants which have been developed as an alternative to

TBP [7]. Various types of ligands bearing S, O and N-donor atoms have been developed for the separation of actinides from lanthanides [8-12]. Organophosphorus esters are the preferred class of compounds for the extraction and separation of actinides. The basic oxygen atom of the phosphoryl group is responsible for the complexing ability of TBP and other organophosphorus ligands. Thus the extraction ability of the organophosphorus extractants depends on the basicity of the phosphoryl oxygen and nature of the substituents attached to the phosphorus atom. It is known that a structural change in the substituent at the phosphorus atom causes a perceptible change in their physicochemical properties and extraction abilities [13]. The extraction ability and the electronegativity of the phosphoryl oxygen can be enhanced by replacing the C–O–P group in the extractant by a C–P group. The size and nature of the organic group in the esters governs the degree of extraction since the solubility of the metal complex in the diluent is an important parameter for higher loadings. The basicity of the phosphoryl oxygen in the neutral organophosphorus extractant series increases in the order: phosphates < phosphonates < phosphinates < phosphine oxides [14]. Phosphine oxides and phosphinates are more basic in nature and hence stripping of metal ion extracted in the organic phase are difficult as compared to phosphate and phosphonates. Phosphonates are moderately basic and the back extraction of the metal ions from the organic phase can be carried out by adjusting the acidity of the aqueous phase.

Extensive studies were carried out employing various H-phosphonates [15, 16], phosphinic acids [17], symmetrical and unsymmetrical dialkylalkyl phosphonates by Brahmmananda Rao et al. [18, 19]. In continuation with these studies on phosphonates, we have synthesized the analogues of TBP by altering one of the butoxy group in the TBP by hydrogen, hydroxyl, alkyl, aryl and amide substituents. The purpose of the present work is to ascertain and understand the extraction behavior of actinides by altering the substituent on TBP molecule. In this manuscript, we describe the extraction properties of compounds **I-VI** (Figure 1) towards U(VI), Th(IV), Pu(IV) and Am(III) in the nitric acid medium at 303K. The extraction behavior of these compounds was compared with TBP (**VII**).

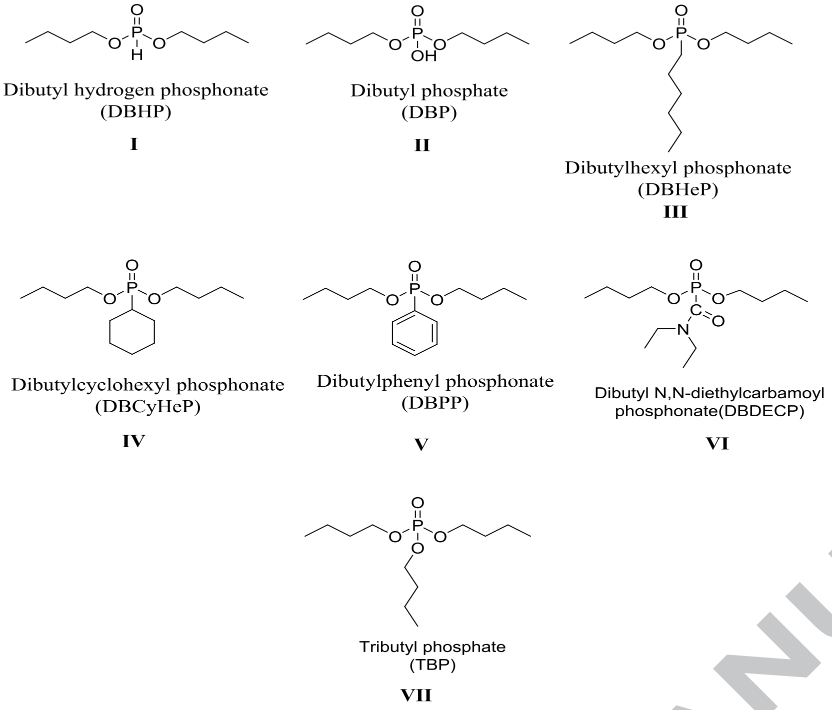


Figure 1. Chemical structures of the extractants **I-VII** used in this study.

2. Experimental Section

2.1. Materials and Instrumentation

Phosphorus trichloride, 1-bromohexane, cyclohexyl bromide, l-butanol, sodium, Arsenazo-III were procured from SD-Fine chemicals, India. Phenylphosphonic dichloride, tributyl phosphite, tributyl phosphate (TBP), dibutyl phosphate, diethylcarbamoyl chloride were procured from Sigma Aldrich. The solvents *n*-dodecane and xylene were purchased from Fluka. The actinides, ^{233}U, ^{239}Pu and ^{241}Am tracers were used from laboratory stock solutions. All other chemicals used for synthesis and other experimental work are of reagent grade and used without further purification.

The ^{1}H, ^{13}C, and ^{31}P-NMR spectra were recorded using BRUKER DMX-400 spectrometer in appropriate deuterated solvents. FT-IR spectra were recorded on SHIMADZU Affinity-1 FT-IR spectrometer with KBr pellet. UV–Vis absorption spectra were recorded using SHIMADZU UV-3600 double-beam spectrophotometer. GC-MS spectra were recorded on Perkin-Elmer Clarus 680 (GC) and Clarus 600 (EI Mass). Thermogravimetric analysis (TGA) was carried out using a TA Thermogravimetric analyzer model Q500 from 25 °C to 300 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

2.2. Synthesis of extractants

The extractants **I**, **III-VI** were synthesized according to the modified literature reports [20-23] and the synthetic routes were shown in Figure 2. Extractants **II** and **VII** were obtained from the commercial sources.

Dibutylhydrogen phosphonate (DBHP) (I): 1-Butanol (76 g, 1.02 mol) was added drop-wise to a mixture of phosphorus trichloride (47 g, 0.343 mol) in 200 mL of dichloromethane at 0 °C under constant stirring. The mixture was stirred for 4 h at room temperature. Subsequently, the reaction mixture was further diluted with dichloromethane and washed with saturated solution of sodium carbonate, water and the organic phase was concentrated under reduced pressure. 60 g (90% yield) of DBHP was collected as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-5.92 (d, $^{1}J_{PH}$ = 692 Hz, 1H), 4.08–4.03 (m, 4H), 1.69–1.69 (m, 4H), 1.44–1.35 (m, 4H), 0.94–0.90 (t, 3H), ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): δ= 10.04-5.56(d, $^{1}J_{PH}$ = 691 Hz) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ: 65.54, 65.48, 32.43, 32.40, 18.69, 13.50. GCMS (m/z): 195.21 $[M]^+$.

Dibutylhexyl phosphonate (DBHeP) (III): Dibutyl H-phosphonate (40 g, 0.2 mol) was added dropwise over a period of 30 min to a suspension of metallic sodium (5.68 g, 0.247 mol) in 100 mL toluene. After the metal had dissolved completely, freshly distilled n-bromohexane (37.5 g, 0.22 mol) was added. The mixture was refluxed for 5 h and the completion of the reaction was monitored by ^{31}P-NMR. The byproduct sodium bromide was separated by centrifugation, and the solution was washed with distilled water and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using 10% ethyl acetate/ n-hexane as an eluent. 37.5 g (65% yield) of DBHeP was collected after column purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.92-3.81 (m, 4H), 1.72–1.64 (m, 2H), 1.57–1.44 (m, 6H), 1.37–1.24 (m, 10H), 0.90-0.84 (m, 9H) ppm. ^{31}P NMR (161.97 MHz, DMSO-d_6): δ= 31.96 ppm.^{13}C NMR (100 MHz, DMSO-d_6) δ: 64.31, 64.24, 32.09, 32.04, 30.75, 29.48, 29.32, 22.06, 22.01, 21.87, 18.25, 13.76, 13.35. GCMS (m/z): 279.25 $[M]^+$.

Dibutylcyclohexyl phosphonate (DBCyHeP) (IV): The procedure adopted for the synthesis of DBCyHeP is similar to DBHeP. The compound was prepared from dibutyl H-phosphonate (50 g, 0.25 mol) and bromocyclohexane (42 g, 0.25mol). The yield of the product is 42 g (60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.94-3.86 (m, 4H), 1.73–1.64 (m, 2H), 1.59–1.52 (m, 4H), 1.47–1.29 (m, 8H), 0.90-0.84 (m, 9H) ppm. ^{31}P NMR (161.97 MHz, DMSO-d$_6$): δ= 31.99 ppm.^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 64.35, 64.29, 39.10, 38.89, 32.11, 32.05, 24.24, 24.19, 23.0, 22.84, 18.27, 13.40. GCMS (m/z): 277.30 [M]$^+$.

Dibutylphenyl phosphonate (DBPP) (V): To a solution of n-butanol (24 g, 0.323 mol) and triethylamine (32.69 g, 0.323 mol) in 100 mL of dichloromethane was added dichlorophenylphosphine (30 g, 0.152 mol) in 30 mL of dichloromethane at 0 °C under nitrogen atmosphere. The reaction mixture was subsequently stirred at room temperature for 24 h. The resultant triethylamine hydrochloride in the reaction mixture was quenched with ice cold water. The organic layer was separated and washed with saturated sodium bicarbonate, dried over sodium sulfate and concentrated under reduced pressure to yield a colorless liquid. The yield of the product is 33 g (80%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.73-7.68 (m, 2H), 7.65–7.54 (m, 3H), 3.94-3.94 (m, 4H), 1.60–1.53 (m, 4H), 1.36-1.37 (m, 4H), 0.87-0.83 (t, 3H) ppm. ^{31}P NMR (161.97 MHz, DMSO-d$_6$): δ= 17.93 ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 132.44, 131.25, 131.15, 129.23, 128.74, 128.60, 127.47, 65.17, 65.11, 31.89, 31.83, 18.20, 13.31. GCMS (m/z): 271.18 [M]$^+$.

Dibutyldiethylcarbamoyl phosphonate (DBDECP) (VI): Diethylcarbamoyl chloride (17.87 g, 0.131 mol) was taken in a Schlenk tube with a magnetic stirring bar. To this tributyl phosphite (30 g, 0.119 mol) was added drop-wise at 0 °C and refluxed at 100 °C for 12 h. The reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography using 50% ethyl acetate in n-hexane as eluent resulted in a brown color liquid. The yield of the product is 25g (71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.23-4.11 (m, 4H), 3.75–3.5 (q, 2H), 3.72-3.42 (q, 2H), 1.73–1.66 (m, 6H), 1.44-1.38 (m, 4H), 1.25-1.21 (t, 3H), 1.44-1.38 (m, 4H) 1.16-1.13(t 3H), 0.91-0.95(t, 3H) ppm. ^{31}P NMR (161.97 MHz, CDCl$_3$): δ= 0.39 ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ: 166.48, 164.22, 67.50, 67.42, 42.04, 39.8, 39.75, 32.40, 32.34, 18.77, 18.65, 14.24, 13.53, 12.45. GCMS (m/z): 294.27 [M]$^+$

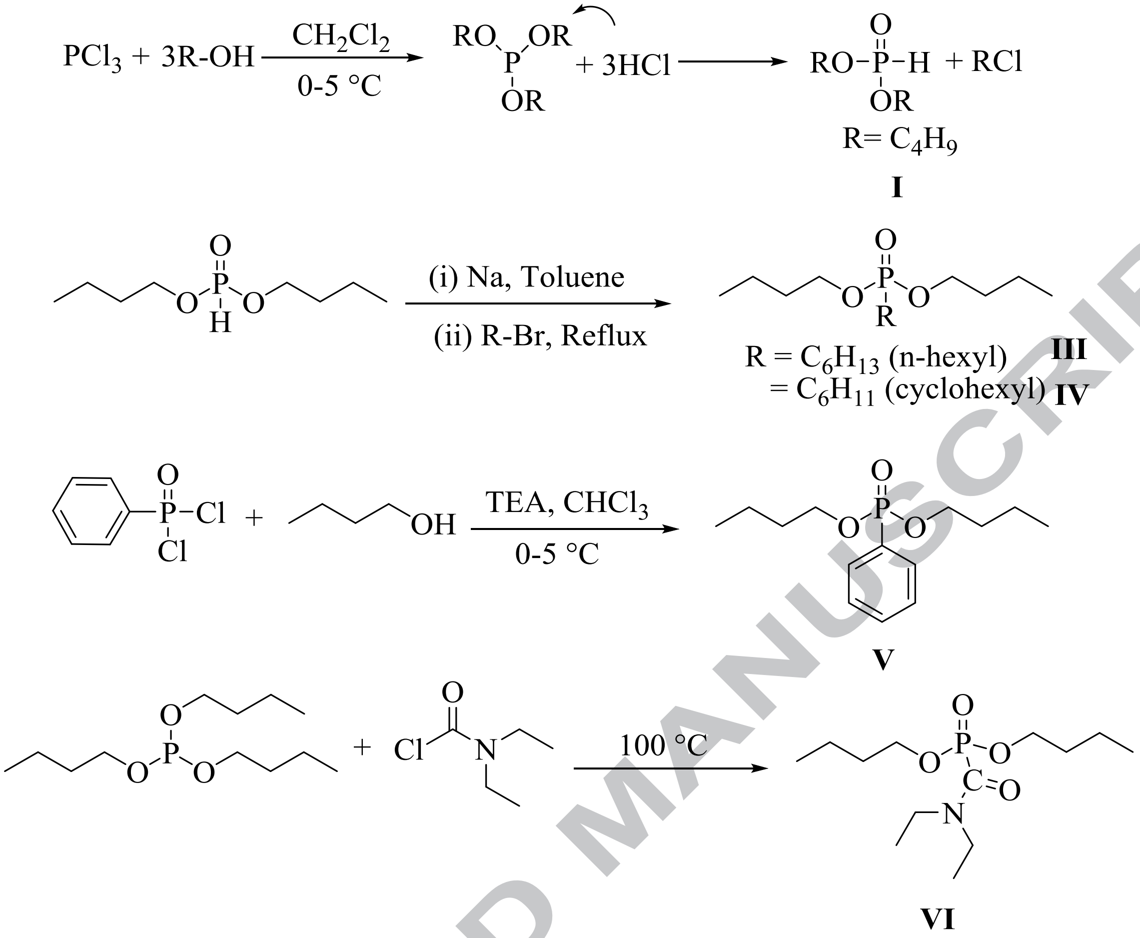


Figure 2. Schematic illustration of the synthesis of extractants **I, III-VI.**

2.3. Physicochemical properties

2.3.1. Density measurements

The undiluted, as well as 1.1 M solutions of extractants **I-VII** in corresponding diluents (2 mL) were equilibrated at 303K with an equal volume of the aqueous phase of the appropriate nitric acid concentration ranging from 0.01 to 6 M for 1 h. The density of the organic phase was measured in triplicate by weighing 500 µL of the sample in a glass micropipette using an analytical balance of ± 0.1 mg sensitivity.

2.3.2. Viscosity measurements

The viscosity of extractants **I-VII** was measured by Oswald viscometer [24]. A known volume (~ 15 mL) of liquid was taken in a viscometer and the time taken by the liquid to flow through the marked region of the Oswald viscometer was measured as a function of temperature.

The driving pressure *p* at all stages of the flow of a liquid is given by hρg, where h is the difference in the heights of the liquid in upper and lower bulb, ρ density of the liquid and g acceleration due to gravity. The viscosity of the fluid can be determined using the following expression.

$$\eta_f = \eta_w\,(\rho_f\, t_f / \rho_w\, t_w) \qquad (1)$$

Where η_f, ρ_w and t_f are viscosity, density and time taken for the fluid to pass through a marked region of the viscometer. The η_w, ρ_w and t_w are viscosity, density and time for the water system under identical conditions.

2.3.3. Nitric acid extraction

Equal volumes (each 2 mL) of organic solution (1.1 M solutions) and the required nitric acid solution taken in a glass stoppered test tube were equilibrated at 303 K. After equilibrating the solutions for an hour, the phases were allowed to settle by gravity. Suitable aliquots were withdrawn from both the phases and analyzed for their acid concentration. The acid in the organic phase was stripped by contacting three times with equal volume of deionized water and quantitatively analyzed using standardized NaOH solution as titrant using phenolphthalein indicator.

2.3.4. Distribution measurements

All the extractants of 1.1M solutions were prepared in corresponding diluent (n-dodecane/xylene). Compounds **I-IV** and **VII** were diluted in n-dodecane and compounds **V** and **VI** were diluted in xylene. The solubility of extractants **V** and **VI** was observed to be poor in n-dodecane and the third phase was observed when pre-equilibrated with nitric acid because of the limited solubility of the hydrogen complexed ligand in non-polar dodecane. All the diluted extractants were washed with 5N sodium hydroxide to remove undesired acidic impurities. All the experiments were carried out in triplicate. Radiometric assay of ^{233}U and ^{239}Pu was carried by liquid scintillation counting technique employing an LSC system (Hidex, Finland) coupled to a multi-channel analyzer using a dioxane-based scintillator cocktail [25]. ^{241}Am was assayed by a well-type Na(Tl) detector coupled to a multi-channel analyzer (ECIL, India).

(a) U(VI), Pu(IV) and Am(III) extraction

The extractants were pre-equilibrated with appropriate nitric acid concentration. A 2 mL of the extractant and 2 mL of nitric acid (containing a requisite quantity of ^{233}U, ^{239}Pu and ^{241}Am tracer) were equilibrated in a constant-temperature bath at 303 K for 1 h. After attainment of equilibrium, suitable aliquots from the both the phases (e.g.100µL) were taken for radiometric assay of the actinides. The distribution ratio (D_M) was calculated as the ratio of concentration (radioactivity per unit volume per unit time) of metal ions in the organic phase to that in the aqueous phase.

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \tag{2}$$

Where $[M]_{org}$ and $[M]_{aq}$ are the metal ion concentration in the organic and aqueous phases, respectively.

(b) Th(IV) extraction

The experimental procedure used for the extraction of Th(IV) by 1.1 M extractants was similar to that of uranium extraction. The thorium concentrations in the initial aqueous phase, as well as at equilibrium were determined spectrophotometrically using Arsenazo-III as the chromogenic agent [26]. The concentration of thorium in the organic samples was estimated by subtracting the equilibrium aqueous concentration from the initial feed concentration. The distribution ratio can then be defined as

$$D_M = \frac{[M]_{i,aq} - [M]_{f,aq}}{[M]_{f,\,aq}} \tag{3}$$

Where $[M]_{i,aq.}$ and $[M]_{f,aq.}$are the initial and final concentration of metal ion in the aqueous phase.

2.4. Computational methods

Density functional theory (DFT) was applied to study the electronic structure and geometries of the ligands DBHP **(I)**, DBP **(II)**, DBHeP **(III)**, DBCyHeP **(IV)**, DBPP **(V)**, DBDECP **(VI)** and TBP **(VII)**. All geometry optimizations were performed at density functional theory (DFT) level employing B3LYP functional [27, 28] in conjunction with triple-ζdef2-TZVP basis sets [29, 30]. 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) [31, 32]. Increased integration grids (Grid6 in ORCA convention) and tight SCF convergence criteria were used throughout the calculations. All quantum chemical calculations were performed with ORCA version 3.0.3 program package [33]. In order to derive AIM charges, the corresponding wavefunction files were generated at B3LYP/def2-TZVP level combining ORCA program package and Molden2AIM utility [34] and analyzed using AIMAll program package [35]. The natural charges were derived by performing natural population analysis using NBO program package version 6.0 [36].

3. Results and Discussion

3.1. Characterization

We have synthesized six analogues of TBP by altering one of the butoxy group in the TBP **(VII)** by hydrogen **(I)**, hydroxyl **(II)**, alkyl **(III, IV)**, aryl **(V)** and amide **(VI)** substituents respectively. The structures of the synthesized products **I, III-VI** were confirmed by IR, multinuclear NMR and mass spectral analysis. Figure 3 shows the overlay of ^{31}P NMR of compounds **I-VII**. The phosphorus in the phosphonate is more deshielded than phosphates because of the higher electron density at the phosphoryl oxygen. The ^{31}P chemical shift values (ppm) for the compounds **I-VII** follows the order **VII > VI > II > I > V > III ≅ IV** are shown in Table 1.

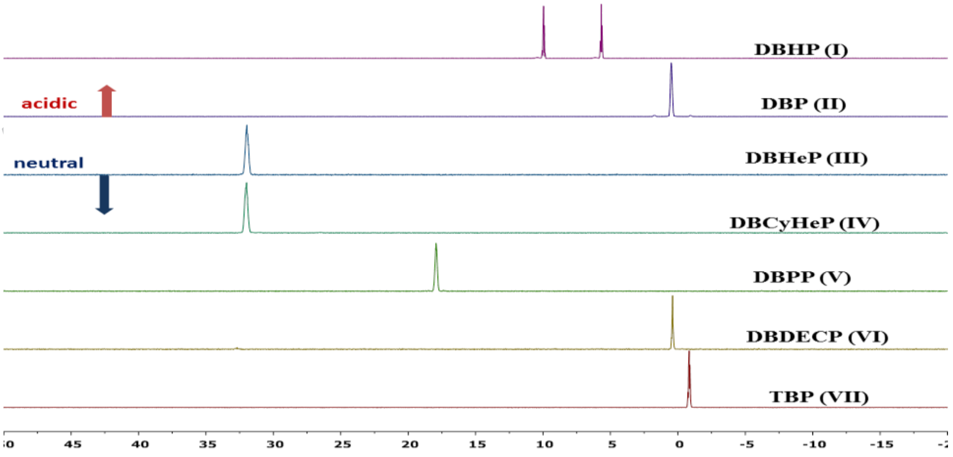


Figure 3. ^{31}P NMR overlay of extractants **I-VII.**

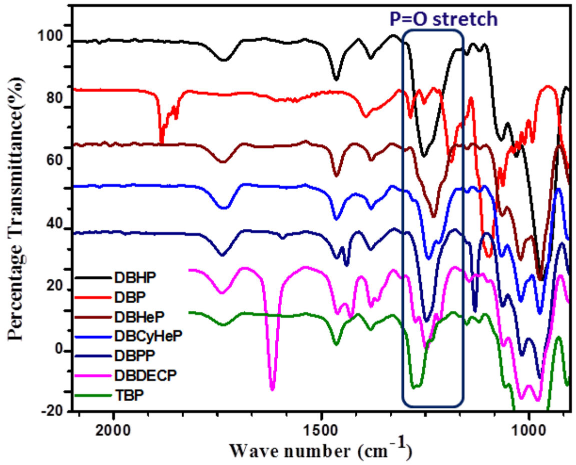


Figure 4. FT-IR overlay of extractants **I-VII**.

The IR spectra of organophosphorus compounds contain characteristic bands attributed to P=O and P–O–C vibrations. The position of the P–H and P=O absorption bands depend largely on the type of substituents. The stretching frequency of P=O was employed as an index of electron density at phosphoryl oxygen. The electron density at the phosphoryl oxygen is attributed to the mesomeric and inductive effect of -OR groups. The replacement of -OR by -R eliminates the mesomeric effect and the inductive nature changes from -I to +I effect, which increases the electron density and the basicity of phosphoryl oxygen atom. This increase in the basicity makes the P=O bond behaves more like a single bond and hence stretching frequency of P=O in phosphonate is lower than that of phosphates (Figure 4). The P=O stretching frequency of the compounds **I-VII** follows the same trend as ^{31}P NMR (see Table 1).

Table 1. Spectral characteristics of the extractants **I-VII**.

Extractant	^{31}P Shift (ppm)	P=O Stretching Frequency (cm^{-1})	Calculated P=O stretching frequencies (cm^{-1}) at B3LYP/def2-TZVP level
DBHP **(I)**	6,10	1251	1287
DBP **(II)**	0.49	1220	1291
DBHeP **(III)**	31.95	1230	1276
DBCyHeP **(IV)**	31.99	1242	1277
DBPP **(V)**	17.93	1246	1286

DBDECP **(VI)**	0.35	1247	1283
TBP **(VII)**	-0.4	1276	1290

The thermal stability of extractants **I-VII** was studied by thermogravimetric (TG) analysis and the results are summarized in Table 2. Among seven extractants, DBP (**II**) showed highest thermal stability (started decomposing after 200 °C), whereas DBHP (**I**) showed least thermal stability as can be seen in Figure 5.

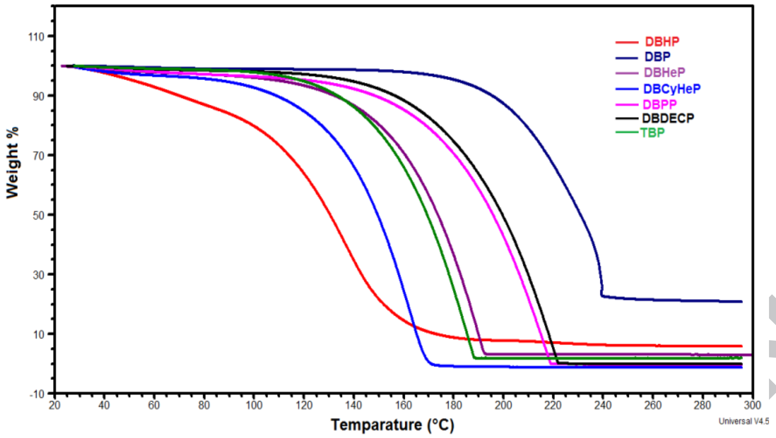


Figure 5. Thermogravimetric analytic curves of extractants **I-VII**.

Table 2. Thermal degradation data of extractants **I-VII** derived from TGA.

Extractant	T_d 5%[a] (°C)	T_d 10%[b] (°C)	T_d max%[c] (°C)
DBHP **(I)**	51.00	69.38	185.00
DBP **(II)**	181.54	194.59	239.34
DBHeP **(III)**	108.53	131.62	192.89
DBCyHeP **(IV)**	83.77	108.54	171.41
DBPP **(V)**	122.13	147.17	219.10
DBDECP **(VI)**	137.85	156.23	222.03
TBP **(VII)**	118.93	132.52	188.73

[a] Temperature at weight loss value of 5% for non-isothermal degradation.
[b] Temperature at weight loss value of 10% for non-isothermal degradation.
[c] Temperature at which a maximum decomposition rate is reached for non-isothermal degradation.

3.2. Density

The density difference between the organic phase and the aqueous phase is an important parameter which decides the phase separation time (PST) in liquid–liquid extraction. Figure 6 shows the variation in density of nitric acid loaded organic phase with the equilibrium aqueous nitric acid at 303 K. The density of organic phase increases with an increase of nitric acid concentration in the organic phase. In our case, a marginal increase in the density of the organic phase was noticed as the aqueous phase acidity increases from 0.01 M to 6 M nitric acid concentration. In the case of DBP, the density decreases with increasing acid concentration due to the increase in the aqueous solubility of DBP in nitric acid medium. A similar trend was observed for DBHP up to 2M followed by a rise in the density above 2M nitric acid concentration. The uncertainty in the estimation of density in these studies is ±0.2%.

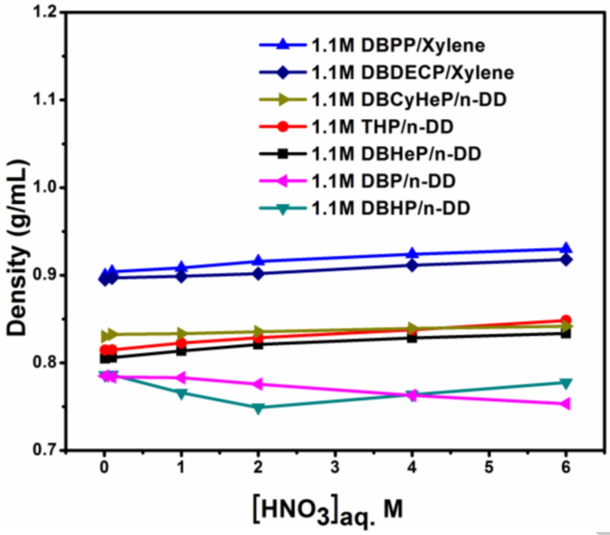


Figure 6. Density variations of extractants **I-VII** with an initial concentration of nitric acid at 303 K.

3.3. Viscosity

The variation in the viscosity of extractants **I-VII** as a function of temperature is shown in Figure S30 (ESI). The relative standard deviation for the measurement of viscosity by Oswald viscometer is 1-2%. The deviations can be maximum at higher temperatures due to an error in the assumption of invariance in density as a function of temperature. In case of water, density at 303K and 323 K is 0.997 and 0.988 g/mL respectively. This corresponds to an uncertainty of 1% in the calculation of viscosity by this method. Among all the extractants, DBP (II) exhibits high viscosity due to the presence intramolecular hydrogen bonding between the -OH groups. The effect of temperature on the viscosity can be fitted with the Arrhenius type of relationship as shown in Eq.4

$$?? = ??_0??^{????/????}$$

(4)

Where ??$_0$ is dynamic viscosity (Pa·s); ?? is the pre-exponential factor (Pa·s); ??$_{??}$ is the exponential constant which is known as activation energy (J/mol); ?? is the gas constant (J/mol.K) and ?? is the absolute temperature (K). The plot of ln?? against 1/?? for phosphonates is shown in Figure 7. At 303K, the activation energy ??$_{??}$ (calculated from the slope of the straight lines) values for **I-VII** are 12.13, 23.99, 17.96, 12.83, 17.15, 25.19, 14.63 kJ/mol respectively.

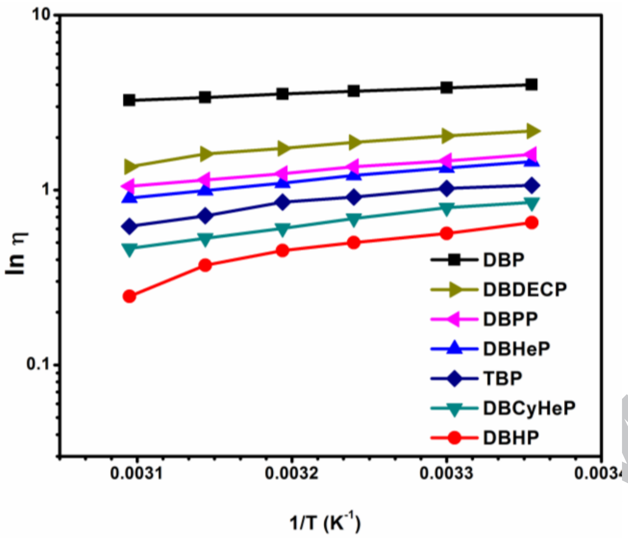


Figure 7. Arrhenius plot for the variation in viscosity for the extractants **I-VII** with temperature.

3.4. Nitric acid extraction

The basicity of neutral extractants is an important parameter that decides the efficiency towards metal ion extraction. Ligand basicity can be determined to a certain extent on the basis of nitric acid extraction. Figure 8 shows the extraction of nitric acid by 1.1 M solutions of **I-VI** in n-dodecane/xylene at 303 K in comparison with extraction of nitric acid by 1.1 M TBP/n-dodecane at 303 K [37]. Extraction of nitric acid by DBHeP **(III)**, DBCyHeP **(IV)** and DBPP **(V)** is almost same throughout the acidities. The presence of carbonyl group (C=O) in DBDECP **(VI)** strongly decreases the electron density at phosphoryl oxygen, resulting in lower nitric acid extraction, which is nearly similar to TBP **(VII)**. The presence of free -OH group in DBP **(II)** and tri-coordinated phosphite form [38] of DBHP **(I)** contribute to the acidity to the molecule and hence are not reported here.

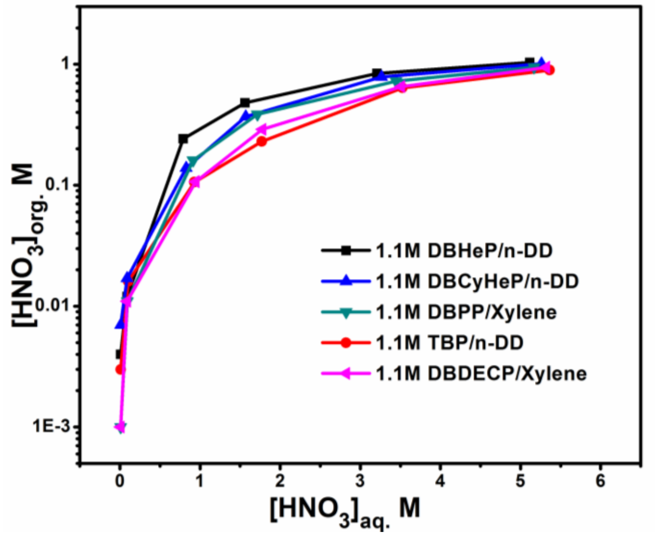
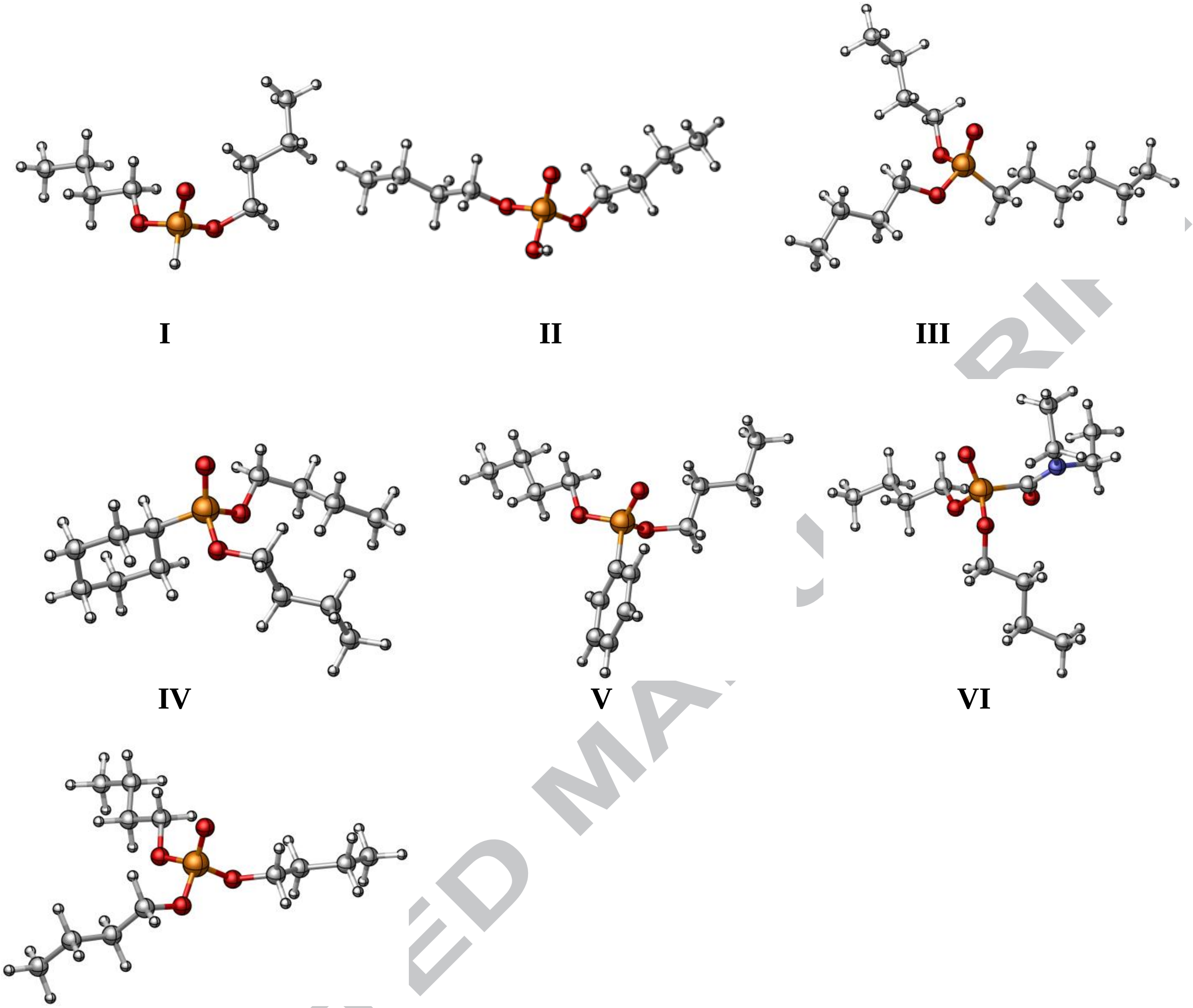


Figure 8. Variation in nitric acid concentration of extractants **I-VII** in organic phase as a function of initial aqueous nitric acid concentration.

3.5. Density Functional Theory Studies

We have applied DFT calculations to probe the effect of structural change on the electronic structure of the ligands. The ligand geometries were systematically optimized considering ten starting geometrical conformers resulting from C-C single bond rotation. Our calculations suggested that the energy difference between these conformers is relatively small (~5 kcal/mol) and suggests the conformational flexibility of the system under room temperature. This is in accordance with our previous studies reported on di-n-alkyl phosphine oxides [39] and tri-n-butyl phosphate ligands [40, 41]. Therefore we have considered the lowest energy conformer in each set as the representative structure for each ligand. The optimized geometries of the ligands DBHP **(I)**, DBP **(II)**, DBHeP **(III)**, DBCyHeP **(IV)**, DBPP **(V),** DBDECP **(VI)** and TBP **(VII)** are illustrated in Figure 9. The lowest energy conformer for TBP **(VII)** is already reported in the literature [41] and therefore considered from the corresponding reference. The calculated gas phase P=O stretching frequencies for all ligands were in agreement with the corresponding values derived experimentally (Table 1). There is also a general trend in computed P=O stretching frequencies in neutral compounds, as we move from DBHeP to TBP, *i.e.* from 1276 cm^{-1} to 1290 cm^{-1}.



I

II

III

IV

V

VI

VII

Figure 9. Optimized geometries of ligands **I-VII** considered in the present study at B3LYP/def2-TZVP level. Color code: Orange ball is phosphorus, red balls are oxygen, blue ball is nitrogen, grey balls are carbon, and white balls are hydrogen atoms

It is conventionally understood that replacement of –OR group by –R increases basicity of the phosphoryl oxygen atom. In order to verify this hypothesis, we have performed electron population analysis on computationally derived representative structures. To check the sensitivity of the computed charges, we have compared the Mulliken electron population and that derived using advanced methodologies, such as natural bond orbital (NBO) and AIM. Upon structural modification, the phosphoryl oxygen atom shows no considerable change in electron population. This can be reconfirmed by comparing trends in computed electronic charges at phosphoryl oxygen using three different methodologies, viz. Mulliken, NBO and AIM (Table S1, ESI). On the other hand, the absolute values of computed charges at phosphorus atom show small numerical differences for different ligands. A general trend such as a large positive charge on phosphorous for TBP **(VII)** and a small value for phosphorous on DBHeP **(III)** was observed and this trend is in agreement with the trend in ^{31}P chemical shift values. In summary, the difference in extraction behavior of ligands considered in the present study cannot be attributed alone to the difference in electron density at phosphoryl oxygen arising from the structural modification. Factors other than basicity of P=O group, such as geometry of the corresponding complexes, nitrate ion concentration, etc. will also contribute to the *D* value.

3.6. Distribution studies of U(VI), Th(IV), Pu(IV) and Am(III)

The extracting power of neutral organophosphorus extractants can be enhanced by an increase in the electron availability on the donor atom. The introduction of longer alkyl chain, branching in the alkyl groups near the donor atom are likely to make a marginal increase in the basicity of the extractant. However, extraction is also decided by the stability of the metal complex and on the structure of the extractant.

The data on the variation in D for the trace level extraction of U(VI) by 1.1M solutions of extractants **I-VII** with equilibrium aqueous nitric acid concentrations from 0.01 to 6M at 303 K are shown in Figure 10 and compared with 1.1 M TBP/n-dodecane. The variation in distribution ratio for U(VI) by 1.1M dibutyl phosphate (DBP) as a function of nitric acid concentrations was investigated and it was observed that at lower acidity $D_{U(VI)}$ value for DBP **(II)** is considerably large and it decreases gradually with the increase of acid concentration. A high distribution value of DBP **(II)** at lower acidity is attributed to cation exchange mechanism [39] and involves the following reaction.

$$\mathrm{nRPO\text{-}H} + \mathrm{mM_{aq}}^{n+} \Longleftrightarrow \mathrm{RPO\text{-}M_{org}} + \mathrm{nH^+} \qquad (5)$$

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

$$K_{eq} \;=\; [\mathrm{RPO\text{-}M}]_{org}\,[\mathrm{H^+}]^n \;/\; [\mathrm{RPO\text{-}H}]^n\, \mathrm{M_{aq}}^{n+} \qquad (6)$$

Rearranging eq. (6),

$$D = K_{eq}\,[\mathrm{RPO\text{-}H}]^n / [\mathrm{H^+}]^n \qquad (7)$$

DBP **(II)** has two chelating sites, viz. P=O and P-OH groups, at lower acidity ion exchange mechanism is the predominant mode of extraction of actinides, at higher acidity, the higher concentration of H^+ drives the reaction to the reactant side with no metal complex formation. The phosphoryl group is thus solely responsible for the extraction at higher acidity. The $D_{U(VI)}$ values of DBHP **(I)** are high at low acidities as compared to those of TBP under similar conditions. At lower acidities, the DBHP **(I)** behave like acidic extractant via cation exchange mechanism, while at higher acidity the extraction occurs through solvation as that of DBP **(II)**. The graph also shows the comparative data for the extraction of U(VI) for DBHeP **(III)**, DBCyHeP **(IV)**, and DBPP **(V)**. Among the three hexyl derivatives, DBPP **(V)** shows lower distribution values compared to DBHeP **(III)**, due to the presence of phenyl group, which is moderately activating group compared to the n-hexyl group. The decrease in electron density on phosphoryl oxygen leading to the formation of the weaker complex bond, thereby it resulting low distribution values compared to DBHeP **(III)** and DBCyHeP **(IV)**. $D_{U(VI)}$ values for DBDECP **(VI)** were lower and closer to TBP **(VII)** due to electron withdrawing carbonyl group (C=O), which is directly attached to the central phosphorus atom and it decreases the electron density on phosphoryl oxygen.

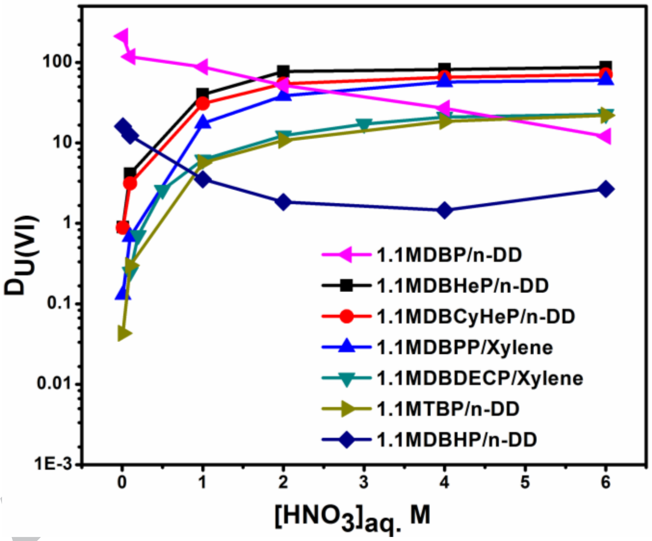


Figure 10. Variation in the $??_{U(VI)}$ of extractants **I-VII** in organic phase with equilibrium aqueous phase nitric acid at 303 K.

Figure 11 shows the variation in $??_{Th(IV)}$ as a function of nitric acid concentration. The trend in thorium is similar to U(VI). The D values of Th(IV) for all four phosphonates are in the same order and increased with nitric acid concentration. The uptake of Th(IV) reaches steady value at 2M acidity after which there is only a marginal increase. Distribution values for the phosphonate systems are significantly higher than those of TBP **(VII)** system and DBDECP **(VI)** distribution is almost similar to TBP **(VII)**. The presence of cyclic ring in the DBCyHeP **(IV)** and DBPP **(V)** causes steric effect resulting in large variation of the $D_{Th(IV)}$ values compared to the open chain in DBHeP **(III)**. The decrease in D values of thorium is more profound in thorium system than uranium. This may be due to the higher solvation number i.e. trisolvate nature of Th solvate compared to the disolvate uranium complex [42], which reduces the amount of free extractant in thorium extraction compared to uranium. Distribution studies of Th(IV) for DBP **(II)** and DBHP **(I)** could not be carried out, because of the formation of emulsion at lower acidities. As mentioned earlier, nature of substituent and steric effects have a predominant effect in the extraction behavior of the metals.

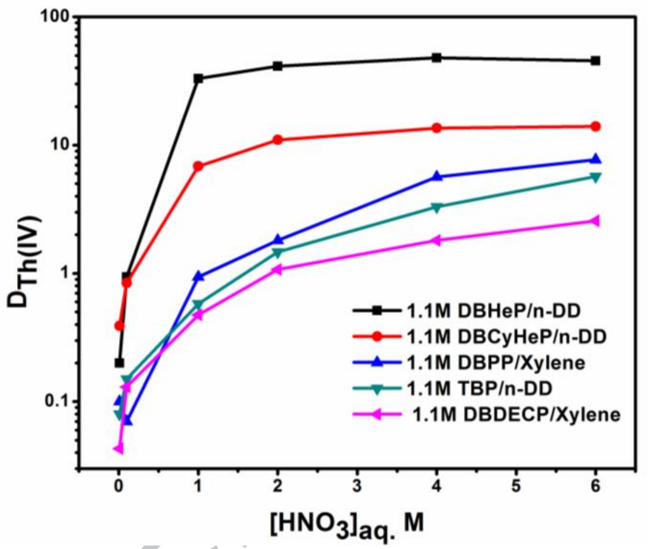


Figure 11. Variation in the $??_{Th(IV)}$ of extractants **III-VII** in organic phase with equilibrium aqueous phase nitric acid at 303 K.

The batch studies for the extraction of Pu(IV) was carried out as a function of nitric acid ranging from 0.01- 6M. The effect of the different structures of extractants **I-VII** on the distribution ratios of plutonium is similar to that observed for uranium. Figure 12 gives the variation of distribution ratios of Pu(IV) by 1.1M to solutions of extractants **I-VI** with equilibrium aqueous nitric acid 303 K. This system is compared with 1.1M TBP/n-dodecane under identical conditions. The $D_{Pu(IV)}$ increases steeply for the extractants **III-VI** as compared to

VII. A decrease in D values of plutonium is observed as the nitric acid concentration is varied from 0.01- 6M for the extractants **I-II**. The fall in the D values can be explained based on the cation exchange mechanism operating in these systems.

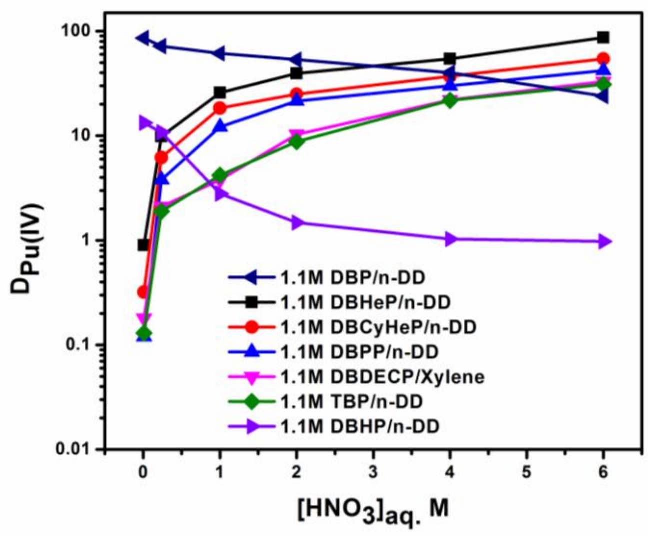


Figure 12. Variation in the ??$_{Pu(IV)}$ of extractants I-VII in organic phase with equilibrium aqueous phase nitric acid at 303 K.

The effect of equilibrium aqueous phase nitric acid concentration on the extraction of Am(III) with 1.1M solutions of **I-VI** at 303K are compared with 1.1M TBP/n-dodecane under identical conditions are shown in Figure 13. The extraction behavior of these ligands towards Am(III) follows the same trend as that of U(VI). The data suggest that the extraction of Am(III) is poor compared to that of tetravalent (Th) and hexavalent (U) actinide ions. The extraction values of Am(III) by TBP **(VII)** and phosphonates are very low and hence cannot be used for practical application in the solvent extraction mode. In absolute terms, the D values of phosphonates are ten times higher than those of TBP **(VII)**, suggesting the higher basicity of phosphonates over phosphates.

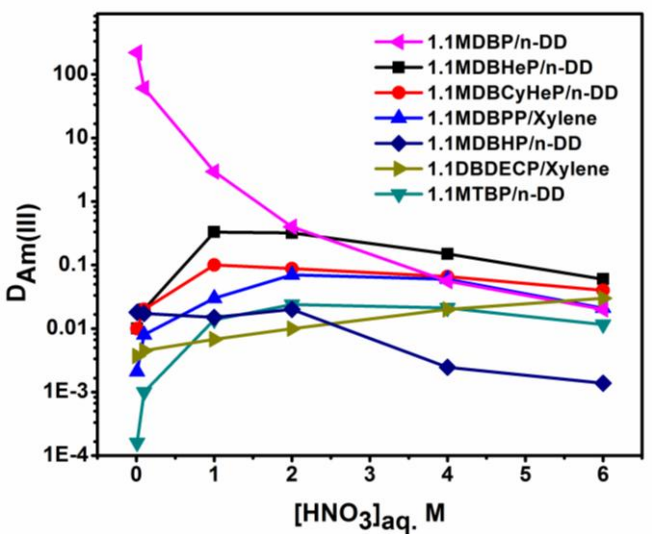


Figure 13. Variation in the ??$_{\text{Am(III)}}$ of extractants **I-VII** in organic phase with equilibrium aqueous phase nitric acid at 303 K.

3.7 Effect of $NaNO_3$ on extraction of Uranium

The effect of ionic strength on the extraction of U(VI) was studied at varying concentrations of $NaNO_3$ (0.0–6 M) in 0.1M HNO_3. The effect of variation of salt on extraction by extractants **III-VII** showed that the distribution ratio increases with the increase in $NaNO_3$ concentration in these systems as shown in Table 3. This is explained by the increase in the thermodynamic activity of the metal and concomitant decreases in the activity of water. The ionic strength of the solution increases and hence behaves like salting out agent. The efficiency of extraction increases with the increase in the concentration of nitrate anions, because these species are considered as weak complexing anions and thus behave as salting out agents. This supports the nitrate complex is being extracted because of the higher the ionic strength of the solution. On the other hand, to evaluate the effect of acid (protons) on extraction, we have carried out the extraction of U(VI) with the extractants **III-VI** by varying the nitric acid to sodium nitrate concentration where the total nitrate concentration is fixed at 2M. Distribution ratios are greatly increased with the decrease in H^+ concentration and increase in nitrate ion concentration as shown in Table 4. This observation can be attributed to the salting out effect of nitrate ions and decrease in competition between acid and metal ions for the extraction.

Table 3. Variation of $D_{U(VI)}$ with varying nitrate concentration at fixed 0.1M HNO_3.

$[NO_3^-]$		$D_{U(VI)}$				
$[HNO_3]$ M	$[NaNO_3]$ M	DBHeP **(III)**	DBCyHeP **(IV)**	DBPP **(V)**	DBDECP **(VI)**	TBP **(VII)**
0.1	0	6.0	2.6	0.98	0.43	0.29
0.1	0.4	18.60	7.48	4.67	1.76	0.91
0.1	0.9	38.02	18.51	9.5	5.3	4.23
0.1	1.9	54.01	25	20.6	14.7	12.70
0.1	3.9	105.21	94	67.8	45.4	39.70
0.1	5.9	128.13	102	86	58.68	52.29

Table 4. Variation of $D_{U(VI)}$ with varying nitrate concentration with respect to HNO_3.

$[NO_3^-]$		$D_{U(VI)}$				
$[HNO_3]$ M	$[NaNO_3]$ M	DBHeP **(III)**	DBCyHeP **(IV)**	DBPP **(V)**	DBDECP **(VI)**	TBP **(VII)**
2.0	0	74.01	57.83	41.88	12.08	7.75
1.75	0.25	84.12	64.34	47.70	13.44	9.89
1.5	0.5	91.15	68.3	48.14	15.69	11.75
1.0	1.0	101.03	76.91	55.75	17.46	15.81
0.5	1.5	119.36	93.51	71.12	23.12	18.5
0	2.0	141.02	114	95.26	29.63	19.2

3.8 Effect of temperature on extraction of uranium and thorium

Temperature plays an important role in solvent extraction studies. In order to determine the effect of temperature on extraction of these metals, variable temperature extraction studies were carried out with extractants **III-VII** at 2M nitric acid concentration with U(V1) and Th(IV). Figure 14 and Figure 15 illustrated the variation of distribution ratio of U(VI) and Th(IV) with the temperature. The extraction of uranium and thorium decreases monotonically with an increase in the temperature within the range of experiment (290–333 K), which confirms that the extraction of these metals with the extractants **III-VII** is exothermic in nature. The reeducation in temperature aids the extraction of U(VI) and Th(IV). The D_M data of U(VI) and Th(IV) obtained for extractants at different temperature were plotted as log D_M vs (l/T) and the plots for 2.0 M HNO_3 are shown in Figure 16 and Figure 17.

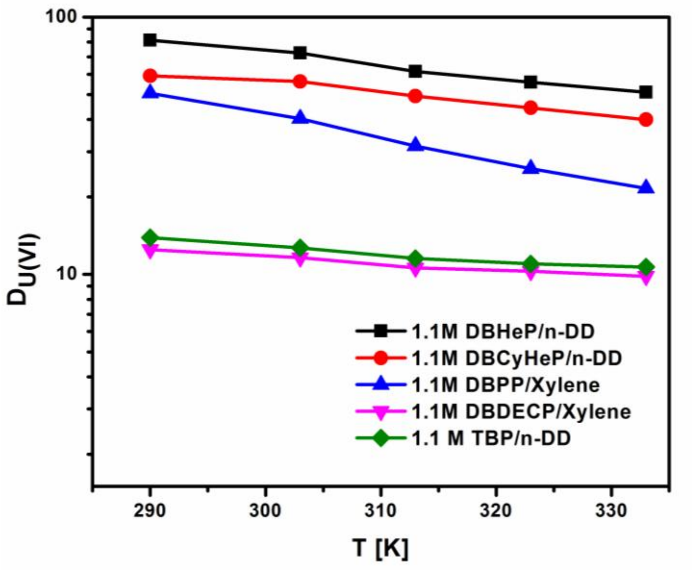


Figure 14. Effect of temperature on the distribution ratio for extraction of U(VI) by 1.1 M extractants **III-VII** at equilibrium 2M nitric acid.

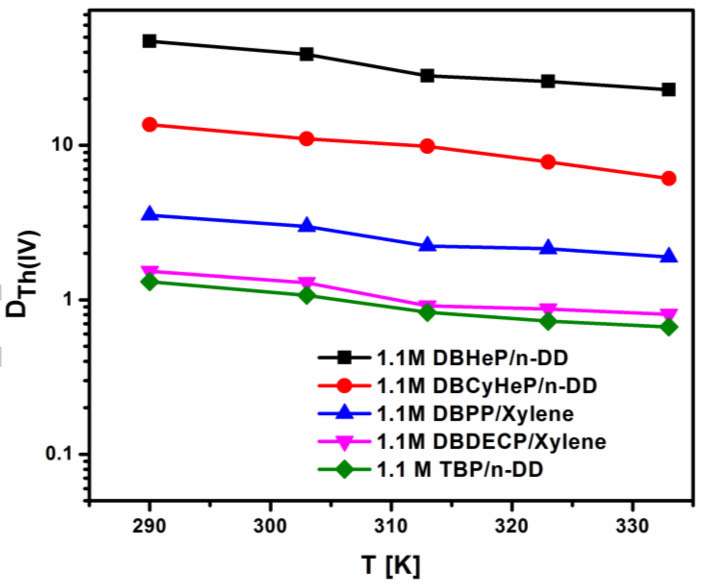


Figure 15. Effect of temperature on the distribution ratio for extraction of Th(IV) by 1.1 M extractants **III-VII** at equilibrium 2M nitric acid.

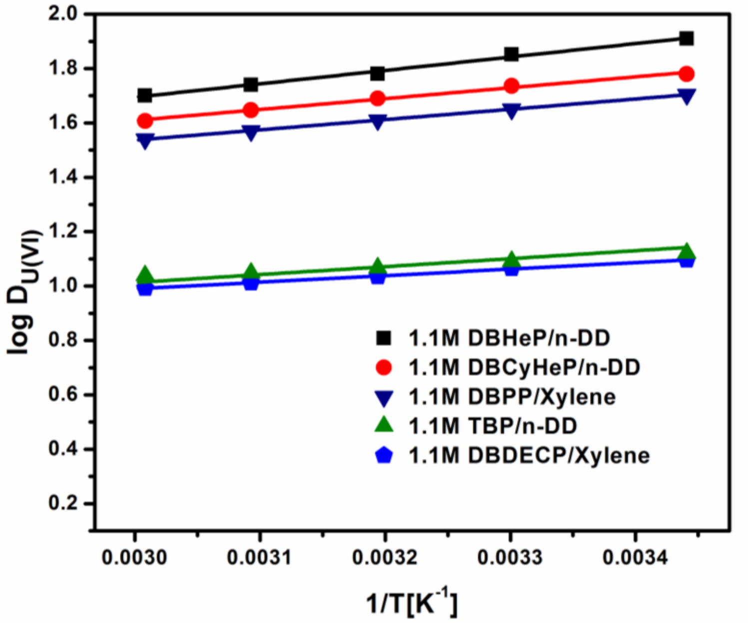


Figure 16. Variation of log $D_{U(VI)}$ against 1/T for the extractants **III-IV** at equilibrium 2M nitric acid.

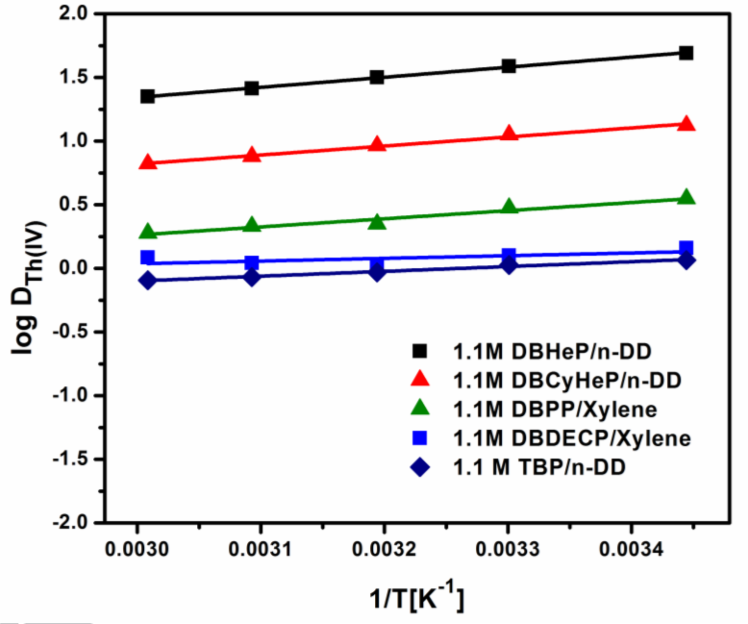


Figure 17. Variation of log $D_{Th(IV)}$ against 1/T for the extractants **III-IV** at equilibrium 2M nitric acid.

Table 5. Enthalpy Change of Extraction of U(VI) and Th(IV) with 1.1M extractants **III-VII** at equilibrium 2M nitric acid.

Extractant	-ΔH(kJ/mol)	
	U(VI)	Th(IV)
DBHeP **(III)**	9.48	15.16
DBCyHeP **(IV)**	7.7	13.58
DBPP**(IV)**	7.27	12.21
DBDECP **(VI)**	4.63	7.23
TBP **(VII)**	3.74	4.04

From the slope of the straight lines, the enthalpy change ΔH for the extraction can be calculated using the Van’t Hoff equation:

$$\frac{\Delta \log D_M}{\Delta \log (1/T)} = \frac{-\Delta H}{2.303R} \quad (8)$$

and the calculated values are summarized in Table 5. The negative ΔH value further suggests that the extraction reaction of uranium and thorium by the extractants **III-VII** is exothermic in nature.

4. Conclusions

We have prepared six different analogues of TBP by altering one of its butoxy group by hydrogen, hydroxyl, hexyl, cyclohexyl, phenyl and amide substituents. The synthesized TBP derivatives were well characterized by spectroscopic methods and also measured their physical properties such as density and viscosity. The ^{31}P chemical shift values (ppm) for the compound **I-VII** follows the order **VII** > **VI** > **II** > **I** > **V** > **III** ≅ **IV**. This trend suggests that phosphorus in the phosphonate is more deshielded than in the case of phosphates because of the higher electron density at the phosphoryl oxygen. IR studies revealed that the P=O stretching frequency of the compounds **I-VII** follows the same trend as that of ^{31}P NMR. The DFT calculated P=O stretching frequencies for extractants **I-VII** were in agreement with experimental values.

The solvent extraction behavior of synthesized extractants towards U(VI), Th(IV), Pu(IV) and Am(III) were studied and compared with standard TBP. It was found that the variations in the distribution ratios of U(VI), Th(IV) and Am(III) were influenced by the basicity of the phosphoryl oxygen (P=O), which correlated with the nature and size of the inductive effective substituent, and distribution ratios are greatly influenced by the increase of sodium nitrate. The extraction process of U(VI) and Th(IV) is exothermic. ^{31}P chemical shift values, FT-IR absorption frequency values are good agreement and evident for the electron density (basicity) of the phosphoryl oxygen (P=O). Thus the field of organophosphorus based extractants are seems to be wide open for exciting investigations.

Acknowledgements

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Highlights

Six different analogues of TBP were prepared and evaluated for their solvent extraction behavior towards U(VI), Th(IV) and Am(III).

The distribution coefficient values (for U(VI), Th(IV) and Am(III))

Are strongly depend on the nature and size of the substituents. Presence of electron donating groups enhances the uptake of the actinides.

Graphical abstract