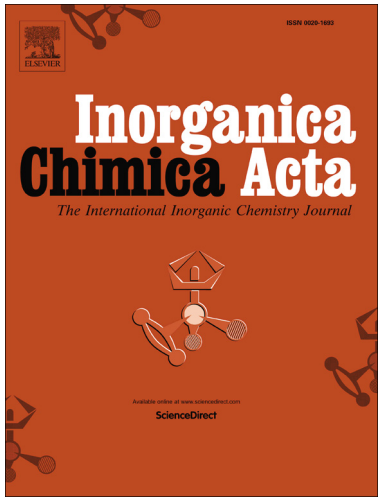

Research paper

Synthesis and Extraction behavior of Alkyl and Cyclic Aminophosphonates towards Actinides

Dhrubajyoti Das, C.V.S. Brahmmananda Rao, N. Sivaraman, Akella Sivaramakrishna, Kari Vijayakrishna

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Synthesis and Extraction behavior of Alkyl and Cyclic Aminophosphonates towards Actinides

Dhrubajyoti Das[a], C.V.S. Brahmmananda Rao,[b] N. Sivaraman,[b] Akella Sivaramakrishna,[a] Kari Vijayakrishna,[a,*]

[a]*Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India*

[b]*Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam 603 102, Tamil Nadu, India*

Corresponding Author: Kari Vijayakrishna
E-mail: kari@vit.ac.in and vijayakrishnakari@gmail.com

Abstract

Alkyl and cyclic substituted aminophosphonates (AmPs) were synthesized and characterized with various spectroscopic techniques. The molecular structures of diphenyl phenyl aminophosphonate (DPhPhAmP) and diphenyl cyclohexyl aminophosphonate (DPhCyAmP) were elucidated based on the single crystal XRD analysis. Extraction behavior of these synthesized AmPs were investigated with some actinides [U(VI), Th(IV), and Am(III)] and also studied their acid uptake as a function of nitric acid concentration. Here we have compared the extraction behavior of aminophosphonates (AmPs) towards actinides as a function of alkyl, cyclic and alicyclic substituents.

Keywords: Aminophosphonates;Solvent extraction; Actinides; Uranium; Thorium

1. Introduction

Nuclear spent fuel contains a large amount of different actinide ions along with many fission products [1]. Recovery of those actinides from other metal ions is a challenging task and also plays an important role in nuclear waste management [2]. Over these years various processes were adopted for the separation of actinides including precipitation, co-precipitation, ion exchange and solvent extraction methods [3, 4]. Solvent extraction process has been proved to be the most favorable method for separation and purification of actinides in large scale. Organophosphorous and amide based neutral and acidic extractants like TBP (tri-n-butyl phosphate) [5], CMPO (octyl, phenyl- *N, N*-diisobutyl carbamoylmethyl phosphine oxide) [6], TRPO (trialkyl phosphine oxides) [7, 8] HD2EHP (di(2-ethylhexyl) phosphoric acid) [9], DIDPA (di-isodecyl phosphoric acid) [10], DMDBTDMA (*N,N,N′,N′*- dimethyldibutyl tetradecyl malonamide) [11], TODGA (*N,N,N′,N′*- tetraoctyl malonamide) [12] are being used in many processes like PUREX [13], TRUEX [14] and DIAMEX [15] which are used for the separation of actinides and lanthanides (not on commercial scale). N-donor extractants like BTP (2,6-di(1,2,4-triazin-3-yl)pyridine) and BTBPs (6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bypiridines) also used for the separation and extraction of Am(III). Recently a tetradentate N-donor ligand *N,N'*-diethyl-*N,N'*-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen) was reported as a promising ligand for the separation and extraction of actinides from nuclear waste stream [16-19]. TBP has been extensively used in nuclear repossessing industry for the recovery of uranium and plutonium from irradiated fuel since last six decades [20]. TBP is a mild extractant and can extract actinides at higher acidity and strip at lower acidity. Being hard acids, actinides prefer oxygen donor ligands like organophosphorous esters as the preferred class of

compounds for actinides recovery [21]. Extraction of actinides depends on the basicity of the phosphoryl oxygen, as well as it is related to the substituents of the extractants [22]. The nature of the substituents also plays an important role on the extractability. Numerous classes of dialkyl alkyl phosphonates [23-26] and their functionalized resin [27], H-phosphonates [28, 29] and di-*n*-alkyl phosphine oxides [30, 31] (DAPOs) were synthesized and their extraction behavior towards actinides was studied and reported earlier [32-35]. In the literature a variety of phosphates with various substituents have been employed for the extraction of actinide.

Aminophosphonates (AmPs), also known as phosphoramidates are relatively new class of ligands derived from the very well-known phosphine oxide family and offer fascinating opportunities. This area has the potential to grow as increasing demand for carefully designed ligands of this type in the nuclear industry towards the treatment and separation of nuclear waste. It seemed a constructive exercise to analyze the nature of these ligands in the coordination spheres of some selected actinides, especially as these complexes possess potentially reactive P–N, P–C–N and P–N–C linkages. Eventually, our search for newer ligands has lead us to investigate the extraction behavior of phosphonates towards the actinide ions having a primary amine group in the phosphonate moiety. Also we wanted to study the effect of linear, aromatic and cyclic substitutions in distribution ratio of actinides. In this connection, we have synthesized a class of alkyl and cyclic substituted aminophosphonates (AmPs) and studied their extraction behavior towards various actinides.

2. Experimental

2.1. Materials and Instrumentation

Cyclohexyl amine, aniline, phenylphosphinic dichloride, diphenylphosphoryl chloride and $CDCl_3$ (Sigma-Aldrich) were used as received. Butyl, hexyl and octyl amine were purchased from Sigma Aldrich and used without any further purification. All the alcohols and solvents were purchased from SD fine chemicals. Solvents were distilled prior to use. Radiotracers were used from laboratory stock and their radiochemical purity was checked prior to their use.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded by BRUKER DMX-400 and ^{1}H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 298 K, $CDCl_3$). H_3PO_4 was used as an external standard for ^{31}P NMR. FT-IR spectra were recorded on SHIMADZU Affinity 1 FT-IR spectrometer using KBr pellet. The spectra were recorded at ambient temperature by making pressed pellets of the compound. UV–vis absorption spectra were recorded with a UNICAM UV4-100 type double-beam spectrophotometer (ATI UNICAM, Cambridge, UK). Radiometric assay of ^{233}U was carried out using a liquid scintillation counting technique using an LSC system (Hidex, Finland) coupled to a multi-channel analyzer using a dioxane-based scintillator cocktail.

2.2. Single crystal X-ray analysis

Single crystal X-ray diffraction analysis was performed by Bruker AXS SMART APE XII single crystal X-ray diffractometer equipped with graphite monochromatic MoKα (λ = 0.71073 Å) radiation and 62 mm square CCD detector. Intensity data was collected at room temperature (293K). The unit cell parameters were determined from 36 frames measured (0.5˚ phi-scan) from different crystallographic zones using the method of difference vectors. The intensity data were collected with an average fourfold redundancy per reflection and optimum resolution (0.80 Å). The intensity data collection, frames integration, Lorentz and polarization corrections and decay

correction were carried out using SAINT-NT (version 7.06a) software. An empirical absorption correction (multi-scan) was performed using the SADABS program. The crystal structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares using SHELXL-97 [35]. Molecular geometry was calculated using PARST. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the ORTEP-PLATON program. The CCDC deposition number for diphenyl phenyl aminophosphonate (DPhPhAmP) and diphenyl cyclohexyl aminophosphonate (DPhCyAmP) are CCDC 1820500 and CCDC 1820498 respectively.

2.3. Synthesis of Dibutyl butyl aminophosphonates (DBBAmP)

Dibutyl butyl aminophosphonate was synthesized by Atherton–Todd reaction [37] (Scheme 1). Ten grams (51.54 mmol) of dibutyl hydrogen phosphonate (DBP) was taken in a two neck RB containing 25 g of CCl_4 in 50 mL of dry THF. The mixture was stirred for 2 h in an ice bath. To this mixture of 4.46g (61.23 mmol) of butylamine and 15.45 g (154.63 mmol) of triethylamine (dissolving in 100 mL of THF) was added drop wise over a period of 45-60 minutes. Reaction mixture was allowed to stir for overnight. Hydrochloride salt of TEA was filtered. The organic layer was washed with water (3X50 mL), separated and dried over anhydrous Na_2SO_4. Solvent and other volatile impurities were removed using rotary evaporator and then further dried the compound through high vacuum pump for 2 h to obtain viscous yellow liquid in 12.56 g (92% isolated yield). Similar procedure was followed to synthesize DHHAmP, DOOAmP and DCyCyAmP. IR (cm^{-1}): 1022.37 (P=O), 3111.85 (N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 0.91-

0.94(t, CH_3CH_2, 9 H), 3.94-4.01 (m, P-O-CH_2, 4 H), 1.32-1.68 (m, CH_3CH_2, 14 H), ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): 9.27

2.4. Dihexyl hexyl aminophosphonates (DHHAmP): IR (cm^{-1}): 1065.43 (P=O), 3140.11(N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 0.86-0.88 (t, CH_3CH_2, 9 H), 2.83-2.89 (m, P-O-CH_2, 4 H), 1.28-1.67 (m, CH_3CH_2, 24 H), 3.93-3.99 (m, $NHCH_2$, 2 H). ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): 9.27.

2.5. Dioctyl octyl aminophosphonates (DOOAmP): IR (cm^{-1}): 1036.81 (P=O), 3221.12 (N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 0.86-0.89 (t, CH_3CH_2, 9 H), 2.84-2.89 (m, P-O-CH_2, 4 H), 1.27-1.67 (m, CH_3CH_2, 36 H), 3.93-3.99 (m, $NHCH_2$, 2 H), ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): 9.43.

2.6. Dicyclohexylcyclohxyl aminophosphonate (DCyCyAmP): IR (cm^{-1}): 1220.94 (P=O), 3226.91 (N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 4.281(m, P-O-CH, 2 H), 2.95(m, P-NH-CH, 1 H), 1.1-1.93 (m, $CH_2CH_2CH_2$, 30 H). ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): 6.58.

2.7. Synthesis of Diphenylcyclohexyl aminophosphonate (DPhCyAmP)

In an two neck RB 10g (37.22 mmol) of diphenyl phosphoryl chloride dissolved in 80 mL dry THF was taken and to that mixture of 4.54g (45.73 mmol) of cyclohexylamine and 11.21g (111.3 mmol) of triethylamine (dissolving in 100 ml of THF) was added drop wise over a period of 45-60 min in an ice bath. Reaction was carried out in nitrogen atmosphere. The reaction mixture allowed to reach at room temperature and kept for overnight stirring. White precipitate of hydrochloride salt of TEA was filtered. Organic layer was washed with water (3X50 mL), separated and dried over anhydrous Na_2SO_4 and the volatile solvent and other impurities was removed using rotary evaporator. Required compound was obtained as colorless solid (isolated yield 87.5%). Same procedure was used for the synthesis of diphenylphenyl aminophosphonate

(DPhPhAmP) and monophenyldicyclohexyl aminophosphonate (MPhDcyAmP) ligands. IR (cm^{-1}): 1190.08 (P=O), 3207.62 (N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 7.27 (d, Ar-*o*, 4 H), 7.33 (t, Ar-*m*, 4 H), 7.16 (t, Ar-*p*, 2 H), 3.26 (m, P-NH-*CH*, 1 H), 1.14-1.195 (m, $CH_2CH_2CH_2$, 24 H). ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): -1.68. ^{13}C-NMR (δ, 100 MHz, $CDCl_3$): 24.98, 25.32, 35.39, 51.26, 120.23, 124.76, 129.62, 151.03.

2.8. Diphenylphenyl aminophosphonate (DPhPhAmP): Ten grams (37.22 mmol) of diphenyl phosphoryl chloride in 80 mL dry THF, was made to reacted with 4.25g of aniline (45.73 mmol) in presence of 11.21g (111.3 mmol) of triethylamine (dissolving in 100 mL of THF) in ice cooled condition and the reaction was allowed to stir overnight. White precipitate of hydrochloride salt of TEA was filtered from the reaction mixture. The organic layer was washed with water (3X50 mL), separated, dried over anhydrous Na_2SO_4 and the volatile solvent was removed using rotary evaporator. Required compound was obtained as colorless solid (isolated yield 84.29%). IR (cm^{-1}): 1176.58 (P=O), 3170.97 (N-H). ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 7.03 (t, NH-Ar-*p*, 1 H), 7.03 (m, Ar-*o, m, p* 14 H). ^{31}P-NMR (δ, 162 MHz, $CDCl_3$): -6.81. ^{13}C-NMR (δ, 100 MHz, $CDCl_3$): 118.22, 120.39 122.25, 125.31, 129.30, 129.75, 139.12, 150.33.

2.9. Monophenyl dicyclohexyl aminophosphonate (MPhDCyAmP): Ten grams (47.39 mmol) of phenyl dichlorophosphate in 80 mL of dry THF was made to react with two equivalent of cyclohexyl amine (9.4g, 94.78 mmol) in presence of excess of triethylamine (17. 65 g, 189.56 mmol) (dissolving in 150 mL of THF) at ice cooled condition. The reaction was allowed to stir overnight. After filtering the white precipitate of hydrochloride salt of TEA the organic layer was washed with water (3X50 mL), separated and dried over anhydrous Na_2SO_4. The volatile solvent was removed using rotary evaporator. Required compound was obtained as colorless solid

(isolated yield 86%). IR (cm^{-1}): 1199.72 (P=O), 3228.84 (N-H). ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 7.16 (d, Ar-*o*, 2 H), 7.24 (t, Ar-*m*, 2 H), 7.03 (t, Ar-*p*, 1 H), 3.034 (m, P-NH-CH, 2 H), 1.05-1.86 (m, $CH_2CH_2CH_2$, 20 H).^{31}P NMR (δ, 162 MHz, $CDCl_3$): 9.34. ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 25.1, 25.44, 35.87, 50.6, 120.26, 123.97, 129.45, 151.54.

2.10. Batch studies of actinides by solvent extraction

Uranium and Americium: The extractant was pre-equilibrated with appropriate nitric acid concentration prior to the extraction studies. 2 mL of ligand solution (0.01 molar) in xylene and 2 mL of corresponding nitric acid solutions were taken in an equilibration tube, spiked with $^{233}U/^{241}Am$ tracer and equilibrated in a constant temperature bath at 303K for 2 h. After attainment of equilibrium, suitable aliquots from both the 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 concentrations of U(VI) in both the phases were measured. The equilibrium concentration of Am (III) in the aqueous and organic phases was computed by measuring the activities of the 60 keV γ photons of the respective phases using NaI(Tl) 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

$$\mathbf{D_M = \frac{[M]_{org}}{[M]_{aq}}} \qquad (1)$$

Where $[M]_{org.}$ and $[M]_{aq.}$ are the concentrations of metal ion in organic and aqueous phases respectively. All the experiment was carried out at various nitric acid concentrations ranging from 0.01M to 6 M.

Thorium: The extraction of Th(IV) was performed by following the similar experimental procedure mentioned for uranium using 0.01M solutions of extractant in xylene. Thorium amount was calculated spectrophotometrically using arsenazo-III as the chromogenic agent [38] 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

$$\mathbf{D_M = \frac{[M]_{aq(i)} - [M]_{aq(f)}}{[M]_{aq(f)}}} \quad (2)$$

Where $[M]_{aq(i)}$ and $[M]_{aq(f)}$ concentration of metal ions before and after contact with organic phase.

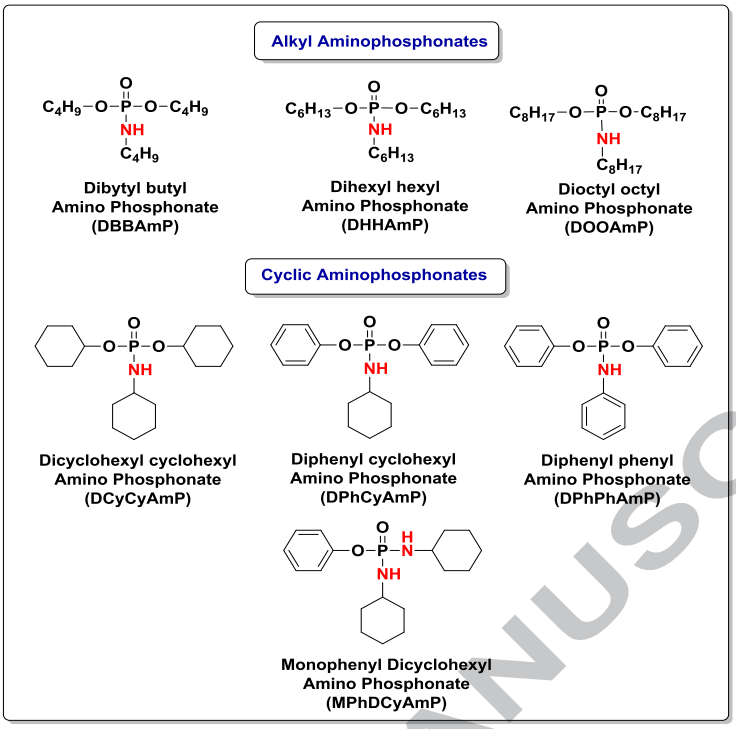


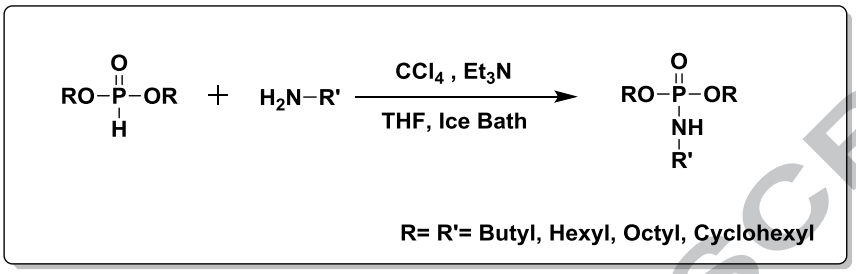
Figure 1. Ligands used in the present study

3. Results and discussions

3.1. Synthesis of aminophosphonates

All aminophosphonates were synthesized by modified literature report [37]. Purity and structural conformations of all synthesized AmPs were established by various spectroscopic techniques such as ^{31}P, ^{1}H and ^{13}C NMR (See supporting information for spectral data). Three alkyl aminophosphonates *viz.* DBBAmP, DHHAmP, DOOAmP and one cyclic aminophosphonate, DCyCyAmP were synthesized from their corresponding H-phosphonates by reacting with appropriate amines in presence of CCl_4 and TEA as shown in Scheme 1. In ^{31}P-NMR, a substantial downfield shift was observed in the AmPs compared to their precursor the H-phosphonate. Also a singlet was observed in the final aminophosphonate whereas the H-

phosphonate appears as a doublet in ^{31}P NMR suggesting the formation of the compound. For example, DCyCyAmP appears as a singlet at δ 6.58 where the starting material dicyclohexyl H-phosphonate resonates as doublet at δ 4.52 which confirms the complete conversion (Figure 2).



Scheme 1. Synthesis of alkyl aminophosphonates (AmPs)

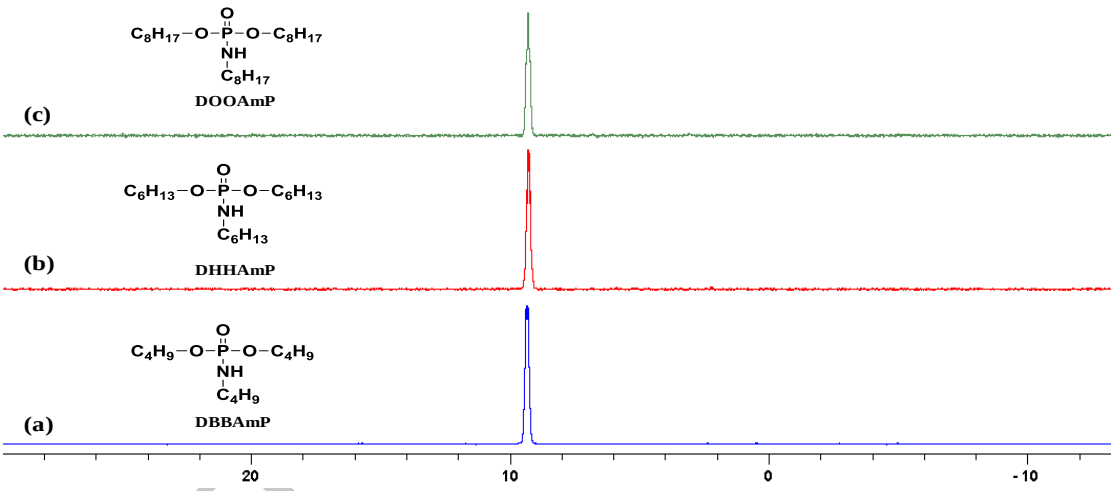
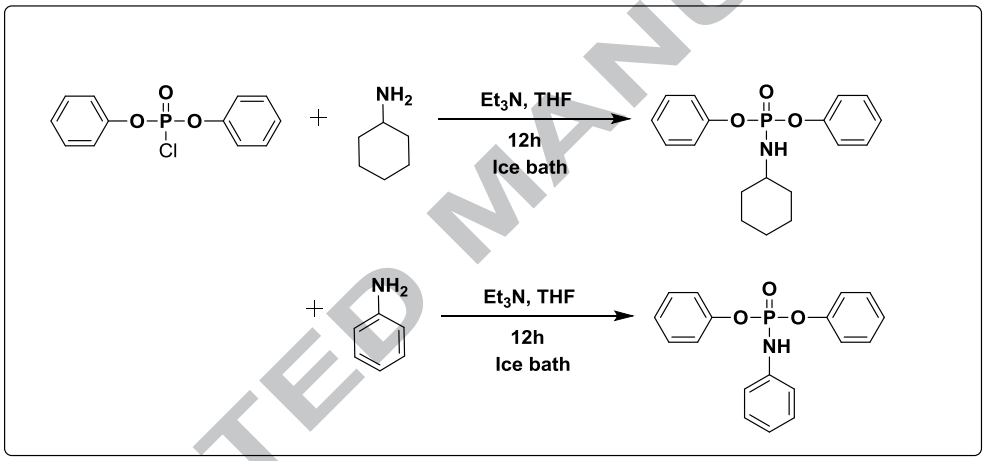


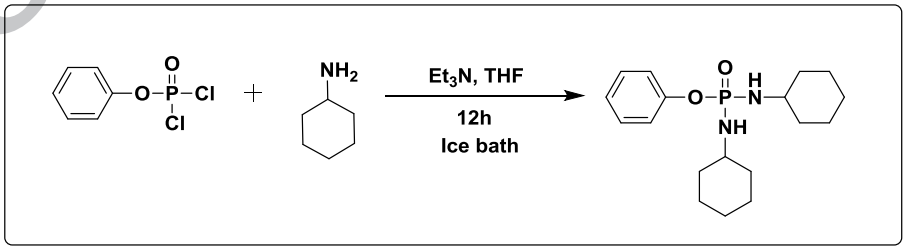
Figure 2. ^{31}P NMR overlay of alkyl aminophosphonates

Similarly DPhCyAmP (^{31}P = δ -1.68) and DPhPhAmP (^{31}P = δ -6.81) were synthesized from diphenyl phosphoryl chloride (^{31}P = δ 6.1) reacting cyclohexyl amine and phenyl amine respectively (Scheme 2), which has shown a significant up-field shift in ^{31}P NMR compared to the starting material. Two equivalents of cyclohexyl amine was reacted with one equivalent of phenylphosphinic dichloride to form MPhDCyAmP (Scheme 3) and the product derived from this reaction mixture gives a singlet at δ 9.34 which is much more deshielded than the precursor

resonating at δ -1.8 in ^{31}P NMR (Figure 3). All these AmPs showed strong infrared absorptions in the range of 1100-1200 cm^{-1} due to phosphoryl groups. The molecular structures of DPhCyAmP (Figure 4) and DPhPhAmP (Figure 5) were further confirmed by single crystal X-ray analysis. Both the molecules showed significantly short P=O bond distances as 1.4565(16) and 1.4663(11) Å respectively. The P-O bond lengths were observed in the range of 1.5785(11) to 1.5924(17) Å. In DPhPhAmP molecule, the P-N bond length was slightly longer (1.6249(13) Å) when compared to DPhCyAmP (1.6062(18) Å). Both the structures did not exhibit any considerable changes in the bond angles.



Scheme 2. Preparation of diphenylcyclohexyl aminophosphonate (DPhCyAmP) and diphenyl phenyl aminophosphonate (DPhPhAmP)



Scheme 3. Preparation of monophenyl dicyclohexyl aminophosphonate (MPhDCyAmP)

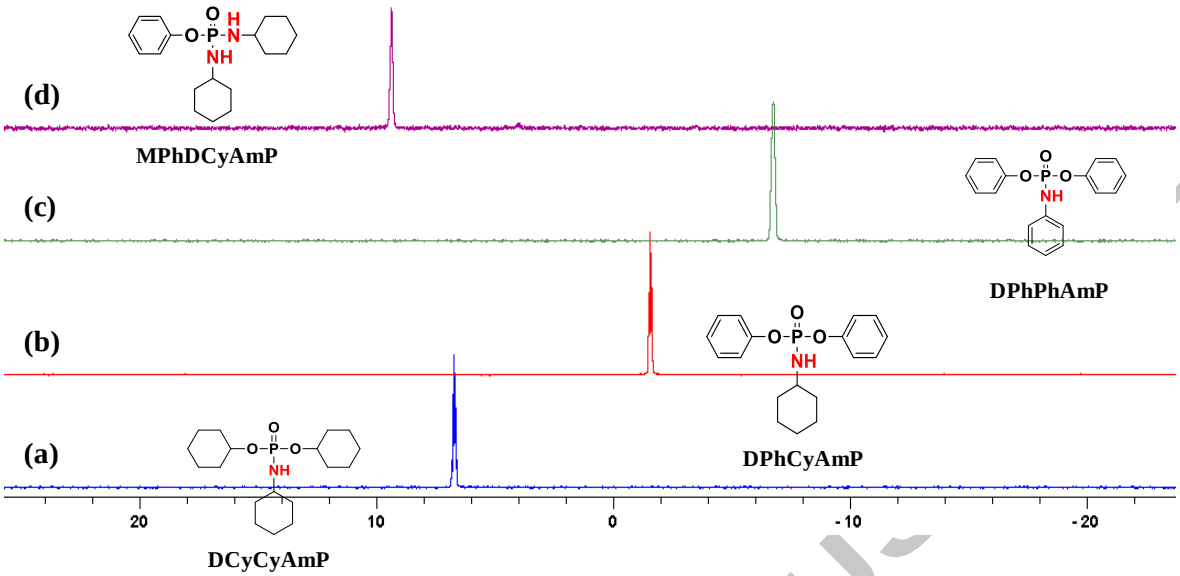


Figure 3. ^{31}P NMR overlay of cyclic aminophosphonates

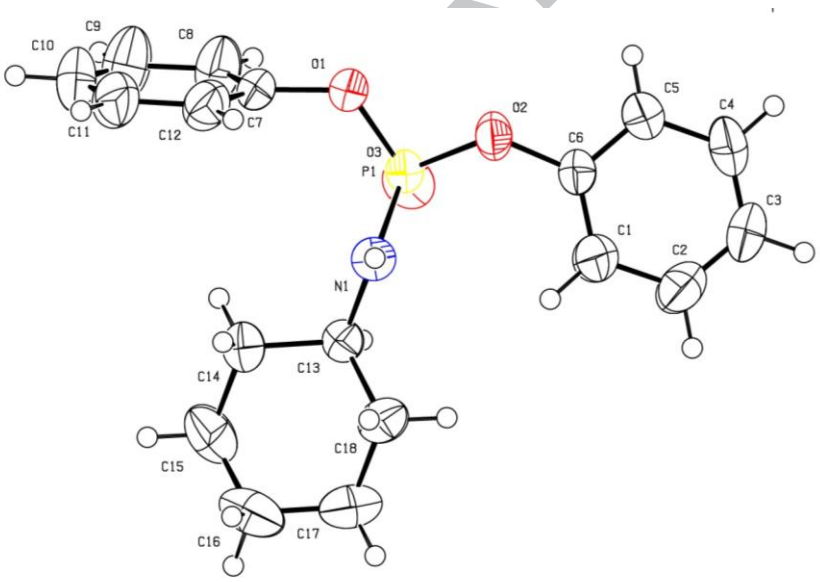


Figure 4. Molecular structure (ORTEP) of DPhCyAmP obtained by single crystal X-Ray analysis at 40 % ellipsoid levels. Some selected bond lengths (Å) are given here: P1 O2 1.4565(16), P1 O3 1.5912(15), P1 O1 1.5924(17) and P1 N1 1.6062(18); selected bond angles (°):O3 P1 O2 114.21(9), O3 P1 O1 116.64(10), O2 P1 O1 93.18(9), O3 P1 N1 113.15(10), O2 P1 N1 109.37(9) and O1 P1 N1 108.51(9).

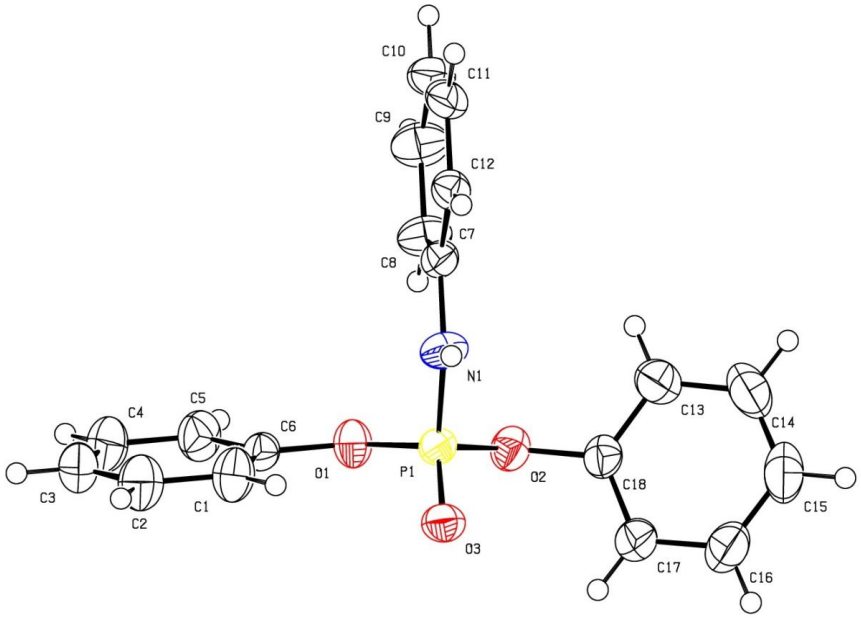


Figure 5. The ORTEP diagram of DPhPhAmP derived from single crystal XRD data drawn at 40 % ellipsoid levels; Some selected bond lengths (Å) are given here: N1 P1 1.6249(13), O1 P1 1.5785(11), O2 P1 1.5881(11) and O3 P1 1.4663(11); selected bond angles (°):O3 P1 O1 116.95(7), O3 P1 O2 114.70(7), O1 P1 O2 94.99(6), O3 P1 N1 110.08(6), O1 P1 N1 109.03(7) and O2 P1 N1 110.18(7).

3.2. Distribution studies of aminophosphonates

3.2.1 Effect of alkyl chain length in distribution studies

In the present study, 0.2 M solutions of alkyl AmPs in xylene were used. Figure 6a gives the variation of distribution coefficient of the for U(VI) by alkyl AmPs at 303K in different nitric acid concentration ranging from 0.01 – 6M. The distribution values increased gradually with the increase in nitric acid concentration. Alkyl AmPs are neutral ligands and only extracts through P=O coordination. The alkyl chain length also plays an important role in the distribution coefficient where we can see distribution value is increasing with the decrease of alkyl chain length. DBBAmP shows highest distribution among all three followed by DHHAmP and DOOAmP which suggests that lesser the steric hindrance leads to more distribution.

$$UO_2^{++}{}_{(aq)} + 2NO_3^-{}_{(aq)} + 2APA_{(org)} \rightleftharpoons UO_2(NO_3)_2 \,.\, 2APA_{(org)} \quad (3)$$

As shown in Figure 6b, $D_{Th(IV)}$ increased with increase in nitric acid concentration and reached maximum at 2M nitric acid concentration. The decrease in the D value at higher acidity is due to the inextractable anionic species and considerable extraction of nitric acid. At higher acid concentration, variation of $D_{Th(IV)}$ is greater than $D_{U(VI)}$ and this may be due to their varied solvation numbers [25].

$$Th^{4+}{}_{(aq)} + 4NO_3^-{}_{(aq)} + 3APA_{(org)} \rightleftharpoons Th(NO_3)_4 \,.\, 3APA_{(org)} \quad (4)$$

The distribution trend for Am(III) followed the same trend as that of thorium (Figure 6c). However the distribution of Am(III) is very less for alkyl AmPs as these compounds are not suitable for extraction of Am(III).

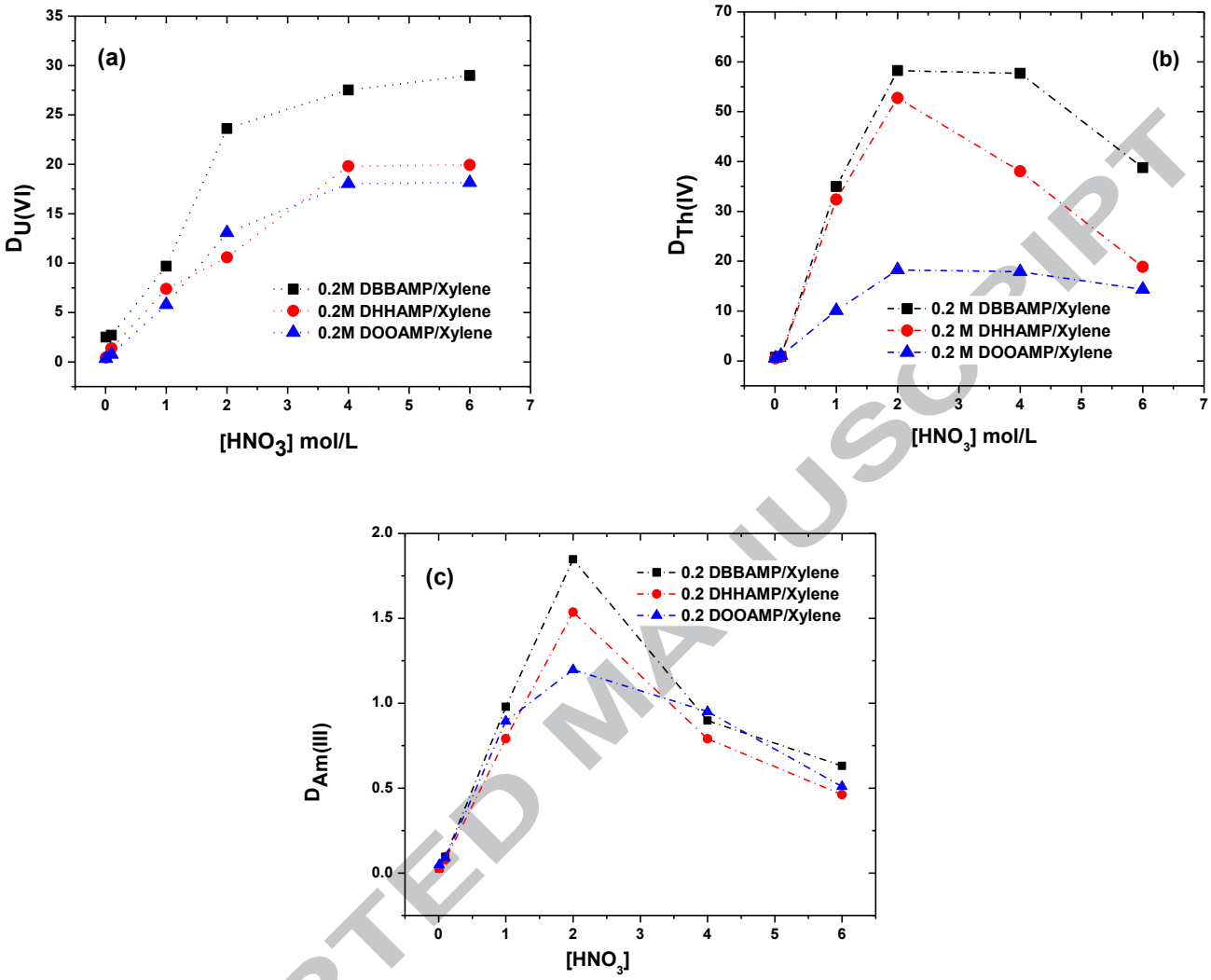


Figure 6. Variation of (a) $D_{U(VI)}$, (b) $DTh_{(IV)}$ and (c) $D_{am(III)}$ as a function of nitric acid concentration for alkyl AmPs at 303 K

3.2.2 Effect of cyclic substitution in distribution studies

Due to poor solubility of the cyclic substituted ligands (cyclic AmPs) in xylene, we have taken chloroform as diluent. Figure 7 shows the distribution coefficients of uranium and thorium at 303K as a function of nitric acid concentration for a fixed concentration of cyclic aminophosphonates (0.2 M) in chloroform. Uranium extraction was observed only in case of DCyCyAmP and MPhDCyAmP, where as DPhCyAmP and DPhPhAmP showed very less or no

distribution values. The distribution ratio of $D_{U(VI)}$ for DCyCyAmP and MPhDCyAmP increased with increase in nitric acid concentrations. Among four cyclic AmPs, only DCyCyAmP showed some significant distribution value for thorium (Figure 7b). These cyclic aminophosphonates did not show any extraction for Am(III).

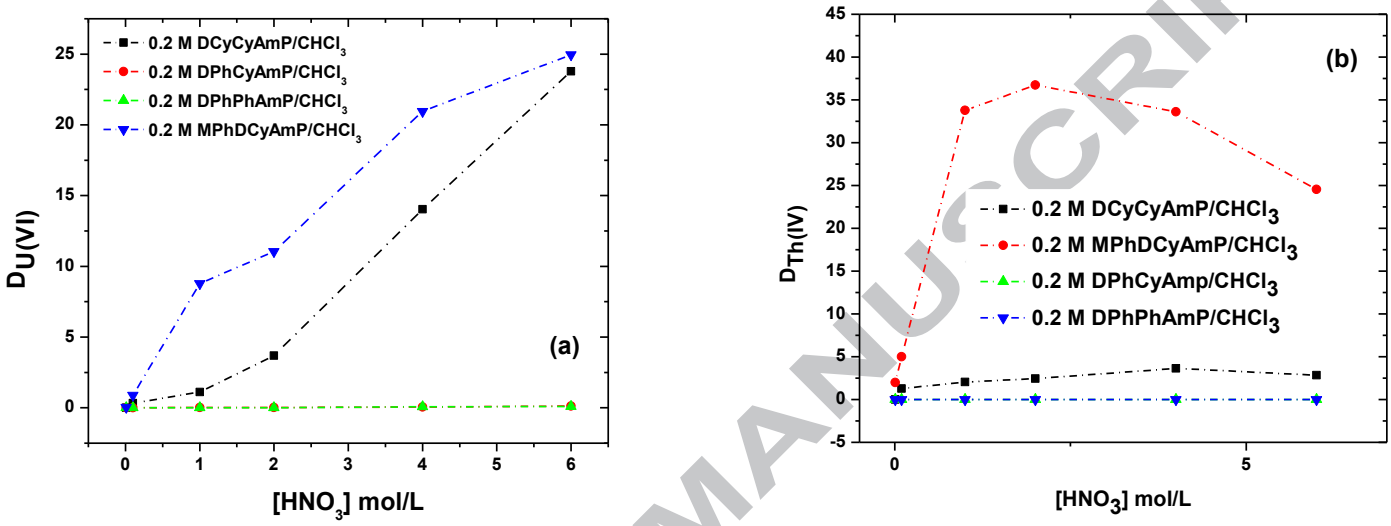


Figure 7. Variation of (a) $D_{U(VI)}$ and (b) $D_{Th(IV)}$ as a function of nitric acid concentration for cyclic AmPs at 303 K

Among these alkyl and cyclic substituted aminophosphonates, alkyl aminophosphonates showed better extraction compared to the cyclic aminophosphonate. In case of alkyl AmPs, dibutyl butyl aminophosphonate showed a better extraction for all the three actinides *viz.* U(VI), Th(IV) and Am(III). The lesser alkyl chain length makes the compound less hindered and this leads to an efficient coordination with the metal ion present in the solution. The extraction behavior of these alkyl AmPs towards U(VI), Th(IV) and Am(III) is in the following order: DBBAmP > DHHAmP > DOOAmP (Figure 8). Among the four cyclic AmPs used, MPhDCyAmP showed the highest extraction, whereas DPhPhCyAmP and DPhCyAmP did not show any extraction at all. The lower extractability of these cyclic AmPs (DPhPhCyAmP and DPhCyAmP) is due to the bulky phenyl groups that makes phosphonate more hindered and less available for the coordination with metal ions. But the different structural conformations of cyclohexyl substitution make the phosphonate more active towards the metal centre.

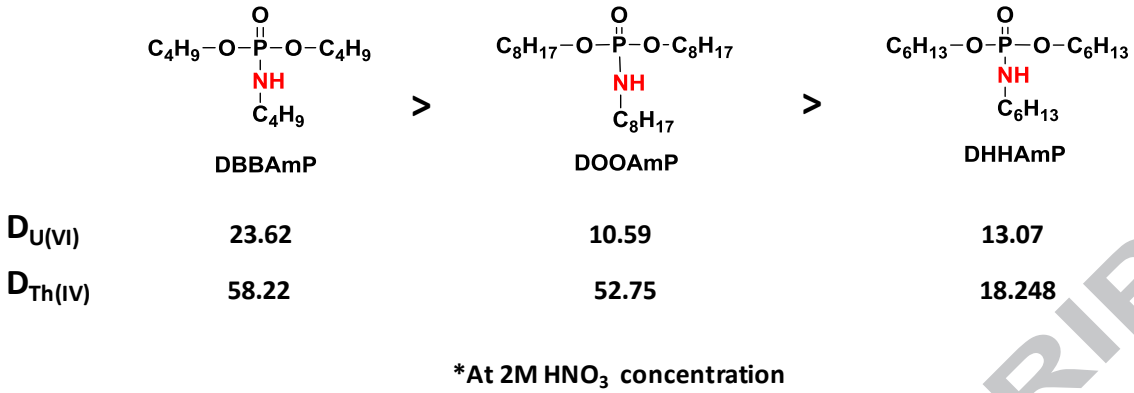


Figure 8. Distribution trends for alkyl AmPs towards $D_{U(VI)}$ and $D_{Th(IV)}$ at 2M nitric acid concentration at 303 K

In another study, we have taken 0.2M TBP solution in xylene where the distribution of U(VI) was measured in 4M HNO_3 and compared with $D_{U(VI)}$ of DBBAmP under identical experimental conditions. A significant difference in distribution was found between the $D_{U(VI)}$ of TBP and DBBAmP. TBP showed distribution value of 6, whereas DBBAmP showed four times higher $D_{U(VI)}$ value (than TBP) i,e 28. This suggests that the displacement of one of the butoxy group (-OC_4H_9) in TBP with butylamine (-NH C_4H_9) can enhance the extractability of uranium.

4. Conclusions

Seven different aminophosphonates with alkyl, cyclohexyl and phenyl substitution were synthesized and characterized with various spectroscopic techniques, such as FT-IR, ^{1}H, ^{13}C, and ^{31}P NMR. The molecular structure of diphenyl phenyl aminophopshonate (DPhPhAmP) and diphenyl cyclohexyl aminophosphonate (DPhCyAmP) were elucidated based on the single crystal XRD analysis. These synthesized AmPs were tested for extraction of U(VI), Th(IV), and Am(III). Among these AmPs, alkyl substituted ones (alkyl AmPs) showed better distribution towards the actinides compared to the cyclic substituted aminophosphonates (cyclic AmPs). Among the three different alkyl substituted aminophosphonates, DBBAmP showed better

extraction towards the actinides studied. The extraction behavior of these alkyl substituted AmPs are in the following order: DBBAmP > DHHAmP > DOOAmP. The influence of various substituents on AmPs was clearly seen on the distribution values, where short alkyl chain length makes the compound less hindered and more available for the binding with metal ions. In case of the cyclic substituted AmPs, only MPhDCyAmP showed the significant extraction of uranium and thorium, among the four. We have demonstrated that DBBAmP shows four fold better extractability of uranium when compared with commonly used TBP extractant at 4M HNO_3 concentration.

References

[1] X. Sun, H. Luo, S. Dai, Chem. Rev. 112 (2011) 2100-2128.

[2] W.D. Bond, Thorex Process, in: L.L.B. W.W. Schulz, J.D. Navratil and K.P. Bender (Ed.), Science and Technology of Tributyl Phosphate, CRC Press, Florida, 1990, pp. 225-247.

[3] Solvent extraction principle and practice, 2 ed., Marcel Dekker, New York 2004.

[4] S.A. Ansari, P. Pathak, P.K. Mohapatra, V.K. Manchanda, Sep. Purif. Rev. 40 (2011) 43-76.

[5] T.H.P. M. Benedict, H.W. Levi., Nucl. Chem. Eng., McGraw-Hill, New York, 1981.

[6] J. Mathur, M. Murali, K. Nash, Solvent Extr. Ion Exchn. 19 (2001) 357-390.

[7] C. Apostolidis, R. De Meester, L. Koch, R. Molinet, J. Liang, Y. Zhu, The Extraction of Acitnides and Other Constituents from Highly Active Waste (HAW) by Trialkyl Phosphine Oxide (TRPO), New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications, Springer1991, pp. 80-86.

[8] M. Murali, J. Mathur, Solvent Extr. Ion Exch. 19 (2001) 61-77.

[9] T. Sato, J. Inorg. Nucl. Chem. 24 (1962) 699-706.

[10] Y. Morita, M. Kubota, Journal of Nucl. Sci. Technol. 24 (1987) 227-232.

[11] V. Manchanda, P. Pathak, Sep. Purif. Technol. 35 (2004) 85-103.

[12] S. Ansari, P. Pathak, V. Manchanda, M. Husain, A. Prasad, V. Parmar, Solvent Extr. Ion Exch. 23 (2005) 463-479.

[13] H. Mckay, The PUREX process, Science and technology of tribuytl phosphate1990.

[14] E. Philip Horwitz, D.C. Kalina, H. Diamond, G.F. Vandegrift, W.W. Schulz, Solvent Extr. Ion Exch. 3 (1985) 75-109.

[15] C. Madic, P. Blanc, N. Condamines, P. Baron, L. Berthon, C. Nicol, C. Pozo, M. Lecomte, M. Philippe, M. Masson, Actinide partitioning from high level liquid waste using the DIAMEX process, CEA Centre d'Etudes de la Vallee du Rhone, 1994.

[16] N. Boubals, M.G.B. Drew, C. Hill, M.J. Hudson, P.B. Iveson, C. Madic, M.L. Russell, T.G.A. Youngs, Dalton Trans. (2001) 55-62.

[17] C. L. Xiao, C. Z. Wang, L. Mei, X. R. Zhang, N. Wall, Y. L. Zhao, Z. F. Chai, W. Q. Shi, Dalton Trans. 44 (2015) 14376 - 14387

[18] J. H. Lan, W. Q. Shi, L. Y. Yuan, J. Li, Y. L. Zhao, Z. F. Chai, Coord. Chem. Rev. 256 (2012) 1406 – 1417

[19] W. Q. Shi , L.Y. Yuan , C. Z. Wang , L. Wang , L. Mei , C. L. Xiao , L. Zhang , Z. J. Li , Y. L. Zhao , Z. F. Chai, Adv. Mater. 26 (2014) 7807–7848

[20] D.L. Clark, S.S. Hecker, G.D. Jarvinen, M.P. Neu, in: L. R., N.M.E. Morss, J. Fuger (Eds.), The Chemistry of the Actinide and Transactinide Elements, Springer, Netherlands, 2006.

[21] S. Ahrland, J. O. Lijenzin, R. Rydberg, in: J. Bailar, H. Emeleus, R. Nyholm (Eds.), Comprehensive inorganic chemistry, Pergamon Press, Oxford, 1975, p. 337.

[22] G.W. Mason, H.E. Griffin, Demonstration of the Potential for Designing Extractants with Preselected Extraction Properties: Possible Application to Reactor Fuel Reprocessing, Actinide Separations, American Chemical Society1980, pp. 89-99.

[23] C. V. S. Brahmmananda Rao, T. Srinivasan, P. Vasudeva Rao, Solvent Extr. Ion Exch. 28 (2010) 202-224.

[24] C. V. S. Brahmmananda Rao, T. Srinivasan, P. Vasudeva Rao, Solvent Extr. Ion Exch. 30 (2012) 262-277.

[25] C. V. S. Brahmmananda Rao, T. Srinivasan, P. Vasudeva Rao, Solvent Extr. Ion Exch. 25 (2007) 771-789.

[26] S. Annam, G. Gopakumar, C.V.S. Brahmmananda Rao, N. Sivaraman, A. Sivaramakrishna, K. Vijayakrishna, Inorg. Chim. Acta 469 (2018) 123-132.

[27] D. Das, A. Sivaramakrishna, C.V.S. Brahmmananda Rao, N. Sivaraman, K. Vijayakrishna, Polym. Int. 67 (2018) 374-379.

[28] C. V. S. Brahmmananda Rao, S. Jayalakshmi, S. Subramaniam, N. Sivaraman, P. Vasudeva Rao, Radiochim. Acta 103 (2015) 345-358.

[29] S. Annam, G. Gopakumar, C. V. S. Brahmmananda Rao, N. Sivaraman, A. Sivaramakrishna, K. Vijayakrishna, Radiochim. Acta 105 (2017) 329-339.

[30] D. Das, E.V. Goud, S. Annam, S. Jayalakshmi, G. Gopakumar, C.V.S. Brahmmananda Rao, N. Sivaraman, A. Sivaramakrishna, K. Vijayakrishna, RSC Adv. 5 (2015) 107421-107429.

[31] D. Das, G. Gopakumar, C.V.S. Brahmmananda Rao, N. Sivaraman, A. Sivaramakrishna, K. Vijayakrishna, J. Coord. Chem. 70 (2017) 3338-3352.

[32] T. Siddall III, Industrial and Engineering Chemistry (US) Formerly J. Ind. Eng. Chem. Superseded by Chem. Technol. 51 (1959).

[33] D. Madigan, R. Cattrall, Journal of Inorg. and Nuclear Chem. 21 (1961) 334-338.

[34] C. V. S. Brahmmananda Rao, S. Jayalakshmi, N. Sivaraman, P. Vasudeva Rao, Radiochim. Acta 103 (2015) 235-243.

[35] D. Das, A. Sivaramakrishna, G. Gopakumar, C.V.S. Brahmmananda Rao, N. Sivaraman, K. Vijayakrishna, Polyhedron 141 (2018) 215-222.

[36] G. Sheldrick, SHELXL-97 and SHELXS-97, University of Göttingen, Germany (1997).

[37] S.S. Le Corre, M. Berchel, H. Couthon-Gourvès, J.-P. Haelters, P.-A. Jaffrès, Beilstein J. Org. Chem. 10 (2014) 1166-1196.

[38] J. Pérez-Bustamante, F.P. Delgado, Analyst 96 (1971) 407-422.

Highlights

A study on the extraction behavior of aminophosphonates (AmPs) to wards actinides as a function of alkyl, cyclic and alicyclic substituents. From these studies it is observed that aminopphosphonates bearing alkyl substation are better for actinide extraction. Its worth mentioning that aromatic substituted AmPs did not showed any extraction towards the actinides.