Research paper

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PII: S0020-1693(19)30362-7
DOI: https://doi.org/10.1016/j.ica.2019.05.034
Reference: ICA 18935

To appear in: *Inorganica Chimica Acta*

Received Date: 19 March 2019
Revised Date: 17 May 2019
Accepted Date: 18 May 2019

Please cite this article as: G. Jegan, A. Suresh, C.V.S. Brahmmananda Rao, B. Sreenivasalu, N. Sivaraman, Synthesis, characterization and evaluation of phosphoramides for actinide extraction, *Inorganica Chimica Acta* (2019), doi: https://doi.org/10.1016/j.ica.2019.05.034

Synthesis, characterization and evaluation of phosphoramides for actinide extraction

G. Jegan, A. Suresh*, C.V.S. Brahmmananda Rao, B. Sreenivasalu, N. Sivaraman
Homi Bhabha National institute, MC&MFCG, IGCAR, Kalpakkam-603102

Abstract

A new class of extractants called hexaalkylphosphoramides has been chosen for actinide separation applications in the present study. Hexaalkylphosphoramides [$(NR_2)_3P=O$] are compounds which possess three nitrogen sub-units along with a strong donor oxygen atom. The studies on them provide an opportunity to synthesize a large variety of structurally diverse analogs. Thus, the desired properties of the extractant can be tuned for a specific application. We discuss the synthesis, purification, and characterization of two such hexaalkylphosphoramides (Propyl and Butyl) in this paper. Their physico-chemical properties were measured and the extraction behavior was evaluated with U(VI), Th(IV) and Pu(IV). The results were compared with trialkyl phosphates such as tri-*n*-butyl phosphate (TBP) and tri-n-amyl phosphate (TAP). The results revealed that the extraction behaviors of phosphoramides are comparable to trialkyl phosphates.

Keywords: Trialkyl phosphates, alternate extractants, phosphoramides, physical properties, actinides separation.

1 Introduction

In recent years, there has been increasing interest in the reprocessing of spent nuclear fuels for the effective utilization of the fissile and fertile materials of the irradiated fuel. PUREX **[1]** and THOREX **[2]** processes have been widely employed for the processing of uranium and thorium based irradiated fuels, respectively. In PUREX process, 1.1 M solution of TBP in *n*-dodecane has

been used as the solvent. TBP has excellent extraction properties albeit with some limitations with respect to third phase formation in the extraction of tetravalent metal ions such as Th(IV), Pu(IV) and Zr(IV) **[3]**. TBP also exhibits poor selectivity of uranium over thorium which is crucial in U/Th separation during reprocessing of thorium based irradiated fuels. In PUREX process, TBP undergoes hydrolyses and form dibutylphosphoric acid (HDBP) and monobutyl phosphoric acid (H2MBP). The above hydrolyzed products formed during the processing have the strong complexing ability towards fission products like Zr and Ru thereby reducing the decontamination factors **[4 - 6]**. The third phase formation and solvent degradation are the main concerns in fast reactor fuel reprocessing due to high plutonium content and activity of the dissolver solutions. Therefore, the development of an alternate extractant is needed for spent fuel reprocessing, especially, for the fast reactor fuel reprocessing. In order to identify an alternate extractant to overcome these limitations, higher homologs of TBP such as Tri-*n*-amyl phosphate (TAP), Tri-iso-amyl phosphate (TiAP), Tris-2-methylbutyl phosphate (T2MBP), etc. were investigated in our laboratory **[7]**. Our studies revealed that TiAP and T2MBP are potential extractants for fast reactor spent fuel reprocessing. These studies further revealed that with an increase in carbon chain length of alkyl groups increases the hydrophobicity of the solvent. The metal solvate is more compatible with the diluent, thereby reducing the tendency to form the third phase. We have also established that TsBP is suitable for U/Th separation. The results of the investigation indicated that branching adjacent to the P=O group of the ligand, increases the separation factor for U and Th. Studies on N, N-dialkyl amides also revealed that increase in the carbon number of the extractant as well as the branching around the donor group of the ligand, significantly influences the metal ion extraction thereby yielding higher U/Th separation factor **[8 - 11].**

The *n*-alkyl and cyclic amino phosphine oxides, which are structural analogs to TBP have also been investigated for the selective extraction of actinide metal ions **[12]**. Their study also revealed that the structural modification of phosphine oxides by its alkyl substituents significantly changes the basicity of the compound. Investigations on phosphonates and its derivatives also concluded that modification of the alkyl substituent around P=O group in the molecule has its influence on the basicity of the coordinating group thereby altering the extraction behavior **[13, 14].**

Hexamethylphosphoramide (HMPA) and hexaethylphosphoramide (HEPA) are phosphoramides, which finds applications in catalysis for organic synthesis **[15]**. The strong basic nature of the HMPA also makes it a good ligand and form complexes with various metal ions **[16, 17]**. Moreover, the phosphoramide based compounds are used as inhibitors for the enzymatic reaction such as the urease **[18]**, acetyl cholinesterase **[19]** and butyl cholinesterase **[20]**. In addition, these find applications in agriculture as pesticides and insecticides **[21, 22]**.

A large number of trialkyl phosphates and dialkyl amides have been developed over the past three decades in order to overcome the limitations of TBP. However, phosphoramides have not been investigated for the extraction of actinides. We ventured to investigate the extraction behavior of actinides and fission products with phosphoramides. The results of our investigation were compared with TBP. The feasibility of hexaalkylphosphoramides [$(R_2N)_3PO$ (R=Propyl (HPPA) and Butyl (HBPA)] for actinides separations have been examined in this paper. The

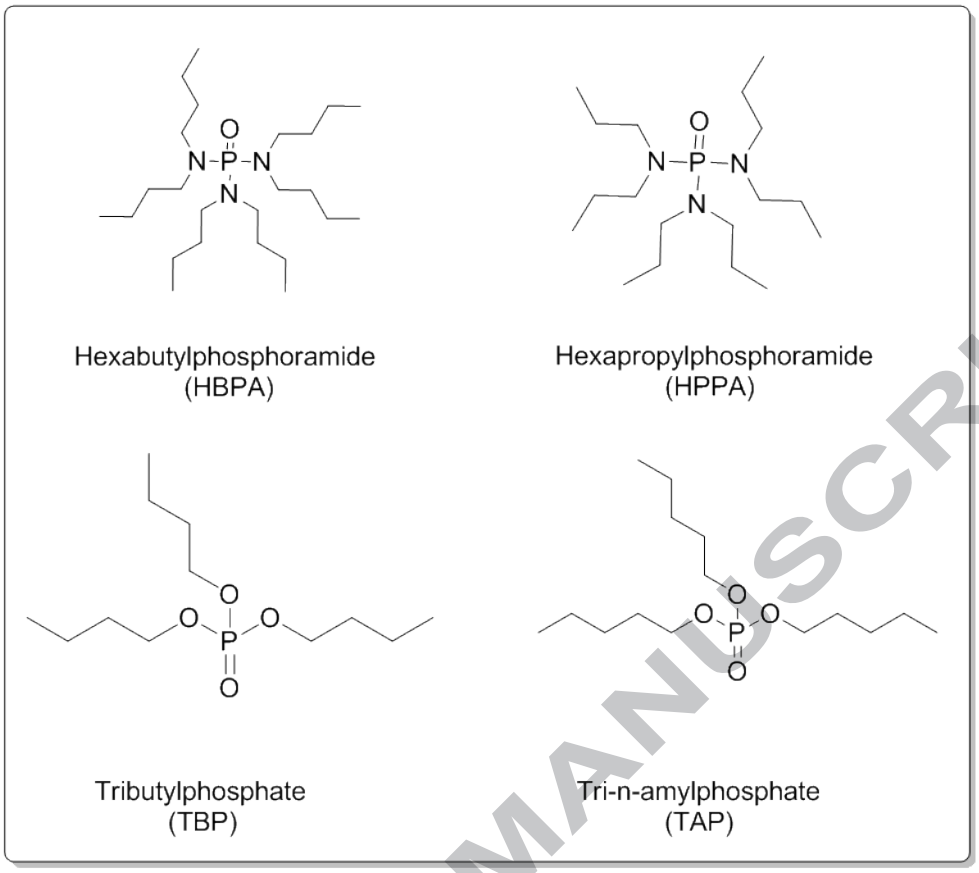

Fig. 1. Chemical structures of the extractants used for actinide extraction.

chemical structure of the phosphoramides and trialkyl phosphates are shown in Fig.1. In the present study, hexapropylphosphoramide (HPPA) and hexabutylphosphoramide (HBPA) were synthesized, purified, and characterized by using analytical techniques like NMR (^{31}P, ^{1}H& ^{13}C), IR spectroscopy, mass spectrometry (GC-MS).

Physicochemical properties like density, aqueous solubility, and solubility of water in phosphoramides have been measured. The extraction behavior of U(VI), Th(IV) and Pu(IV) with 1.1M solutions of HBPA and HPPA in *n*-dodecane have been investigated as a function of equilibrium aqueous phase nitric acid concentration.

2 Experimental

2.1 Materials

Phosphoryl chloride ($POCl_3$), triethylamine, Di-*n*-butylamine, Di-*n*-Propylamine, Silica gel (60-120 mesh), *n*-dodecane, hexane, ethyl acetate, 1-(2-Arsonophenylazo)-2-naphthol-3,6-disulfonic acid disodium salt (Arsenazo-III), 2-(3,6-Disulfo-2-hydroxy-1-naphthylazo)benzene arsonic acid disodium salt (Thoron), 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAD) and dichloromethane (DCM) (M/s. Merck.) were used as received. Nuclear grade thorium nitrate received from Indian Rare Earths Ltd., Mumbai, India was used without further treatment. $UO_2(NO_3)_2.6H_2O$ obtained from BDH, Poole, England was used as received. Plutonium (principal isotope: ^{239}Pu) is used as radioactive tracer. Plutonium was purified with 0.5M TTA/xylene for the removal of americium. Plutonium was selectively extracted with 0.5M TTA/xylene at 1M HNO_3 leaving Am in the aqueous phase followed by scrubbing with 7M HNO_3. Subsequently, the plutonium loaded in 0.5M TTA/xylene was stripped into aqueous phase using 8M HNO_3. The stripped plutonium is used as radioactive tracer. 1.1M solutions of phosphoramides were prepared by taking the required quantity of phosphoramides and *n*-dodecane in volumetric flasks.

2.2 Synthesis of extractants

Phosphoramides were synthesized by the condensation reaction between $POCl_3$ and corresponding dialkyl amines as shown in Fig. 2.

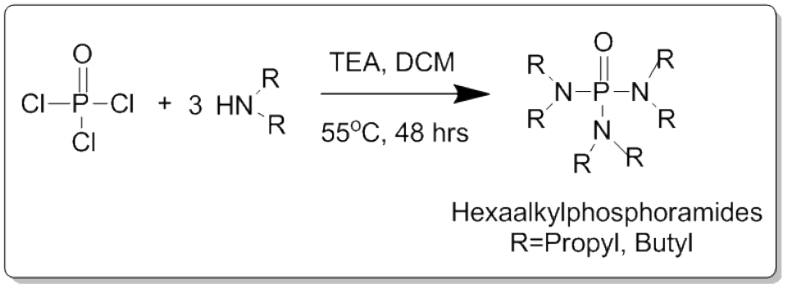

Fig. 2. Schematic representation for synthesis of Hexaalkylphosphoramide.

2.2.1. Synthesis of Hexabutylphosphoramide (HBPA)

To a round bottom flask, triethylamine (0.3 mol) and DCM (100 mL) were added. Then, the solutions of di-*n*-butylamine (0.3 mol) in DCM (100 mL) and phosphoryl chloride (0.1 mol) in DCM (25 mL) were added drop wise for 2 hrs. under reflux conditions (~55^{0}C). After the addition, the solution was refluxed for 48 hrs and subsequently treated with 50 mL of 4N HCl followed by deionized water. The crude product was obtained by evaporating DCM by using rotary evaporator. The crude product was made into slurry with silica gel (60-120 mesh). In a glass column, it was packed in the ratio of 1:10 with respect to slurry and silica gel. Hexane was passed through the column to remove non-polar impurities. Phosphoramide compound was eluted from a column with the mixture of hexane and ethyl acetate. (SiO_2, 60-120 mesh, hexane/EtOAc 9.5/0.5) and the yield is around 65%. ^{1}H NMR (400 MHz, $CDCl_3$); d=0.84-0.88 (t, 18H), 1.18 - 2.26 (m, 12H), 1.44 -1.52 (m, 12H), 2.94 – 3.01 (m, 12H) ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$); d = 28.28–28.78 (m, $^1J_{PH}$ = 691 Hz) ppm. ^{13}C NMR (162.01 MHz, $CDCl_3$); 13.51, 19.91, 29.90, 45.66 ppm.

2.2.2 Synthesis of Hexapropylphosphoramide (HPPA)

HPPA was synthesized from Di-n-propyl amine and the synthetic route for HPPA is similar to HBPA. The yield is around 66%. ^{1}H NMR (400 MHz, $CDCl_3$); d = 0.80 - 0.84 (t, 18H), 1.48 - 1.56 (m, 12H), 2.91 – 2.98 (m, 12H) ppm. ^{31}PNMR (162.01 MHz, $CDCl_3$); d = 28.15–28.64 (m, $^{1}J_{PH}$ = 691 Hz) ppm. ^{13}C NMR (162.01 MHz, $CDCl_3$); 10.88, 20.90, 47.65 ppm.

2.3 Instrumentation

The structures of the extractants were elucidated by using Bruker DMX-400 spectrometer for ^{1}H, ^{13}C, and ^{31}P NMR spectra. All the ^{1}H chemical shifts were reported with respect to tetramethyl silane (TMS) (all at 298 K, $CDCl_3$). The characteristic stretching frequencies of functional groups of the extractants were identified by using Shimadzu Affinity 1 FT-IR Spectrometer. SHIMADZU UV-3600 double-beam spectrophotometer was employed for determining U(VI) and Th(IV) present in the organic and aqueous phases using the methods described below. The concentration of Pu(IV) was analyzed by using Liquid Scintillation Counter (LSC) (300SL TDCR liquid scintillation analyzer, Hidex, Finland).

2.4 Physical properties of extractants

2.4.1 Density measurement

The density of phosphoramides (undiluted and 1.1M solution in *n*-dodecane) was measured using mass(m) to volume(v) ratio of the compound. In this method, a glass micropipette (500µL, BOROSIL®, India) was filled with a phosphoramide and weighed by using an analytical balance of ±0.1mg sensitivity at 299 ±1K. In this experiment, previously weighed glass micropipette was used for weighing the sample.

2.4.2 Solubility of water in phosphoramides

The solubility of water in phosphoramides was measured using the gravimetric method. Phosphoramide (5 mL) was equilibrated with an equal volume of deionized water for an hour at 299±1K. After equilibration and centrifugation, the organic and aqueous layers were separated. A known amount of separated organic layer (3-4 g) was taken into a previously weighed 25 mL round-bottomed flask. The dissolved water from the sample was removed by vacuum using a rotary evaporator. Once the sample has attained constant weight after the complete removal of water, the RB was weighed. The solubility of water in phosphoramides was obtained from the weight difference of the flask containing the sample before and after the evaporation. The aqueous phase collected from this experiment was used for measuring the aqueous solubility of phosphoramide. Karl Fischer method was also employed to find out the water content present in phosphoramides (undiluted as well as the 1.1M solution).

2.4.3 Solubility of phosphoramides in water

Aqueous phase collected from the above experiment was transferred into a separating funnel and allowed to settle. The top portion of the aqueous phase in the separating funnel was discarded to ensure the complete elimination of organics from the aqueous sample and centrifuged prior to the analysis. The aqueous sample was analyzed for carbon by using TOC analyzer (SHIMADZU model TOC-V_{CPH}).

2.5 Procedure for Solvent Extraction Experiments

2.5.1 Extraction of Nitric Acid

The extraction of nitric acid by phosphoramides was investigated by equilibrating 1.1 M phosphoramides in *n*-dodecane (2 mL) with an equal volume of nitric acid solutions for 2 hrs. at 303±1K. After equilibration, the phases were allowed to settle by gravity. Nitric acid in organic

and aqueous samples was estimated by titrating suitable aliquot with standardized NaOH solution using phenolphthalein as the indicator.

2.5.2 Extraction of U(VI), Pu(IV) and Th(IV) as a function of equilibrium aqueous phase nitric acid concentration

Stock solutions containing 500 and 600 µg/mL of Th(IV) and U(VI), respectively were prepared in various nitric acid media (0.01 M to 6M). The extraction behavior of U(VI), Pu(IV) and Th(IV) was investigated as a function of equilibrium aqueous phase nitric acid concentration (0.01M to 6M). 1.1M solution of a phosphoramide in *n*-dodecane (2 mL) was equilibrated with an equal volume of nitric acid solution containing the metal ion (Th(IV) or U(VI)) for one hour by using a magnetic stirrer. The temperature was maintained at 303±1K using a constant temperature water bath. In the case of Pu(IV), plutonium tracer (10^{-4} to 10^{-5} M) (major isotope: ^{239}Pu) was added to the aqueous phase. After equilibration, the phases were allowed to settle by gravity. Metal ion concentrations in aqueous and organic phases were estimated by suitable methods by taking appropriate aliquots. From equation 1, D values were obtained for actinide metal ions.

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

2.5.3 Analytical Procedures

The Spectrophotometric method was employed for the estimation of U(VI) and Th(IV) in the aqueous and organic phases. The U(VI) was estimated by using Br-PADAP as the chromogenic agent by measuring the absorbance at λ_{max} of 577±1 nm. Th(IV) was estimated using Thoron as the chromogenic agent by measuring the absorbance at λ_{max} of 541±1 nm **[23-26].** The precision

of spectrophotometric determination was better than ±3% and nitric acid estimation was better than ±1%. The amount of Pu(IV) in aqueous and organic phases was measured by liquid scintillation counting (LSC) technique by taking suitable aliquots and precision of the method is ±1%.

3 Results and discussion

3.1 Density of hexaalkylphosphoramides

Density is an important physical property of the extractant for separation processes. An optimum difference in densities of the aqueous and organic phases results in faster separation of the phases after extraction.

Table 1. Density of phosphoramides and trialkyl phosphates (dry, water-saturated (WS) and 1.1 M solutions in *n*-dodecane) at 299±1K

	Density, ρ (g/mL)		
	Undiluted		
Extractants	**Dry**	**WS**	**1.1 M solutions in *n*-DD**
HPPA	0.971	0.981	0.826
HBPA	0.924	0.954	0.834
TBP	0.976	0.980	0.812
TAP	0.954	0.960	0.814

*precision of the density measurement is ±0.2%

The trends in the variation of density as a function of the number of carbon atoms present in the molecule for various systems (*n*-alkyl phosphoramides, n-alkanes, n-alkyl phosphates) are shown in (Fig.3.)

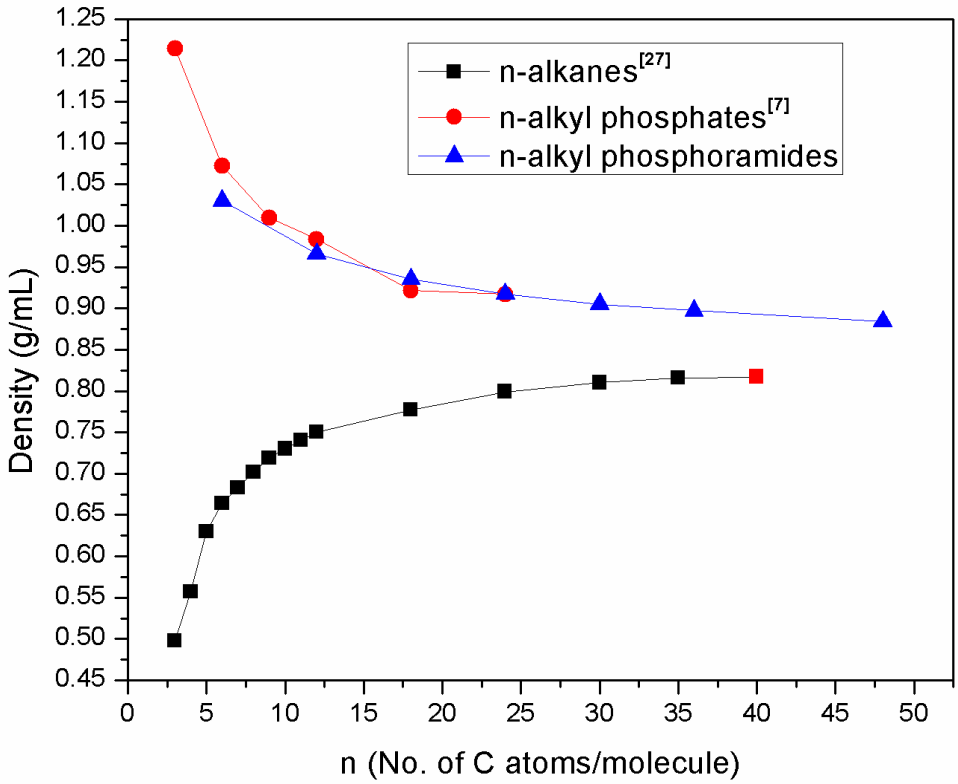

Fig. 3. Density variation of the extractants (phosphoramides and phosphates) and hydrocarbons with an increase in the carbon atoms.

The density of an organic compound depends on its mass, shape and intermolecular interactions. In the case of linear hydrocarbons, the density gradually increases with an increase in the number of carbon atoms **[27]**. This can be attributed to "Van der Waals" interaction between the molecules. Therefore, the strength of Van der Waals force is directly related to its size of the molecule. Hence, there is an increase in density with an increase in the carbon number in the case of hydrocarbons. For trialkyl phosphates, the density of the compound decreases with increase in molecular mass. It is reported that there is a decrease in density of trialkyl phosphates with an increase in the number of carbon atoms **[7]**. Unlike hydrocarbons, trialkyl phosphates

have dipole-dipole interactions operate between the molecules besides van der Waals interaction. If the size of the molecule is small, intermolecular dipole-dipole interaction between the P=O groups of molecules is predominant and leads to close packing of molecules. The dipole-dipole interaction diminishes and the Van der Waals force of attraction becomes dominant with the increase in the number of carbon atoms. In such cases, the net effect is a reduction in density due to the close packing of molecules. Therefore, phosphoramides having non-polar alkyl groups and polar P=O entity also likely to exhibit similar trends. This can be illustrated by comparing different phosphoramides with a large difference in carbon number. For example, hexamethyl phosphoramide (HMPA) with six carbon atoms has a density of around 1.030 g/mL, whereas, hexahexyl phosphoramide (HHPA) with thirty-six carbon atoms has a density of around 0.812 g/mL **[31]**. The present study also indicates that the crowding near P=O group of the extractant as in the case of phosphoramides due to the presence of more number of alkyl groups diminishes the dipole-dipole interaction and lowers the density of the molecule. This effect can be seen from Table 1 which provides a comparison of densities between trialkyl phosphates and hexaalkyl phosphoramides containing three and six alkyl groups, respectively. It is interesting to note that despite the higher molecular weight, both the phosphoramides (HPPA and HBPA) exhibit lower density of 0.971 g/mL and 0.921 g/mL, respectively, as compared to TBP (0.976 g/mL). However, the densities of 1.1M solutions of phosphoramides in *n*-DD are comparable to that of 1.1M TBP/*n*-DD due to the presence of higher volume fraction of the extractant.

3.2 Solubility of Water in phosphoramides

Table 2. Data on solubility of water in Phosphoramides and Trialkyl phosphates at 299±1K

Extractants	**Solubility of H_2O in extractant**				**1.1 M solutions in *n*-DD**	
	mg/mL	**mg/mL**	**mg/mL**	**mol/L**	**mg/mL**	**mol/Lit**

	(1)	(2)	average			
HPPA	204.8	201.2	203.0	11.27	44.6	2.477
HBPA	74.8	71.6	73.2	4.06	31.1	1.727
TBP	66.3	67.7	67.0	3.37	9.1	0.506
TAP	41.4	40.0	40.6	2.26	7.8	0.433

*(1) Gravimetry method: Precision of solubility measurement is ±3%.
(2) Karl Fischer titration: Precision of solubility measurement by Karl Fischer titration is ±3%.

The solubility of water in trialkyl phosphates is attributed to hydrogen bonding between the P=O group of the extractant and water molecules **[7]**. Earlier, we have investigated the effect of structural modification of trialkyl phosphates on the solubility of water in these extractants. In the present study, similar measurements have been made with phosphoramides. Results indicated that the solubility of water in phosphoramides decreases with an increase in the number of carbon atoms. This is in accordance with the hydrophobicity of the extractants, i.e. solubility of water decreases with an increase in the hydrophobicity of the extractants. Therefore, the structural modification of the extractant by varying the alkyl groups can significantly influence the solubility of the water in phosphoramides. Data on the solubility of water in undiluted HPPA and HBPA at 298±1K are given in Table 2 and found to be 203 mg/mL and 73.2 mg/mL, respectively. The results obtained from both the methods (gravimetry as well as Karl Fischer method) have shown excellent agreement.

3.3 Solubility of phosphoramides in water

The solubility of extractants in water is decided by dipole-dipole interactions of the P=O group in extractant and water molecules **[7]**. Generally, aqueous solubility decreases with an increase in the carbon number and also branching near the P=O group of the extractant.

Table 3. Data on the aqueous solubility of undiluted (neat) phosphoramides and trialkyl phosphates.

Extractants	Solubility in mg/L
HPPA	80
HBPA	60
TBP	388
TAP	19

*Precision of TOC analysis: ±3%

Moreover, the hydrophobicity of the extractant also increases by increasing the alkyl chain length of the extractant. Data on the aqueous solubility of HBPA and HPPA are given in Table 3. The results presented in this work clearly revealed that HPPA (80 mg/mL) with eighteen carbon atoms have higher aqueous solubility than that HBPA (60 mg/L) with twenty-six carbon atoms. The aqueous solubility of an extractant is an important concern with respect to safety considerations due to 'red oil" formation. Some incidents reported related to "red oil" formation was due to the higher solubility of TBP in water and nitric acid medium [32]. In addition, loss of extractant is also important during reprocessing of spent nuclear fuels due to its aqueous solubility. Therefore, it is always desirable to employ an extractant with lower aqueous solubility. The solubility of phosphoramides is significantly lower than that of TBP (388 mg/L) and is an advantage of phosphoramides for nuclear materials processing applications.

3.4 Extraction of Nitric acid

Table 4. Data on extraction of nitric acid by 1.1 M solutions of phosphoramides in *n*-DD at 303±1K.

Initial acidity (mol/L)	$[HNO_3]$(mol/L)			
	HPPA		HBPA	
	org	aq	org	aq
0.14	0.01	0.11	0.01	0.10
0.99	0.17	0.81	0.17	0.78
2.09	0.44	1.62	0.62	1.36
3.95	0.81	3.13	0.85	2.70
5.77	1.11	4.25	1.11	4.09

*Precision of nitric acid determination is ±1%

Basicity of neutral extractants can be correlated with nitric acid extraction. Horwitz *et al*. have studied the extraction of nitric acid by replacing the alkoxy groups with alkyl groups on N, N-diethylcarbamoylmethyl phosphoryl derivatives and the results indicated that extraction of nitric acid is enhanced by increasing the basicity of the extractant **[28]**. Generally, a significant change in the nitric acid extraction is not observed within the family of extractant by increasing its alkyl chain length. In the present work, the extraction of nitric acid by HBPA and HPPA have been studied (Fig. 4) and the results were compared with 1.1M solutions of TBP and TAP in *n*-DD (Table 4) under identical conditions **[29]**. Moreover, for better comparison, the distribution data for the extraction of nitric acid by 1.1M solutions of HPPA and HBPA in n-DD at 303±1K are presented in Table 4.

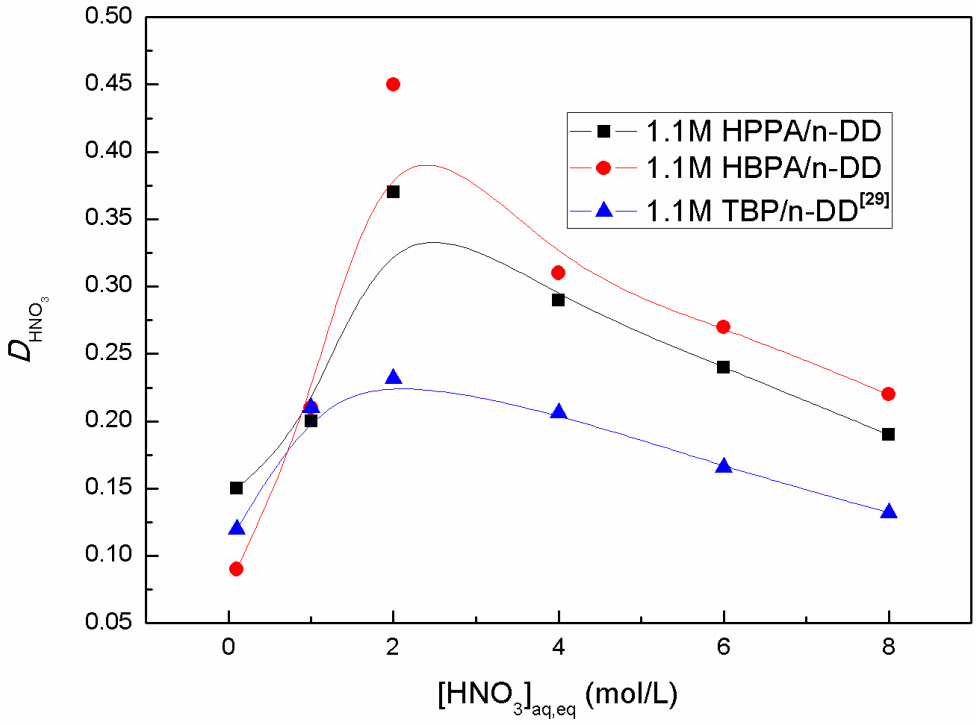

Fig. 4. Variation of distribution ratio for nitric acid extraction by 1.1 M solutions of phosphoramides and TBP in *n*-dodecane as a function of aqueous phase nitric acid concentration at 303±1K.

From the data shown in Fig. 4, it can be concluded that the phosphoramides are relatively more basic than trialkyl phosphates. Therefore, the extraction of nitric acid by phosphoramides is marginally higher than that of trialkyl phosphates. The nitric acid extraction isotherms by HPPA and HBPA are also shown in Fig. 5.

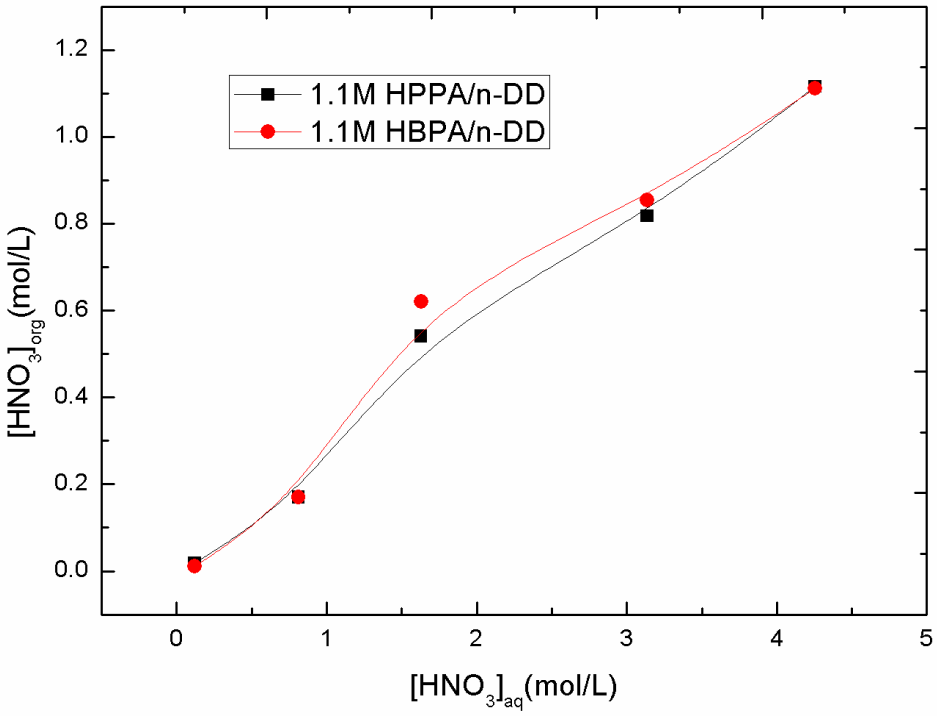

Fig. 5. Variation in the organic phase nitric acid concentration for 1.1 M solutions of phosphoramides in *n*-dodecane as a function of aqueous phase nitric acid concentration at 303±1K.

3. 5 Extraction of U (VI)

Table 5. Data on the extraction of U (VI) by 1.1M solutions of phosphoramides and trialkyl phosphates in *n*-DD from nitric acid media at 303±1K ($ - This work)

			$D_{U(VI)}$	
Acidity	**HPPA**	**HBPA**	**TBP**	**TAP**
0.01M	0.35	0.45	0.01	0.01
0.1 M	1.81	0.62	0.34	0.40
1 M	3.21	2.46	7.30	8.76
2 M	4.8	3.13	16.10	19.6
4 M	13.3	16.88	30.90	35.2
6 M	28.00	29.98	35.70	40.3
Ref	$	$	**[7]**	**[7]**

Precision of $D_{U(VI)}$ measurements: ±4%.

The extraction of U(VI) by 1.1M solutions of HBPA and HPPA in *n*-dodecane has been investigated as a function of equilibrium aqueous phase nitric acid concentration at 303±1K (Fig.6). The extraction data are shown in Table 5 and Fig. 6 provide the U(VI) extraction data of trialkyl phosphate systems for comparison.

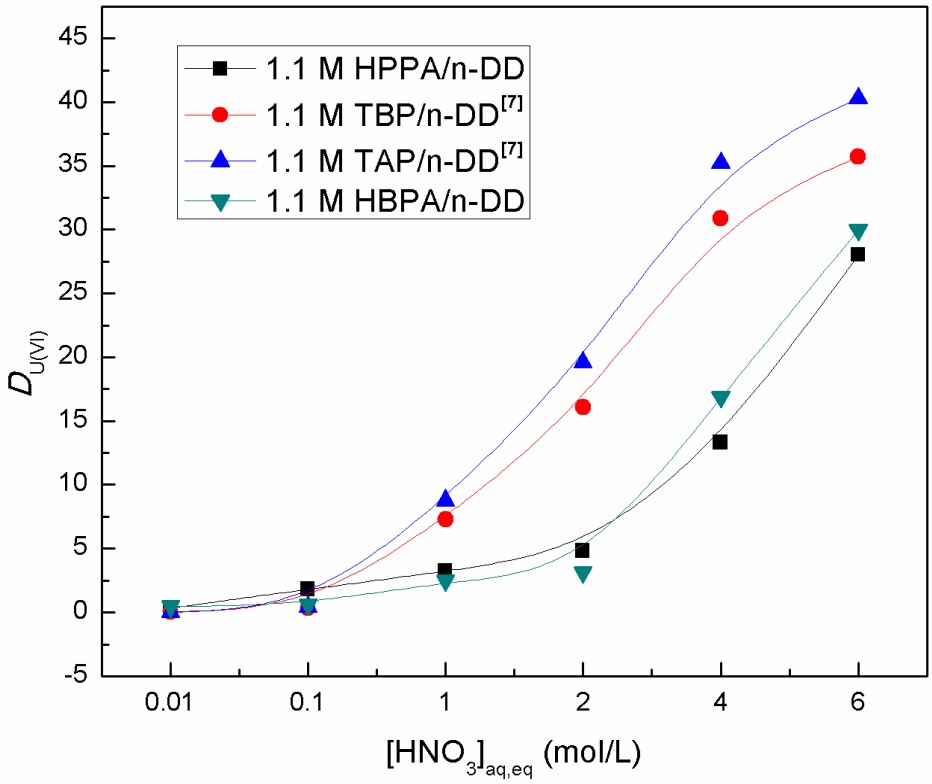

Fig. 6. Variation in the $D_{U(VI)}$ for 1.1 M phosphoramides and trialkylphosphates as a function of aqueous phase nitric acid concentration at 303±1K..

The trends in the variation of $D_{U(VI)}$ as a function of nitric acid concentration for phosphoramides and trialkyl phosphates are similar. In both the cases, the $D_{U(VI)}$ increases with nitric acid

concentration and this is a typical trend shown by neutral extractants. However, $D_{U(VI)}$ values for phosphoramide systems are marginally lower than that of phosphates. It can be seen that $D_{U(VI)}$ reaches a maximum at around 6M HNO_3 for trialkyl phosphates. Moreover, the $D_{U(VI)}$ of phosphoramide systems gradually increases between 4-6 M HNO_3. The initial increase in $D_{U(VI)}$ is attributed to salting out effect and the further decrease is due to decrease in the free extractant concentration and also the competition between the U(VI) and HNO_3 for free extractant molecules. The gradual increase after 4M HNO_3 might be due to the preferential compound formation between the protonated phosphoramides and metal nitrate. Furthermore, the formation of protonated extractant is favored by increasing the nitric acid concentration. Thus, there is a gradual increase in the $D_{U(VI)}$ with increasing nitric acid concentration in 4-6 M region. Further studies are in progress to understand the mechanism of extraction for phosphoramides. The extraction of U(VI) by phosphoramides as well as trialkyl phosphates increases with increase in number of carbon atoms **[7]**. For example, the extraction of U(VI) increases by 14 % from TBP to TAP but it is 26% from HPPA to HBPA at 4M HNO_3.

3.6 Extraction of Pu(IV)

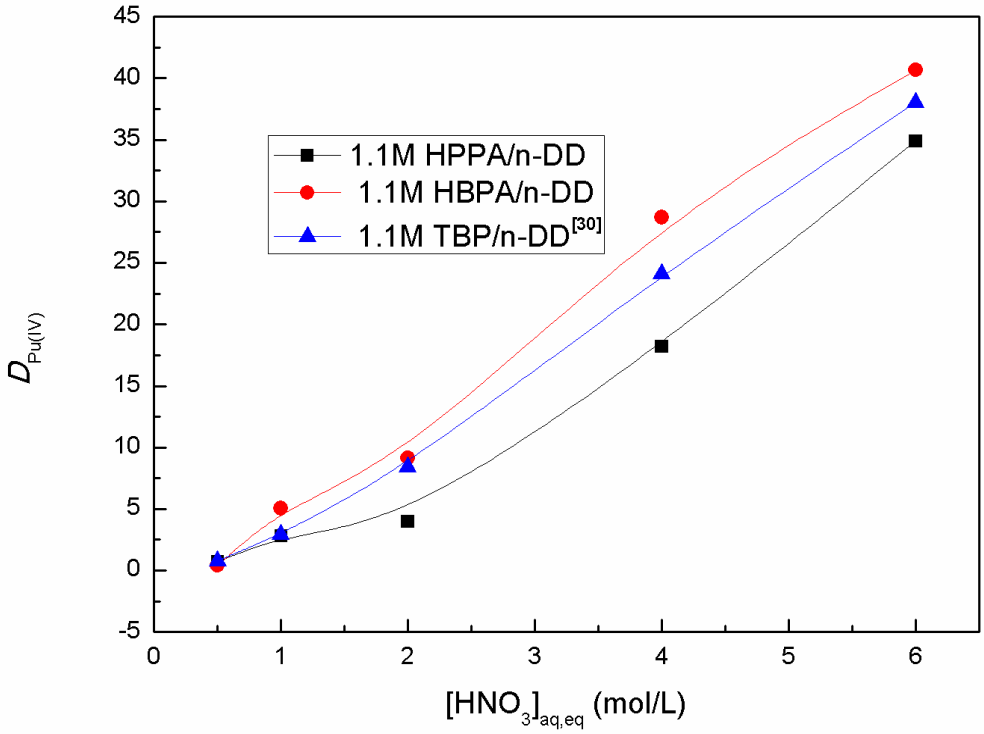

Fig. 7. Variation in the $D_{Pu(IV)}$ for 1.1M phosphoramides and trialkylphosphates as a function of aqueous phase nitric acid concentration at 303±1K..

The extraction of Pu(IV) by 1.1M HPPA and HBPA in *n*-DD has been investigated as a function of equilibrium aqueous phase nitric acid concentration. The extraction data are shown in Fig. 7 and Table 6. Our earlier data on the extraction of Pu(IV) by TBP and TAP are also included to compare phosphate and phosphoramide systems.

Table 6. $D_{Pu(IV)}$ Values for the extraction by 1.1 M phosphoramides and trialkyl phosphates in *n*-dodecane at 303±1K ($ - This work)

Extractants	0.5 M	1M	2M	4M	6M	Ref
HPPA	0.7	2.83	4.0	18.2	34.9	$
HBPA	0.4	5.07	9.15	28.71	40.65	$
TBP	0.81	2.91	8.42	24.12	38.33	**[30]**
TAP	0.95	3.36	9.43	29.33	42.51	**[30]**

Precision of $D_{Pu(IV)}$ measurements: ±1%.

Results indicated that $D_{Pu(IV)}$ for phosphoramides increases with nitric acid concentration and $D_{Pu(IV)}$ for HBPA is marginally higher than that of HPPA (Fig. 7). At lower nitric acid concentration, the D values for Pu(IV) extraction by phosphoramides are marginally lower than that of trialkyl phosphates. For example, $D_{Pu(IV)}$ values for HPPA and HBPA are 0.4 and 0.7, respectively, at 0.5M HNO_3, whereas for TBP and TAP, $D_{Pu(IV)}$ values are 0.81 and 0.9. Results also revealed that for phosphoramides the $D_{Pu(IV)}$ is higher than that of $D_{U(VI)}$ indicating that phosphoramides extract Pu(IV) higher than U(VI) at a given nitric acid concentration, whereas in the case of trialkyl phosphates, the $D_{U(VI)}$ is higher than that of $D_{Pu(IV)}$.

3. 7 Extraction of Th(IV).

The extraction of Th(IV) by 1.1M solutions of phosphoramides in *n*-dodecane has been investigated as a function of equilibrium aqueous phase nitric acid concentration at 303±1K.

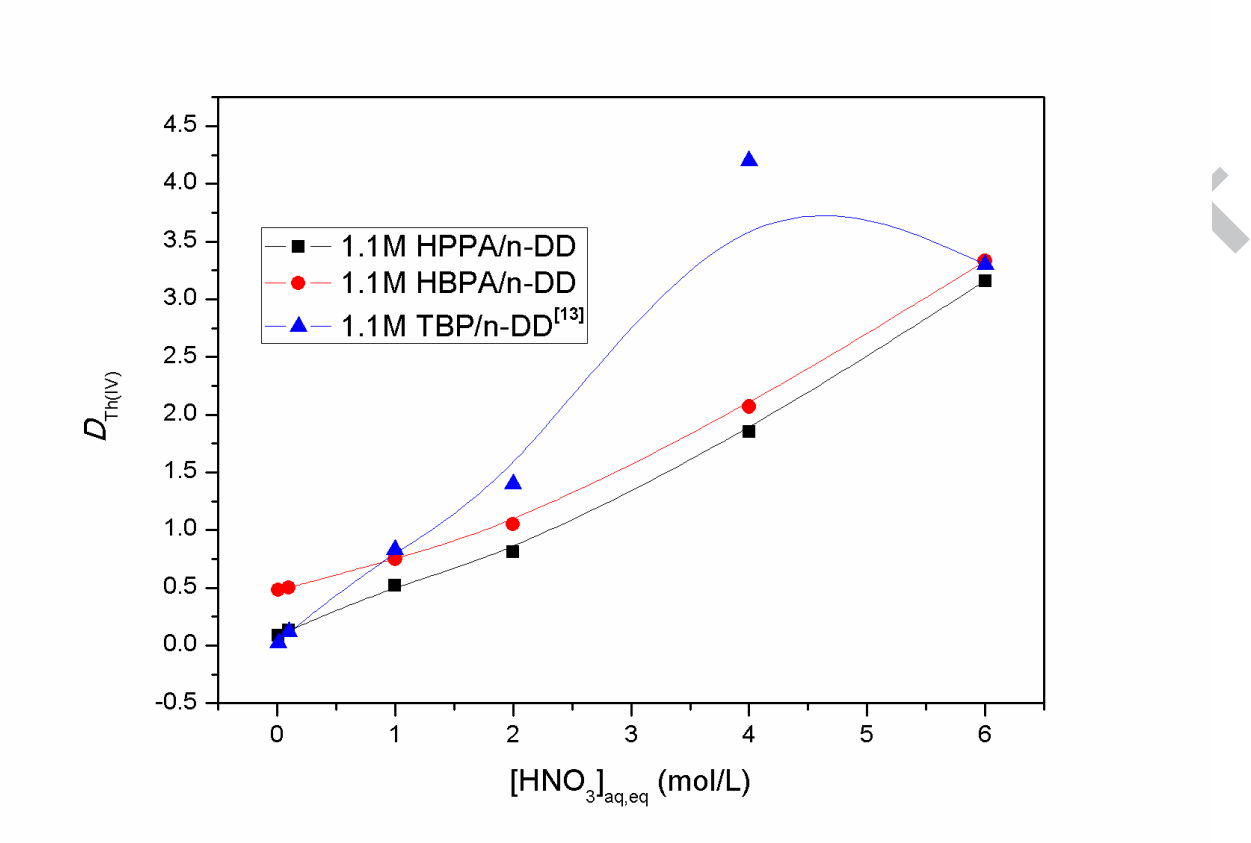

Fig. 8. Variation in the $D_{Th(IV)}$ for by 1.1M phosphoramides and trialkyl phosphates as a function of aqueous phase nitric acid concentration at 303±1K.

The thorium extraction data of phosphoramides along with our earlier data on TBP system are shown in Fig. 8 and Table 7. Results indicated that *D* values are lower for phosphoramides as compared to TBP, especially in the extraction from 2-4 M HNO_3 media. Probably the presence of the six alkyl groups around the P=O group in phosphoramides may be responsible for the suppression of $D_{Th(IV)}$ value due to steric hindrance in Th(IV) extraction. However, at higher acidity (eg: 6 M) there is no difference in $D_{Th(IV)}$ value between TBP and phosphoramides.

Table 7. $D_{Th(IV)}$ Values for the extraction by 1.1 M phosphoramides and trialkyl phosphates in *n*-dodecane at 303±1K ($ - This work)

Extractants	0.01 M	0.1M	1M	2M	4M	6M	Reference
HPPA	0.09	0.13	0.52	0.81	1.85	3.16	$

HBPA	0.48	0.5	0.75	1.05	2.07	3.33	$
TBP	0.02	0.12	0.83	1.4	4.2	3.3	**[13]**

Precision of $D_{Th(IV)}$ measurements: ±4%.

Conclusion

We have synthesized and purified two hexaalkyl phosphoramides, HBPA and HPPA. These phosphoramides were well characterized by spectroscopic techniques such as NMR (^{1}H, ^{31}P & ^{13}C), IR and mass analysis. Their physicochemical properties were measured and extraction behavior with U(VI), Th(IV) and Pu(IV) was investigated. Lesser density and lower aqueous solubility of phosphoramides are attractive features to make these compounds as suitable for solvent extraction applications. The overall results obtained from this study suggest that phosphoramides are potential ligands for actinides separations.

The present study is only the beginning of an investigation to explore hexaalkyl phosphoramides for actinide separations. Clearly, further studies on third phase formation, fission product extraction, degradation aspects (thermal, chemical and radiolytical), etc. have to be carried out to have a thorough understanding of these extraction systems prior to their deployment for separation processes.

Acknowledgements

The author's thanks to Dr. Kari Vijayakrishna and Dr. Suresh Reddy of Department of chemistry, VIT University, Vellore, India-632 014 for their support and assistance in the synthesis and characterization of phosphoramides.

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Highlights:

1. Two hexaalkylphosphoramides, HBPA and HPPA have been synthesized, purified and characterized successfully by using analytical techniques (^{1}H, ^{13}C, ^{31}P and Mass spectrometry(GC-MS))
2. Extraction studies on phosphoramides with U(VI), Pu(IV) and Th(IV) were evaluated and results compared with Tri-n-butyl phosphate (TBP)
3. The phosphoramides have lower density and lesser aqueous solubility than TBP