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Liquid–Liquid Extraction of Actinides from Nitric Acid Feeds Using Two Hexa-*n*-alkylnitrilotriacetamides

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ABSTRACT

Solutions of two nitrilotriacetamide (NTA) ligands, viz., *N,N,N',N'',N''*-hexa-*n*-butylnitrilotriacetamide (HBNTA) and *N,N,N',N'',N'',N''*-hexa-*n*-hexylnitrilotriacetamide (HHNTA) in 20% isodecanol–80% *n*-dodecane were employed for the extraction of U(VI), Np(IV), Pu(IV), and Am(III) from nitric acid feed solutions. Limitations of ligand solubility and third-phase formation when contacted with nitric acid solutions led to the choice of the diluent composition of 20% isodecanol and 80% *n*-dodecane. The results of the solvent extraction studies indicated poor extraction of the metal ions with HBNTA as compared to that with HHNTA as the extractant and hence, major part of this work involved HHNTA. Slope analysis suggested extraction of 1:1 (ML) species with Np(IV) and Pu(IV) at 3 M HNO₃ and mixed 1:2 (ML₂) and 1:3 (ML₃) species with U(VI) at pH 2. At 0.5 M HNO₃, the observed trend for extraction was Pu(IV) > Np(IV) >> Am(III) > U(VI).

KEYWORDS

Nitrilotriacetamide;
actinides; solvent extraction;
separation

Introduction

The high-level waste (HLW) emanating from the reprocessing of spent nuclear fuel contains long-lived minor actinides (Am, Cm, Np), unextracted uranium and plutonium from the PUREX (Plutonium Uranium Reduction Extraction) cycle, fission products including some of the lanthanides, Cs, Sr, Mo, Tc, Zr, platinum group metals, and structural materials.^[1–3] The proposed strategy for the safe and long-term management of HLW is the partitioning of the long-lived actinides^[4] followed by their transmutation to form short-lived or stable elements in accelerator-driven subcritical systems (ADSS) or high-flux nuclear reactors.^[5] However, in both cases, the separation of actinides from the HLW is required. Since lanthanides possess similar chemical properties as that of minor actinides, their extraction tends to occur simultaneously with the minor actinides. In view of

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the fact that some of the lanthanides have high neutron-absorption cross sections that can effectively reduce the transmutation efficiency of the actinides,^[6] the mutual separation of actinides and lanthanides is one of the most important tasks in the back end of the nuclear fuel cycle prior to the transmutation stage.^[6] It is important to mention here that the HLW, sans the actinides, can be vitrified in glass matrices followed by burial into the deep geological repositories. If the long-lived actinides and fission products (i.e., ¹³⁵Cs, ¹²⁹I, ¹⁰⁷Pd, ⁹⁹Tc, and ⁹³Zr, etc.) are not separated from the HLW prior to the vitrification of the waste blocks, then long-term surveillance (up to millions of years) is needed, which could impose a huge economic burden to the society.

However, selective separation of the long-lived minor actinides is not an easy task. A large number of ligands with high extraction efficiency were designed, synthesized and tested for extraction of the minor actinides from nitric acid feed solutions (HLW contains 3–4 M HNO₃). Some notable examples of the selective extractants are: a) CMPO (carbamoylmethylphosphine oxide)^[7] with TBP (tri-*n*-butyl phosphate); b) TRPO (trialkylphosphine oxide)^[8]; c) DIDPA (diisodecyl phosphoric acid)^[9]; d) malonamides^[10]; e) diglycolamides,^[11] etc., which have all shown encouraging results in laboratory studies. However, these solvent systems co-extract the lanthanides along with minor actinides. The mutual separation of actinides and lanthanides is quite a challenging task and is generally performed using aqueous soluble complexing agents, such as diethylenetriamine *N,N,N',N''*, *N''*-pentaacetic acid (DTPA) or 2,6-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)pyridine (SO₃-Ph-BTP), which selectively complex with the actinides.^[12,13] Alternatively, soft donor extractants containing 'N' or 'S' donor atoms have been evaluated.^[14–17] Diglycolamide extractants such as TODGA (*N,N,N',N''*-tetra-*n*-octyl diglycolamide, Figure 1a) is reported to show preferential extraction of Eu³⁺ (a representative trivalent lanthanide ion) vis-à-vis Am³⁺ (a representative trivalent minor actinide ion) with a separation factor ($SF = D_{Eu}/D_{Am}$) ca. 9 at 1 M HNO₃.^[11] In case of the N-pivot tripodal diglycolamide extractant, TREN-DGA (Figure 1b), on the other hand, the SF values decreased significantly probably due to coordination of the central 'N' atom to Am.

N-pivot tripodal amides viz. *N,N,N',N'',N''*-hexa-*n*-octylnitrilotriacetamide (HONTA, Figure 1c) are alternative 'green' CHON type ligands where three acetamide groups are appended onto a central nitrogen atom to form a tripodal ligand structure with both hard (O) and soft (N) donor atoms. Though the extractant was first reported by Iqbal et al.^[18,19] a subsequent study by Sasaki et al., used HONTA solutions in *n*-dodecane and indicated selective extraction of Am and Cm with respect to lanthanides at lower nitric acid concentrations.^[20] They also reported high extraction of Pu and other relevant fission product elements such as Mo, Tc, and Pt group metals.^[20,21] The mixer-settler data showed very encouraging results for the separation of Am and Cm from Ln.^[22] Recently, we reported the effect of different alkyl derivatives of NTA on the complexation with Eu³⁺ using fluorescence and DFT studies.^[23] Usually, when longer alkyl

Figure 1. Structural formula of (a) TODGA, (b) tripodal DGA ligands, and (c) N,N,N',N',N'',N'' -hexa- n -alkylnitrilotriacetamides.

chains are substituted, the extraction efficiency of the ligand increases in view of the higher lipophilicity.^[24] On the other hand, shorter alkyl chain-based ligands increase the ease of aqueous complexation and hence, indirectly can enhance the extraction efficiency.^[11] This suggests that an optimal alkyl chain length of the NTA derivative should be used. Although, most of the recent studies by different authors concerned the use of HONTA which yielded encouraging results for the actinide and lanthanide partitioning, very limited studies were reported with the lower homologues of HONTA, especially with the n -butyl (HBNTA) and n -hexyl (HHNTA) homologs, on the extraction of actinides. In a recent study, Wang et al. pointed out that with the increase of the alkyl chain length, the extractability of the NTA derivative increases.^[24] Recent studies using NTA derivatives are focused on the extraction of Am(III) and Eu(III) and there are very little available literature reports on the extraction of other relevant actinide ions such as U(VI), Np(IV), and Pu(IV). Therefore, it is very important to investigate the extraction behavior of actinides with the lower homologs of HONTA. Though Am(III) extraction was reported by us before, data on Am(III) extraction, generated under identical experimental conditions, are also included for comparison purposes.

The present study involves the extraction of U(VI), Np(IV), and Pu(IV) from nitric acid medium using N,N,N',N',N'',N'' -hexa- n -butylnitrilotriacetamide (HBNTA) and N,N,N',N',N'',N'' -hexa- n -hexylnitrilotriacetamide (HHNTA; Figure 1c) in a mixture of isodecanol and n -dodecane.

Experimental

Chemicals

The ligands HBNTA and HHNTA were synthesized as per a reported procedure^[23] and were characterized using ^1H NMR and HR-MS, and the

purity was found to be more than 95%. The diluents, *n*-dodecane (Lancaster, UK, purity >99%), isodecanol (SRL, Mumbai, purity >99%) and xylene (Merck, Germany) were used as received. 2-Thenoyltrifluoroacetone (TTA) was purchased from Sigma-Aldrich (USA) and was used without further purification after checking the melting point (42 °C). Suprapur nitric acid (Merck, Germany) was used for the preparation of nitric acid solutions using MilliQ water (Millipore, USA). The strength of nitric acid was standardized using a standard NaOH solution, where the end point was detected by adding phenolphthalein (Fluka) as indicator. All the other chemicals were of AR grade.

Reagent solutions

A 0.5 M TTA solution was made in xylene for the extraction studies involving Np(IV) and Pu(IV) and was stored in a dark bottle to prevent photolytic degradation. A fresh solution of ferrous sulfamate (0.3 M) was prepared by dissolving the required amount of Fe powder (BDH) in sulfamic acid (Aldrich). Hydroxylamine (assay: 50 wt%; Lancaster, UK) was neutralized by concentrated HNO₃ at 2–4 °C using an ice bath for subsequent use.

Radiotracers

Pu (²³⁹Pu mainly) was purified from the ²⁴¹Am, grown from the decay of ²⁴¹Pu, using an anion exchange resin (DOWEX 1x8, chloride form, 100–200 mesh). The oxidation state of Pu was adjusted to +4 by adding NaNO₂ (0.05 M) and ammonium metavanadate (0.005 M) as the holding agent in 1 M HNO₃ followed by extraction with 0.5 M HTTA in xylene.^[25] Pu(IV) was stripped from the organic phase by contacting with 8 M HNO₃. The purity was checked by alpha and gamma spectrometry which indicated a pure solution of Pu.

²³³U was purified from its daughter products using an anion exchange resin column (DOWEX 1x8, chloride form, 100–200 mesh) and the radiochemical purity of ²³³U isotope was ascertained by alpha spectrometry.

²³⁹Np was obtained by irradiating natural uranium in the Dhruva reactor (BARC, Mumbai) at a thermal neutron flux of 1×10^{13} n/cm²/s. The ²³⁹Np thus produced was separated from the accompanying fission products and the bulk of uranium by adjusting the oxidation state of Np to Np(IV) using a mixture of ferrous sulfamate (0.005 M) and hydroxylamine (0.25 M) as reducing agent in 1 M HNO₃ followed by extraction with 0.5 M HTTA in xylene.^[26] The organic phase was contacted with 8 M HNO₃ to strip Np(IV) to the aqueous solution. The Np(IV) containing aqueous solution was washed with xylene for two to three times to discard any traces of organic phases present. The purity of the product was confirmed using alpha spectrometry. The valency of Pu(IV) and

Np(IV) was confirmed from the slope analysis of the linear fitting plot of $\log$ - $\log$ of D_{Pu} or D_{Np} with HTTA in xylene and was confirmed by UV-vis spectrophotometry as well.^[27] The concentrations of ^{239}Np , ^{233}U , and Pu generally used for the experiments were 10^{-12} M, 10^{-5} M and 10^{-6} M, respectively.

Distribution studies

The solvent extraction studies were carried by contacting equal volumes (usually 1 mL) of the organic phase, containing the extractant, and the aqueous phase, containing the radiotracer at the pre-decided concentration of nitric acid, phases in leak-tight stoppered Pyrex glass tubes (10 mL capacity). The tubes, sealed in PVC bags, were agitated at a constant speed (vertical rotation, 20 rpm) in a constant temperature water bath ($25 \pm 0.1^\circ\text{C}$) for about one hour. The tubes were subsequently taken out of the bath, rested for 10 minutes, and centrifuged at 5000 rpm for five minutes to enable clear phase separation. Suitable aliquots (0.05–0.1 mL) of the organic and aqueous phases were pipetted out carefully and assayed radiometrically. ^{233}U and Pu were assayed in a liquid scintillation counter (Hidex, Finland) using an Ultima Gold scintillator cocktail, whereas ^{239}Np and ^{241}Am were assayed by a well-type NaI(Tl) scintillation counter (Para electronics) coupled to a multichannel analyzer (ECIL, India). The distribution ratio (D_M) of the metal ion ($M = \text{U, Np, Pu}$ or Am, as the case may be) was determined using the following formula:

$$D_M = \frac{\text{Amount of the metal ion present per unit volume of the organic phase}}{\text{Amount of the metal ion present per unit volume of the aqueous phase}} \quad (1)$$

In the present case, where radiotracers are used, the amount of the metal ion is expressed as counts per minute.

All the experiments were done in duplicate, the reproducibility in the D values being within $\pm 2\%$. The mass balance was found to be within $\pm 5\%$ (it is defined as the difference between the counts per minute of the aqueous phase in 100 μL before the start of the experiment and the total counts per minute of the aqueous and organic phases in 100 μL after reaching the equilibrium).

Extraction of nitric acid

The determination of $D_{(\text{HNO}_3)}$ as a function of feed nitric acid concentration was made by equilibrating the organic phase (0.08 M HHNTA in 20% iso-decanol-80% *n*-dodecane) with the aqueous phase (0.01–6 M HNO_3) taking 1 mL of each of the phases in a Pyrex glass tube similar to the studies on the extraction of metal ions by HHNTA (*vide supra*). Hydrogen ion concentrations in both the organic and aqueous phases were determined by titration

using standard NaOH (previously standardized using standard phthalic acid) and phenolphthalin as the indicator. For the titrations involving the organic phases, 5 mL of 50% ethanol–water mixture (which was previously standardized to neutralize traces of acid) was used. The $D_{(\text{HNO}_3)}$ was determined by taking the ratio of the acid concentrations in the organic and the aqueous phases.

Results and discussion

Ligand solubility and third-phase formation

Prior to the two-phase extraction studies, it was important to ensure the complete dissolution of the extractant into the diluents and also to test the integrity of the phases after mixing, which could be ascertained from the mass balance (total counts in the organic and the aqueous phases put together should be near about constant). Many times, the two phases became turbid after mixing and a third phase appeared at the interphase of the organic and the aqueous phases, which could be due to either acid loading or metal ion loading.^[28,29] As the present studies involved radiotracers, metal ion loading is ruled out. Consequently, the possibility of third-phase formation, if any, should be due to the acid loading into the organic phase. In such a case, the third-phase formation can be alleviated by changing the polarity of the diluent. In view of this, a mixture of *n*-dodecane and isodecanol was used, where the latter was used to enhance the polarity of the diluent mixture.

HBNTA could not be easily dissolved in *n*-dodecane, while HHNTA was completely dissolved in the diluent and a 0.1 M solution was prepared for subsequent extraction studies. Surprisingly, 0.1 M HHNTA in *n*-dodecane forms a third phase when contacted with 0.1–3 M HNO_3 (Table 1). For optimization studies, a 0.1 M HHNTA solution was prepared using diluent mixtures containing varying isodecanol contents (5%, 10%, and 20%), and the resultant solutions were contacted with three different HNO_3 concentrations (Table 1). As clearly seen from the table, it is required to use a 20% isodecanol–80% *n*-dodecane mixture for preparing a 0.1 M HHNTA solution, which can be used for the extraction experiments in the HNO_3 concentration range of 0.1–6 M without the formation of a third phase.

It is understood that nitric acid is extracted into the organic phase by the extractant (HHNTA in this case) and hence, the extractant concentration is also linked to third-phase formation. While using 0.05 M HHNTA in 5% isodecanol–95% *n*-dodecane, a third phase did not appear up to 1 M HNO_3 , but the phase integrity was lost at higher nitric acid concentrations. Carrying out analogous studies with HBNTA, third-phase formation was observed even with 0.1 M ligand at 6 M HNO_3 , however, this was not the case using 0.08 M

Table 1. Phase integrity data as a function of nitric acid concentration and isodecanol content in the solvent containing 0.1 M HHNTA in the diluent mixture of *n*-dodecane + isodecanol.

[HNO ₃], M	Phase integrity with isodecanol content			
	Nil	5%	10%	20%
0.1	Third phase	Clear	Clear	Clear
1	Third phase	Third phase	Clear	Clear
3	Third phase	Third phase	Clear	Clear
6	Third phase	Third phase	Third phase	Clear

HBNTA. In view of this, all subsequent studies were carried out using 0.08 M concentrations of both HHNTA as well as HBNTA.

Extraction of HNO₃

Determination of the acid uptake by the organic phase containing the extractant is very important, as the metal ion extraction involved acidic feed solutions. The extraction of metal ions (Equation 2) generally competes with the acid uptake (Equation 3) for the neutral solvating-type ligands according to the following equations, where A is the NTA ligand.

where, the subscripts, 'aq' and 'org' represent species in the aqueous and organic phases, respectively, while K_{ex} is the two-phase extraction constant and K_H is the acid uptake constant of the extractant. The acid uptake generally gives an idea about the free ligand (ligand which is not forming an adduct with HNO₃) concentration. The acid uptake of the phase containing 0.08 M HHNTA in 20% isodecanol–80% *n*-dodecane was 4.8% at equilibrium when the organic phase was contacted with 3 M nitric acid (D_{HNO_3} : 0.05) (Figure 2). This is lower than the reported value of nitric acid uptake by 0.1 M HHNTA in *n*-dodecane (D_{HNO_3} : 0.164) at 3 M HNO₃.^[30] We would like to comment on the lack of third-phase formation in the literature report and hence, the reliability of the reported data. It has to be mentioned here that the diluent mixture itself (without the extractant) can extract nitric acid to some extent. Sharma et al. reported a nitric acid uptake of <0.02 M by a diluent mixture containing 20% isodecanol–80% *n*-dodecane when contacted with 3.5 M HNO₃,^[31] suggesting that the acid uptake by the organic phase is predominantly due to HHNTA. Figure 2 exhibits that the percent acid uptake (% extraction) decreases with increasing nitric acid concentration up to 3 M HNO₃, while beyond that, there is a marginal increase. The acid extraction was found to be mainly due to the 20% isodecanol present in the diluent

Figure 2. Extraction of nitric acid in the organic phase, 0.08 M HHNTA in 20% isodecanol-*n*-dodecane from the feed phase (1–6 M HNO₃).

mixture and to a much lower extent due to the extractant. For example, with 6 M HNO₃ as the aqueous phase, 0.402 M HNO₃ was extracted into the organic phase containing the diluent mixture (20% isodecanol + 80% *n*-dodecane) while 0.463 M HNO₃ was extracted with 0.08 M HHNTA in the diluent mixture. Overall, an acid uptake value <5% is considered acceptable. It is beneficial in terms of ease of stripping of metal ions from the organic phase compared to cases where the acid loading in the organic phase is higher.

The lower acid uptake in the presence of isodecanol may be due to the interaction of part of the HHNTA with isodecanol, resulting in a decrease in the effective concentration of HHNTA for acid extraction at a given nitric acid concentration. Sengupta et al. also reported a lower acid^[32] uptake constant (K_H) of the combined system (0.2 M CMPO + isodecanol) than that with CMPO alone (K_H : 2.0).^[33] We, however, encountered third-phase formation when 0.1 M HHNTA in *n*-dodecane was contacted with 3 M HNO₃ (*vide supra*). On the other hand, with 0.5 M TODGA in *n*-dodecane, D_{HNO_3} is 0.173 at 3 M HNO₃.^[30] Assuming a 1:1 adduct with HHNTA and HNO₃ and a linear plot of $\log D_{\text{HNO}_3}$ vs. $\log [\text{HHNTA}]$ up to 0.5 M HHNTA in 20% isodecanol–80% *n*-dodecane, the D_{HNO_3} with 0.5 M HHNTA in 20% isodecanol–80% *n*-dodecane would be 1.8 times higher than the D_{HNO_3} in 0.5 M TODGA-*n*-dodecane, which may be due to the more basic nature of HHNTA compared to TODGA.

Optimization of contact time

It was required to optimize the contact time (time required to attain equilibrium D values while agitating in the water bath as mentioned above) for the solvent extraction studies. The studies were carried out in the equilibration time range of 5–60 minutes and the equilibrium distribution ratio values along with the time taken to attain those are presented in Figure 3. These experiments were carried out for U(VI) at pH 2.0, while those for Pu(IV) and Np(IV) were performed at 3 M HNO_3 using 0.08 M HHNTA in 20% isodecanol–80% n -dodecane. Figure 3 shows that the equilibrium attainment was rather fast; about 10 minutes were needed to get plateaus at 25 °C. However, for all subsequent extractions, 60 minutes of equilibration time was chosen for the sake of convenience.

Extraction of actinide ions

When the extraction experiments were carried out with the barren diluent mixture (without HHNTA), the metal ion extraction (U(VI) and Pu(IV)) was negligible ($D < 0.001$). On the other hand, when the extraction studies were carried out using 0.08 M HHNTA in 20% isodecanol–80% n -dodecane, there

Figure 3. Kinetics of extraction. Org. phase: 0.08 M HHNTA in 20% isodecanol–80% n -dodecane. Aq. Phase: Np(IV) at 3 M HNO_3 ; Pu(IV) at 3 M HNO_3 ; U(VI) at pH 2.0.

was a remarkable enhancement in the extraction of the metal ions as shown in Table 2. Out of the actinide ions, the extraction of U(VI) was studied in greater detail for the optimization of the ligand concentration and isodecanol content in the diluent mixture. While increasing the ligand concentration enhanced the extraction of U(VI), increasing the isodecanol content in the diluent mixture resulted in a decrease in the metal ion extraction (D_U decreased from 4.47 ± 0.02 for 5% isodecanol to 1.57 ± 0.01 for 20% isodecanol, both data obtained at 0.1 M HNO_3). Out of the two extractants used in the present study, HHNTA resulted in significantly larger extraction of the metal ions as compared to HBNTA (Table 2) which is in line with the solubility results presented above. In view of this, most of the studies on varying extractant concentration, diluent composition and feed nitric acid concentration were carried out using HHNTA. Some studies were also carried out using HBNTA for comparison purpose.

The extraction behavior of Np(IV) and Am(III) was studied from nitric acid solutions using 0.08 M HBNTA as well as HHNTA in 20% isodecanol–80% *n*-dodecane at 0.5 M HNO_3 , while that of Pu(IV) was done from 3 M HNO_3 and the data are presented in Table 2. The trend of metal ion extraction was found to be $\text{Pu(IV)} > \text{Np(IV)} > \text{Am(III)} > \text{U(VI)}$. Though ionic potential considerations alone would suggest a higher extraction of U(VI) vis-à-vis Am(III), the possibility of binding of the latter to the ‘N’ atom of the tripodal ligands (due to ‘soft-soft interaction’) could lead to a reversal in the extraction trend. Also, due to the presence of two axial oxygen atoms in the UO_2^{2+} ion, the binding of the NTA ligand with the metal ion result in an unfavorable structure leading to its poor extraction.

Effect of nitric acid concentration

It was of great relevance to study the effect of the nitric acid concentration on the metal ion extraction, since the extractions/separations of actinides involve nitric acid-based feed conditions in the nuclear fuel cycle. As mentioned above (Table 2), the preliminary extraction studies of U(VI), Np(IV), Pu(IV), and Am(III) with 0.08 M HHNTA in 20% isodecanol–80% *n*-dodecane at 0.5 M HNO_3 indicated very encouraging results, which lead us to investigate the dependency of the D_M of the metal ions on the nitric acid concentration (Figure 4) in the range starting

Table 2. Distribution data of actinide ions using 0.08 M HBNTA and 0.08 M HHNTA in 20% isodecanol–80% *n*-dodecane.

Solvent	[HNO_3]	$D_{\text{U(VI)}}$	$D_{\text{Np(IV)}}$	$D_{\text{Pu(IV)}}$	$D_{\text{Am(III)}}$
No ligand	0.5 M	<0.001	–	<0.001	–
HHNTA	0.5 M	0.14 ± 0.00	45.7 ± 0.9	76.2 ± 1.50	0.69 ± 0.03
HHNTA	3 M	0.28 ± 0.00	83.3 ± 0.2	210 ± 4.21	–
HBNTA	0.5 M	0.01 ± 0.00	0.26 ± 0.00	– (3.3) ^a	0.08 ± 0.00

^aValue inside the parenthesis refers to 3 M HNO_3 as the aqueous phase

from 0.01 M to 6 M using 0.08 M HHNTA in 20% isodecanol–80% *n*-dodecane. For HBNTA, a few data points were generated for U(VI) alone for comparison purposes. Figure 4 shows that the D_M values of U(VI) decrease sharply up to 0.5 M HNO_3 and thereafter increase slowly up to 6 M HNO_3 . The initial decrease of the D_M of U(VI) with HNO_3 may be due to the protonation of the central nitrogen atom of the ligand molecule, which effectively reduces the ligand reactivity towards the metal ion coordination, while the increase may be due to a concomitant increase in the metal ion extraction with increasing nitrate ion concentration based on a solvation mechanism. The participation of the central N atom in the coordination of the metal ion was indicated by EXAFS and DFT calculations of the NTA-based ligands.^[17,34] The slow increase above 0.5 M HNO_3 may be explained by the slightly predominant extraction of U(VI) by an ion-pair mechanism due to the increase in the nitrate ion reactivity at higher nitric acid concentrations as compared to a decrease in the ligand reactivity due to acid uptake. On the other hand, an increasing trend in the extraction of Pu(IV) from 0.5 M HNO_3 to 6 M HNO_3 was observed, in a manner similar to the latter part of the extraction curve for U(VI) (above 0.5 M HNO_3), indicating that the extraction follows an ion-pair mechanism. The higher extraction of Pu(IV) than U(VI) follows the trend of a higher ionic potential of the former. As can be seen from

Figure 4. Effect of nitric acid on the distribution ratio of U(VI), Pu(IV), Np(IV), and Am(III). [HHNTA]: 0.08 M in 20% isodecanol–80% *n*-dodecane.

Table 2, the D_M values follows the trend $\text{Pu(IV)} > \text{Np(IV)} \gg \text{Am(III)} > \text{U(VI)}$. The higher D_M of Am(III) than U(VI) cannot be explained on the basis of the ionic potential. However, if one considers the binding of the central 'N' atom to the Am^{3+} ion, then it is possible to explain the trend. Such preferential binding of Am^{3+} ion to the 'N' atoms (compared to the Eu^{3+} ion) has been reported before.^[23]

Huang et al. observed that the D_M value of Th(IV) decreased up to 1 M HNO_3 and thereafter increased till 10 M HNO_3 ^[35] with hexaocetylnitrilotriacetamide (HONTA) in kerosene. A similar extraction trend was also reported for Pu(IV) by Sasaki et al. with HONTA in *n*-dodecane.^[21] On the other hand, the authors reported an increasing trend of $D_{\text{U(VI)}}$ upon increasing nitric acid concentrations starting from 0.2 M HNO_3 .^[21] These observations clearly show a different extraction behavior of the actinides below 1 M HNO_3 depending on the nature of the extractant.

Extraction of fission product ions

Apart from the actinide ion extraction (**Table 2**), it was required to carry out the extraction of some of the fission product ions such as Eu^{3+} (surrogate for the rare earth ions), Sr^{2+} and Cs^+ . **Table 3** gives the extraction data of these metal ions from 0.5 M HNO_3 as the aqueous phase and 0.08 M in 20% isodecanol–80% *n*-dodecane as the organic phase. It is important to mention here that the extraction of the fission products is to a much lower extent as compared to the tetravalent actinide ions while that of Eu(III) was found to be closer to that of the Am(III) ion. The higher extraction of Am(III) as compared to Eu(III) is due to binding of the former to the central 'N' donor atom in a manner similar to that was reported with the *n*-octyl homolog, HONTA.^[21]

Nature of the extracted species

It is very important to determine the stoichiometry of the extracted metal-ligand complex (ligand to metal ratio, L/M) and the extraction equilibrium constant (K_{ex}) to understand the extractability of the metal-ligand complex into the organic phase. As per the generic equation given above for metal ion extraction using a neutral donor extractant (Equation (2)), the metal ion can get extracted to the organic phase with the help of the required number of nitrate ions (equal to the charge on the metal ion), for charge neutralization

Table 3. Extraction at 0.5 M HNO_3 with 0.08 M HHNTA in 20% isodecanol–80% *n*-dodecane.

Metal ion	D_M
Eu (III)	0.156 ± 0.003
Sr(II)	<0.001
Cs(I)	<0.001

purpose, along with 'x' number of ligands that enhance the lipophilicity of the extracted species. The two-phase extraction equilibrium constant (K_{ex}) is defined as follows:

$$K_{ex} = \frac{[M(NO_3)_n \bullet xA]_{org}}{[M^{n+}]_{aq} [NO_3^-]_{aq}^n [A]_{org}^x} \quad (4)$$

The distribution ratio (D_M) is defined as the ratio of all the metal-bearing species in the organic to those in the aqueous phase and is given as:

$$D_M = \frac{[M(NO_3)_n \bullet xA]_{org}}{[M^{n+}]_{aq} (1 + X)} \quad (5)$$

where $X = \sum \beta_i [NO_3^-]^i$ and $i = 1$ to n . Using Equation (5), Equation (4) can be further simplified as

$$K_{ex} = \frac{D_M (1 + X)}{[NO_3^-]_{aq}^n [A]_{org}^x} \quad (6)$$

taking the logarithm and after rearrangement, one would get

$$\log D_M = \log K_{ex} - \log (1 + X) + n \log [NO_3^-]_{aq} + x \log [A]_{org} \quad (7)$$

Upon further simplification, with the assumption that the $\log K_{ex}'$ is the conditional extraction constant defined as $\log K_{ex} - \log (1 + X) + n \log [NO_3^-]_{aq}$, one would get

$$\log D_M = \log K_{ex}' + x \log [A]_{org} \quad (8)$$

The stoichiometries of the complexes of HHNTA with U(VI), Pu(IV) and Np(IV) were determined from the slope of the log-log plots of D vs. HHNTA concentration (Figure 5) at a given nitric acid concentration. Since the metal ion concentrations are significantly lower than that of the extractant concentrations used in these studies (*vide supra*), the free ligand concentration can be taken as the initial ligand concentration. On the other hand, a constant fraction of ligand is always protonated in each nitric acid solution which will not complex with the metal ion and hence, will not alter the slopes^[36] in Figure 5. The slope analysis of the studies on the U(VI)-HHNTA extraction system was done at pH 2.0, whereas that of Pu(IV) and Np(IV) was carried out at 3 M HNO₃ at room temperature. The simple and effective way to obtain the L/M ratio of the extracted complex in a solvent extraction process is by determining the slope of the linear fitting plot of $\log D_M$ versus the $\log [\text{ligand}]$, while the $\log K_{ex}'$ can be obtained from the intercept of the linear fitting of Equation (8). As can be seen from Figure 5, all the log-log plots are linear with slope values of 2.45 ± 0.06 , 1.43 ± 0.16 , 1.16 ± 0.05 , and 1.12 ± 0.03 for U(VI), Am(III),

Figure 5. Effect of variation of ligand concentration on the distribution ratio of Np(IV), Pu(IV), Am(III) and U(VI). Organic phase: varying [HHNTA] in 20% isodecanol–80% *n*-dodecane. Aqueous phase: Np(IV) extraction in 3 M HNO₃, Pu(IV) extraction in 3 M HNO₃, Am(III) extraction at pH 2.0, U(VI) extraction at pH 2.0.

Np(IV), and Pu(IV), respectively. This suggests the extraction of ML type species with Np(IV) and Pu(IV), while mixed species of the type ML and ML₂ and ML₂ and ML₃ are extracted for Am(III) and U(VI), respectively. Huang et al. also reported the extraction of ML type^[35] species for the extraction of Th(IV) with HONTA in kerosene at 3 M HNO₃. Similarly, Sasaki et al. have reported the extraction of ML type species for Pu(IV) at 3 M HNO₃ with HONTA in *n*-dodecane.^[21] However, in sharp contrast to the present study, the above authors have reported the extraction of ML type species for U(VI) as well with the higher homolog, HONTA.^[21] The comparatively lesser number of extractant molecules with U(VI) in Sasaki's case is probably due to the availability of a lower effective concentration of ligand at 3 M HNO₃ than that at pH 2.0 due to more acid uptake by the solvent. The lower stoichiometry of metal-ligand at higher nitric acid concentration was reported by Sasaki et al., where two molecules of HONTA were associated in the extraction of Am(III) at 0.2 M HNO₃ in *n*-dodecane,^[30] which changed to one molecule of HONTA when extracted at 1 M HNO₃.

Plotting of $\log D_M$ vs. $\log [A]$, yielded slope y , the number of ligands associated with the metal ion extraction, and from the intercept the $\log K_{ex}$ value can be obtained at a given nitrate ion concentration. The values of $\log$

K_{ex} for Np(IV) and Pu(IV) were obtained as 1.50 ± 0.07 and 1.85 ± 0.05 , respectively, at 3 M HNO_3 . The molar concentration of nitrate ion was obtained from the dissociation constant of nitric acid at 25°C ($\log K$: 23.5), while the number of nitrate ions involved in the extracted species was considered as 4 to make charge neutralized extracted species. The $\log K_{\text{ex}}$ data indicated a higher extraction of Pu(IV) than of Np(IV) with HHNTA from an aqueous nitric acid solution. The $\log K_{\text{ex}}$ of Np(IV) complex was compared with that of two N-pivoted tripodal diglycolamide (DGA) ligands viz. TRPN-DGA and *i*-Pr₃-TREN-DGA (Figure 1b), which displayed a higher extractability of Np(IV) with the DGA ligands ($\log K_{\text{ex}}$ values for Np(IV) are reported as 2.87 ± 0.17 and 3.52 ± 0.15 , respectively^[33]) possibly due to the coordination to three 'O' atoms in a DGA moiety than only one 'O' atom in the amide arm of the present set of tripodal ligands.

Effect of isodecanol content

As mentioned in Section 3.1, isodecanol was added to enhance the solubility of the ligand in *n*-dodecane and also to alleviate the third-phase formation issues. The effect of isodecanol on the D_{U} value at 0.1 M HNO_3 was studied with 0.1 M HHNTA in *n*-dodecane in the range of 5–20% of isodecanol (Figure 6). The data presented in the figure can be fitted to a first-order exponential decay equation, $y = 1.6 + 11 \exp(-x/7.17)$, where y is D_{U} and x is the percentage of isodecanol at a fixed concentration of HHNTA (0.1 M for the present case) in *n*-dodecane. Extrapolation of the exponential plot to zero percentage of isodecanol gives a value of 12.6 being the D_{U} in 0.1 M HNO_3 with 0.1 M HHNTA in *n*-dodecane, which otherwise could not be determined due to formation of a third phase. The decreasing trend of extraction of U(VI) with increasing isodecanol content in *n*-dodecane points to the interaction of isodecanol with HHNTA resulting in a decrease in its reactivity to metal ion coordination in presence of isodecanol.

Comparative extraction of Np(IV) and Pu(IV) with other ligands

A comparison of the extraction of Np(IV) and Pu(IV) was made with tripodal amides such as HBNTA, HHNTA, and HONTA as well as diglycolamides (DGA) such as TODGA (Figure 1a) and its tripodal variants (Figure 1b) TREN-DGA (N-pivoted tripodal DGA with C₂ spacer), TRPN-DGA (N-pivoted tripodal DGA with C₃ spacer) and *i*-Pr₃-TREN-DGA (N-pivoted tripodal DGA with C₂ spacer with an isopropyl group on each amidic N atom) to understand the performance of the ligands. Although the difference in the DGA and amide classes of ligands is quite significant in the sense that the former involves metal ion binding through three 'O' atoms (two amidic and one etheric 'O' atom), the latter class involves binding through a single

Figure 6. Effect of isodecanol on the distribution ratio of U(VI) at 0.1 M HNO_3 . Organic phase: 0.1 M HHNTA in isodecanol–*n*-dodecane.

carbonyl ‘O’ atom. On the other hand, while a tripodal amide like HHNTA can bind the metal ion in a ‘crab like’ grip, a similar configuration involving the tripodal DGA ligands may lead to steric crowding and hence a less stable complex. While the central ‘N’ atom in the NTA ligands may be able to bind to the metal ion in certain cases (for example to the trivalent actinide ions such as Am^{3+}), it is rather difficult for such binding in case of the tripodal DGA ligands. A comparison of these ligands for the extraction of Np(IV) and Pu(IV) is made, and the data are summarized in Table 8. At the present experimental conditions, HHNTA is a superior ligand in the extraction of Np(IV) and Pu(IV) compared to HBNTA and HONTA, the order being HBNTA < HONTA $\ll$ HHNTA. However, HHNTA is less efficient with respect to the DGA-based ligands. Although, the D_M values for Np(IV) and Pu(IV) extraction with TREN-DGA and TRPN-DGA are lower at the concentrations quoted in Table 4, they would be significantly higher if the extractant concentration is extrapolated to 0.08 M, as ML type species are expected to be extracted with this type of ligands.^[38,39]

Proposed structure of the An(IV) complex

A probable structure of the formed species of HHNTA with tetravalent Np or Pu is shown in Figure 7 in which the metal ion is bonded with three carbonyl oxygen atoms and the central nitrogen atom of the ligand, and four nitrate ions bind in a monodentate fashion. Similar binding has been reported from EXAFS studies involving the TREN-DGA ligand, suggesting that this is a possibility when there are too many coordinating arms crowding the central metal ion.^[40] It is speculated that the three DGA arms of the tripodal DGA ligands may not bind to the metal ion simultaneously due to steric crowding, but only a single DGA arm binds to the metal ion.^[38] On the other hand, for HHNTA, though one is tempted to suggest binding by all the three amide arms, this may lead to steric crowding and hence may be the reason for the lower extraction of metal ions with HHNTA compared to the tripodal DGA ligands (*vide supra*). Structural investigations are, therefore, required to get a clear picture of this bonding aspect of metal-ligand complexation.

Conclusions

The hexaalkyl nitrilotriacetamide ligands, HBNTA and HHNTA, were studied for the extraction of U(VI), Np(IV), Pu(IV), and Am(III) from nitric acid feed solutions in the diluent mixture 20% isodecanol–80% *n*-dodecane (due to solubility reasons and to avoid third-phase formation). HHNTA

Table 4. Distribution ratios of Np(IV) and Pu(IV) with the tripodal ligands at 3 M HNO₃.

Extractants	$D_{\text{Np(IV)}}$	$D_{\text{Pu(IV)}}$	Ref.
0.1 M TODGA in <i>n</i> -dodecane	>100	>1000	[37]
1×10^{-3} M TREN-DGA in 5% isodecanol–95% <i>n</i> -dodecane	3.8	8.7	[38]
1×10^{-3} M TRPN-DGA in 5% isodecanol–95% <i>n</i> -dodecane	17.9 ± 0.89	134 ± 1.51	[39]
1.0×10^{-3} M <i>i</i> -Pr ₃ -TREN-DGA in 5% isodecanol–95% <i>n</i> -dodecane	147 ± 7.35	315 ± 2.70	[39]
0.1 M HONTA in <i>n</i> -dodecane	–	~ 12	[21]
0.08 M HHNTA in 20% isodecanol–80% <i>n</i> -dodecane	83.3 ± 0.21	210 ± 4.20	This work
0.08 M HBNTA in 20% isodecanol–80% <i>n</i> -dodecane	0.26 ^a	3.3	This work

^aData obtained at 0.5 M HNO₃.

Figure 7. Probable structure of the complex of HHNTA with M(IV) ions extracted from nitric acid.

showed better extraction properties than HBNTA, the observed trend being $\text{Pu(IV)} > \text{Np(IV)} \gg \text{Am(III)} > \text{U(VI)}$ at 0.5 M HNO_3 . In case of HHNTA, slope analysis indicated the extraction of 1:1 (ML) species with Np(IV) and Pu(IV) at 3 M HNO_3 and mixed 1:2 (ML_2) and 1:3 (ML_3) species with U(VI) at pH 2. For the ML species, it is speculated that the metal ion binds with the three carbonyl oxygen atoms and the central nitrogen atom of the ligand and with four nitrate ions.

Though one would expect better extraction performance with HBNTA and HHNTA when compared to HONTA, on the basis of shorter chain alkyl substituents, the major bottleneck with these ligands has been their solubility. While HONTA is freely soluble in only *n*-dodecane, HBNTA requires 20% isodecanol as the phase modifier. However, as mentioned in Table 4 above, HHNTA is a stronger extractants for Pu(IV) as compared to both HBNTA and HONTA, with about 20% lower extractant concentration. It is proposed to carry out separations involving actual radioactive waste solutions using HHNTA in the future.

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Disclosure statement

There are no conflicts of interest to declare.

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