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Unusual Reversal in Pu and U Extraction in an Ionic Liquid Using Two Tripodal Diglycolamide Ligands: Experimental and DFT Studies

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ABSTRACT

The extraction of UO_2^{2+} and Pu^{4+} ions was studied from nitric acid medium using three diglycolamide (DGA) extractants, viz. TODGA (N,N,N',N'-tetra-n-octyldiglycolamide), T-DGA (tripodal diglycolamide), and TREN-DGA (N-pivot tripodal diglycolamide) in a molecular diluent mixture (9:1 mixture of n-dodecane and iso-decanol) and an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][Tf_2N]). Using 1.0×10^{-3} M solutions of the ligands in [C_4mim][Tf_2N], T-DGA yielded an exceptionally high extraction of Pu^{4+} ion ($D_{Pu} > 3.2 \times 10^3$) from 3 M HNO_3 as compared to D_{Pu} values of 4 and 17 obtained with TREN-DGA and TODGA, respectively. Similarly, while the extraction of UO_2^{2+} ion was significantly lower than that of Am^{3+} ion for all the three DGA ligands in the molecular diluent and with TODGA and TREN-DGA in [C_4mim][Tf_2N], a reversal in the extraction trend was found in the case of T-DGA. Density Functional Theory (DFT) computational studies were carried out to understand the structures of the extracted complexes. $PuL_2(NO_3)_n^{(4-n)+}$ species with n = 2, 3, or 4 were considered for the geometry optimization. DFT data indicated longer M–O bonds with the etheric 'O' atom as compared to the carbonyl 'O' atom. The metal-ligand bond length and bond order analysis indicated the extraction of neutral complexes of the type $PuL_2(NO_3)_4$ as compared to cationic species of the type $PuL_2(NO_3)_2^{2+}$ and $PuL_2(NO_3)_3^+$ for all the three types of ligands (TODGA, TREN-DGA, and T-DGA).

Introduction

The extraction of trivalent actinide ions from acidic feeds is the key feature of the "Actinide Partitioning" strategy which uses extractants such as carbamoylmethylphosphine oxide,[1] malonamides, etc.[2] Recently, diglycolamide (DGA) extractants are reported to be much more efficient for the same purpose and extract the trivalent actinides to a much greater extent than Pu^{4+} and UO_2^{2+}.[3–5] This extraction trend has been attributed to a reverse micellar extraction mechanism in the case of DGA ligands such as TODGA (N,N,N',N'-tetra-n-octyldiglycolamide, Figure 1).[6] The formation of the reverse micellar aggregates is facilitated in apolar diluents such as n-dodecane. In view of the presence of 3–4 TODGA molecules in the extracted species containing trivalent lanthanide ions,[7] DGA functionalized ligands with 3–4 DGA pendant arms have been synthesized and evaluated for actinide ion extraction.[8,9] A C-pivot tripodal diglycolamide (T-DGA, Figure 1) extractant has been used for the extraction of trivalent lanthanide/actinide ions[10] and the results

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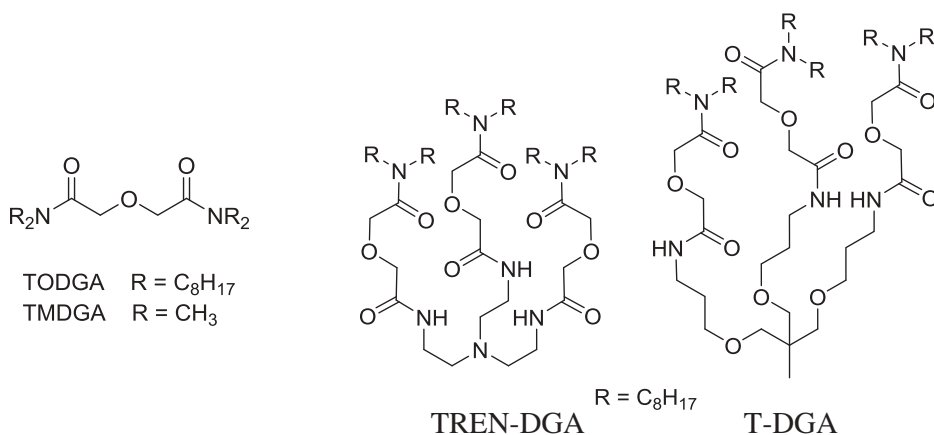
Figure 1. Structural formulae of TODGA, TMDGA, TREN-DGA, and T-DGA.

yielded very high distribution ratios even at millimolar concentrations.[11] The selectivities obtained with TODGA were retained in T-DGA in a diluent mixture of 90% *n*-dodecane and 10% iso-decanol. However, the poor extraction of UO_2^{2+} was a remarkable feature with the tripodal DGA ligand.

Room temperature ionic liquids are being proposed as alternatives to the molecular diluents due to attractive properties such as, low vapor pressure, nonflammability, large electrochemical window, possibility to tune the diluent properties by changing the cation or the anion, etc.[12–16] There are reports proposing their possible applications as alternative diluents for solvent extraction,[17–19] which are based on large enhancements in the metal ion extraction in many cases.[20] The extraction of trivalent lanthanide and actinide ions is studied using TODGA as well as T-DGA in ionic liquids.[21–24] In these studies, the separation efficiency (defined as separation factor or S.F. which is the ratio of the *D* values of the concerned metal ions) was found to increase with respect to the UO_2^{2+} ion, while an opposite trend was seen for the Pu^{4+} ion.[22] The higher separation efficiency is due to an enhanced extraction of Am^{3+} in ionic liquids with a concomitant decrease in the extraction of the UO_2^{2+} ion. It has also been reported that, whereas T-DGA is a highly efficient extractant for Am^{3+} in molecular diluents, it is not the case in ionic liquids, especially at higher HNO_3 concentrations. Typically, the D_{Am} value obtained using 1.0×10^{-3} M T-DGA at 3 M HNO_3 was 0.6 in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide ([C_4mim][Tf_2N]). On the other hand, the distribution ratio was ca. 30 under identical experimental conditions when a molecular diluent mixture (90% *n*-dodecane and 10% iso-decanol) was used.[24] In most of the reported literature, the extraction of UO_2^{2+} and Pu^{4+} ions has not been studied in detail. However, in view of the presence of U and Pu in the high-level waste in significant amounts (due to the PUREX losses), it is worth investigating their extraction behavior using ionic liquid based solvents containing TODGA and T-DGA.

Recently, an *N*-pivot T-DGA ligand, termed as TREN-DGA (Figure 1), was found to be a highly efficient extractant for trivalent lanthanide/actinide ions in ionic liquid medium.[25] Interestingly, the extraction of the metal ions was rather poor in a molecular diluent mixture. The D_{Am} values using 1.0×10^{-3} M TREN-DGA in [C_4mim][Tf_2N] and a molecular diluent (90% *n*-dodecane + 10% iso-decanol) were reported to be 161 and 0.36, respectively, which is the opposite of the trend in the case of T-DGA. However, detailed investigations with UO_2^{2+} and Pu^{4+} are lacking. It was, therefore, of interest to make a comparative evaluation of the extraction behavior of the most important actinide ions in the nuclear fuel cycle, viz. UO_2^{2+} and Pu^{4+}, using TODGA, T-DGA, and TREN-DGA in both a molecular diluent (90% *n*-dodecane + 10% iso-decanol) as well as an ionic liquid ([C_4mim][Tf_2N]). The extraction data of Am^{3+} are also included for comparison purposes.[25] The present article describes an unusual (in most DGA functionalized ligands, the D_U is very low)[24] increase in UO_2^{2+}

ion extraction in T-DGA containing ionic liquids with a concomitant decrease in Am^{3+} extraction making $D_U > D_{Am}$. Finally, DFT computational studies were carried out to understand this extraction/separation behavior of the metal ions.

Experimental

Reagents

TODGA (99%) was obtained from Thermax Ltd (Pune, India) and was used as received. T-DGA and TREN-DGA were synthesized as per the reported procedures.[11,25] n-Dodecane (Lancaster, UK) and iso-decanol (SRL, Mumbai) were obtained at >99% purities and were used without any further purification. The ionic liquid, $[C_4mim][Tf_2N]$, was purchased from IoliTec, Germany, at 99% purity and was used as obtained. Suprapur nitric acid (Merck, Germany) and MilliQ (Millipore) water were used for the preparation of nitric acid solutions, which were standardized using acid–base titrations using phenolphthalein (Fluka, Switzerland) as the indicator.

Radiotracers

^{233}U (obtained after irradiation of ^{232}Th) was purified using an anion-exchange method (Dowex 1 × 8, Cl⁻ form resin was used) as reported previously to get rid of its major decay products such as ^{228}Th (daughter product of ^{232}U which is present in a small quantity along with ^{233}U) and its daughter products.[26] It is well known that in 6 M HCl, anionic complexes of U are held onto the column, while ^{232}Th and its daughter products pass through.[26] The loaded U was subsequently eluted with dilute HCl. Alpha spectrometry of the purified ^{233}U stock indicated it to be free from ^{232}Th and its daughter products.

   Pu (obtained from irradiation of natural U target) was purified from its major decay product ^{235}U and ^{241}Am (from beta decay of ^{241}Pu) by 2-thenoyltrifluoroacetone (TTA) extraction (using 0.5 M TTA in xylene) from an aqueous phase containing 1 M HNO_3.[27] Under these conditions, Am^{3+} and UO_2^{2+} are not extracted, while Pu^{4+} is extracted quantitatively. Pu was subsequently stripped by 8 M HNO_3 and alpha spectrometry of the purified stock was carried out to rule out the presence of impurities.

   The oxidation state of Pu was adjusted to the +4 state by first drying a known amount of Pu (about 20 μg) under an infrared lamp. Subsequently, the Pu was dissolved in 1 mL of 1 M HNO_3, whereupon a few drops of 0.005 M $NaNO_2$ solution were added to change the oxidation state from the +3 and +6 state to the +4 state. The aqueous solution was contacted with 1 mL of 0.5 M TTA in xylene for 30 min. The extracted Pu^{4+} (the unconverted Pu^{3+} and PuO_2^{2+} were not extracted under these conditions) was subsequently stripped using 8 M HNO_3 and kept for subsequent studies involving Pu^{4+}. The oxidation state of Pu^{4+} was intermittently checked by TTA extraction (the log D vs log TTA concentration plot gave a slope close to 4). The Pu^{4+} stock solution, thus prepared, was found to be stable for about 1 month.

Radiometric assay

The alpha particle emitting radionuclides (such as ^{233}U and ^{239}Pu) were counted using a liquid scintillation counter (Hidex, Finland). The sample preparation involves adding the required aliquot (about 100–200 μL) into 5 mL of the Ultima Gold scintillator cocktail (Perkin Elmer). The count rate was obtained after background correction and counting for a sufficiently long time to ensure that statistical errors were <1%. The error due to quenching was found to be negligible (<2%).

Liquid–liquid extraction

Solvent extraction studies were carried out by equilibrating equal volumes of the organic and the aqueous phases in leak-tight Pyrex glass tubes in a thermostated water bath at 25 ± 0.2°C. Usually, the organic phase contained 1.0×10^{-3} M solutions of TODGA, T-DGA, or TREN-DGA in the molecular diluent mixture or [C$_4$mim][Tf$_2$N] while the aqueous solutions contained HNO$_3$ solutions spiked with the required radiotracer. The time to attain equilibrium was determined by obtaining metal ion extraction data as a function of time till nearly constant D values were obtained. All subsequent experiments with the given extraction systems were carried out by keeping the corresponding equilibration time which ensured equilibrium D values. The ligand concentration variation studies were carried out by measuring D values obtained with varying concentrations of the ligands (prepared by taking appropriate concentrations of a stock solution of the ligand and making up with the ionic liquid to obtain the required ligand concentrations) at a fixed nitric acid concentration. For these studies, non-pre-equilibrated ionic liquid phases containing the extractants were used. After equilibration, the tubes were rested and centrifuged at 5,000 rpm for 2 min, after which aliquots were taken from both phases for radiometric assay (vide supra). The distribution ratio of the metal ion was defined as the ratio of the counts per minute of the radionuclide per unit volume in the organic phase to that in the aqueous phase. All liquid–liquid extraction experiments were conducted in duplicate and the results were reproducible within ±5%. For cases where the D values were >100, a higher aqueous phase aliquot volume (0.5 mL) was used for assaying. Counting statistics errors were minimized to <1% by counting the samples for longer time (ranging up to several hours). The concentrations of the metal ions used in the present study are 10^{-6} and 10^{-5} M for Pu^{4+} and UO$_2^{2+}$ ions, respectively. The acid uptake in the ionic liquids (in the absence of the ligand and metal ions) was determined by volumetric titrations in methanol medium using standard NaOH (BDH) and phenolphthalein (Merck) indicator.

Computational methodology

The minimum energy structures of the free DGA ligands, TMDGA (tetramethyldiglycolamide), TREN-DGA, and T-DGA (for both the tripodal DGA ligands, the methyl derivations were taken in place of the *n*-octyl derivatives indicated in Figure 1 for convenience), and their Pu^{4+} complexes were calculated using the hybrid B3LYP[28,29] functional employing the split valence plus polarization (SVP) basis set[30] as available in the Turbomole suite of programs.[31–33] In the case of Pu^{4+}, an ECP core potential was used, where 60 electrons are kept in the core of Pu.[34–36] The single point energies for the free ligands and their Pu^{4+} complexes were calculated using the B3LYP functional employing the triple zeta valence plus double polarization basis set[37,38] using equilibrated structures obtained at the B3LYP/SVP level of theory. The calculations of the Pu^{4+} complexes were performed using the quintet spin state. The COSMO solvation scheme was used to account for the solvent effects on the energetic parameters.[39] The default COSMO radii were used for all the elements except for Pu^{4+} for which the values of COSMO radii used were 2.00 Å. A dielectric constant (ε) of 2.1 was used to represent the *n*-dodecane/iso-decanol (9:1) mixture.

Results and discussion

Extraction

The extraction of UO$_2^{2+}$ and Pu^{4+} was insignificant in the absence of the ligands in the case of the molecular diluent mixture of *n*-dodecane (90%) + iso-decanol (10%) over the entire HNO$_3$ concentration range of 0.01–6 M. On the other hand, when the pure ionic liquid, [C$_4$mim][Tf$_2$N], was contacted with the metal ions, though the extraction of the metal ions was negligible at lower HNO$_3$ concentrations, reasonable U extraction (ca. 7.5%) was obtained at 6 M HNO$_3$ (Table 1). Interestingly, Pu^{4+} extraction was even higher

Table 1. Acid dependence of the extraction of Pu^{4+} and UO_2^{2+} by [C_4mim][Tf_2N] in the absence of DGA ligands and extraction of HNO_3. Time of equilibration: 1 h.

[HNO$_3$], M	D_U	D_{Pu}	%Acid uptake
0.01	$<1.0 \times 10^{-2}$	–	–
0.1	$<1.0 \times 10^{-2}$	–	7.6
0.5	$<1.0 \times 10^{-2}$	$<1.0 \times 10^{-2}$	7.3
1	$<1.0 \times 10^{-2}$	$<1.0 \times 10^{-2}$	3.9
2	$<1.0 \times 10^{-2}$	0.185	3.7
3	1.7×10^{-2}	2.62	4.5
6	8.2×10^{-2}	14.3	9.4

(>93%) at that acidity, and also in contrast to that at lower acid concentrations, which may be attributed to an anion-exchange mechanism,[40,41] given below:

$$Pu^{4+}_{aq} + xNO_3{-}_{aq} + 2Tf_2N^-_{IL} \rightleftharpoons Pu(NO_3)_{xIL}^{(x-4)-} + 2Tf_2N^-_{aq} \qquad (1)$$
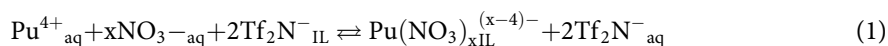
where $x > 4$ and the subscripts, "aq" and "IL" represent the species present in the aqueous and the ionic liquid phases, respectively. In view of the significantly lesser possibility of formation of anionic species with the uranyl ion in the acid concentration range studied, such an anion-exchange-mechanism is not invoked. As will be discussed below, the D values, particularly those of Pu^{4+}, increased enormously in the ionic liquid when the DGA-based ligands were used. There are examples where the extraction of Pu^{4+} in the ionic liquid ([C_4mim][Tf_2N]) was reported to be as high as ca. 15 at 6 M HNO_3 even in the absence of any organic extractant.[42]

Table 1 also lists the % acid uptake data as a function of the HNO_3 concentration which were in the range of ca. 4–9%. It was not very surprising and in line with the relatively high (as compared to <0.1% in molecular diluents such as *n*-dodecane) water extraction ability of the ionic liquid (ca. 0.5%).[43] Such high acid extraction has been previously reported in many diluents such as alcohols, ketones, and carboxylic acids, which are known to extract nitric acid to varying degrees depending on their alkyl chain length which is reflected in their polarity.[44]

Time of equilibration

In the case of multiple-DGA functionalized ligands such as T-DGA and TREN-DGA, it is expected that the lesser degrees of freedom of the three DGA moieties (as compared to three TODGA molecules) may result in a slower complex formation rate, which may in turn affect the kinetics of the metal ion extraction. It was found that equilibrium D values were obtained in only ca. 20 minutes when the molecular diluent mixture was used (Figure 2). We have reported that extraction of UO_2^{2+} and Pu^{4+} reach a steady value after about 10 min when a solution of TODGA in a molecular diluent was used.[45,46] On the other hand, ionic liquids, due to their high viscosities, lead to slower metal ion extraction kinetics.[24] A detailed investigation was carried out on the kinetics of the extraction of UO_2^{2+} and Pu^{4+} with T-DGA and TREN-DGA using [C_4mim][Tf_2N]. For comparison purpose, data on the extraction of the metal ions were also determined with TODGA in [C_4mim][Tf_2N] (Table 2). The times required to attain equilibrium for Pu^{4+} extraction using T-DGA and TREN-DGA in [C_4mim][Tf_2N] are 30 and 2 h, respectively. Though the exact reason for this drastic difference in the equilibration times is not understood, it is suggested that binding in T-DGA takes place by coordination to all the three DGA moieties.[10] This would require more time to undergo conformational changes, which becomes rather slow in the more viscous ionic liquid diluent as compared to the molecular diluent. On the other hand, TREN-DGA has been reported to bind through only one DGA moiety,[25] thereby avoiding such steric constraints. As discussed below, ML_2 type species are formed with T-DGA as well with increasing ligand
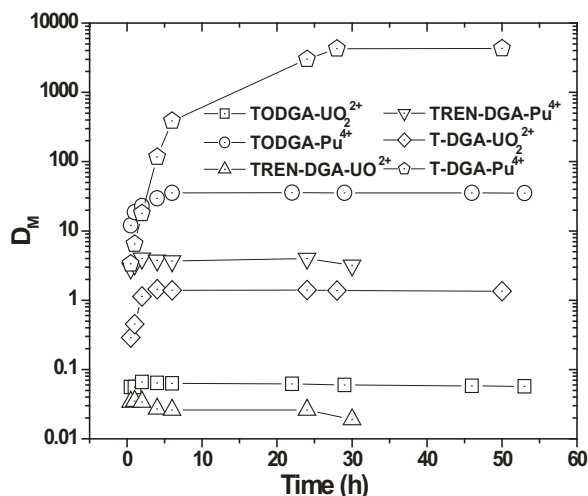
Figure 2. Dependence of metal ion extraction on the equilibration time using 1.0×10^{-3} M concentrations of all the three DGA ligands in $[C_4mim][Tf_2N]$ using. Aqueous phase: 1 M HNO_3.

Table 2. Time of equilibration of the extraction of Pu^{4+} and UO_2^{2+} using 1.0×10^{-3} M TODGA, T-DGA, and TREN-DGA in a molecular diluent and $[C_4mim][Tf_2N]$. Aqueous phase: 3M HNO_3.

	Time to attain equilibrium (h)	
Solvent system	U	Pu
TODGA – n-dodecane + iso-decanol (9:1)	<0.17[a]	<0.17[b]
TODGA-$[C_4mim][Tf_2N]$	0.5	6
T-DGA – n-dodecane + iso-decanol (9:1)	<0.35	<0.35
T-DGA-$[C_4mim][Tf_2N]$	4	30
TREN-DGA – n-dodecane + iso-decanol (9:1)	<0.35	<0.35
TREN-DGA-$[C_4mim][Tf_2N]$	0.5	2

[a] Data taken from ref. 43; [b] Data taken from ref. 44.

concentration. DFT computations suggest that in such cases the metal ion binds to only one DGA pendant arm.

It was interesting to note that the attainment of equilibrium in the case of UO_2^{2+} was relatively faster with all the three ligands in $[C_4mim][Tf_2N]$. The slow attainment of equilibrium in the case of TODGA is not understood at this stage and needs further investigations (may be using molecular dynamics simulations). The higher flexibility of the pendant arms in the T-DGA (five spacer atoms) as compared to TREN-DGA (two spacer atoms) is reflected in the significantly higher D_{Pu} values for the former as compared to those obtained with TREN-DGA.

Effect of HNO₃ concentration

In all these experiments, the concentration of the extractants was kept constant at 1.0×10^{-3} M. For the extraction of UO_2^{2+}, the HNO_3 concentration range was chosen as 0.01–6 M, while for Pu^{4+} extraction studies the acid concentration range was 0.5–6 M; the lower limit of 0.5 M HNO_3 was kept due to possible hydrolysis of the metal ion.[47]

The extraction of UO_2^{2+} and Pu^{4+} ions using solutions of T-DGA and TREN-DGA in the molecular diluent mixture of 90% n-dodecane and 10% iso-decanol increases upon increasing HNO_3 concentration (Figure 3a). For comparison purpose, the extraction profiles of both metal ions with 1.0×10^{-3} M TODGA are also included in the figure. From the solvent
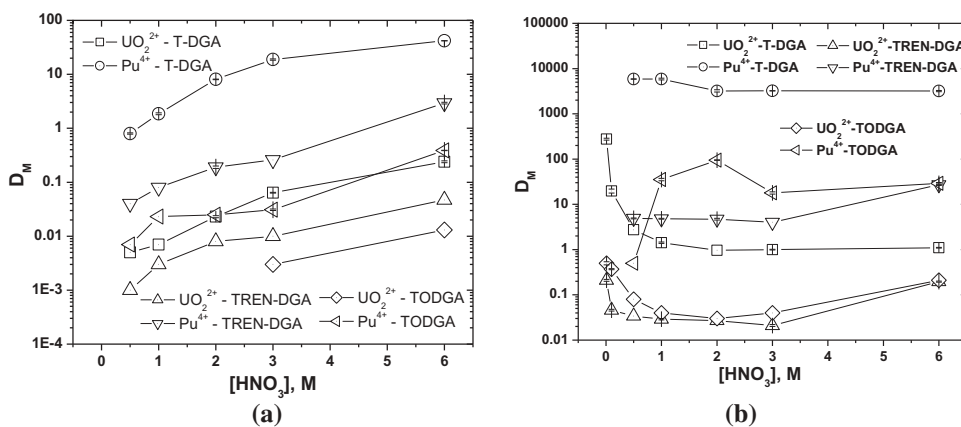
Figure 3. Dependence of aqueous phase HNO₃ concentration on the metal ion extraction using 1.0×10^{-3} M ligand; (a) in the molecular diluent mixture; Equilibration time: 1 h; (b) in [C₄mim][Tf₂N]; Equilibration time: 50 h.

extraction data, the following observations can be made, (i) the general trend of the metal ion extraction is: T-DGA > TREN-DGA > TODGA and (ii) the extraction of Pu^{4+} is significantly larger than that of UO$_2^{2+}$, in line with the results available in the literature.[3–5] Obviously, the mechanism of extraction is of the solvation type.[19] The higher extraction ability of T-DGA as compared to that of TREN-DGA can be attributed to several factors out of which the most prominent is the lipophilicity of the extracted complex. In this context, the flexibility of the ligand may play an important role (vide supra). Though one may be tempted to assume that the protonation of the N atom in TREN-DGA may be the reason for its lower binding as compared to that of T-DGA, the large values reported for Am^{3+} and Eu^{3+} ion extraction do not corroborate this.[25]

The results of the metal ion extraction studies using 1.0×10^{-3} M ligands in [C₄mim][Tf₂N] as a function of the HNO₃ concentration are presented in Figure 3b. It shows that, though the metal ion extraction trend in the ionic liquid medium was the same as for the molecular diluent mixture (Pu^{4+} is extracted to a greater extent than UO$_2^{2+}$), the separation factors are more than two orders of magnitude larger in the former (vide infra). The extraction mechanism appears to be of the cation-exchange type for UO$_2^{2+}$ ion (where the metal ion is extracted to the RTIL phase with a simultaneous partitioning of two C₄mim$^+$ ions toward the aqueous phase), as the characteristic decrease in metal ion extraction with increasing HNO₃ concentration was seen at the lower HNO₃ concentrations followed by marginal or no increase at higher acidities (Figure 3b). The extraction trend of the ligands followed the order: T-DGA > TODGA > TREN-DGA for both Pu^{4+} and UO$_2^{2+}$, which was different from that observed in the molecular diluent mixture (vide supra). At 0.5 M HNO₃, Pu^{4+} extraction was lower with TODGA than with TREN-DGA. However, at 1 M HNO₃ and higher, the D_{Pu} values were clearly higher with TODGA as compared to those with TREN-DGA. Interestingly, the D_{Pu} values with both the extractants were comparable at 6 M HNO₃ (Figure 3b). With all the three ligands in [C₄mim][Tf₂N], Pu^{4+} extraction appears to be independent of the HNO₃ concentration, at least in considerable concentration ranges in a way similar to the "solvation" mechanism seen with TODGA in molecular diluents.[5] The apparent increase in Pu^{4+} extraction with TREN-DGA in [C₄mim][Tf₂N] at 6 M HNO₃ can be attributed to the contribution of the extraction of anionic complexes of Pu^{4+} by the ionic liquid alone, following an anion-exchange mechanism (vide supra).[34–36]

Separation behavior

The tripodal DGA ligands have been used for the extraction of trivalent lanthanide/actinide ions from HNO_3 feed solutions,[2] which is otherwise hard to achieve with conventional extractants like tributyl phosphate. Therefore, to make a better comparison of the data, D values of Am^{3+} are included in Table 3 (taken from ref. 24 and 25). The extraction trend with TREN-DGA in the molecular diluent as well as in $[C_4mim][Tf_2N]$ is: $Am^{3+} > Pu^{4+} \gg UO_2^{2+}$ (Table 3). Though modest separation factors (S.F.) were obtained for Pu^{4+} with respect to Am^{3+} in $[C_4mim][Tf_2N]$, the S.F. (Am/U) of >8,000 is worth mentioning. The S.F. significantly increased (by >200 times) just by changing the diluent system from the molecular diluent mixture to $[C_4mim][Tf_2N]$. A similar enhancement in the S.F. (Pu/U) was observed, being ca. 25 in the molecular diluent and increasing to ca. 200 in $[C_4mim][Tf_2N]$.

In the case of T-DGA, the metal ion extraction trend in the molecular diluent mixture was $Pu^{4+} > Am^{3+} \gg UO_2^{2+}$, which changed to $Pu^{4+} \gg UO_2^{2+} > Am^{3+}$ in the ionic liquid (Table 3). To our knowledge, the D_{Pu} value of ca. 3.2×10^3 obtained with 1.0×10^{-3} M T-DGA for 3 M HNO_3 as the aqueous feed is one of the highest D values reported with such a low ligand concentration and may have interesting separation possibilities (though one may expect large errors in such high D values, we have taken care by assaying 0.5 mL lots from the aqueous phase and counting for long time so that the counting statistics errors were kept at minimum). The value of S.F. (Pu/Am) is exceptionally high (ca. 40,000) in $[C_4mim][Tf_2N]$, compared to a mere 1.7 in the molecular diluent mixture. The S.F. (Pu/U) value is ca. 316 in the molecular diluent mixture, which showed a more than ten-fold increase when the diluent was changed into the ionic liquid.

When 1.0×10^{-3} M TODGA was used as the extractant, the metal ion extraction was very low in the molecular diluent mixture. The extraction trend in the ionic liquid medium was found to be $Pu^{4+} > Am^{3+} > UO_2^{2+}$. While the S.F. (Pu/Am) value in the TODGA ionic liquid system is ca. 70, the S.F. (Pu/U) value is ca. 450.

Nature of the extracted species

In view of the rather low metal ion extraction in the molecular diluent mixture and also due to the significantly higher extraction of Pu^{4+} as compared to UO_2^{2+}, it was logical to investigate the nature of the extracted species of Pu^{4+} in $[C_4mim][Tf_2N]$. The extracted species are expected to be quite different with T-DGA, TREN-DGA, and TODGA and can be ascertained by the slope analysis method by carrying out ligand concentration variation experiments at 3 M HNO_3. In the ligand concentration variation plots, the total concentration of the ligand was used in place of the "free" ligand concentration in view of the very low amount of ligand used in metal ion extraction in view of the low metal ion concentrations used in these studies. It is clear from Figure 4 that ML_2 type species are dominating (slope: 1.87 ± 0.11) for Pu^{4+} ion extraction when TODGA was used as the extractant. In the case of T-DGA as the extractant, while ML species are extracted at lower ligand concentrations (slope: 0.94 ± 0.06), there is a tendency to extract species of higher ligand to metal ratio at higher ligand concentrations, especially at $>4.0 \times 10^{-4}$ M (slope: 2.64 ± 0.20). On the other hand, in the case of TREN-DGA, the ligand dependence was very low at lower

Table 3. Comparative distribution ratio and separation factor values with respect to Am^{3+} (in brackets) of the extraction of Pu^{4+} and UO_2^{2+} by the DGA ligands. Feed: 3 M HNO_3. Ligand concentration: 1.0×10^{-3} M.

Metal ion (M)	D_M values with TREN-DGA		D_M values with T-DGA		D_M values with TODGA	
	n-Dodecane + IDA[a] (9:1)	$[C_4mim][Tf_2N]$	n-Dodecane + IDA (9:1)	$[C_4mim][Tf_2N]$	n-Dodecane + IDA (9:1)	$[C_4mim][Tf_2N]$
Am^{3+}	0.36 ± 0.02[b]	161 ± 2.3[b]	11.1 ± 0.06[b]	0.081 ± 0.21[b]	0.003[c]	0.25[c]
Pu^{4+}	0.25 ± 0.01 (1.44)	4.0 ± 0.1 (40.2)	19.0 ± 1.1 (0.58)	3227 ± 40 (2.5×10^{-5})	0.03 ± 0.00	17.9 ± 1.0 (0.014)
UO_2^{2+}	0.01 ± 0.00 (36)	0.02 ± 0.00 (8050)	0.06 ± 0.01 (185)	1.00 ± 0.01(0.081)	< 0.01	0.04 ± 0.0 (6.25)

[a] IDA: iso-decanol; [b] Data taken from ref. 25; [c] Data taken from ref. 24.
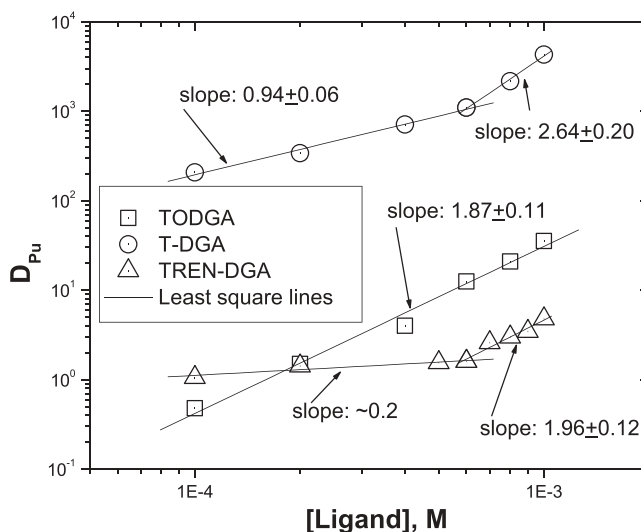
Figure 4. Dependence of ligand concentration on the metal ion extraction of all three DGA ligands in [C$_4$mim][Tf$_2$N]. Aqueous phase: 3 M HNO$_3$; Equilibration time: 50 h.

ligand concentrations and the extraction of species of the type ML$_2$ (slope: 1.96 ± 0.12) was seen in the concentration range of 5.0×10^{-4}–1.0×10^{-3} M. This striking difference in the two types of tripodal ligands suggests that metal ion extraction is not very favorable with TREN-DGA, probably on account of steric constrains due to the presence of two spacer atoms as compared to five spacer atoms in the case of T-DGA and also due to the central "N" atom which can interact with the H$^+$ ion, which are present at a significantly large concentration. This indicates that the former ligand is significantly strained if all the nine "O" atoms are required to coordinate with the Pu^{4+} ion during the extraction of ML type species. Evidence for the "non-inclusion" complexes in the case of both types of tripodal ligands (where all the three DGA moieties are bound to the Pu^{4+} ion) comes from the DFT computation data (vide infra). This may be the reason for the preference for 1:2 (M:L) complex formation at higher ligand concentrations. In such ML$_2$ type complexes, all the "O" atoms from the extractant are not necessarily required to coordinate to the metal ion, suggesting a more favorable extraction mechanism.

In the case of T-DGA, steric constraints are present to a much lower extent, giving rise to the extraction of ML type of species at lower ligand concentrations. At higher concentrations, however, ML$_2$ type species are formed in a manner analogous to that with TREN-DGA. In the case of TODGA, there are no such steric constraints and hence ML$_2$ species are formed in the entire range. Such coordinatively unsaturated complexes suggest the presence of nitrate ions in the extracted species. Usually, with these ligands, extraction of charge neutralized species of the type ML$_n$(NO$_3$)$_4$ (where n = 1–3 depending on the nature of the extractant) are suggested for the Pu^{4+} ion. In view of the possibility of a parallel anion-exchange extraction mechanism in the absence of the extractants (vide supra), nitrate concentration variation studies will be rather complex and hence, were not attempted. On the other hand, cation-exchange species[17] of the type UO$_2$L$_n$$^{2+}$ may be extracted in the case of the uranyl ion. Though the value of n can be determined from ligand concentration variation studies, those were not performed in view of the very low D_U values.

DFT Computations

The experimental studies indicated the formation of 1:2 complexes of Pu^{4+} with both T-DGA and TREN-DGA. The same metal-ligand stoichiometry was, therefore, maintained for the computational studies. The number of nitrate ions, however, varied from 2 to 4 forming bi-positive to neutral complexes. Similar types

of complexes were reported earlier for Eu^{3+}.[25] For comparison, the calculations were also performed on the similar Pu^{4+} complexes of TMDGA (taken as a homolog of TODGA). It may be noted here that the time required to do computation with TODGA becomes very large in view of the large number of atoms (214 atoms for 2 TODGA) involved in such a complex vis-à-vis only 46 atoms in the case of 2 units of TMDGA. In a similar manner, the methyl analogs of T-DGA and TREN-DGA were used for the computations. Furthermore, for a more simplified approach, the anionic complexes of Pu^{4+} were not considered. The optimized geometries of the free ligands are shown in Fig. S1 (ESI) and those of the respective Pu^{4+} complexes are shown in Figures 5–7. In all the complexes, Pu^{4+} was connected to three different kinds of oxygen atoms, viz. carbonyl ($O_{carbonyl}$), etheric (O_{ether}), and nitrate (O_{nit}) (Table 4). Though the $Pu–O_{carbonyl}$ distances are in the range of 2.35–2.54 Å, the $Pu–O_{ether}$ distances are much larger ranging from 2.576–3.812 Å, which indicates a weaker interaction with the etheric oxygen atoms of the DGA units. Analogous results have been reported in computational[48] as well as structural studies.[49]
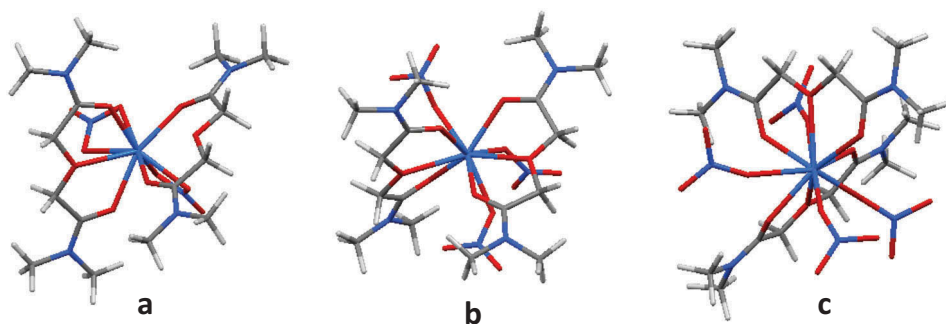
Figure 5. Optimized structures of different possible Pu^{4+} complexes of TMDGA (L) (a) $PuL_2(NO_3)_2{}^{2+}$, (b) $PuL_2(NO_3)_3{}^+$, and (c) $PuL_2(NO_3)_4$.
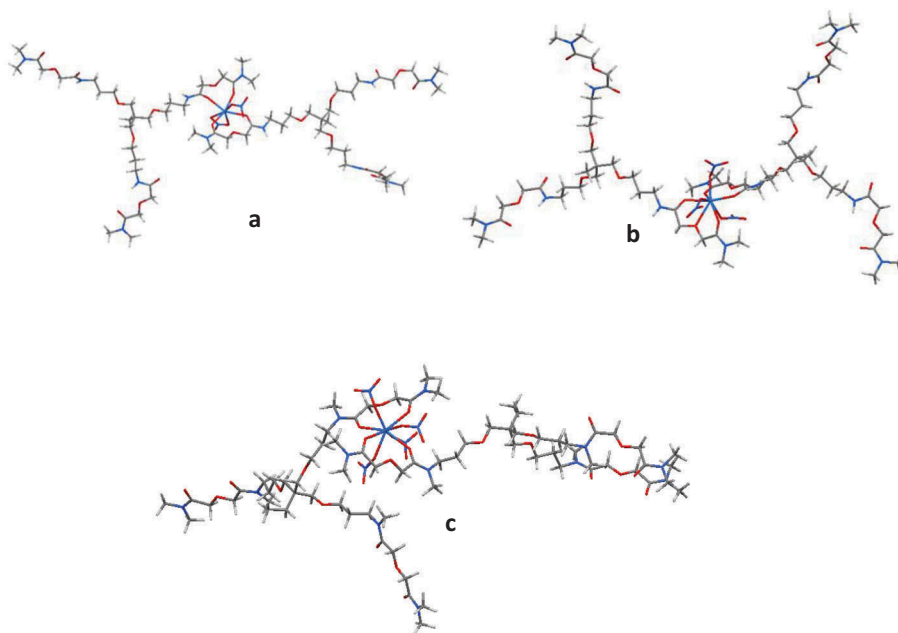
Figure 6. Optimized structures of different possible Pu^{4+} complexes of T-DGA (L) (a) $PuL_2(NO_3)_2{}^{2+}$, (b) $PuL_2(NO_3)_3{}^+$, and (c) $PuL_2(NO_3)_4$.
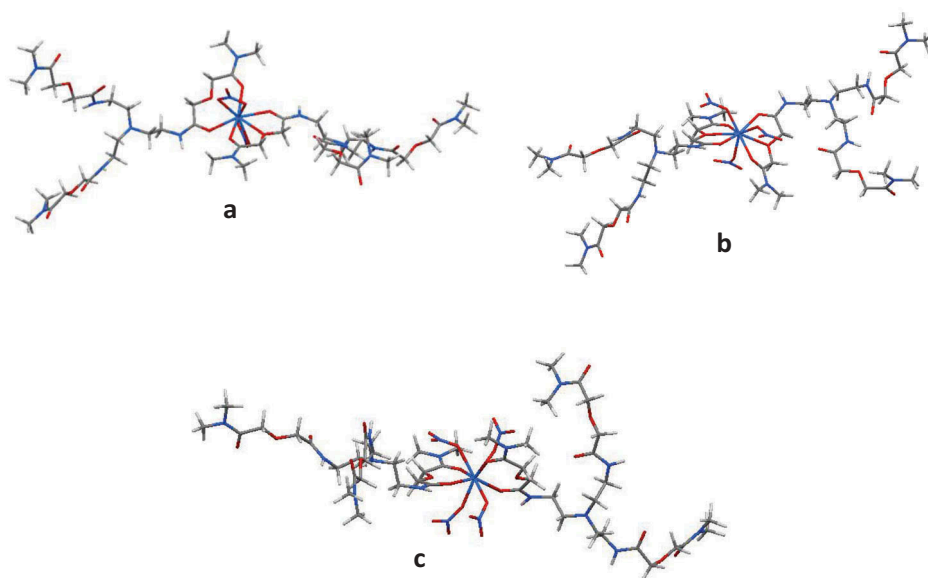
Figure 7. Optimized structures of different possible Pu^{4+} complexes of TREN-DGA (L) (a) $PuL_2(NO_3)_2^{2+}$, (b) $PuL_2(NO_3)_3^+$, and (c) $PuL_2(NO_3)_4$.

Table 4. Calculated structural parameters (Å) of different Pu^{4+} complexes of TMDGA, T-DGA, and TREN-DGA.

Ligand (L)	Complex	Pu–$O_{carbonyl}$	Pu–O_{ether}	Pu–O_{nit}
TMDGA	$PuL_2(NO_3)_2^{2+}$	2.351, 2.419, 2.362, 2.366	2.656, 2.778	2.373/2.393,[a] 2.428/2.421[a]
	$PuL_2(NO_3)_3^+$	2.408, 2.337, 2.405, 2.540	2.576, 2.579	2.231, 2.376, 2.195
	$PuL_2(NO_3)_4$	2.431, 2.446, 2.427, 2.452	2.635, 2.656	2.295, 2.365, 2.327, 2.248
T-DGA	$PuL_2(NO_3)_2^{2+}$	2.370, 2.415, 2.424, 2.481	2.682, 3.812	2.462/2.481,[a] 2.295
	$PuL_2(NO_3)_3^+$	2.358, 2.453, 2.388, 2.441	2.692, 2.635	2.229, 2.202, 2.333
	$PuL_2(NO_3)_4$	2.355, 2.444, 2.406, 2.386	2.778, 2.923	2.395, 2.282, 2.406, 2.287
TREN-DGA	$PuL_2(NO_3)_2^{2+}$	2.414, 2.446, 2.432, 2.424	2.646, 2.737	2.455/2.476,[a] 2.460/2.423[a]
	$PuL_2(NO_3)_3^+$	2.391, 2.450, 2.358, 2.398	2.604, 2.658	2.241, 2.340, 2.227
	$PuL_2(NO_3)_4$	2.407, 2.454, 2.475, 2.372	2.788, 2.823	2.283, 2.380, 2.395, 2.253

[a] These bonds refer to bidentate nitrates. All other are monodentate nitrates.

Two kinds of nitrate ions were observed, bidentate and monodentate. While the Pu–O_{nit} bond distances were larger for the bidentate nitrates ranging from 2.37 to 2.46 Å, that for the monodentate nitrates varied from 2.195 to 2.395 Å. In the gas phase, the complexation becomes more and more favorable upon increasing the number of nitrate ions, resulting in a neutral complex of the type PuL_2 $(NO_3)_4$ which became the most favorable with the highest interaction energy for all the three ligands (TMDGA, T-DGA, and TREN-DGA). In the solution phase, however, a similar trend was only observed in the case of T-DGA. On the other hand, the mono-positive $PuL_2(NO_3)_3^+$ complex was found to be most favorable for TREN-DGA in the solution phase. This explains the better extraction of TREN-DGA complexes in ionic liquid medium where the cationic species may be extracted.[17,18] Comparison of the interaction energies (Table 5) for various complexes, those of TMDGA showed much stronger interactions than those of both T-DGA and TREN-DGA, probably because of the absence of steric crowding from non-coordinating DGA arms in TMDGA. In the cases of T-DGA and TREN-DGA, however, out of the three DGA arms only one is coordinating, whereas the other two remain non-coordinated and induce steric hindrance leading to a poor interaction. If we compare three different complexes of TMDGA, TREN-DGA and T-DGA, it is to be noted that only in the case of the neutral Pu^{4+} complex with all the four nitrate in the inner sphere, the order of

Table 5. Gas and solution phase binding energies (ΔE in kcal mol^{-1}) for the different possible complexes of Pu^{4+} with the ligands TMDGA, T-DGA, and TREN-DGA with metal-ligand stoichiometry of 1:2.

Ligand (L)	Complex	Gas phase	Solution phase
TMDGA	PuL$_2$(NO$_3$)$_2^{2+}$	−3520.0	−1111.4
	PuL$_2$(NO$_3$)$_3^+$	−4153.8	−1146.2
	PuL$_2$(NO$_3$)$_4$	−4432.6	−1130.7
T-DGA	PuL$_2$(NO$_3$)$_2^{2+}$	−2598.9	−188.4
	PuL$_2$(NO$_3$)$_3^+$	−3238.9	−246.5
	PuL$_2$(NO$_3$)$_4$	−3783.3	−270.9
TREN-DGA	PuL$_2$(NO$_3$)$_2^{2+}$	−2584.1	−184.0
	PuL$_2$(NO$_3$)$_3^+$	−3223.5	−231.6
	PuL$_2$(NO$_3$)$_4$	−3764.8	−207.5

"Pu−O$_{carbonyl}$" bond distances suggest strongest complexation with T-DGA, followed by TREN-DGA and TMDGA (Table 4). This observation is in line with the results obtained from the solvent extraction study in n-dodecane medium, where highest extraction is observed in the case of T-DGA followed by TREN-DGA and TMDGA. This indicates that Pu^{4+} preferably forms a neutral complex of the type PuL$_2$(NO$_3$)$_4$ in the case of all the three ligands.

The Wiberg bond order has been defined for the closed shell semi-empirical molecular orbital theory using complete neglect of differential overlap approximation and therefore, an orthonormal condition of the basis function is assumed. The Mayer Bond order, however, is more a generalization of the WBO, where the overlap matrix is taken into account and it can be used for non-orthonormal basis functions and in addition it can nicely handle the open shell systems.[50–53] Wiberg[50,51] and Mayer[52,53] bond orders for the "Pu−O" bonds for the carbonyl and ethereal oxygen atoms of the DGA moieties were calculated using AOMIX and the results are listed in Tables 6–8.[54,55] In the cases of ethereal oxygen atoms, the maximum "Pu−O$_{ether}$" bond orders were 0.14 in the case of the PuL$_2$(NO$_3$)$_2^{2+}$ complex of TMDGA. On the other hand, the "Pu−O$_{carbonyl}$" bond orders were in the range of 0.2–0.5, which is much higher than that of the "Pu−O$_{ether}$" bond. This clearly supports the observation of a weaker interaction of the ethereal oxygen as compared to the carbonyl oxygen atoms. Comparing the total bond order, considering all the "Pu−O" bonds from the two DGA moieties for the three types of complexes varying the number of nitrate ions, it has to be noted that in the case of the PuL$_2$(NO$_3$)$_2^{2+}$ type of complex the total bond order (both WBO and MBO) is the lowest for T-DGA. This contradicts the experimental results showing the highest extraction efficiency for T-DGA. Considering the PuL$_2$(NO$_3$)$_3^+$ type of

Table 6. Wiberg's (WBO) and Mayer's (MBO) bond order between Pu^{4+} and coordinating carbonyl and ethereal oxygens of two DGA moieties in the Pu^{4+}-TMDGA complex.

Complex	Bond	Pu−O$_{car1}$	Pu−O$_{car1}$	Pu−O$_{car2}$	Pu−O$_{car2}$	Pu−O$_{ether1}$	Pu−O$_{ether2}$	Total
PuL$_2$(NO$_3$)$_2^{2+}$	WBO	0.384	0.454	0.418	0.458	0.065	0.139	1.918
	MBO	0.392	0.465	0.428	0.467	0.066	0.14	1.958
PuL$_2$(NO$_3$)$_3^+$	WBO	0.419	0.461	0.32	0.463	0.084	0.102	1.849
	MBO	0.425	0.471	0.323	0.471	0.087	0.104	1.881
PuL$_2$(NO$_3$)$_4$	WBO	0.196	0.336	0.228	0.32	0.068	0.068	1.216
	MBO	0.203	0.339	0.233	0.324	0.07	0.07	1.239

Table 7. Wiberg's (WBO) and Mayer's (MBO) bond order between Pu^{4+} and coordinating carbonyl and ethereal oxygens of two DGA moieties in the Pu^{4+}-T-DGA complex.

Complex	Bond	Pu−O$_{car1}$	Pu−O$_{car1}$	Pu−O$_{car2}$	Pu−O$_{car2}$	Pu−O$_{ether1}$	Pu−O$_{ether2}$	Total
PuL$_2$(NO$_3$)$_2^{2+}$	WBO	0.299	0.339	0.327	0.302	0.080	<0.05	1.397
	MBO	0.303	0.344	0.33	0.305	0.081	<0.05	1.413
PuL$_2$(NO$_3$)$_3^+$	WBO	0.435	0.357	0.346	0.47	0.121	0.086	1.815
	MBO	0.44	0.364	0.355	0.476	0.123	0.088	1.846
PuL$_2$(NO$_3$)$_4$	WBO	0.428	0.342	0.421	0.405	0.074	0.088	1.758
	MBO	0.436	0.349	0.428	0.413	0.074	0.089	1.789

Table 8. Wiberg's (WBO) and Mayer's (MBO) bond order between Pu^{4+} and coordinating carbonyl and ethereal oxygens of two DGA moieties in the Pu^{4+}-TREN-DGA complex.

Complex	Bond	Pu–O_{car1}	Pu–O_{car1}	Pu–O_{car2}	Pu–O_{car2}	Pu–O_{eth1}	Pu–O_{eth2}	Total
$PuL_2(NO_3)_2^{2+}$	WBO	0.394	0.341	0.377	0.481	0.104	0.084	1.781
	MBO	0.399	0.346	0.381	0.486	0.105	0.085	1.802
$PuL_2(NO_3)_3^{+}$	WBO	0.47	0.382	0.461	0.401	0.171	0.073	1.958
	MBO	0.476	0.388	0.468	0.411	0.175	0.074	1.992
$PuL_2(NO_3)_4$	WBO	0.39	0.355	0.304	0.429	0.101	< 0.05	1.629
	MBO	0.397	0.361	0.311	0.436	0.102	< 0.05	1.657

Table 9. Natural charges on plutonium and electronic population in "*s*", "*p*", "*d*", and "*f*" orbitals in its complexes with different DGA derivatives obtained from the natural population analysis.

Ligand	Complex	Natural charge	$n(s)$	$n(p)$	$n(d)$	$n(f)$
TMDGA	$PuL_2(NO_3)_2^{2+}$	1.639	4.202	11.990	11.066	5.101
	$PuL_2(NO_3)_3^{+}$	1.702	4.188	11.973	11.060	5.075
	$PuL_2(NO_3)_4$	1.641	4.147	11.965	11.117	5.125
T-DGA	$PuL_2(NO_3)_2^{2+}$	1.837	4.159	11.981	10.984	5.036
	$PuL_2(NO_3)_3^{+}$	1.742	4.184	11.972	11.053	5.047
	$PuL_2(NO_3)_4$	1.643	4.199	11.972	11.108	5.074
TREN-DGA	$PuL_2(NO_3)_2^{2+}$	1.660	4.198	11.993	10.967	5.180
	$PuL_2(NO_3)_3^{+}$	1.722	4.185	11.974	11.055	5.062
	$PuL_2(NO_3)_4$	1.633	4.201	11.973	11.113	5.077

complex, the highest complexation efficiency should be reflected for TREN-DGA and this also contradicts the experimental observations. The total bond order from the DGA moieties is found to be the highest for T-DGA when we consider the neutral complex of the type $PuL_2(NO_3)_4$. The highest bond order for the Pu–O bond for the TDGA followed by TREN-DGA and TMDGA complex can explain the trends in the "Pu–$O_{carbonyl}$" bond distances in the neutral Pu^{4+} complexes of all the three ligands. Similar to the trends in the "Pu–$O_{carbonyl}$" bond distances, bond order analysis, therefore, also supports the experimental observation of the highest extraction efficiency with T-DGA which is followed by TREN-DGA and TODGA shows the lowest extractability for Pu^{4+} in *n*-dodecane medium.

Charges for different Pu^{4+} complexes were calculated using natural population analysis (NPA)[56,57] and are listed in Table 9. Significant electron density has been transferred from the ligand (DGA and nitrate) to the plutonium ion in the case of all the complexes. A minimal change of the electron density is noticed in the 5*p* and 6*p* orbitals of plutonium. However, the electron density in the 6*d* and 5*f* orbitals is significantly increased. More than two electrons are transferred from the ligand molecules to the "*d*" and "*f*" orbitals of the plutonium ion, indicating significant degrees of covalence in the plutonium complexes.

Conclusions

The extraction of UO_2^{2+} and Pu^{4+} using two different TDGAs showed drastic differences in their extraction and selectivities. While the extraction of the metal ions was relatively low with TREN-DGA in the molecular diluent mixture of *n*-dodecane and iso-decanol (9:1), a significant enhancement in the distribution ratios was observed using the ionic liquid $[C_4mim][Tf_2N]$ as the diluent. In general, UO_2^{2+} extraction was faster as compared to that of Pu^{4+}. Furthermore, while the extraction kinetics was significantly slower in $[C_4mim][Tf_2N]$ vis-à-vis that in the molecular diluent mixture, extraction with T-DGA was significantly slower than with TREN-DGA, which was attributed to the higher flexibility of the former leading to less preorganization of the pendant DGA groups. As UO_2^{2+} extraction was rather low in all cases, the *S.F.* values with respect to UO_2^{2+} are impressive. Especially, the *S.F.* (Pu/Am) value of >40,000 in the case of T-DGA in $[C_4mim][Tf_2N]$ is one of the important findings of this study. From the slope analysis, the nature of the extracted species for Pu^{4+} ion extraction in the ionic liquid medium

was determined to be of the ML_2 type for TODGA in the entire concentration range and for TREN-DGA at relatively high ligand concentrations. In the case of T-DGA, both ML and ML_2 type complexes were reported, namely, ML species occurring at lower ligand concentrations changing to ML_2 type species at higher ligand concentrations. DFT studies indicated coordination of only one DGA pendent arm out of three such arms present in TREN-DGA as well as T-DGA, the free ones leading to steric constraints. The order of extractability of T-DGA > TREN-DGA > TMDGA for Pu^{4+} in *n*-dodecane medium from the solvent extraction study could be explained on the basis of the trends in the "Pu–$O_{carbonyl}$" bond distances and "Pu–O" bond orders only in the case of the neutral complex of the type $PuL_2(NO_3)_4$. This suggested that Pu^{4+} was preferably extracted as the neutral complex (mentioned above) in the case of all the three ligands.

Acknowledgments

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