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

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\textbf{ABSTRACT}

The extraction of UO\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{4+} ions was studied from nitric acid medium using three diglycolamide (DGA) extractants, viz. TODGA (\(N,N,N',N'-\text{tetra-}\text{-}n\text{-}octyldiglycolamide), T-DGA (tripodal diglycolamide), and TREN-DGA (\(N\text{-}pivot\text{-}tripodal\text{-}diglycolamide\) in a molecular diluent mixture (9:1 mixture of \(n\text{-}dodecane\ and iso\text{-}decanol) and an ionic liquid, 1-butyl-3-methylimidazolium bis\text{(trifluoromethanesulfonyl)imide (\([C_4\text{mim}]\text{[Tf}_2\text{N}]\). Using 1.0 \times 10\textsuperscript{-3} M solutions of the ligands in \([C_4\text{mim}]\text{[Tf}_2\text{N}]\, T-DGA yielded an exceptionally high extraction of Pu\textsuperscript{4+} ion (\(D_{Pu} > 3.2 \times 10\textsuperscript{3}\)) from 3 M HNO\textsubscript{3} as compared to \(D_{Pu}\) values of 4 and 17 obtained with TREN-DGA and TODGA, respectively. Similarly, while the extraction of UO\textsubscript{2}\textsuperscript{2+} ion was significantly lower than that of Am\textsuperscript{3+} ion for all the three DGA ligands in the molecular diluent and with TODGA and TREN-DGA in \([C_4\text{mim}]\text{[Tf}_2\text{N}]\, 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\textsubscript{2}(NO\textsubscript{3})\textsubscript{n}\textsuperscript{4+} 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\textsubscript{2}(NO\textsubscript{3})\textsubscript{4} as compared to cationic species of the type PuL\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}\textsuperscript{2+} and PuL\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}\textsuperscript{+} for all the three types of ligands (TODGA, TREN-DGA, and T-DGA).

\textbf{KEYWORDS}

Diglycolamides; actinides; ionic liquid; solvent extraction; DFT computations

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,\textsuperscript{[1]} malonamides, etc.\textsuperscript{[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\textsuperscript{4+} and UO\textsubscript{2}\textsuperscript{2+}\textsuperscript{[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'-\text{tetra-}\text{-}n\text{-}octyldiglycolamide, Figure 1).\textsuperscript{[6]} The formation of the reverse micellar aggregates is facilitated in apolar diluents such as \(n\text{-}dodecane\). In view of the presence of 3–4 TODGA molecules in the extracted species containing trivalent lanthanide ions,\textsuperscript{[7]} DGA functionalized ligands with 3–4 DGA pendent arms have been synthesized and evaluated for actinide ion extraction.\textsuperscript{[8,9]} A C-pivot tripodal diglycolamide (T-DGA, Figure 1) extractant has been used for the extraction of trivalent lanthanide/actinide ions\textsuperscript{[10]} and the results...
yielded very high distribution ratios even at millimolar concentrations.\textsuperscript{[11]} The selectivities obtained with TODGA were retained in T-DGA in a diluent mixture of 90% \textit{n}-dodecane and 10% iso-decanol. However, the poor extraction of UO\textsubscript{2}\textsuperscript{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.\textsuperscript{[12–16]} There are reports proposing their possible applications as alternative diluents for solvent extraction,\textsuperscript{[17–19]} which are based on large enhancements in the metal ion extraction in many cases.\textsuperscript{[20]} The extraction of trivalent lanthanide and actinide ions is studied using TODGA as well as T-DGA in ionic liquids.\textsuperscript{[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\textsubscript{2}\textsuperscript{2+} ion, while an opposite trend was seen for the Pu\textsuperscript{4+} ion.\textsuperscript{[22]} The higher separation efficiency is due to an enhanced extraction of Am\textsuperscript{3+} in ionic liquids with a concomitant decrease in the extraction of the UO\textsubscript{2}\textsuperscript{2+} ion. It has also been reported that, whereas T-DGA is a highly efficient extractant for Am\textsuperscript{3+} in molecular diluents, it is not the case in ionic liquids, especially at higher HNO\textsubscript{3} concentrations. Typically, the \(D_{\text{Am}}\) value obtained using \(1.0 \times 10^{-3}\) M T-DGA at 3 M HNO\textsubscript{3} was 0.6 in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonfonyl)imide ([C\textsubscript{4}mim][Tf\textsubscript{2}N]). On the other hand, the distribution ratio was ca. 30 under identical experimental conditions when a molecular diluent mixture (90\% \textit{n}-dodecane and 10\% iso-decanol) was used.\textsuperscript{[24]} In most of the reported literature, the extraction of UO\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{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 \textit{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.\textsuperscript{[25]} Interestingly, the extraction of the metal ions was rather poor in a molecular diluent mixture. The \(D_{\text{Am}}\) values using \(1.0 \times 10^{-3}\) M TREN-DGA in [C\textsubscript{4}mim][Tf\textsubscript{2}N] and a molecular diluent (90\% \textit{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\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{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\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{4+}, using TODGA, T-DGA, and TREN-DGA in both a molecular diluent (90\% \textit{n}-dodecane + 10\% iso-decanol) as well as an ionic liquid ([C\textsubscript{4}mim][Tf\textsubscript{2}N]). The extraction data of Am\textsuperscript{3+} are also included for comparison purposes.\textsuperscript{[25]} The present article describes an unusual (in most DGA functionalized ligands, the \(D_U\) is very low)\textsuperscript{[24]} increase in UO\textsubscript{2}\textsuperscript{2+} extraction efficiency using TREN-DGA.

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Figure 1. Structural formulae of TODGA, TMDGA, TREN-DGA, and T-DGA.
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.\(^\text{[11,25]}\) 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\(_4\)mim][Tf\(_2\)N], 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.\(^\text{[26]}\) 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.\(^\text{[26]}\) 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\(_3\).\(^\text{[27]}\) 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 \(\mu\)g) 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 \(\mu\)L) 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.
At that acidity, and also in contrast to that at lower acid concentrations, which may be attributed to an anion-exchange mechanism,\textsuperscript{[40,41]} given below:

\[
\text{Pu}^{4+}_{\text{aq}} + x\text{NO}_3^{-\text{aq}} + 2\text{Tf}_2\text{N}^{-\text{IL}} \rightleftharpoons \text{Pu(NO}_3^3)^{(x-4)^-}_{\text{IL}} + 2\text{Tf}_2\text{N}^{-\text{aq}}
\]  

(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 \(\text{Pu}^{4+}\), increased enormously in the ionic liquid when the DGA-based ligands were used. There are examples where the extraction of \(\text{Pu}^{4+}\) in the ionic liquid ([C\text{4}mim][Tf\text{2}N]) was reported to be as high as ca. 15 at 6 M HNO\(_3\) even in the absence of any organic extractant.\textsuperscript{[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%).\textsuperscript{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.\textsuperscript{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 \(\text{UO}_2^{2+}\) and \(\text{Pu}^{4+}\) reach a steady value after about 10 min when a solution of TODGA in a molecular diluent was used.\textsuperscript{[45,46]} On the other hand, ionic liquids, due to their high viscosities, lead to slower metal ion extraction kinetics.\textsuperscript{24} A detailed investigation was carried out on the kinetics of the extraction of \(\text{UO}_2^{2+}\) and \(\text{Pu}^{4+}\) with T-DGA and TREN-DGA using [C\text{4}mim][Tf\text{2}N]. For comparison purpose, data on the extraction of the metal ions were also determined with TODGA in [C\text{4}mim][Tf\text{2}N] (Table 2). The times required to attain equilibrium for \(\text{Pu}^{4+}\) extraction using T-DGA and TREN-DGA in [C\text{4}mim][Tf\text{2}N] 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.\textsuperscript{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,\textsuperscript{25} thereby avoiding such steric constraints. As discussed below, ML\(_2\) type species are formed with T-DGA as well with increasing ligand
concentration. DFT computations suggest that in such cases the metal ion binds to only one DGA pendent 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 $[C_{4}mim][Tf_{2}N]$. 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 HNO$_3$ concentration**

In all these experiments, the concentration of the extractants was kept constant at $1.0 \times 10^{-3}$ 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. 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 $1.0 \times 10^{-3}$ M TODGA are also included in the figure. From the solvent concentration. DFT computations suggest that in such cases the metal ion binds to only one DGA pendent arm.
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 [C\(_4\)mim][Tf\(_2\)N] as a function of the HNO\(_3\) 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 C\(_4\)mim\(^+\) ions toward the aqueous phase), as the characteristic decrease in metal ion extraction with increasing HNO\(_3\) concentration was seen at the lower HNO\(_3\) 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 HNO\(_3\), Pu\(^{4+}\) extraction was lower with TODGA than with TREN-DGA. However, at 1 M HNO\(_3\) 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 HNO\(_3\) (Figure 3b). With all the three ligands in [C\(_4\)mim][Tf\(_2\)N], Pu\(^{4+}\) extraction appears to be independent of the HNO\(_3\) 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 [C\(_4\)mim][Tf\(_2\)N] at 6 M HNO\(_3\) 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 HNO₃ feed solutions, which is otherwise hard to achieve with conventional extractants like tributyl phosphate. Therefore, to make a better comparison of the data, D values of Am³⁺ 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 [C₄mim][Tf₂N] is: Am³⁺ > Pu⁴⁺ > UO₂²⁺ (Table 3). Though modest separation factors (S.F.) were obtained for Pu⁴⁺ with respect to Am³⁺ in [C₄mim][Tf₂N], 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 [C₄mim][Tf₂N]. A similar enhancement in the S.F. (Pu/U) was observed, being ca. 25 in the molecular diluent and increasing to ca. 200 in [C₄mim][Tf₂N].

In the case of T-DGA, the metal ion extraction trend in the molecular diluent mixture was Pu⁴⁺ > Am³⁺ > UO₂²⁺, which changed to Pu⁴⁺ > UO₂²⁺ > Am³⁺ in the ionic liquid (Table 3). To our knowledge, the $D_{Pu}$ value of ca. $3.2 \times 10^3$ obtained with $1.0 \times 10^{-3}$ M T-DGA for 3 M HNO₃ 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 [C₄mim][Tf₂N], 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 $1.0 \times 10^{-3}$ 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 Pu⁴⁺ > Am³⁺ > UO₂²⁺. 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 Pu⁴⁺ as compared to UO₂²⁺, it was logical to investigate the nature of the extracted species of Pu⁴⁺ in [C₄mim][Tf₂N]. 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 HNO₃. In the ligand concentration variation plots, the total concentration of the ligand was used in place of the free ligand concentrations, especially at >4.0 × $10^{-4}$ M (slope: 2.64 ± 0.20). On the other hand, in the case of TREN-DGA, the ligand dependence was very low at lower

| Metal ion (M) | $D_M$ values with TREN-DGA | $D_M$ values with T-DGA | $D_M$ values with TODGA |
|---------------|---------------------------|-------------------------|------------------------|
|               | $n$-Dodecane + IDA⁴⁺       | $n$-Dodecane + IDA⁴⁺    | $n$-Dodecane + IDA⁴⁺   |
|               | (9:1) [C₄mim][Tf₂N]      | (9:1) [C₄mim][Tf₂N]    | (9:1) [C₄mim][Tf₂N]   |
| Am³⁺          | 0.36 ± 0.02⁵              | 161 ± 2.3⁵              | 11.1 ± 0.06⁵           |
| Pu⁴⁺          | 0.25 ± 0.01 (1.44)        | 4.0 ± 0.1 (40.2)        | 19.0 ± 1.1 (0.58)      |
| UO₂²⁺         | 0.01 ± 0.00 (36)          | 0.02 ± 0.00 (8050)      | 0.06 ± 0.01 (185)      |

⁴⁺ IDA: iso-decanol; ⁵ Data taken from ref. 24; ¹ Data taken from ref. 25.

![Table 3](image-url)
ligand concentrations and the extraction of species of the type $\text{ML}_2$ (slope: $1.96 \pm 0.12$) was seen in the concentration range of $5.0 \times 10^{-4}$–$1.0 \times 10^{-3}$ 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 $\text{H}^+$ 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 $\text{Pu}^{4+}$ 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 $\text{Pu}^{4+}$ 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 $\text{ML}_n(\text{NO}_3)_4$ (where $n = 1$–3 depending on the nature of the extractant) are suggested for the $\text{Pu}^{4+}$ 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 $\text{UO}_2\text{L}_n^{2+}$ 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 $\text{Pu}^{4+}$ 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$_{\text{carbonyl}}$), etheric (O$_{\text{ether}}$), and nitrate (O$_{\text{nitr}}$) (Table 4). Though the Pu–O$_{\text{carbonyl}}$ distances are in the range of 2.35–2.54 Å, the Pu–O$_{\text{ether}}$ 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$_3$)$_4$. 
Two kinds of nitrate ions were observed, bidentate and monodentate. While the Pu–O
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
(\textit{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
(\textit{NO}_3)^3\textit{+} 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\cite{17,18}.

Comparison of the interaction energies (\textit{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\textsuperscript{4+} complex with all the four nitrate in the inner sphere, the order of

\begin{table}
\centering
\begin{tabular}{lllll}
\hline
Ligand (L) & Complex & Pu–O\textsubscript{Carbonyl} & Pu–O\textsubscript{Ether} & Pu–O\textsubscript{nit} \\
\hline
TMDGA & PuL\textsubscript{2}(\textit{NO}_3)^{2\textit{+}} & 2.351, 2.419, 2.362, 2.366 & 2.656, 2.778 & 2.373/2.393, \textit{a} \textit{PuL}2(\textit{NO}_3)^{3\textit{+}} & 2.408, 2.337, 2.405, 2.540 & 2.576, 2.579 & 2.231, 2.376, 2.195 \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{3\textit{+}} & 2.431, 2.446, 2.427, 2.452 & 2.635, 2.656 & 2.295, 2.365, 2.327, 2.248 \\
& PuL\textsubscript{2}(\textit{NO}_3)^{4} & 2.370, 2.415, 2.424, 2.481 & 2.682, 3.812 & 2.462/2.481, \textit{a} 2.295 \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{4} & 2.358, 2.453, 2.388, 2.441 & 2.692, 2.635 & 2.229, 2.202, 2.333 \\
T-DGA & PuL\textsubscript{2}(\textit{NO}_3)^{2\textit{+}} & 2.355, 2.444, 2.406, 2.386 & 2.778, 2.923 & 2.395, 2.282, 2.406, 2.287 \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{3\textit{+}} & 2.414, 2.446, 2.432, 2.424 & 2.646, 2.737 & 2.455/2.476, \textit{a} 2.460/2.423 \textit{a} \\
& PuL\textsubscript{2}(\textit{NO}_3)^{4} & 2.391, 2.450, 2.358, 2.398 & 2.604, 2.658 & 2.241, 2.340, 2.227 \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{4} & 2.407, 2.452, 2.475, 2.372 & 2.788, 2.823 & 2.283, 2.380, 2.395, 2.253 \\
TREN-DGA & PuL\textsubscript{2}(\textit{NO}_3)^{2\textit{+}} & 2.414, 2.446, 2.432, 2.424 & 2.646, 2.737 & 2.455/2.476, \textit{a} 2.460/2.423 \textit{a} \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{3\textit{+}} & 2.391, 2.450, 2.358, 2.398 & 2.604, 2.658 & 2.241, 2.340, 2.227 \\
& & & & & & & & \\
& PuL\textsubscript{2}(\textit{NO}_3)^{4} & 2.407, 2.452, 2.475, 2.372 & 2.788, 2.823 & 2.283, 2.380, 2.395, 2.253 \\
\hline
\end{tabular}
\caption{Calculated structural parameters (Å) of different Pu\textsuperscript{4+} complexes of TMDGA, T-DGA, and TREN-DGA.}
\end{table}

\textit{a} These bonds refer to bidentate nitrates. All other are monodentate nitrates.
Gas and solution phase binding energies (ΔE in kcal mol⁻¹) for the different possible complexes of Pu⁴⁺ with the ligands TMDGA, T-DGA, and TREN-DGA with metal-ligand stoichiometry of 1:2.

| Ligand (L) | Complex            | Gas phase | Solution phase |
|------------|--------------------|-----------|----------------|
|            | Pu₂(NO₃)₂²⁺         | -3520.0   | -1111.4        |
|            | Pu₂(NO₃)₃⁺         | -4153.8   | -1146.2        |
| T-DGA      | Pu₂(NO₃)₂²⁺         | -4432.6   | -1180.7        |
|            | Pu₂(NO₃)₃⁺         | -2959.9   | -188.4         |
|            | Pu₂(NO₃)₄₁        | -3238.9   | -246.5         |
| TREN-DGA   | Pu₂(NO₃)₂²⁺         | -3783.3   | -270.9         |
|            | Pu₂(NO₃)₃⁺         | -3223.5   | -231.6         |
|            | Pu₂(NO₃)₄₁        | -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 Pu⁴⁺ preferably forms a neutral complex of the type PuL₂(NO₃)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 PuL₂(NO₃)₂²⁺ 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 PuL₂(NO₃)₂²⁺ 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 PuL₂(NO₃)₃⁺ type of

| Complex          | Bond | Pu–O\_car1 | Pu–O\_car1 | Pu–O\_car2 | Pu–O\_car2 | Pu–O\_ether1 | Pu–O\_ether2 | Total  |
|------------------|------|-----------|-----------|-----------|-----------|--------------|--------------|--------|
| Pu₂(NO₃)₂²⁺       | 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  |
| Pu₂(NO₃)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  |
| Pu₂(NO₃)₄₁       | 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  |

| Complex          | Bond | Pu–O\_car1 | Pu–O\_car1 | Pu–O\_car2 | Pu–O\_car2 | Pu–O\_ether1 | Pu–O\_ether2 | Total  |
|------------------|------|-----------|-----------|-----------|-----------|--------------|--------------|--------|
| Pu₂(NO₃)₂²⁺       | 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  |
| Pu₂(NO₃)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  |
| Pu₂(NO₃)₄₁       | 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  |
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$_3$)$_3$. 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)\cite{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.

**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$_{car2}$ | 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 |

**Conclusions**

The extraction of UO$_2$$^{2+}$ and Pu$^{4+}$ using two different TDGAs showed drastic differences in their extraction and selectivities. While the extraction of the metal ions was relatively low with TREN-DGA in the molecular diluent mixture of n-dodecane and iso-decanol (9:1), a significant enhancement in the distribution ratios was observed using the ionic liquid [C$_4$ mim][TF$_2$N] as the diluent. In general, UO$_2$$^{2+}$ extraction was faster as compared to that of Pu$^{4+}$. Furthermore, while the extraction kinetics was significantly slower in [C$_4$ mim][TF$_2$N] 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$_4$ mim][TF$_2$N] 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 ML₂ 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 ML₂ type complexes were reported, namely, ML species occurring at lower ligand concentrations changing to ML₂ 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 Pu⁴⁺ 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 PuL₂(NO₃)₄. This suggested that Pu⁴⁺ was preferably extracted as the neutral complex (mentioned above) in the case of all the three ligands.

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