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Diglycolamide-Functionalized Calix[4]arenes Showing Unusual Complexation of Actinide Ions in Room Temperature Ionic Liquids: Role of Ligand Structure, Radiolytic Stability, Emission Spectroscopy, and Thermodynamic Studies

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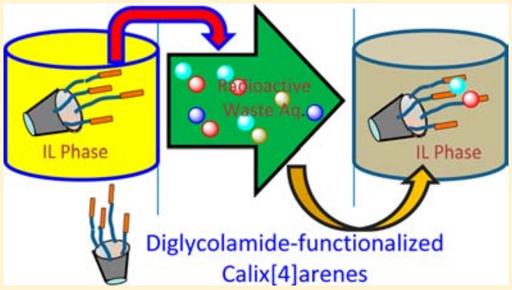
Supporting Information



ABSTRACT: Diglycolamide-functionalized calix[4]arenes (C4DGAs) with varying structural modifications were evaluated for actinide complexation from their extraction behavior toward actinide ions such as UO_2^{2+}, Pu^{4+}, PuO_2^{2+}, and Am^{3+} in the room temperature ionic liquid (RTIL) 1-*n*-octyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ($C_8mimNTf_2$). The formation constants were calculated for Am^{3+} which showed a significant role of ligand structure, nature of substituents, and spacer length. Although the alkyl substituents on the amidic nitrogen increase the extraction efficiency of americium at lower acidity because of the inductive effect of the alkyl groups, at higher acidity the steric crowding around the ligating site determines the extraction efficiency. All C4DGAs formed 1:1 complexes with Am^{3+} while for the analogous Eu^{3+} complexes no inner sphere water molecules were detected and the asymmetry of the metal ligand complex differed from one another as proved by time-resolved laser induced fluorescence spectroscopy (TRLIFS). Thermodynamic studies indicated that the extraction process, predominant by the Am^{3+}-C4DGA complexation reaction, is exothermic. The unique role of the medium on Am^{3+} complexation with the C4DGA molecules with varying spacer length, **L-IV** and **L-V**, was noticed for the first time with a reversal in the trend observed in the RTIL compared to that seen in a nonpolar molecular diluent like *n*-dodecane. Various factors leading to a more preorganized structure were responsible for favorable metal ion complexation. The solvent systems show promise to be employed for nuclear waste remediation, and sustainability options were evaluated from radiolytic stability as well as stripping studies.

1. INTRODUCTION

Room-temperature ionic liquids (RTILs) are currently being evaluated as alternative solvents with low volatile organic content (VOC) burden on the environment. Their diverse applications include synthesis,[1] catalysis,[2] electrochemistry,[3] and separations.[4] Because of their favorable properties including low vapor pressure, good radiation and chemical stability, high degree of solubility, noninflammability, wide liquid range, and so forth, in comparison with conventional molecular diluents, RTILs have of late been evaluated for metal ion extraction.[5] Out of these, there is a growing interest in their application in actinide extractions in the front as well as back end of the nuclear fuel cycle, which has been reviewed recently.[6] These studies include extraction of actinides using neutral extractants like TBP (tri-*n*-butyl phosphate),[7] CMPO (carbamoylmethylphosphine oxide),[8] malonamides,[9] and so forth, chelating acidic extractants like TTA (thenoyltrifluoroacetone),[10] D2EHPA (di-2-ethylhexylphosphoric acid),[11] and basic extractants like amines.[12] Out of these extractants, the neutral donor ligands have been extensively studied for actinide extraction, out of which, diglycolamide extractants have been found to be the most promising.[13] Solvent extraction studies with the diglycolamide extractants such as TODGA (*N*,*N*,*N*′,*N*′-tetra-*n*-octyldiglycolamide) and T2EHDGA (*N*,*N*,*N*′,*N*′-tetra-2-ethylhexyldiglycolamide) in molecular diluents have shown great promise. There are several reports on counter-current extraction studies for actinide extraction from either simulated[14] or hot high level waste (the raffinate emanating from the PUREX cycle for recovering U and Pu from the spent nuclear fuel)[15] suggesting the possible application of these extractants for “actinide partitioning”,[16] a key step in the safe management of radioactive wastes.

The superior extraction properties of TODGA have been attributed to a reverse micellar extraction mechanism where 4 extractant molecules are involved in the formation of an aggregate.[17] The aggregate formation is, however, dependent on the nature of the diluent.[18] Therefore, TODGA moieties were appended onto a calix[4]arene platform to get diluent independent metal extraction properties. Our previous efforts

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in this direction have clearly demonstrated the superior extraction properties of the TODGA appended calix[4]arenes, termed alternatively as diglycolamide-functionalized calix[4]-arenes or C4DGAs, for trivalent and tetravalent actinide ions.[19] Extraction of actinides using C4DGA extractants in RTILs resulted in a significant enhancement in metal ion extraction. A unique separation method for preferential Am^{3+} extraction has been reported using 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ($C_8mim^+\cdot PF_6^-$).[20] The DGA-functionalized calix[4]arenes (C4DGA) not only showed a favorable extraction of the trivalent actinide ions, the extraction of UO_2^{2+} and Sr^{2+} was spectacularly suppressed indicating the unique separation ability of these solvent systems. Recently, we demonstrated that the nature of the alkyl substituents on the nitrogen atom of the DGA units and the spacer length play a significant role in the metal ion extraction.[19a] Therefore, it was of interest to investigate the effect of these changes in the C4DGA ligands on their extraction behavior in ionic liquid-based diluents. Because of the release of the corrosive fluoride ion (F^-) in contact with high feed acidity, PF_6^- based ionic liquids were not used in the present study; only a RTIL having a NTf_2^- (bis(trifluoromethane)sulfonamide) anion was used. The extraction behavior of actinides with a novel both-sides DGA-functionalized calix[4]arene with eight DGA pendent arms was studied, and the results were reported to be highly encouraging.[21]

Here we describe the results of a study on the actinide extraction of solvent systems composed of four different C4DGA ligands, namely, **L-I**, **L-II**, **L-III**, and **L-IV** (Figure 1), in the RTIL $C_8mimNTf_2$ from acidic feed solutions. The nature of the extracted species was ascertained from acid concentration as well as ligand concentration variation studies. It was also corroborated from time-resolved laser induced fluorescence as well as thermodynamic studies. Stripping, separation behavior, and radiolytic stability studies were carried out to evaluate the possible applicability in high level waste remediation as an alternative solvent system to the existing ones based on TODGA in molecular diluents such as *n*-dodecane.

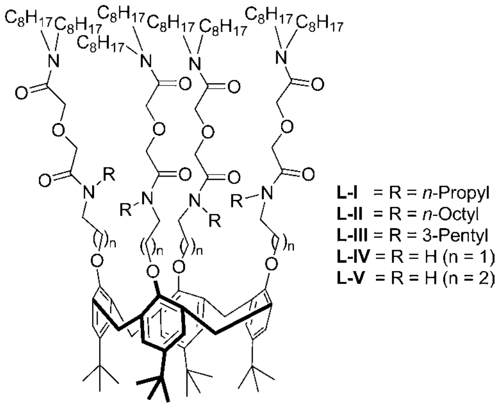

Figure 1. Structural formulas of the C4DGA extractants. The spacer length (*n*) is 2 for **L-I**, **L-II**, and **L-III**.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-*n*-Octyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ($C8mimNTf_2$) (>99%) was obtained from IoliTec, Germany, and was used as received. The purity of the ionic liquid was checked by measuring various physical parameters such as density and viscosity and also by measuring distribution coefficients of reported systems (U–TBP).[7b] DTPA (diethylenetriamine-*N,N,N′,N″,N′*-pentaacetic acid) and EDTA (ethylenediamine-*N,N,N′,N′*-tetraacetic acid) were obtained from Aldrich (U.S.A.), while formic acid, citric acid, and hydrazine hydrate were purchased from Merck (Germany). Suprapur nitric acid (Merck) and Millipore water were used for preparing nitric acid solutions. All the other reagents were of AR grade.

^{241}Am, Pu (mainly ^{239}Pu), and ^{233}U tracers were purified prior to their use by ion-exchange methods, while $^{85,89}Sr$ and ^{137}Cs and $^{152,154}Eu$ tracers were purchased from BRIT (Board of Radiation and Isotope Technology), Mumbai, and were used after checking their radiochemical purity. Assaying of ^{241}Am, ^{137}Cs, $^{85,89}Sr$, and $^{152,154}Eu$ was done by gamma counting using a NaI(Tl) scintillation counter (Para Electronics, India), while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting (Hidex, Finland) using toluene-based scintillator cocktails (Sisco Research Laboratory, Mumbai). The concentrations of the metal ions were about 10^{-7} M for Am, 10^{-6} M for Pu and Cs, 10^{-5} M for Eu and U, and 10^{-4} M for Sr. The oxidation states of Pu in the +4 and +6 states were maintained following literature methods using $NaNO_2$ and AgO, respectively.[22,23]

2.1.1. Synthesis of the Diglycolamide-Functionalized Calix[4]-arenes. The C4DGA ligands **L-I**–**L-V** were prepared as recently described.[19a] The purity of the compounds was checked by standard physicochemical methods.

2.2. Methods. *2.2.1. Distribution Studies.* The metal ion distribution studies were carried out by vortexing a mixture of equal volumes of the aqueous phase spiked with the respective radiotracer and RTIL phase (usually 1 mL) containing the required concentration of the ligand solution in Pyrex tubes in a thermostatted water bath at 25 ± 0.1 °C for about 3 h, which was optimized after the studies with varying equilibration time. After centrifugation, the phases were separated and assayed radiometrically as mentioned above. The distribution ratio of the metal ion was calculated from the ratio of the activity per unit volume in the ionic liquid phase to that in the aqueous phase. It has been reported[13] that because of the uncertainties involved in sampling due to the high viscosity of the ionic liquid phase, the distribution ratio (D) values could be calculated from the aqueous phase counts before and after the equilibrium is reached from the following expression:

$$D = (C_i - C_f)/(C_f) \quad (1)$$

Where, C_i and C_f are the initial and final counts in the aqueous phases, respectively. Stripping studies were carried out in an identical manner described above, with the difference that the radiotracer loaded RTIL phase was equilibrated with the required strippant solutions, which were buffered solutions of complexing agents such as EDTA and DTPA.[24] The experiments were carried out in duplicate, and the precision was within ±5%.

A calibrated ^{60}Co irradiation source (using Fricke dosimetry[25]) was used for the radiolytic degradation with a dose rate of 1.6 kGy/h. The temperature variation studies were carried out in a manner similar to that mentioned above using a thermostatted water bath at varying temperatures in the range of 20–40 °C. Aliquots from both phases were taken, while keeping the equilibration tubes in the thermostat, and the temperature changes were kept within ±0.2 °C of the set temperature.

2.2.2. Luminescence Studies. Time resolved laser induced fluorescence (TRLFS) studies of the Eu^{3+} complexes, in dilute nitric acid as well as in the ionic liquid ($C_8mimNTf_2$) extracts, were carried out using a fluorescence spectrometer (Edinburgh Analytical Instruments, U.K.) controlled by a CD 920 controller and equipped with an OPO laser. The Eu^{3+} sample (1.0×10^{-3} M) in dilute nitric acid (0.5 M HNO_3) mixture was scanned in the entire range of 250 to 500 nm. Eu^{3+}-C4DGA complexes were obtained by contacting the Eu^{3+} solutions (1.0×10^{-3} M) in dilute nitric acid (0.5 M HNO_3) with the corresponding C4DGA solution in ionic liquid ($C_8mimNTf_2$). The samples were excited at 395 nm, while the emission spectra were recorded in the range of 575–750 nm. After checking the reproducibility of the emission spectra in five successive runs, the results were used for the calculation of the number of inner-sphere water molecules (N_{H2O}) based on the lifetime (τ) according to the formula[26]

$$N_{H2O} = (1.06/\tau) - 0.19 \tag{2}$$

The emission decay curves were fitted into the exponential function to obtain the lifetimes/decay rates of the excited states using inbuilt software GEM/3 (Edinburgh) with a reproducibility of the lifetimes of the excited states within ±3 μs.

3. RESULTS AND DISCUSSION

3.1. Extraction Profile of Americium at Different Feed Acidities. A systematic study was carried out to establish the extraction profile of americium at different feed acidities using the different diglycolamide-functionalized calixarenes **L-I**−**L-IV** in $C_8mimNTf_2$. It was observed (Figure 2) that in all cases the D_{Am} value decreases drastically up to 0.5 M HNO_3 followed by a moderate decrease. Similar to diglycolamides like TODGA,[27] the C4DGAs can form an adduct of the type C4DGA·HNO_3 at higher acidity, suggesting that the H^+ ion competes with the metal ion, and hence the distribution ratio of americium decreases with increasing feed acidity. This suggests that the extraction of americium using the C4DGAs in $C_8mimNTf_2$ follows an ion exchange mechanism throughout the acidity range and can be expressed by eq 3.

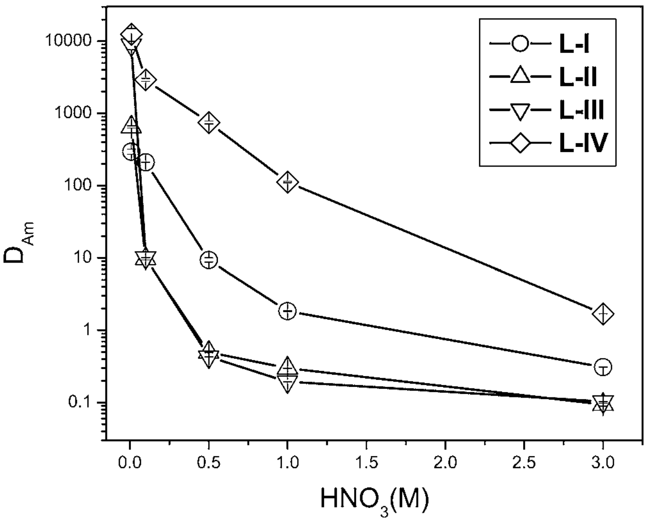

Figure 2. Extraction profile of Am^{3+} from different aqueous phase acidities into the C4DGA-RTIL phase, equilibration time: 2 h; [C4DGA]: 5.0 × 10^{-4} M; Diluent: $C_8mimNTf_2$.

$$\begin{aligned} &Am^{3+}_{aq} + nC4DGA_{IL} + 3C_8mim^{+}_{IL} \\ &\quad = Am[C4DGA]_n{}^{3+}_{IL} + 3C_8mim^{+}_{aq} \end{aligned} \tag{3}$$

The species with the subscripts ‘aq’ and ‘IL’ refer to those in the aqueous phase and in the RTIL phase, respectively. A strong influence of H^+ on the Am(III) extraction can be explained on the basis of a competing equilibrium reaction as follows:

$$\begin{aligned} &H^{+}_{aq} + C4DGA_{IL} + C_nmim^{+}_{IL} \\ &\quad = H\cdot C4DGA^{+}_{IL} + C_nmim^{+}_{aq} \end{aligned} \tag{4}$$

Other than the influence of eq 4 on lowering the Am^{3+} extraction with increased acidity, the nitrate complexation can play a significant role, especially at higher nitric acid concentrations, leading to the formation of ion-pair complexes which can enhance metal ion extraction. At 0.01 M HNO_3 the distribution ratios of americium follow the order, $D_{Am}{}^{L\text{-}IV}$ (12423) > $D_{Am}{}^{L\text{-}III}$ (8856) > $D_{Am}{}^{L\text{-}II}$ (647) > $D_{Am}{}^{L\text{-}I}$ (294), while at 0.5 M HNO_3 the order becomes $D_{Am}{}^{L\text{-}IV}$ (748) > $D_{Am}{}^{L\text{-}I}$ (9.7) > $D_{Am}{}^{L\text{-}III}$ (0.43) ~ $D_{Am}{}^{L\text{-}II}$ (0.49). **L-IV** with a spacer chain length of two carbon atoms is a better extractant in comparison to its analogue **L-V** with a longer spacer chain length (3 C atoms). On the other hand, an opposite trend was observed with molecular diluents as has been reported previously.[19a] Though any concrete evidence is not available at this moment to clearly explain the reasoning for this unusual extraction behavior, a possible explanation can be given on the basis of preorganized structure of the ligands. It seems that the ligands with lower spacer length (for example, **L-IV**) can impart certain amount of rigidity to the pendent arms (due to lower flexibility) leading to a relatively more preorganized structure. Therefore, **L-V**, with longer spacer length can have less probability of a preorganized structure which explains its lower complexation tendency in ionic liquid medium. The reversal in the extraction trend of the ligands **L-IV** and **L-V** switching from a molecular diluent[19a] to an ionic liquid (Table 1) is an interesting observation and is reported here for the first time. This unusual favorable extraction of Am^{3+} with relatively poor extraction of other metal ions (with the exception of Eu^{3+}) was reflected in very high selectivities (vide infra).

Table 1. Evaluation of C4DGA−RTIL Based Solvent Systems L-I, L-IV, and L-V for the Extraction of Actinides and Fission Product Elements[a]

metal ion	L-I	L-IV	L-V[b]	$SF_{L\text{-}I}$[c]	$SF_{L\text{-}IV}$[c]	$SF_{L\text{-}V}$[b,c]
$D_{Am(III)}$	9.34	748	397			
$D_{U(VI)}$	0.07	0.16	0.41	133	4675	968
$D_{Eu(III)}$	143	879	561	0.065	0.85	0.71
$D_{Cs(I)}$	0.009	0.057	0.08	1038	13123	4963
$D_{Sr(II)}$	0.02	0.15	0.15	467	4987	2647
$D_{Pu(IV)}$	2.88	5.62	6.17	3.24	133	64.3
$D_{Pu(VI)}$	0.1	0.18	0.60	93.4	4156	662

[a] Ligand concentration: 5.0 × 10^{-4} M; equilibration time: 3 h; feed acidity: 0.5 M HNO_3; diluent: $C_8mimNTf_2$. [b] Data from ref 21. [c] SF means the separation factor values of Am(III) with respect to other metal ions, i.e., SF = D_{Am}/D_M.

At lower feed acidity, that is, 0.01 M HNO_3, the ligating ability of the carbonyl oxygen will be enhanced if the adjacent amidic nitrogen atom contains any group having a +I (inductive) effect. Since the +I effect of 3-pentyl > *n*-octyl > *n*-propyl group, the electron density on the concerning amidic nitrogen atoms will follow the same order. As a consequence, the extraction efficiencies follow the same order, namely, **L-III** > **L-II** > **L-I**. This trend changes at comparatively higher feed acidities where the amidic nitrogen is protonated and becomes pyramidal and only steric factors become of interest. As a consequence, at 0.5 M HNO_3, the least sterically crowded **L-I** is the best extractant of the four C4DGAs, while **L-III**, containing four 3-pentyl groups shows the least complexing ability. Since at 0.5 M HNO_3, **L-I** and **L-IV** showed good extraction efficiencies for americium, this condition and these ligands were used for further studies.

3.2. Extraction Kinetics. To obtain the distribution data at equilibrium, extraction kinetics studies were carried out. In view of the high viscosity of the RTILs, it is expected that the mass transfer rate will be slower and consequently, the equilibrium will be attained at a relatively longer time than those observed with common molecular diluents. In case of ligands **L-I** and **L-IV**, the distribution ratios of americium in C_8mimNTf$_2$ increased with increasing equilibration time up to 120 min with D_{Am} values of 9.4 and 740, respectively, while beyond 120 min a plateau was observed in both cases (Figure 3). A similar observation of slow extraction kinetics was also found for the extraction of americium into C_8mimNTf$_2$ by a tripodal diglycolamide (T-DGA).[28] Although **L-I** and **L-IV** have a different spacer length of 3 and 2 carbon atoms, respectively, the time required to attain equilibrium is nearly the same in both cases. This suggests that the reorientation during complexation from the free ligand structure has a minimum barrier. The slow attainment of equilibrium is mainly attributed to the viscosity effect of the diluents, which is responsible for the slow mass transfer rates.

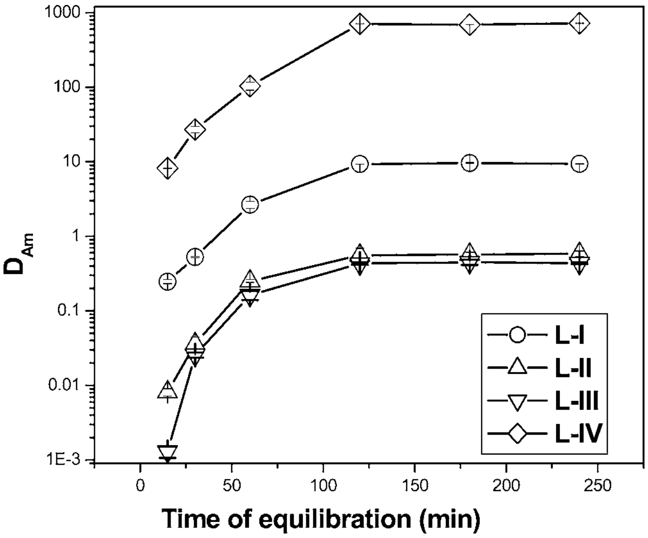

Figure 3. Extraction kinetics of Am^{3+} at different equilibration times into the C4DGA-RTIL phase. Aqueous phase: 0.5 M HNO_3; organic phase: 5.0×10^{-4} M C4DGA in C_8mimNTf$_2$.

3.3. Evaluation of Actinide Extraction and Separation Behavior.

Apart from the Am^{3+} ion, the extraction of several actinide ions, namely, UO_2^{2+} and Pu^{4+}, was also investigated using 0.5 M HNO_3 as the aqueous feed and 5.0×10^{-4} M C4DGAs **L-I** and **L-IV** in C_8mimNTf$_2$ as the organic phase; the results are listed in Table 1. Distribution ratio data for some important fission product elements were also determined under identical experimental conditions. The results are also included in Table 1 for comparison purposes; the extraction trend being $Eu^{3+} > Am^{3+} > Pu^{4+} > UO_2^{2+} > Sr^{2+} > Cs^{+}$. The extractability trend for the different elements is similar to that reported for the T-DGA-*n*-dodecane-*iso*-decanol system[29] as well as the T-DGA-RTIL system.[28] The higher extraction efficiency for the trivalent lanthanide ion, Eu^{3+}, in comparison to the trivalent actinide ion, Am^{3+}, can be attributed to the hard-hard interaction of the former metal ion with the oxygen atoms of the extractant molecules. It is interesting to note that **L-I** has higher relative extraction of Eu^{3+} vs Am^{3+} than **L-IV**, which can be utilized for lanthanide−actinide separation, a relevant step in the high level waste remediation through the "partitioning and transmutation" strategy.[30] The lower distribution ratio values of hexa- and tetravalent actinide ions, as compared to the trivalent ones, are in line with our previous studies with analogous ligands.[27a,28] The separation factors (SF) for Am^{3+} with respect to UO_2^{2+}, Cs(I), Sr(II), Pu(IV), and PuO_2^{2+} are 133, 1038, 467, 3.24, and 93, respectively with **L-I** in C_8mimNTf$_2$, which increased enormously to 4675, 13122, 4987, 133, and 4156, respectively, for **L-IV** in C_8mimNTf$_2$. It can be inferred that **L-IV** is not only a better ligand with respect to the higher extraction efficiency of americium, it also shows a significantly favorable separation behavior. This may have applications in the selective recovery of actinides from radioactive wastes by the now well-known "actinide partitioning" process. Typically, the HLW solution contains about 10^{-4} M Am, implying the solvent system should contain about 10^{-3} M C4DGA ligand. The ligand inventory can, therefore, be significantly lower than the other reported solvent systems for actinide partitioning, making the C4DGA based separations not only cost-effective but also holding promise for significant reduction in the secondary waste volumes.

3.4. Effect of C4DGA Concentration.

The nature of the extracted species, from available literature on analogous extraction systems, has been indicated in eq 3 (vide supra). However, the number of C4DGA molecules involved in the metal ion extraction can be easily found out by carrying out Am^{3+} extraction studies at varying C4DGA concentrations. From eq 3, the two-phase extraction equilibrium constant (K_{ex}) can be expressed as

$$K_{ex} = \frac{[\mathrm{Am(C4DGA)}_n{}^{3+}{}_{\mathrm{IL}}][[\mathrm{C_8mim}^+]^3{}_{\mathrm{aq}}]}{[\mathrm{Am}^{3+}]_{\mathrm{aq}}[\mathrm{C4DGA}]^n{}_{\mathrm{IL}}[\mathrm{C_8mim}^+]^3{}_{\mathrm{IL}}} \tag{5}$$

$$K_{ex} = \frac{D_{\mathrm{Am}}[\mathrm{C_8mim}^+]^3{}_{\mathrm{aq}}}{[\mathrm{C4DGA}]^n{}_{\mathrm{IL}}[\mathrm{C_8mim}^+]^3{}_{\mathrm{IL}}} \tag{6}$$

$$\begin{aligned}&(K_{ex}\cdot[\mathrm{C_8mim}^+]^3{}_{\mathrm{IL}})/[\mathrm{C_8mim}^+]^3{}_{\mathrm{aq}}\\ &\quad = D_{\mathrm{Am}}/[\mathrm{C4DGA}]^n{}_{\mathrm{IL}}\\ &\quad = K'_{ex}\end{aligned} \tag{7}$$

where K'_{ex} is the conditional extraction constant. Taking the logarithm and rearranging, one obtains

$$\log D_{\mathrm{Am}} = \log K'_{ex} + n \log[\mathrm{C4DGA}]_{\mathrm{IL}} \tag{8}$$

The ligand concentration variation studies were carried out using all the C4DGA ligands **L-I**–**L-IV** in C_8mimNTf$_2$ from aqueous feed solutions of 0.5 M HNO_3 (**L-I** and **L-IV**) as well as 0.1 M HNO_3 (**L-II** and **L-III**), while the equilibration time was kept as 2 h. The lower acidity for **L-II** and **L-III** was required to obtain measurable D_{Am} values. The results are presented in Figure 4 (log-log plots of D_{Am} and ligand concentration) and indicate a linear increase in Am(III) extraction with increasing C4DGA concentrations for all four extractants. As per eq 8, the plot of log D_{Am} vs log $[\mathrm{C4DGA}]_{\mathrm{IL}}$ should give a straight line with a slope of *n*, the number of ligand molecules associated with the metal ion, and the intercept as log K'_{ex}. The slope values were found to be very close to 1 for all four C4DGA extractants indicating the stoichiometry of the complex as 1:1. The slopes of the log D-log [Ligand] plots and the conditional extraction constant values are listed in Table 2. The complex formation equilibrium in an ionic liquid can be described by the following equations.

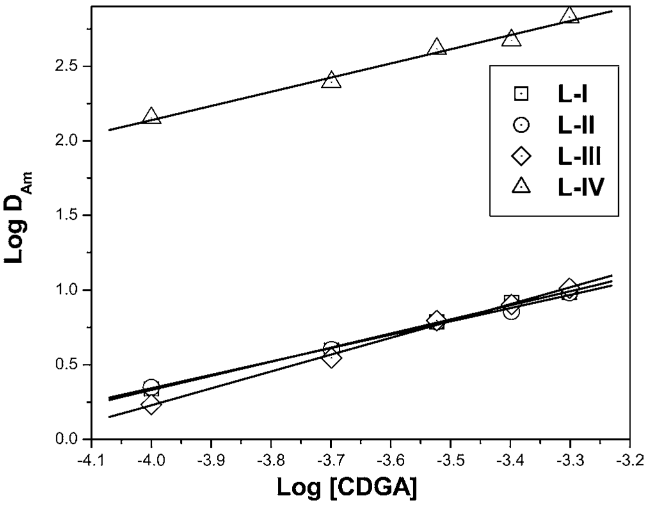

Figure 4. Effect of ligand concentration on the distribution ratio of Am^{3+} into the C4DGA-RTIL phase. Aqueous phase: 0.5 M HNO_3 (for **L-I** and **L-IV**) and 0.1 M HNO_3 (for **L-II** and **L-III**); organic phase: varying concentrations of C4DGA in $C_8mimNTf_2$; equilibration time: 2 h.

$$Am^{3+}{}_{IL} + C4DGA_{IL} = Am(C4DGA)^{3+}{}_{IL} \qquad (9)$$

Table 2. Slopes and Intercepts of the log D_{Am} vs log [C4DGA] Plots Obtained from the Ligand Concentration Variation Experiments[a]

ligand	slope	intercept	log K'_{ex}	log K_{form}[d]
L-I	0.94	4.11	4.11[b]	6.07[b]
L-II	0.89	3.92	3.92[c]	5.88[c]
L-III	1.13	4.74	4.74[c]	6.70[c]
L-IV	0.95	5.94	5.94[b]	7.90[b]

[a]Equilibration time: 3 h; Diluent: $C_8mimNTf_2$. The conditional extraction constants (K'_{Am}) and formation constants (K_{form}) of Am^{3+}-C4DGA complexes in RTIL are also included. [b]Aqueous phase acidity: 0.5 M HNO_3. [c]Aqueous phase acidity: 0.1 M HNO_3. [d]Partition coefficient of Am^{3+} in $C_8mimNTf_2$: 1.09×10^{-2}.

The complex formation constant (K_{form}) can be expressed as

$$K_{form} = [Am(C4DGA)^{3+}]_{IL}/[Am^{3+}]_{IL}[C4DGA]_{IL} \qquad (10)$$

$$K_{form} = (K'_{ex}[Am^{3+}]_{aq})/[Am^{3+}]_{IL} \qquad (11)$$

$$K_{form} = K'_{ex}/P_{Am} \qquad (12)$$

where, P_{Am} is the partition coefficient of Am^{3+} defined as the ratio of the Am^{3+} concentration in the ionic liquid phase to that in the aqueous phase, which was determined to be 1.09×10^{-2}. The K_{form} values are calculated from eq 12 and are listed in Table 2 along with the K'_{ex} values.

3.5. Time Resolved Fluorescence Spectroscopic Study of the Complexation of Eu(III) with C4DGA Ligands L-I–L-IV. Though the number of ligands present in the extracted species can be determined by the slope analysis method as mentioned above, the nature of the coordination is still not clear. Whether the metal ion is bound to the C4DGA ligands through outer-sphere or inner-sphere complexation can be found out by time-resolved laser fluorescence spectroscopy (TRLFS). This gives information about the symmetry of the complexes and also about the number of inner-sphere water molecules. However, due to the very low fluorescence intensity of Am^{3+}, the studies were carried out using the analogous Eu^{3+} ion. The TRLFS studies included monitoring the luminescence of the Eu^{3+} in dilute nitric acid (0.5 M HNO_3) as well as that of Eu^{3+}-C4DGA complexes in $C_8mimNTf_2$ (extracts were prepared from 1.0×10^{-3} M Eu^{3+} in 0.5 M HNO_3). In view of the similarities in the chemical properties of the trivalent actinides and lanthanides, the results of the Eu^{3+} luminescence studies can be extended for the Am^{3+} system as well.

Fluorescence spectroscopic investigations on the Eu^{3+} aqueous complex and Eu^{3+}-C4DGA complexes showed an interesting behavior as the intensity of the characteristics peaks at 617 nm ($^5D_0 \rightarrow {}^7F_2$ hypersensitive transition, electric dipole), 592 nm ($^5D_0 \rightarrow {}^7F_1$ transition, magnetic dipole), and at 690 nm ($^5D_0 \rightarrow {}^7F_4$ transition, electric dipole, sensitive to Eu^{3+} environment) increased significantly (the former by more than 100 times) in case of C4DGA-$C_8mimNTf_2$ as the solvating medium (Figure 5). It is well-known that the luminescence lifetime depends on several radiation (independent of the environment) and radiation-less decay processes and that the number of inner-sphere water molecules is determined by the lifetime of the $^5D_0$ emitting level of Eu^{3+} (eq 2). It is well-known that the Eu^{3+} aquo ion has nine water molecules in its primary co-ordination sphere.[31] In the presence of nitric acid in the aqueous phase, interaction with the nitrate ions can expel the water molecules from the primary hydration sphere, which can be reflected by an increase of the emission lifetime. With a decreasing number of water molecules in the primary hydration sphere, which results in the addition of a C4DGA ligand, the lifetime should show an increasing trend. The luminescence decay profiles of Eu^{3+} and Eu^{3+}-C4DGA in $C_8mimNTf_2$ point to the presence of a single complexed species with 1:1 stoichiometry in all cases.

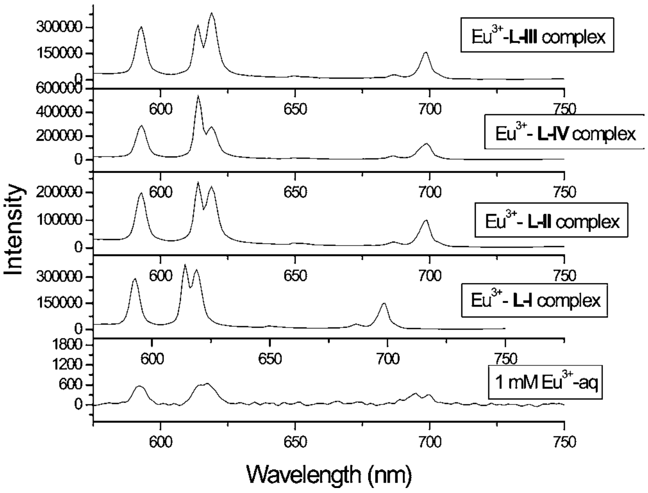

Figure 5. Emission spectra of the Eu^{3+}-aquo and Eu^{3+}-C4DGA complexes in $C_8mimNTf_2$ obtained by time-resolved fluorescence spectroscopy.

The lifetime data are presented in Table 3 which was obtained from the decay curves by single exponential decay fitting. The number of water molecules was calculated from the lifetime (τ) using eq 2. The lifetime of Eu^{3+} in the absence of C4DGA was found to be 115 μs, which increased to about 2.5 ms in the presence of the complexing extractant. It has been reported that the hydrated Eu^{3+} ion with nine inner-sphere water molecules has a fluorescence lifetime of 114 μs, which

Table 3. Determination of Lifetime (τ), Inner Sphere Water Molecule (n), Asymmetric Factor of the Eu^{3+}-C4DGA Complexes in $C_8mimNTf_2$ with the Assignment of the Emission Lines

system	transition	peak positions	asymmetry factor	lifetime (ms)	no of water molecules
Eu^{3+}-Aquo	$^5D_0 \rightarrow {}^7F_0$	not seen			
	$^5D_0 \rightarrow {}^7F_1$	592			
	$^5D_0 \rightarrow {}^7F_2$	617	0.416	0.115	9
	$^5D_0 \rightarrow {}^7F_3$	651			
	$^5D_0 \rightarrow {}^7F_4$	695, 700			
Eu-**L-I** complex	$^5D_0 \rightarrow {}^7F_0$	not seen			
	$^5D_0 \rightarrow {}^7F_1$	593			
	$^5D_0 \rightarrow {}^7F_2$	614, 619(sh)	1.952	1.896	0
	$^5D_0 \rightarrow {}^7F_3$	650			
	$^5D_0 \rightarrow {}^7F_4$	687 (sh), 698			
Eu-**L-II** complex	$^5D_0 \rightarrow {}^7F_0$	not seen			
	$^5D_0 \rightarrow {}^7F_1$	593			
	$^5D_0 \rightarrow {}^7F_2$	614 (h), 619 (sh)	1.819	2.082	0
	$^5D_0 \rightarrow {}^7F_3$	650			
	$^5D_0 \rightarrow {}^7F_4$	687(sh), 699			
Eu-**L-III** complex	$^5D_0 \rightarrow {}^7F_0$	not seen			
	$^5D_0 \rightarrow {}^7F_1$	593			
	$^5D_0 \rightarrow {}^7F_2$	614 (sh), 619	1.908	2.119	0
	$^5D_0 \rightarrow {}^7F_3$	650			
	$^5D_0 \rightarrow {}^7F_4$	687 (sh), 699			
Eu-**L-IV** complex	$^5D_0 \rightarrow {}^7F_2$	614 (h), 619 (sh)			
	$^5D_0 \rightarrow {}^7F_3$	650			
	$^5D_0 \rightarrow {}^7F_4$	686 (sh), 699	2.108	1.544	0
	$^5D_0 \rightarrow {}^7F_0$	not seen			
	$^5D_0 \rightarrow {}^7F_1$	593			

increases in the presence of nitric acid, apparently because of the replacement of some inner-sphere water molecules by the nitrate ions.[32] The appearance of an additional peak at 614 nm indicates a strong interaction with the DGA moieties of the C4DGAs similar to that observed with a calix[4]arene containing four DGA units as well as the T-DGA–RTIL system.[28] The lifetime of the Eu^{3+}-C4DGA complexes were found to be 1.952, 1.819, 1.908, and 2.108 ms for **L-I**, **L-II**, **L-III**, and **L-IV**, respectively. However, the intensity of the split lines at 617 nm changed significantly. These results point to a very strong complex formation with the DGA moieties of the C4DGAs with practically no inner-sphere water molecules. The asymmetric factor ($R = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, where $I(^5D_0 \rightarrow {}^7F_2)$ and $I(^5D_0 \rightarrow {}^7F_1)$ correspond to the intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, respectively) of the Eu^{3+}-C4DGA complexes were calculated, and the symmetry of these complexes in RTIL decreased in the order Eu^{3+}-aq > Eu^{3+}-**L-II** > Eu^{3+}-**L-III** > Eu^{3+}-**L-I** > Eu^{3+}-**L-IV**.

3.6. Radiolytic Degradation Studies.

Though the C4DGA extractants **L-I**–**L-IV** are highly promising extractants for actinide ion extraction, their actual use for actinide ion separation requires testing their long-term reusability, which indirectly means their radiolytic stability. This is because all actinide ions emit high LET (linear energy transfer) alpha particles, which can cause significant radiolytic damage. However, as exposure to the equivalent γ radiation can show the similar effect, it was decided to carry out the radiolytic degradation studies using a ^{60}Co irradiator (vide supra). A systematic study, carried out to investigate the radiolytic stability of the C4DGAs in $C_8mimNTf_2$, indicated that after exposing the organic phase to 500 kGy of absorbed gamma irradiation, the extraction efficiency becomes 72%, 49%, 69%, and 72% of the original D_{Am} values of **L-I**, **L-II**, **L-III**, and **L-IV**, respectively, while after 1000 kGy it becomes 50%, 35%, 50%, and 46%, respectively (Figure 6). This study revealed that **L-I**, **L-III**, and **L-IV** are comparatively more stable with respect to **L-II** up to 500 kGy of absorbed dose, while at the end of 1000 kGy the trend is similar though the degradation has been more pronounced. Apparently, **L-II**, having the largest alkyl group (*n*-octyl) on the amidic nitrogen atom, has a strong tendency for radiolytic degradation. From this study it can be inferred that **L-I** and **L-IV** can be successfully used up to 500 kGy as the radiolytic degradation of the ligands lead to marginal decrease in the overall metal ion extraction. The results are in sharp contrast to previous reports where ionic liquid based solvent systems were highly susceptible to radiolytic degradation.[33] Also, in view of the relatively large D values obtained with the solvent systems in ionic liquids, the % extraction data is not significantly affected even after exposure up to 1000 kGy.

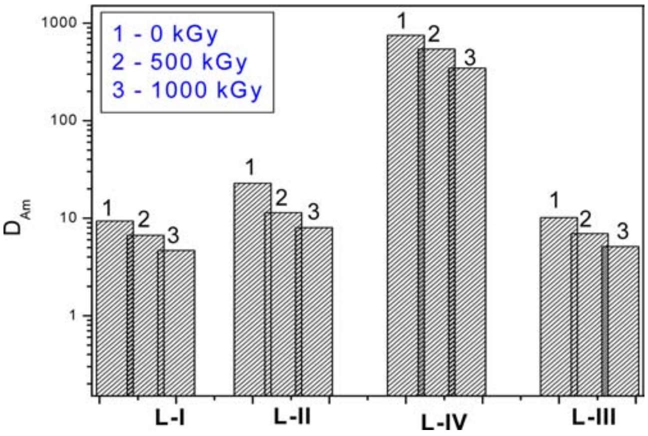

Figure 6. Effect of absorbed dose on the distribution ratio of Am^{3+} into C4DGAs in $C_8mimNTf_2$. Aqueous phase: 0.5 M HNO_3 (for **L-I** and **L-IV**) and 0.1 M HNO_3 (for **L-II** and **L-III**); organic phase: 5.0×10^{-4} M C4DGA in $C_8mimNTf_2$; equilibration time: 2 h.

3.7. Stripping Studies.

Stripping of a metal ion from an ionic liquid phase has always been a challenging task because of the very high distribution ratio values at lower acidities and reasonably good extraction at higher acidities. Though the back extraction of the metal ion is possible at higher acidity, such as 3 M HNO_3, with two of the ligands (**L-II** and **L-III**), it may still be difficult for the other two. Therefore, complexing agents were employed for this purpose with amazingly good results.[24] We have also employed complexing agents such as DTPA and EDTA in a buffered medium to quantitatively back extract Am^{3+}. In the present study, the stripping of Am^{3+} was performed by employing three strippants, namely, (i) 0.05 M DTPA + 1 M guanidine carbonate, (ii) 0.05 M EDTA + 1 M guanidine carbonate, and (iii) a buffer mixture containing 0.4 M formic acid + 0.4 M hydrazine hydrate + 0.2 M citric acid; the

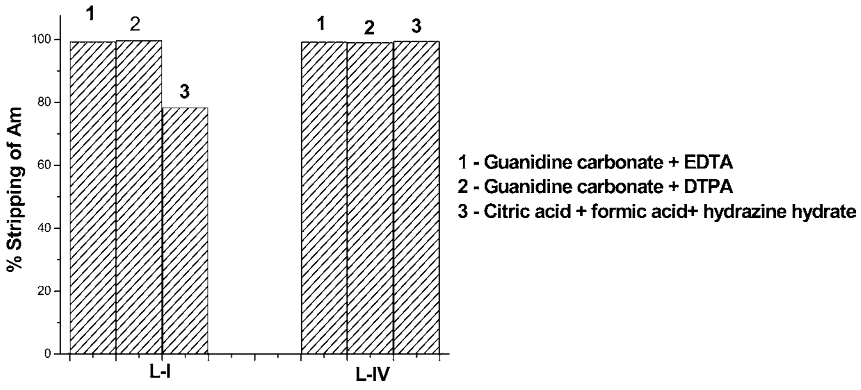

Figure 7. Stripping studies using buffered complexing agent solutions of EDTA and DTPA. A buffer mixture was also used.

results are plotted in Figure 7. The figure shows that near quantitative stripping took place with both complexing agents in a single contact (at a volume ratio of 1:1), while the buffer mixture was not quite efficient for **L-I**. The stripping data are quite encouraging and suggest that the solvent system can be regenerated and reused for further metal ion extraction. Chemical degradation of the ligands were found to be negligible, though long-term use can have transfer of the ionic liquid into the aqueous phase requiring development of alternative diglycolamide-functionalized ionic liquids.[34]

3.8. Determination of Thermodynamic Parameters. The C4DGA ligands **L-I**–**L-IV** have four diglycolamide moieties anchored on a calix[4]arene molecular platform to create a preorganized structure to favor complexation with trivalent lanthanides and actinides. The stereochemical configuration of the calixarenes may also play a role in the complexation. As the conformational changes upon metal ion complex formation are linked to entropy changes, thermodynamic studies were carried out. The metal ion extraction data at varying temperatures (Supporting Information) were used to calculate the thermodynamic parameters, which were subsequently used to understand the complexation of americium with the C4DGAs in $C_8mimNTf_2$ (Table 4). The D_{Am} values decrease with increasing temperature (Figure 8), indicating the complexation to be exothermic in nature. The change in Gibb's energy for the complexation of Am^{3+} with **L-IV** in $C_8mimNTf_2$ is more negative than that of **L-I**, **L-II**, and **L-III**, which reveals that the complex formation of **L-IV** is thermodynamically more favorable than that of the other ligands. These are in the same line as the K_{form} data reported in Table 2.

Table 4. Thermodynamic Parameters for the Extraction of Am^{3+} into the C4DGAs L-I–L-IV in $C_8mimNTf_2$[a]

ligand	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
L-I	−23.6	−84.1	−201
L-II	−22.5	−95.7	−244
L-III	−27.2	−89.3	−388
L-IV	−34.1	−67.2	−110

[a] Aqueous phase acidity: 0.5 M HNO_3; ligand concentration: 5.0 × 10^{-4} M; equilibration time: 3 h.

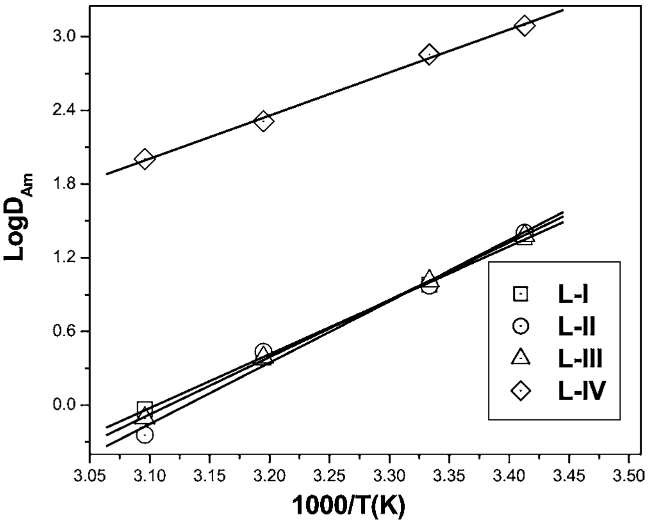

Figure 8. Effect of temperature on the distribution ratio of Am^{3+} into C4DGA in $C_8mimNTf_2$. Aqueous phase: 0.5 M HNO_3 (for **L-I** and **L-IV**) and 0.1 M HNO_3 (for **L-II** and **L-III**); organic phase: 5.0 × 10^{-4} M C4DGA in $C_8mimNTf_2$; equilibration time: 2 h.

The overall enthalpy change during the extraction of Am^{3+} by a C4DGA in $C_8mimNTf_2$ is the sum of mainly three factors: change of enthalpy due to the dehydration of the metal ion (ΔH_1), change in enthalpy due to the complex formation (ΔH_2), and dissolution of the metal ligand complex into the RTIL phase (ΔH_3). In the present study, the contributions of ΔH_1 and ΔH_2 are identical for all the four ligands as it primarily involves the interaction of Am^{3+} with the amidic carbonyl oxygen. The longer spacer length and the *n*-propyl group on the amidic nitrogen atom make the **L-I** metal complex more lipophilic than that of **L-IV** and hence more energy will be released during the dissolution of the Am^{3+}-**L-I** complex into the RTIL phase than in case of the Am^{3+}-**L-IV** complex, which is reflected in the overall enthalpy change (ΔH) of the extraction. The enthalpy changes for **L-I**, **L-II**, and **L-III** are nearly comparable, while that of **L-IV** is less negative, suggesting a relatively weaker interaction with this ligand. The overall entropy change for the extraction is negative for all four extractants, although more negative for **L-III** and less negative for **L-IV**. Since TRLFS studies have indicated the presence of "zero" water molecules in the Eu^{3+}-C4DGA complexes, the net entropy changes can be attributed to conformational changes taking place during complexation. Since the spacer of **L-I** is longer than that of **L-IV**, the C–C bond rotation will be more restricted for **L-I**, which is reflected in the entropy changes upon complexation.

4. CONCLUSIONS

A series of diglycolamide-functionalized calix[4]arenes **L-I–L-IV** in the RTIL $C_8mimNTf_2$ were evaluated for actinide extraction. A decrease in the distribution ratio of americium with increasing aqueous phase acidity was attributed to an ion-exchange mechanism in all cases. In the series **L-I** and **L-IV** were found to be the most promising extractants. Because of the higher viscosity of a RTIL in comparison with molecular diluents,[35] 2 h are required to reach equilibrium. The ligand with a short spacer was found to be a better extractant in comparison to its analogue with a longer spacer probably because of the better preorganization of the diglycolamide moieties on the calixarene platform as a result of restricted C–C single bond rotation. At lower feed acidity, the coordinating ability of the carbonyl oxygen is enhanced because of the electron density on the amidic nitrogen atom to which a group with a +I effect is attached, while at comparatively higher feed acidity the steric crowding around the coordinating group plays a significant role. Both ligands form single complexes with 1:1 stoichiometry. A time-resolved fluorescence study confirmed the strong interaction of the metal ion with the C4DGA ligands in $C_8mimNTf_2$ as single species without inner sphere water molecules. A radiolytic stability study indicated that **L-I** and **L-IV** can be used for actinide partitioning up to a 500 kGy dose, without significant decrease of the extraction efficiency. The trend of the extraction efficiency of the C4DGAs in $C_8mimNTf_2$ was found to be $Eu^{3+} > Am^{3+} > Pu^{4+} > PuO_2^{2+} > UO_2^{2+} > Sr^{2+} > Cs^+$. Metal-C4DGA complex formation is thermodynamically favorable. The overall extraction process is exothermic in nature with a decrease in the overall entropy of the system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details on solvent extraction studies are given in Tables S-1 and S-2 and on fluorescence studies in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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