

Remarkable Improvement in Am³⁺ and Cm³⁺ Separation Using a Cooperative Counter Selectivity Strategy by a Combination of Branched Diglycolamides and Hydrophilic Polyaza-heterocycles

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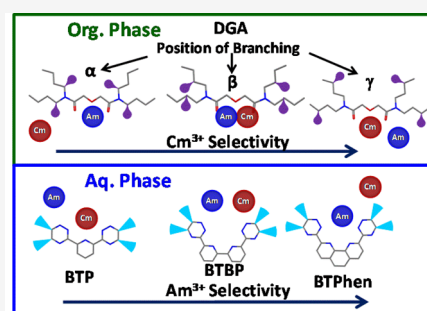


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ABSTRACT: Separation of Am³⁺ and Cm³⁺ is one of the most challenging problems in the back-end of the nuclear fuel cycle. In the present work, we exploited the cooperative effect of the opposite selectivity of hydrophobic branched DGA derivatives and hydrophobic N-donor heterocyclic ligands taken in two different phases to achieve improved separation behavior. A systematic study was performed using a series of DGA derivatives to understand the effect and the position of branching in the alkyl chains on the separation behavior of Am³⁺ and Cm³⁺. A separation factor (S.F.) value as high as 10 for Cm³⁺ over Am³⁺ was obtained in the case of TiBDGA (*N,N,N',N'*-tetra-*iso*-butyl diglycolamide) using SO₃PhBTPhen ((phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayltetrabenzene sulfonic acid) as the aqueous complexant, which is the highest reported value so far for the ligand-based separation of Am³⁺ and Cm³⁺ without involving any oxidation or reduction step. The high selectivity favoring Cm³⁺ ion extraction in the case of this DGA derivative is also explained with the help of computational studies.



Am/Cm selectivity could be tuned by altering the position of branching in the alkyl chain of the DGA in the organic phase and choosing the 'N' donor aqueous soluble ligands suitably to achieve a S.F. ~10 for Cm³⁺ over Am³⁺

INTRODUCTION

Global energy demand is increasing rapidly due to the sharp increase in world population and increased per capita energy consumption in developing countries. Limited resources of fossil fuel and increasing environmental concerns leading to the stringent cutting down of carbon dioxide emission have led to the increasing demand for alternatives such as renewable sources of energy as well as low carbon dioxide emission-based nuclear energy. The major concern for nuclear energy is the generation of a host of radiotoxic elements as the activation and fission products. These highly radiotoxic elements are present in nuclear waste, and if managed with a proper strategy by designing suitable separation schemes, nuclear energy can be a long-term solution for the increasing energy demand worldwide.¹ The radionuclides that seek attention are mainly minor actinides, viz., Am, Cm, and Np, due to their long-term radiotoxicity and α emitting nature.² A separation scheme for Np can be developed by its oxidation state adjustment.^{3,4} The trivalent state is the most stable for Am and Cm in nuclear fuel reprocessing solutions and possesses close chemical similarity with trivalent lanthanide ions.^{5,6} Their separation from trivalent lanthanide ions is, therefore, a challenging task.⁷ Soft S,N-donor ligands show selectivity for the trivalent actinide ions Am³⁺ and Cm³⁺ over lanthanide ions.^{8–10} Mutual separation of Am³⁺ and Cm³⁺ is even more challenging as

those soft donor ligands show poor selectivity between these two adjacent actinide ions in their trivalent state.¹¹ Am/Cm separation is, however, a crucial step for the safe long-term management strategy of nuclear waste. Am isotopes, being longer lived and present in higher amounts than Cm isotopes, are mainly required to be transmuted to shorter-lived radionuclides or stable products. The presence of the short-lived ²⁴⁴Cm isotope, on the other hand, makes fuel fabrication difficult for the recycling of Am for transmutation.^{12–14} The separation of Am³⁺ and Cm³⁺ is addressed by two different approaches. In one case, Am is oxidized to its higher oxidation state and its subsequent separation from Cm³⁺ using conventional extractants, viz., tri-*n*-butyl phosphate (TBP), carbamoylmethylenephosphine oxide (CMPO), or *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA).^{15–17} The major drawback of this approach for Am/Cm separation is the choice of a suitable oxidizing agent that can work under process conditions and the generation of more secondary wastes due

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to the addition of the oxidizing agent. Moreover, maintaining Am in its higher oxidation state is a tricky job, as it is quite sensitive to time and temperature.^{17,18} The oxidation of Am(III) to the +6 state is also done by an electrochemical method in the presence of heteropolyanions (HPA) in the well-known SESAME (Selective Extraction and Separation of Americium by Means of Electrolysis) process.^{19,20} However, HPAs also create secondary wastes, and difficulties are reported in the development of multistage processes. Modolo et al. used a combination of soft S-donor and hard O-donor ligands, viz., bis(*p*-chlorophenyl)dithiophosphinic acid ((ClPh)₂PSSH) and triethylhexylphosphate (TEHP), for the selective extraction of Am³⁺ over Cm³⁺, where they could achieve an S.F. (separation factor) value >7,²¹ which is the highest value reported to date.¹²

An alternative approach to improve the separation of Am³⁺ and Cm³⁺ is by exploiting the cooperative effect of two ligands of opposite selectivity, i.e., one selective for Am³⁺ and the other one for Cm³⁺ taken in two different phases.¹² A significant amount of interest from researchers has recently been drawn to the exploitation of this approach. The Am³⁺ selective lipophilic extractant *N,N,N',N',N'',N''*-hexa-*n*-octyl-nitrilotriacetamide (HONTA) is used in combination with the hydrophilic diglycolamide (DGA) derivative *N,N,N',N'*-tetraethyl diglycolamide (TEDGA) having marginal selectivity for Cm³⁺.²² The lipophilic DGA derivative TODGA (Figure 1f) is also

selectivity between Am³⁺ and Cm³⁺ using TODGA in a room-temperature ionic liquid (RTIL) medium, where the hydrophilic ligand was changed from 6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)pyridine (SO₃PhBTP) to SO₃PhBTBP or 3,3',3'',3'''-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrazenesulfonic acid (SO₃PhBTPhen).²⁷

Recently, we have shown that *N,N,N',N'*-tetrakis-2-ethylhexyl diglycolamide (T2EHDGA), a lipophilic branched DGA derivative, shows selective extraction of Am³⁺ over Cm³⁺ in the presence of SO₃PhBTP in the aqueous phase due to the marginal Cm³⁺ selectivity of this aqueous soluble ligand.²⁸ However, no study on the Am/Cm separation is known that systematically varies the ligands in both organic and aqueous phases to get a clear understanding of the selectivity, resulting in an appropriate combination of ligands. Therefore, it will be of interest to systematically study different lipophilic DGA derivatives along with the hydrophilic aqueous complexants SO₃PhBTP, SO₃PhBTBP, or SO₃PhBTPhen for the separation of Am³⁺ and Cm³⁺. It involves seven different DGA derivatives, viz., *N,N,N',N'*-tetra-*n*-butyl diglycolamide (TBDGA), *N,N,N',N'*-tetra-*iso*-butyl diglycolamide (TiBDGA), *N,N,N',N'*-tetra-*sec*-butyl diglycolamide (TsBDGA), *N,N,N',N'*-tetra-*n*-pentyl diglycolamide (TPDGA), *N,N,N',N'*-tetra-*iso*-pentyl diglycolamide (TiPDGA), TODGA, and T2EHDGA (Figure 1).

EXPERIMENTAL SECTION

Reagents and Chemicals. The ligands TBDGA, TiBDGA, TsBDGA, TPDGA, and TiPDGA were prepared as described before.²⁹ TODGA and T2EHDGA, on the other hand, were synthesized at Thermax India Ltd. using established procedures.³⁰ Detailed synthesis procedures of the hydrophilic N-donor heteropolycyclic ligands SO₃PhBTP, SO₃PhBTBP, and SO₃PhBTPhen (Figure 1) are given in the Supporting Information (Schemes S1–S3). The purities of these ligands were confirmed by ¹H NMR, FT-IR, and mass spectrometry (HR-MS), which are also provided in the Supporting Information. The actinide tracers, ²⁴¹Am and ²⁴⁴Cm, were used from the laboratory stock solutions after their radiochemical purities were confirmed by α spectrometry. Both ²⁴¹Am and ²⁴⁴Cm are highly radiotoxic, and they should be handled with proper care. All other reagents used were of analytical reagent grade.

Liquid–Liquid Extraction Studies. Equal volumes (0.5 mL) of the aqueous phase, containing ²⁴¹Am and ²⁴⁴Cm in varying concentrations of HNO₃, and the organic phase, containing DGAs in different organic diluents, were equilibrated in plastic equilibration tubes for approximately an hour (which ensured attainment of equilibrium) in a thermostated water bath at 25 ± 0.1 °C. Subsequently, the tubes were centrifuged for 2 min, followed by a radiometric assay of the separated aliquots (100 μ L) taken from both phases to calculate the distribution ratio (*D*) value of the metal ions as the ratio of the concentration of the radiotracer (expressed as counts per unit time per unit volume) in the organic phase to that in the aqueous phase, and the S.F. values were calculated as the ratio of the distribution ratio of Cm³⁺ to that of Am³⁺ if not specified separately.

Computational Studies. The structures of the free ligands (TBDGA, TiBDGA, TPDGA, and TiPDGA) and their complexes with Am³⁺ and Cm³⁺ were optimized using def-SV(P) basis sets for all of the atoms as implemented in the TURBOMOLE-7.2.1 suite of program.³¹ The 60-electron effective core potential (ECP) along with the corresponding def-SV(P) basis sets for the valence electrons were considered for the Am³⁺ and Cm³⁺ ions in the case of their DGA complexes.^{32–35} All of the geometry optimizations were performed using the GGA functional BP86,^{36,37} whereas the single point energies of the free ligands and the complexes were calculated using the hybrid functional B3LYP³⁸ and valence triple- ζ (def-TZVP) basis sets.³⁹ All of the calculations were performed in the gas phase, as the complexes of both metal ions (Am³⁺ and Cm³⁺) having very close ionic potential)

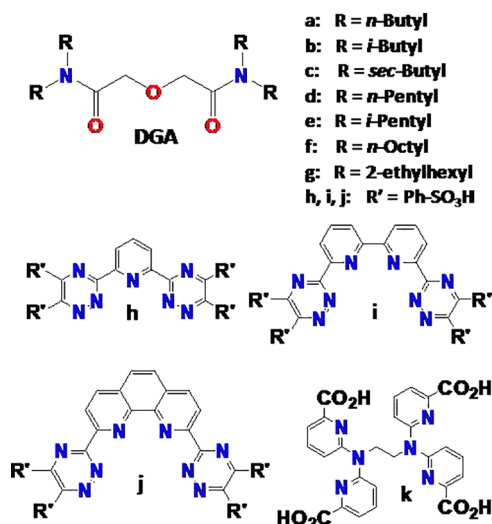


Figure 1. Structures of different ligands used in the present work: (a) TBDGA, (b) TiBDGA, (c) TsBDGA, (d) TPDGA, (e) TiPDGA, (f) TODGA, (g) T2EHDGA, (h) SO₃PhBTP, (i) SO₃PhBTBP, (j) SO₃PhBTPhen (where R = HO₃SPh), and (k) H₄TPAEN.

proposed in combination with the hydrophilic Am³⁺ selective ligand *N,N,N',N'*-tetrakis[(6-carboxypyridin-2-yl)methyl]-ethylenediamine (H₄TPAEN, Figure 1k) to achieve improved separation of Cm³⁺ over Am³⁺ in the Euro-EXAM process under the Euro-SUCCESS program.^{23–25} H₄TPAEN, however, possesses some issues with its solubility depending on its method of preparation or purification.¹² Wagner et al. proposed to use TODGA in combination with the hydrophilic ligand 3,3',3'',3'''-[2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl)tetrabenzene-sulfonic acid (SO₃PhBTBP) in the Americium Selective extraction (AmSel process) from a PUREX raffinate, where an S.F. (separation factor) of 2.5 was achieved for Cm³⁺ over Am³⁺.²⁶ We reported a reversal of

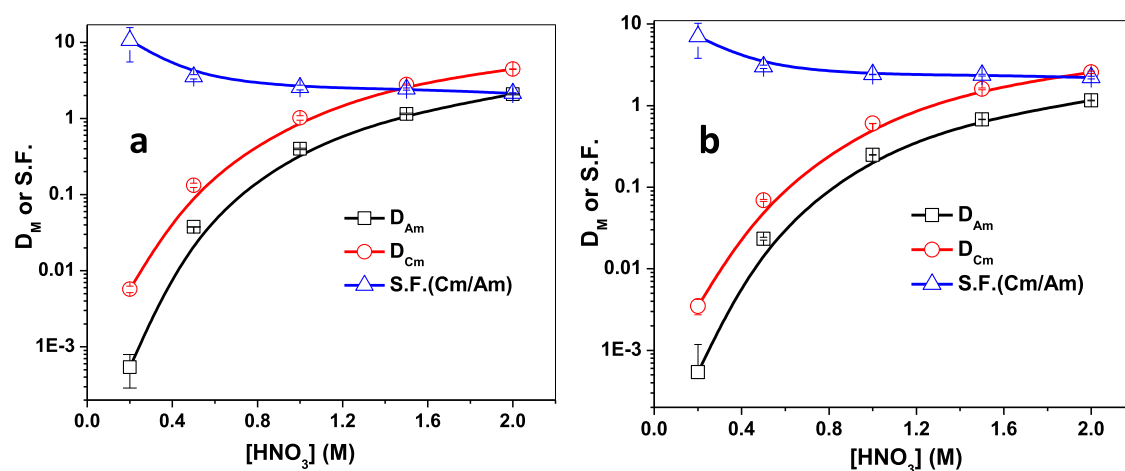


Figure 2. Effect of HNO_3 concentration on the extraction of Am^{3+} and Cm^{3+} by TiBDGA (a) and TiPDGA (b); Org. phase: 20 mM DGA derivatives in *n*-octanol; Aq. phase: 1 mM $\text{SO}_3\text{PhBTPhen}$ in varying concentrations of HNO_3 .

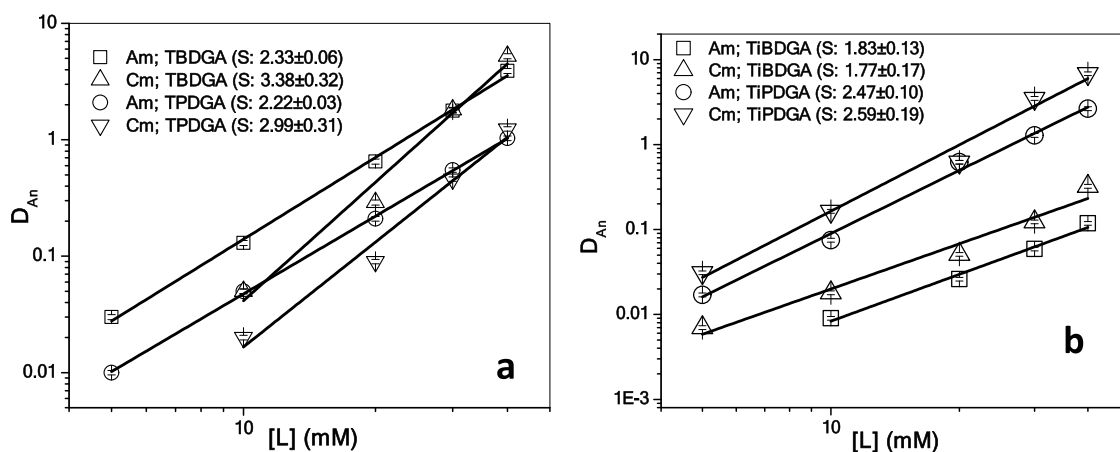


Figure 3. Effect of DGA concentration on the extraction of Am^{3+} and Cm^{3+} ; Org. phase: varying concentrations of DGA derivatives in *n*-octanol; Aq. phase: 1 mM $\text{SO}_3\text{PhBTPhen}$ in 1 M HNO_3 .

have similar structures; therefore, no differences are expected in the relative trends in their complexation ability with the incorporation of the solvent effect.

RESULTS AND DISCUSSION

Effect of an Organic Diluent. Organic diluents have a significant effect on the extraction behavior of metal ions.^{40,41} A number of organic diluents of varying polarity were chosen to study the Am^{3+} and Cm^{3+} separation from a 0.2 M HNO_3 medium containing 1 mM $\text{SO}_3\text{PhBTPhen}$ (Figure S1). TODGA and T2EHDGA were chosen as representative DGA derivatives for the diluent variation studies because of their higher solubility in a wide range of organic diluents as compared to other DGA derivatives having shorter alkyl chains.^{42,43} In our previous report, we observed that among the three aromatic hydrocarbon diluents toluene, *t*Bu-benzene, and tri-*iso*-propylbenzene, the highest selectivity was observed in the case of toluene,²⁸ and therefore, in this study, toluene was chosen. Out of the five diluents, namely, *n*-octanol, *iso*-decanol, toluene, *n*-dodecane, and Solvesso-100 (a high solvency C9 aromatic solvent manufactured from petroleum products), the highest extraction efficiency was observed in the case of *n*-octanol. S.F. values, defined as the ratio of D_{Cm} to D_{Am} , however, were very close for *n*-octanol, *n*-dodecane, and Solvesso-100. Here, *n*-octanol was chosen as the organic

diluent in view of its higher solvating capacity for other DGA derivatives with shorter alkyl chains and the higher extraction of both metal ions without losing their mutual selectivity.

Effect of Aqueous Phase Acidity. It is well known that the extraction efficiency of all metal ions by lipophilic DGA derivatives increases with increasing HNO_3 concentration in the aqueous phase.^{44–46} The complexation ability of the hydrophilic N-donor ligands $\text{SO}_3\text{PhBTPhen}$, SO_3PhBTBP , and $\text{SO}_3\text{PhBTPhen}$, on the other hand, decreases with increasing aqueous phase acidity due to the protonation of the N atoms of the heterocyclic rings.⁴⁷ Our previous study suggested $\text{SO}_3\text{PhBTPhen}$ as the most promising aqueous complexant while studying the $\text{Am}^{3+}/\text{Cm}^{3+}$ separation by TODGA in an RTIL medium.²⁷ Therefore, $\text{SO}_3\text{PhBTPhen}$ is chosen as the representative aqueous complexant for the HNO_3 concentration variation studies along with TiBDGA and TiPDGA as two representative DGA derivatives (Figure 2).

The extraction efficiency increased for both metal ions with increasing aqueous phase acidity. The S.F. values, however, decreased with increasing acidity in the case of both DGA derivatives, and the highest selectivity was observed for 0.2 M HNO_3 . Lower HNO_3 concentrations resulted in an extraction efficiency too low to measure, and therefore, in the subsequent studies, where we aimed to maximize the S.F. values, the aqueous phase HNO_3 concentration was fixed at 0.2 M.

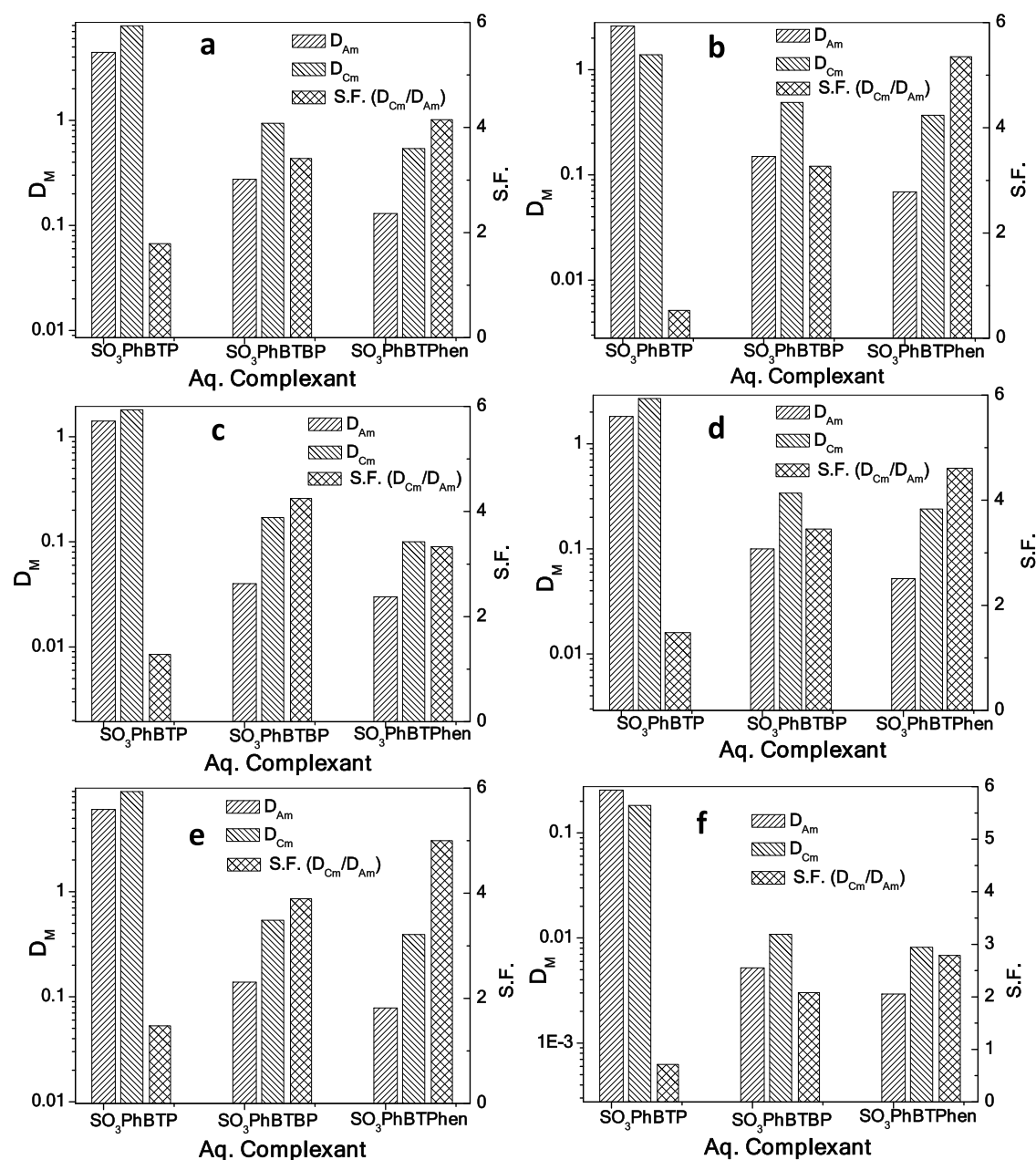


Figure 4. Separation behavior of Am^{3+} and Cm^{3+} using (a) TBDGA, (b) TiBDGA, (c) TPDGA, (d) TiPDGA, (e) TODGA, and (f) T2EHDGA in the presence of a 1 mM aqueous complexant; Org. phase: DGA derivatives (0.1 M for a, b, c, d and 0.2 M for e, f) in *n*-octanol; Aq. phase: a 1 mM aqueous complexant in 0.2 M HNO_3 .

BTPhen derivatives are reported to show selectivity for Am^{3+} over Cm^{3+} .⁴⁸ The stronger complexation ability of $\text{SO}_3\text{PhBTPhen}$ due to its higher $-\text{SO}_3\text{H}$ deprotonation with decreasing HNO_3 concentration in the aqueous phase resulted in a more pronounced decrease in Am^{3+} extraction as compared to Cm^{3+} , leading to the enhancement of the S.F. value for Cm^{3+} over Am^{3+} .

Understanding the Extraction Mechanism. It is relevant to study the role of the concentration of both DGAs and $\text{SO}_3\text{PhBTPhen}$ on the extraction behavior of Am^{3+} and Cm^{3+} in order to understand the mechanism for extraction and separation. The DGA concentration variation study showed that in the cases of TBDGA, TPDGA, and TiPDGA, where either there is no branching in the alkyl chain or the position of the branching is far from the amidic N atoms, higher slope

values are observed for Cm^{3+} than for Am^{3+} . This suggests that Cm^{3+} forms higher stoichiometric complexes than Am^{3+} . While studying the complexation with tetraethyl DGA derivatives, Charbonnel et al. observed that the metal-to-ligand stoichiometry increases as the size of the trivalent 'f' block ion decreases, which is in line with our observation of higher stoichiometric complexes for Cm^{3+} than for Am^{3+} .⁴⁹ In the case of TiBDGA, where the branching is at the β -carbon, the metal–ligand stoichiometries reduced to 2 in the case of both metal ions (Figure 3), indicating that the metal–ligand interactions become weaker in the case of TiBDGA, resulting in a lower metal–ligand stoichiometry in the extracted complex. Formation of lower stoichiometric complexes during the extraction by DGA derivatives with branching at the α - or β -carbon atom is well reported in the literature.^{50,51} Because of

the lower lipophilicity of the lower stoichiometric complexes, these branched DGA derivatives show lower extraction compared to the DGA derivatives having straight alkyl chains or branching away from the amidic N atoms.

Extraction studies of both metal ions by TiBDGA and TiPDGA were also carried out by varying the $\text{SO}_3\text{PhBTPhen}$ concentration, the slope values being ~ 1 in all cases (Figure S2). Similar dependence was also reported by Wagner et al. while performing the extraction of Am^{3+} and Cm^{3+} by TODGA varying the SO_3PhBTBP concentration in the aqueous phase.²⁶ In the case of SO_3PhBTP , however, the dependence was found to be ~ 2 in our previous study.²⁸

Comparison of Different DGA Derivatives and Aqueous Complexants. The aqueous complexants SO_3PhBTP , SO_3PhBTBP , and $\text{SO}_3\text{PhBTPhen}$ (Figure 1h,i,j, respectively) were studied for the $\text{Am}^{3+}/\text{Cm}^{3+}$ separation along with the seven DGA derivatives as listed in Figure 1; the results are shown in Figures 4 and S3. The extraction of both metal ions in the case of the six DGA derivatives (Figure 3) except for TsBDGA (Figure S3) was found to be the highest in the case of SO_3PhBTP . This is probably due to the weaker complexation ability of the tridentate ligand SO_3PhBTP as compared to the tetradentate ligands SO_3PhBTBP and $\text{SO}_3\text{PhBTPhen}$. In general, the selectivity was very poor in the presence of SO_3PhBTP in the aqueous phase in the cases of these six DGA derivatives. In the presence of SO_3PhBTP as the aqueous complexant, Cm^{3+} was extracted with marginal selectivity over Am^{3+} (S.F. values are in the range of 1.3–1.8) in the cases of TBDGA (Figure 4a), TPDGA (Figure 4c), TODGA (Figure 4e), having no branching in the alkyl chain, and TiPDGA (Figure 3d), where the branching is at the away (the γ -carbon atom from the amidic N atom) position from the coordinating sites. In the cases of TiBDGA (Figure 4b) and T2EHDGA (Figure 4f), where the branching will have a significant effect on their complexation behavior, a marginal selectivity was observed for Am^{3+} over Cm^{3+} (S.F. ~ 0.5 – 0.7). It was, therefore, of interest to compare the selectivity of the DGA derivatives between Am^{3+} and Cm^{3+} ions by varying the position of the alkyl branching. Figure 5 shows that the DGA derivatives become more and more Am^{3+} -selective as the branching is closer to the amidic N atoms. The S.F. value becomes 0.23 in the case of TsBDGA, where the methyl branching is at the carbon atom (α -carbon) adjacent to the

amidic N atom. In our previous work, we also observed a higher Am^{3+} selectivity using T2EHDGA as compared to its straight-chain analogue TODGA, where the extraction was carried out even in *n*-dodecane medium in the presence of SO_3PhBTP as the aqueous complexant.²⁸ The exact reason for this selectivity reversal of the DGA derivatives having straight and branched alkyl chains in the presence of SO_3PhBTP as the aqueous complexant is not yet clearly understood. In the cases of the tetradentate aqueous complexants SO_3PhBTBP and $\text{SO}_3\text{PhBTPhen}$, on the other hand, the extraction of Cm^{3+} was always higher than that of Am^{3+} in the case of all of the DGA derivatives studied except for TsBDGA. However, the Am^{3+} selectivity of TsBDGA decreased switching over from the tridentate aqueous complexant SO_3PhBTP to the tetradentate ones SO_3PhBTBP and $\text{SO}_3\text{PhBTPhen}$ (Figure S2). In the case of the other DGA derivatives, Cm^{3+} -selective extraction was observed for both tetradentate aqueous complexants (Figure 4). This is due to the higher preference of the tetradentate N-donor ligands for Am^{3+} over Cm^{3+} .^{52,53}

In most of the cases, $\text{SO}_3\text{PhBTPhen}$ showed the highest S.F. values for Cm^{3+} over Am^{3+} probably due to its selectivity for Am^{3+} as compared to Cm^{3+} . In our previous work on $\text{Am}^{3+}/\text{Cm}^{3+}$ separation studies using TODGA in an RTIL medium, we also observed a reversal of selectivity when we switched over from SO_3PhBTP to $\text{SO}_3\text{PhBTPhen}$ as the aqueous complexant due to the opposite selectivity of these two aqueous complexants as determined from DFT studies.²⁷

Table 1 summarizes the separation behavior of Am^{3+} and Cm^{3+} by different DGA derivatives of varying alkyl chain lengths and branching in the presence and absence of N-donor aqueous complexants. TODGA alone shows very little preference for Cm^{3+} with a poor S.F. value of only 1.2. No improvement in the selectivity was observed when employing SO_3PhBTP as the aqueous complexant. In the presence of SO_3PhBTBP , however, the S.F. value increased to ~ 2 , which was further enhanced to 4.5 using $\text{SO}_3\text{PhBTPhen}$. Marie et al. also reported an improvement in the selectivity for Cm^{3+} over Am^{3+} with an S.F. value of 3.9 by TODGA when the Am^{3+} selective ligand H_4TPAEN (Figure 1k) was present in the aqueous phase.⁵⁴ In the present work, we achieved an S.F. value of 5.1 by using TODGA in *n*-octanol medium where the aqueous phase contained 1 mM $\text{SO}_3\text{PhBTPhen}$. We further checked the effect of varying the TODGA concentration from 0.1 to 0.3 M on the separation behavior of Am^{3+} and Cm^{3+} , and the results indicate that the S.F. values remain almost unaltered (Figure S4). Recently, we reported selective Am^{3+} extraction using T2EHDGA in the presence of SO_3PhBTP as the aqueous complexant with an S.F. value of 2.4.²⁸ Chapron et al. evaluated the role of the position of branching in several DGA derivatives with butyl substituents, viz., TBDGA, TiBDGA, and TsBDGA, and observed that all of them show marginal selectivity toward Cm^{3+} over Am^{3+} with S.F. values in the range of 1.1–1.5. In this study, these DGA derivatives, when used along with $\text{SO}_3\text{PhBTPhen}$ as the aqueous complexant, no improvement in the selectivity was noticed in the case of TsBDGA. TBDGA, however, showed a significant improvement in the selectivity toward Cm^{3+} with an S.F. value of 4.1 for Cm^{3+} over Am^{3+} . TiBDGA exhibited the most promising result with an S.F. value of 5.3. The selectivity for Cm^{3+} over Am^{3+} was further enhanced at lower concentrations of TiBDGA, and an S.F. value of ~ 10 was obtained at 20 mM TiBDGA. Even though the distribution ratio value is quite low at this condition, there may be

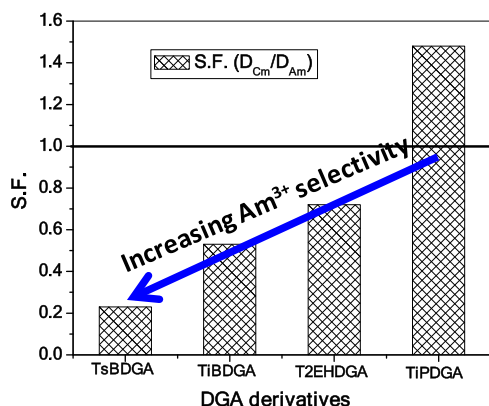


Figure 5. Effect of the position of branching in the alkyl chain of the DGA derivatives on the selectivity between Am^{3+} and Cm^{3+} ; Org. phase 0.1 M DGA (0.2 M for T2EHDGA) in *n*-octanol; Aq. phase: 1 mM SO_3PhBTP in 0.2 M HNO_3 .

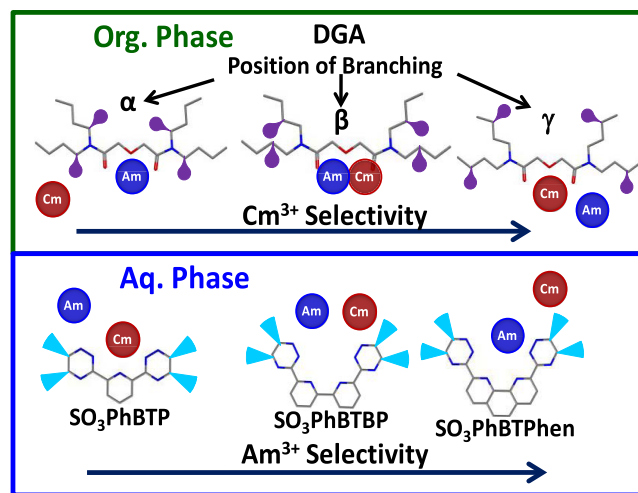
Table 1. Separation Behavior of Am^{3+} and Cm^{3+} Using Six DGA Derivatives Studied in the Present Work; Org. Phase 0.1 or 20 mM DGA in *n*-Octanol; Aq. Phase: 0.2 M HNO_3 Containing 1 mM $\text{SO}_3\text{PhBTPhen}$ (S.F. Values for This Table is Defined as the Ratio of the *D* Values of the Metal Ion Having Higher Extraction to That Having Lower Extraction; the Table Contains Results from Both the Present Study and the Literature)

ligand system	aq. phase	selective for &D	S.F.	refs
5-Br- or 5-(4-hydroxyl-phenyl) substituted $\text{CyMe}_4\text{-BTPhen}$	0.1 M HNO_3	Am^{3+} ($D_{\text{Am}} > 50$)	~ 7	55,56
1 mM Ph_2PyPO in nitrobenzene	1 M HNO_3	Am^{3+} ($D_{\text{Am}} > 30$)	3.5	57
(ClPh) $_2\text{PSSH} + \text{TEHP}$	0.1 M $\text{HNO}_3 + 0.9$ M NaNO_3	Am^{3+} ($D_{\text{Am}} = 5.8$)	> 7	21
0.2 M TODGA in 5% <i>n</i> -octanol/TPH	20 mM $\text{SO}_3\text{PhBTPhen}$ in 0.01–1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} < 1$ at < 0.5 M HNO_3 ; > 1 at > 0.5 M HNO_3)	2.4–4.5	58
0.2 M TODGA in 5% <i>n</i> -octanol/Exxsol D80	20 mM SO_3PhBTBP in 1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} \sim 6$)	~ 2	26
0.2 M TODGA in 5% <i>n</i> -octanol/TPH	20 mM SO_3PhBTP in 1 M HNO_3	no selectivity	~ 1	59
	> 3 mM H_4TPAEN at pH 1	Cm^{3+} ($D_{\text{Cm}} \sim 0.6$)	3.9	54
20 mM TODGA in <i>n</i> -octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} \sim 0.8$)	1.2	60
0.2 M TODGA in <i>n</i> -dodecane	7 mM SO_3PhBTP in 1.5 M HNO_3	no selectivity	~ 1	28
0.1 M TODGA in <i>n</i> -octanol	1 mM $\text{SO}_3\text{PhBTPhen}$ in 0.2 M HNO_3	Cm^{3+} ($D_{\text{Cm}} = 0.066$)	5.1	p.w.
0.2 M T2EHDGA in <i>n</i> -dodecane	7 mM SO_3PhBTP in 1.5 M HNO_3	Am^{3+} ($D_{\text{Am}} = 1.08$)	2.4	28
20 mM TBDGA in <i>n</i> -octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} \sim 4$)	1.5	60
0.1 M TBDGA in <i>n</i> -octanol	1 mM $\text{SO}_3\text{PhBTPhen}$ in 0.2 M HNO_3	Cm^{3+} ($D_{\text{Cm}} = 0.54$)	4.1	p.w.
20 mM TiBDGA in <i>n</i> -octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} \sim 1.5$)	1.3	60
0.1 M TiBDGA in <i>n</i> -octanol	1 mM $\text{SO}_3\text{PhBTPhen}$ in 0.2 M HNO_3	Cm^{3+} ($D_{\text{Cm}} = 0.37$)	5.3	p.w.
20 mM TiBDGA in <i>n</i> -octanol		Cm^{3+} ($D_{\text{Cm}} = 0.006$)	10 ± 5	
0.1 M TsBDGA in <i>n</i> -octanol		Cm^{3+} ($D_{\text{Cm}} = 66.8$)	1.08	
20 mM TsBDGA in <i>n</i> -octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{\text{Cm}} \sim 50$)	1.1	60
0.1 M TPDGA in <i>n</i> -octanol	1 mM $\text{SO}_3\text{PhBTPhen}$ in 0.2 M HNO_3	Cm^{3+} ($D_{\text{Cm}} = 0.1$)	3.3	p.w.
0.1 M TiPDGA in <i>n</i> -octanol		Cm^{3+} ($D_{\text{Cm}} = 0.24$)	4.6	
20 mM TiPDGA in <i>n</i> -octanol		Cm^{3+} ($D_{\text{Cm}} = 0.003$)	7.3 ± 3.0	

possibilities to improve the extraction efficiency without losing much in their selectivity by choosing suitable organic diluents or by playing with the concentration of DGA vis-à-vis $\text{SO}_3\text{PhBTPhen}$. To the best of our knowledge, even after considering the error (calculated using error propagation analysis) on those numbers, such a high S.F. value between Cm^{3+} and Am^{3+} has never been reported using DGA-based extractants. We further extended this separation studies using *n*-pentyl and *iso*-pentyl derivatives of DGA, which also showed a promising separation behavior for Cm^{3+} over Am^{3+} in the presence of $\text{SO}_3\text{PhBTPhen}$ as the aqueous complexant. Improvement of the overall selectivity for Cm^{3+} over Am^{3+} exploiting the cooperative effect of the mutually opposite selectivity of a lipophilic DGA derivative and a hydrophilic N-donor complexant is pictorially shown in Scheme 1.

DFT studies were carried out on four DGA ligands (TBDGA, TiBDGA, TPDGA, and TiPDGA) to check the structural changes in the DGA backbone on changing the alkyl substituents and the position of branching. Optimized structures of the four DGA derivatives are shown in Figure 6. No significant difference in the structural parameters is noticed in the four DGA derivatives except for the angles between the two alkyl C atoms with the amidic N atoms (α_1 and α_2) and the dihedral angles (τ_1 and τ_2) formed between the two planes containing the O and C atoms of the carbonyl group (O_{carb} and C_{carb}) and the ethereal C and O atoms (C_{eth} and O_{eth}). Values of these (dihedral) angles are given in Table S1, showing a slight increase in the values of α_1 and α_2 in the case of TiBDGA, whereas for the other three DGA derivatives, these angles are very close. If we look into the dihedral angles, the highest deviation with respect to TBDGA was observed in the case of TiBDGA, where the τ_1 value increased from 1.24 to

Scheme 1. Improvement of the Overall Selectivity for Cm^{3+} over Am^{3+} Exploiting the Cooperative Effect of the Mutually Opposite Selectivity of a Lipophilic DGA Derivative and a Hydrophilic N-Donor Complexant



16.02°. This higher deviation in the dihedral angles (τ_1 and τ_2) suggests that more preorganization energy is required during the metal ion complexation as compared to the other DGA derivatives, which may result in a weaker complexation ability of TiBDGA.

Optimized structures of the complexes with the four DGA derivatives are shown in Figure 7. Structural parameters of the Am^{3+} and Cm^{3+} complexes with metal–ligand stoichiometries of 1:2 and 1:3 are given in Table 2. In the cases of 1:2 complexes, no significant difference is noticed in the “An–O”

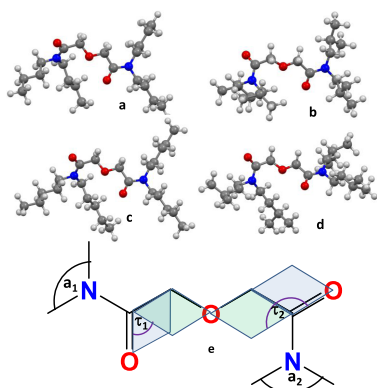
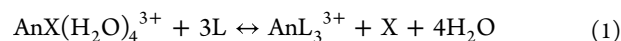


Figure 6. Optimized structures of (a) TBDGA, (b) TiBDGA, (c) TPDGA, and (d) TiPDGA at the BP86/SV(P) level of theory. (e) Schematic representation of the DGA backbone showing angles (a_1 and a_2) and dihedral angles (τ_1 and τ_2) that vary with branching in the alkyl chain.

bond distances for the Am^{3+} and Cm^{3+} complexes of all four DGA derivatives. In the case of the 1:3 complexes, however, the bond distances of the actinide ions and carbonyl O atoms ($\text{An}-\text{O}_{\text{carb}}$) are shorter in the case of TBDGA, TPDGA, and TiPDGA as compared to those in the case of TiBDGA. This indicates that the methyl branching at the β -carbon affects the complexation ability of the DGA derivatives, whereas the branching at the γ -carbon does not have much effect on the coordination ability of this class of ligands. The shorter bond length between the An^{3+} ion and the amidic O atoms, however, resulted in a slight increase in the bond length of the metal ions with the ethereal O atoms ($\text{An}-\text{O}_{\text{eth}}$) in the cases of TBDGA, TPDGA, and TiPDGA as compared to those in TiBDGA (Figure 8).

In order to further compare the interactions of the different DGA derivatives with Am^{3+} vis-à-vis Cm^{3+} in the presence of $\text{SO}_3\text{PhBTPhen}$, the complexation energy for the following complexation reaction (eq 1) was calculated as the difference in the total energies of the products and the reactants.



Here, $\text{X} = \text{BTPhen}$ and $\text{L} = \text{DGA derivative}$. The HO_3SPh group of the ligand $\text{SO}_3\text{PhBTPhen}$ was not considered in the DFT calculations to minimize the computational cost without losing much accuracy, as these groups are present far from the coordinating sites (N atoms of the phenanthroline and triazine rings). In the case of all four DGA derivatives, the complexation energies are higher for the complexation with the Cm^{3+} ion as compared to that with the Am^{3+} ion (Table 3) due to a combined effect of a marginally higher preference of the DGA derivatives for Cm^{3+} over Am^{3+} and the selectivity of the BTPhen derivative for Am^{3+} over Cm^{3+} .^{12,48,60} This combined effect resulted in a higher extraction of Cm^{3+} compared to that of Am^{3+} by these DGA derivatives.

If we compare the complexation energies for TBDGA and TiBDGA, it can be noted that TBDGA forms stronger complexes than TiBDGA with both actinide ions. This is also reflected in the marginally lower ligand-to-metal charge transfer, leading to a higher residual positive charge on the actinide ions in the complexes of TiBDGA. This observation is in line with the longer “ $\text{An}-\text{O}_{\text{amid}}$ ” bond length in the case of the complexes of TiBDGA as compared to those of TBDGA (Table 2). This may explain the poor extraction of both actinide ions by TiBDGA compared to that by TBDGA (Figures 3 and 4). In the case of the pentyl derivatives (*n*-pentyl as well as *iso*-pentyl), on the other hand, different observations were made. TiPDGA formed stronger complexes than TPDGA in the case of both metal ions, which nicely explains the higher extraction capability of TiPDGA as

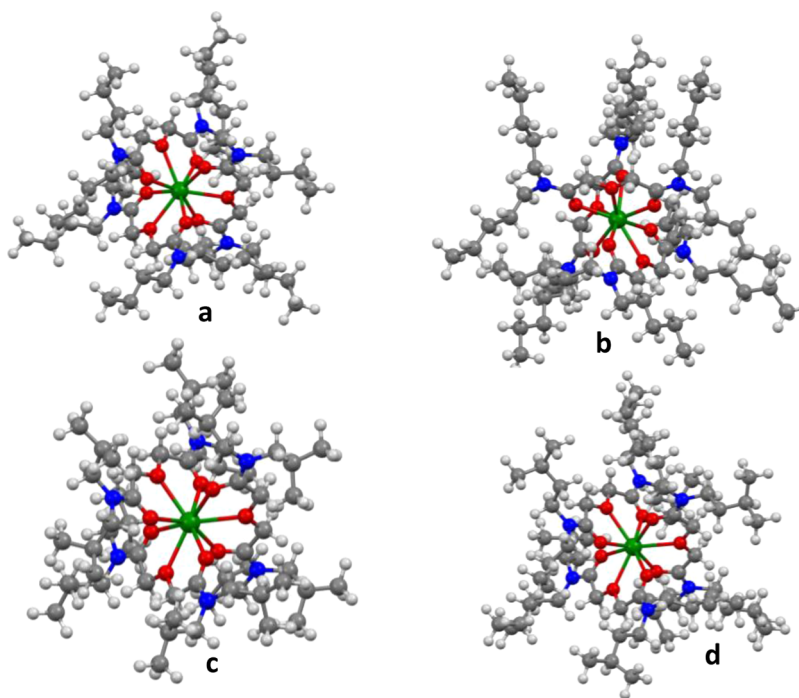
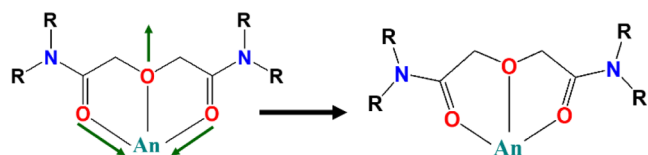


Figure 7. Optimized structures of the Am^{3+} and Cm^{3+} complexes of (a) TnBDGA, (b) TnPDGA, (c) TiBDGA, and (d) TiPDGA of the type AnL_3^{3+} .

Table 2. “An–O” Bond Distances (Å) in Am³⁺ and Cm³⁺ Complexes of Various DGA Derivatives Obtained from the DFT Calculations

complex	Am–O _{carb}	Am–O _{eth}	Cm–O _{carb}	Cm–O _{eth}
An(TBDGA) ₂ (NO ₃) ₂ ²⁺	2.405 ± 0.021	2.566 ± 0.007	2.396 ± 0.008	2.572 ± 0.013
An(TiBDGA) ₂ (NO ₃) ₂ ²⁺	2.405 ± 0.018	2.563 ± 0.012	2.397 ± 0.008	2.574 ± 0.013
An(TPDGA) ₂ (NO ₃) ₂ ²⁺	2.406 ± 0.021	2.565 ± 0.009	2.396 ± 0.009	2.573 ± 0.011
An(TiPDGA) ₂ (NO ₃) ₂ ²⁺	2.405 ± 0.022	2.564 ± 0.011	2.396 ± 0.010	2.573 ± 0.011
An(TBDGA) ₃ ³⁺	2.434 ± 0.016	2.638 ± 0.010	2.432 ± 0.004	2.624 ± 0.001
An(TiBDGA) ₃ ³⁺	2.442 ± 0.015	2.630 ± 0.011	2.439 ± 0.008	2.619 ± 0.006
An(TPDGA) ₃ ³⁺	2.435 ± 0.015	2.635 ± 0.007	2.434 ± 0.016	2.638 ± 0.010
An(TiPDGA) ₃ ³⁺	2.433 ± 0.017	2.637 ± 0.008	2.431 ± 0.004	2.624 ± 0.002

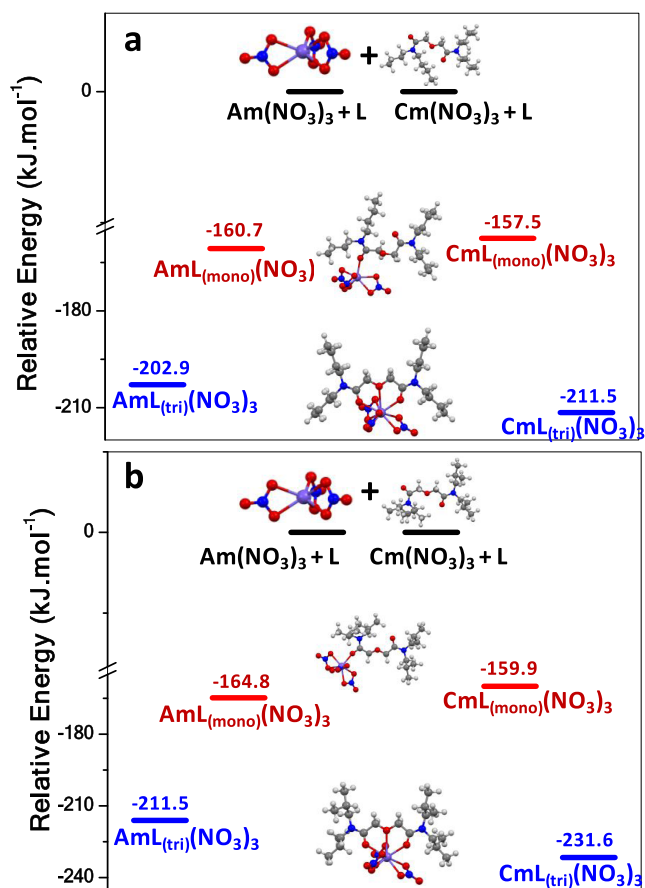
**Figure 8.** Increase in “An–O_{eth}” bond distance with decreasing “An–O_{carb}” bond distances (An = actinide).**Table 3.** Energetics for the Complexation of Am³⁺ and Cm³⁺ with Different DGA Derivatives and Natural Charges on the Actinide Ions (Q_{An}) Calculated at the B3LYP/TZVP//BP86/SV(P) Level of Theory

ligand	An	Q _{An}	comp. energy (kJ mol ^{−1})
TBDGA	Am	1.961	−327.53
	Cm	2.006	−335.11
TiBDGA	Am	1.967	−303.70
	Cm	2.009	−311.26
TPDGA	Am	1.961	−338.65
	Cm	2.012	−346.06
TiPDGA	Am	1.960	−343.48
	Cm	2.005	−351.36

compared to that of TPDGA (Figures 3 and 4). In order to understand the role of branching in the interaction with the metal ions, the relative energies of the metal trinitrato complexes of TBDGA and TiBDGA with respect to the total energies of the two separate moieties (An(NO₃)₃ and L) were calculated considering both mono- and tridentate coordination (Figure 9). The results show that in the case of monodentate coordination, Am³⁺ complexation is marginally favored, whereas considering tridentate coordination, which is the actual coordination mode of the DGA derivatives, Cm³⁺ complexation is favored. The selectivity for Cm³⁺ is higher in the case of TiBDGA as compared to TBDGA, which is in correspondence with its higher S.F. value for Cm³⁺ over Am³⁺ observed in the solvent extraction study (Table 1).

CONCLUSIONS

To explore the cooperative effect of their opposite selectivity toward Am³⁺ and Cm³⁺ separation, studies were performed using a series of DGA derivatives in conjunction with hydrophilic N-donor heteropolycyclic ligands in the aqueous phase. Diluent variation experiments indicated the highest selectivity to be in *n*-octanol. Out of the three N-donor aqueous complexants studied, SO₃PhBTPhen showed the most promising result when used in combination with DGA derivatives with S.F. values in the range of 5–10 for Cm³⁺ over Am³⁺ depending upon the aqueous phase acidity, the character of the alkyl chains of the DGA derivative, and the

**Figure 9.** Relative energies of Am³⁺ and Cm³⁺ complexes of TBDGA and TiBDGA with mono- and tridentate binding mode with respect to the combined energies of An(NO₃)₃ and free DGA ligands.

concentration of the DGA and SO₃PhBTPhen. Despite the decreasing extraction efficiency, lowering the aqueous phase acidity resulted in an improvement in the selectivity for Cm³⁺ over Am³⁺. The highest S.F. value of ~10 was achieved in the case of TiBDGA with branching of the alkyl chains at the β-carbon atom with respect to the amidic N atom, which is the highest value reported so far for the ligand-based separation of Am³⁺ and Cm³⁺ without involving any oxidation or reduction step. The higher selectivity for Cm³⁺ over Am³⁺ by TiBDGA over its straight-chain analogue TBDGA was explained with the help of DFT calculations.

This study not only reports an impressive separation behavior of Am³⁺ and Cm³⁺ using a cooperative effect of the opposite selectivity of two classes of ligands taken in two different phases. It also sheds light on understanding this

phenomenon, which will be helpful in designing ligands for further improvement by making use of mutual selectivity.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c01081>.

Experimental details; Figures S1–S4 showing the effect of diluents and the concentration of $\text{SO}_3\text{PhBTPhen}$ and different DGA derivatives on the separation behavior of Am^{3+} and Cm^{3+} ; computational methodology; Table S1 comparing the angles among the “C” atoms of the alkyl groups and the amidic “N” atom and dihedral angles for the DGA ligands; and Schemes S1–S3 showing the synthesis protocol of SO_3PhBTP , SO_3PhBTBP , and $\text{SO}_3\text{PhBTPhen}$ and their NMR and ESI-MS characterization data (PDF)

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Notes

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