

## PAPER

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7783**Bis-(1,2,4-triazin-3-yl) ligand structure driven selectivity reversal between Am<sup>3+</sup> and Cm<sup>3+</sup>: solvent extraction and DFT studies†**Arunasis Bhattacharyya,<sup>a</sup> S. A. Ansari,<sup>a</sup> N. S. Karthikeyan,<sup>b</sup> C. Ravichandran,<sup>b</sup> B. Venkatachalapathy,<sup>b</sup> T. S. Rao,<sup>c</sup> H. Seshadri<sup>d</sup> and P. K. Mohapatra<sup>a</sup>

Selectivity between Am<sup>3+</sup> and Cm<sup>3+</sup> was investigated after their aqueous complexation with three structurally tailored hydrophilic bis-(1,2,4-triazin-3-yl) ligands followed by their extraction with *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) dissolved in an ionic liquid (C<sub>4</sub>mim-Tf<sub>2</sub>N). The three hydrophilic ligands used were SO<sub>3</sub>PhBTP, SO<sub>3</sub>PhBTBP, and SO<sub>3</sub>PhBTPhen. It was evident from the solvent extraction studies that SO<sub>3</sub>PhBTP formed a stronger complex with Cm<sup>3+</sup> than with Am<sup>3+</sup>, but SO<sub>3</sub>PhBTPhen showed better complexation ability for Am<sup>3+</sup> than for Cm<sup>3+</sup>, and SO<sub>3</sub>PhBTBP showed no selectivity for the two actinide ions. DFT calculations indicated that the coordinating 'N' atoms in BTP were more co-planar in the complex and this co-planarity was higher in the Cm<sup>3+</sup> complex as compared to that in Am<sup>3+</sup>. In the case of BTBP and BTPhen ligands, on the other hand, the co-planarity was more pronounced in the Am<sup>3+</sup> complexes. Mayer's bond order calculations of M–N bonds in the complexes also indicated a reversal of the complexation ability of the BTP and BTPhen ligands for Am<sup>3+</sup> and Cm<sup>3+</sup>. Calculations of the complexation energies further supported the higher selectivity of the BTP ligand for Am<sup>3+</sup> by –52.0 kJ mol<sup>–1</sup>, and better selectivity of the BTPhen ligand for Cm<sup>3+</sup> by –24.7 kJ mol<sup>–1</sup>.

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## 1. Introduction

In the back end of the nuclear fuel cycle, the PUREX (Plutonium Uranium Redox Extraction) raffinate contains a host of radionuclides,<sup>1–3</sup> out of which the major components are short lived and do not require a long term management strategy.<sup>2</sup> On the other hand, the minor components, which include minor actinides (Np, Am and Cm), are of great concern because of their long half-lives and high radiotoxicity.<sup>4,5</sup> To overcome this concern, dedicated efforts have been made worldwide to develop suitable strategies for the partitioning of minor actinides from the host of other elements, especially from lanthanides.<sup>5–8</sup> In this context, a number of soft donor ligands have been identified for the effective and selective recognition of trivalent actinides over lanthanides.<sup>8–10</sup> Whereas a few 'N' donor ligands showed a separation factor (SF) for Am<sup>3+</sup>/Eu<sup>3+</sup> in

the range of few hundreds,<sup>10–12</sup> some 'S' donor ligands gave SF values >1000.<sup>13–15</sup>

Separation of Am<sup>3+</sup> and Cm<sup>3+</sup> is an important step after the group separation of trivalent actinides from lanthanides for better management of the PUREX raffinate. The separation of a small fraction of Cm from Am is important due to its shorter half-life. In addition, it has been shown that the presence of Cm in the Am fraction will create difficulty during the target preparation for the proposed transmutation of long-lived minor actinides.<sup>16</sup> This difficulty primarily arises due to the large neutron and heat output of <sup>244</sup>Cm. The separation of Am<sup>3+</sup> and Cm<sup>3+</sup>, however, is far more challenging than the inter group separation of trivalent actinides and lanthanides.<sup>17</sup> Due to this challenge, only limited literature on Am<sup>3+</sup>/Cm<sup>3+</sup> separation is available.<sup>18</sup> In the proposed SESAME process (selective extraction and separation of americium by means of electrolysis), Am<sup>3+</sup> is oxidized electrochemically in the presence of a heteropolyanion followed by its extraction with TBP and amide based extractants.<sup>19–22</sup> In the EXAM process (extraction of americium process), on the other hand, the slightly higher ionic potential of Cm<sup>3+</sup> is exploited for its selective aqueous complexation with *N,N,N',N'*-tetraethyl diglycolamide (TEDGA) over Am<sup>3+</sup> followed by extraction with a mixture of tetra-alkyl malonamide and HD2EHP (di-2-ethylhexyl phosphoric acid).<sup>23,24</sup> In the LUCA process (Lanthaniden Und Curium

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Americum Trennung process), however, the higher softness of  $\text{Am}^{3+}$  compared to those of  $\text{Cm}^{3+}$  and trivalent lanthanide ions is utilized for its selective extraction with the 'S' donor ligand.<sup>25</sup>

For effective management of the PUREX raffinate, the first proposed step is the recovery of trivalent actinides from the host of other elements in the actinide partitioning step. However, most of the proposed extractants for actinide partitioning cannot differentiate between trivalent actinides and lanthanides due to their similar chemical properties. In this context, dedicated efforts have been made for the selective separation of the trivalent actinides over lanthanides using soft donor ligands.<sup>9</sup> From a large number of ligands evaluated in this context, three main kinds of 'N' donor ligands are found to be the most appropriate ones for the separation of the trivalent actinides over the lanthanides. The three kinds of ligands are (i) tridentate bis-(1,2,4-triazin-3-yl) pyridine (BTP), (ii) tetradentate bis-(1,2,4-triazin-3-yl) bipyridine (BTBP), and (iii) tetradentate bis-(1,2,4-triazin-3-yl) phenanthroline (BTPhen) derivatives.<sup>9,10</sup> In addition to the lanthanide/actinide separation, recent studies of these ligands have been explored for the separation of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ .<sup>18</sup> A hydrophobic BTP derivative has been evaluated extensively for the extraction of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  along with a number of lanthanide ions, where a marginal selectivity towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  has been reported.<sup>26</sup> Geist *et al.*,<sup>27</sup> on the other hand, studied the separation behaviour of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  from the lanthanides by employing a hydrophilic BTP derivative and reported no selectivity between  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  during their extraction with TODGA. It was concluded that the selectivity towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  by TODGA was cancelled out due to the same selectivity of the hydrophilic BTP derivative in the aqueous phase, which leads to the overall loss of selectivity between  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ .<sup>27</sup> Tetradentate hydrophobic BTBP derivatives, on the other hand, were found to be marginally selective towards  $\text{Am}^{3+}$  over  $\text{Cm}^{3+}$  and have been studied for being selective towards  $\text{Am}^{3+}$  over  $\text{Cm}^{3+}$  in nitric acid medium.<sup>28</sup> Moreover, the selectivity of these hydrophobic BTPhen ligands could be further tuned by suitable electronic modulation in the ligands.<sup>29</sup> To our knowledge, there is no report on the selectivity between  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  which is studied systematically using hydrophilic BTP, BTBP and BTPhen derivatives. It will be, therefore, interesting to evaluate the hydrophilic BTP, BTBP and BTPhen derivatives for the selective recognition of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ .

It is well known that diglycolamide derivatives such as TODGA (*N,N,N',N'*-tetraoctyl diglycolamide) dissolved in a molecular solvent show an increasing extraction tendency for trivalent actinides with increasing nitric acid concentration.<sup>30</sup> On the other hand, when they are dissolved in room temperature ionic liquids (RTILs), they show an opposite extraction behaviour where the actinide extraction decreases with increasing aqueous feed acidity.<sup>31,32</sup> Needless to mention, RTILs have been suggested as efficient diluents for nuclear fuel cycle applications.<sup>33–35</sup> It will be interesting, therefore, to investigate their effect on  $\text{Am}^{3+}/\text{Cm}^{3+}$  selectivity by TODGA in the presence

of aqueous complexing heteropolycyclic ligands. With this objective, the present work was aimed to investigate the separation behaviour of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  with the TODGA/RTIL solvent in the presence of three structurally tailored hydrophilic BTP ligands, *viz.*  $\text{SO}_3\text{PhBTP}$ ,  $\text{SO}_3\text{PhBTBP}$ , and  $\text{SO}_3\text{PhBTPhen}$  ligands (Fig. 1). DFT studies were also carried out to rationalize the separation results obtained experimentally.

## 2. Experimental

### 2.1. Materials

*N,N,N',N'*-Tetraoctyl diglycolamide (TODGA) was synthesized at Thermax India Ltd using an established procedure.<sup>36</sup> Detailed synthesis procedures of hydrophilic 'N' donor heteropolycyclic ligands,  $\text{SO}_3\text{PhBTP}$ ,  $\text{SO}_3\text{PhBTBP}$  and  $\text{SO}_3\text{PhBTPhen}$  (Fig. 1) are given in the ESI (see the ESI†). The purities of these ligands were confirmed by  $^1\text{H-NMR}$ , FT-IR and mass spectrometry (HR-MS). The room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ( $\text{C}_4\text{mim}^+\text{Tf}_2\text{N}^-$ ), in 99% purity was procured from Iolitec, Germany. The actinide tracers,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ , were obtained from the laboratory stock after confirming their radiochemical purities by alpha spectrometry. All other reagents used were of analytical reagent grade.

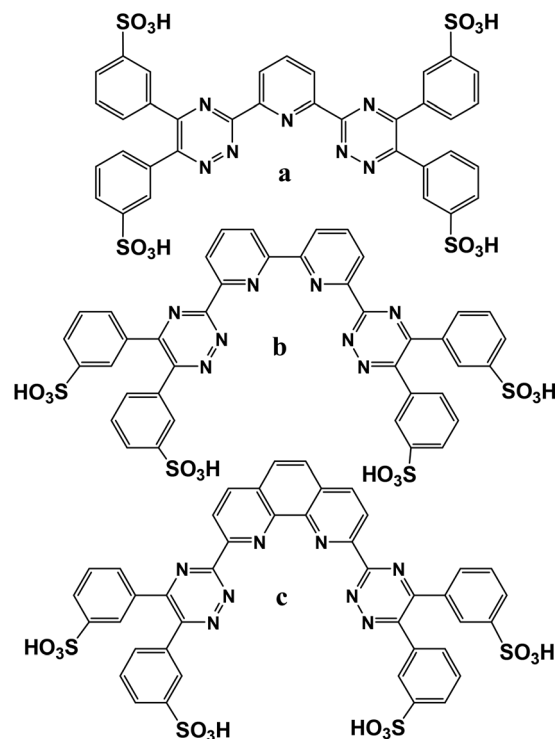


Fig. 1 Structural features of the hydrophilic 'N' donor heteropolycyclic ligands used in this work. (a)  $\text{SO}_3\text{PhBTP}$ , (b)  $\text{SO}_3\text{PhBTBP}$ , and (c)  $\text{SO}_3\text{PhBTPhen}$ .

## 2.2 Distribution measurements

Liquid-liquid extraction studies were carried out by equilibrating equal volumes (usually 1 mL) of the RTIL phase containing 5 mmol L<sup>-1</sup> of TODGA with the desired aqueous phase spiked with the radiotracers. The aqueous phase contained 10 mmol L<sup>-1</sup> BTP ligands at various nitric acid concentrations and either <sup>241</sup>Am or <sup>244</sup>Cm tracers. The concentrations of Am and Cm in these studies were 10<sup>-7</sup> M (~3 × 10<sup>3</sup> Bq ml<sup>-1</sup>) and 10<sup>-9</sup> M (~750 Bq ml<sup>-1</sup>), respectively. The equilibration of the two phases was carried out in a leak tight Pyrex glass tube (10 mL capacity) in a thermostat water bath at 25.0 ± 0.1 °C. The two phase equilibration time was set to be at least 3 h which ensured the attainment of equilibrium conditions. Subsequently, the tubes were centrifuged and 100 µL aliquots were taken out from both the phases for radiometric assay. The assay of <sup>241</sup>Am was carried out using a well type NaI(Tl) scintillation counter (Para Electronics) coupled with a multi-channel analyzer (ECIL, India). On the other hand, the assay of <sup>244</sup>Cm was performed by liquid scintillation counting (Hidex, Finland) using Aqualite + cocktail (Hidex, Finland). The distribution ratio of Am<sup>3+</sup> and Cm<sup>3+</sup> was calculated as the ratio of their radioactivities in unit volume in the RTIL phase to those in the aqueous phase. Each distribution experiment was repeated thrice, and the accepted data were within the relative standard deviation of 5%.

## 2.3 Computational methodology

The geometries of the free ligands and metal/ligand complexes were optimized using the def-SV(P) basis sets for all the atoms as implemented in the TURBOMOLE-7.2 suits of program.<sup>37</sup> For the geometrical optimization of the Am<sup>3+</sup> and Cm<sup>3+</sup> complexes, an electron effective core potential (ECP) of 60 along with the corresponding def-SV(P) basis sets for the valence electrons were used.<sup>38–41</sup> The entire geometrical optimizations were performed using the GGA functional BP86.<sup>42,43</sup> The single point energies of the free ligands and the complexes were calculated using the hybrid functional B3LYP.<sup>44</sup> The basis sets of the valence triple zeta quality; for example, def-TZVP<sup>45</sup> as implemented in the TURBOMOLE-7.2 package were used to calculate the single point energy. The details of the computational methodology are described in the ESI† (see the ESI†).

# 3. Results and discussion

## 3.1 Solvent extraction studies

Fig. 2 shows the distribution behaviour of Am<sup>3+</sup> and Cm<sup>3+</sup> by TODGA in the presence of the three hydrophilic complexing ligands. In the absence of the aqueous complexant, TODGA favors the extraction of Cm<sup>3+</sup> as compared to Am<sup>3+</sup> throughout the aqueous phase acidity of 0.5 to 3 M HNO<sub>3</sub>. This feature is very much expected considering the ionic potential of these two actinides where Cm<sup>3+</sup> has a higher ionic potential than Am<sup>3+</sup>. Similar results were also obtained for solvent extraction studies with the TODGA/*n*-dodecane system, where *D*<sub>Cm</sub> was

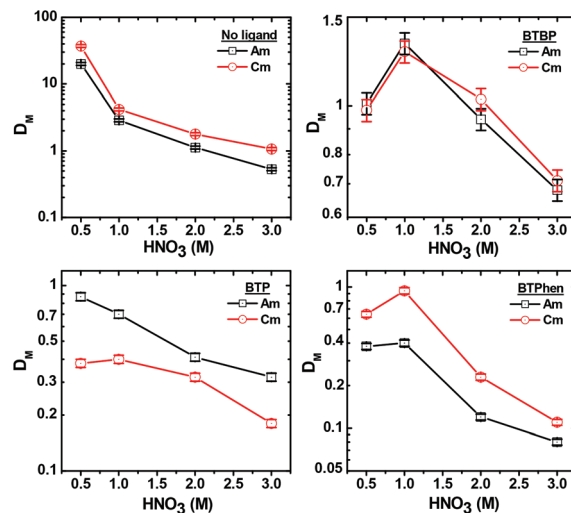


Fig. 2 Effect of aqueous phase acidity on the distribution ratio (*D*<sub>M</sub>) of Am<sup>3+</sup> and Cm<sup>3+</sup> by TODGA in the presence of 10 mM hydrophilic N-donor ligands. RTIL phase: 5 mM TODGA/C<sub>4</sub>mim-Tf<sub>2</sub>N.

found to be higher than that of *D*<sub>Am</sub>.<sup>46</sup> However, the extraction patterns in the *n*-dodecane and RTIL systems are completely opposite. Whereas the *D*<sub>M</sub> value in *n*-dodecane increases with the aqueous phase feed acidity, it decreases with the feed acidity when RTIL is used as the diluent. These two types of extraction patterns are well understood in the light of the two different extraction mechanisms involved in molecular solvents and in ionic liquids.<sup>47</sup> A neutral metal/ligand/nitrate species is extracted by the solvation mechanism in *n*-dodecane but a cationic metal/ligand complex is exchanged by the cationic component of the ionic liquid phase when RTIL is used as the diluent.

As shown in Fig. 2, the extraction of both Am<sup>3+</sup> and Cm<sup>3+</sup> is suppressed significantly (about 40 times) in the presence of the hydrophilic 'N' donor ligands which is attributed to their aqueous complexation. This decrease is, however, different for Am<sup>3+</sup> and Cm<sup>3+</sup> in the case of the three ligands, indicating that these ligands differ in their complexation ability for Am<sup>3+</sup> and Cm<sup>3+</sup>. In the case of SO<sub>3</sub>PhBTBP, Geist *et al.*<sup>27</sup> found that this ligand has marginally higher selectivity for Cm<sup>3+</sup> over Am<sup>3+</sup>. As a result, one may expect a marginally lower extraction of Cm<sup>3+</sup> with TODGA compared to Am<sup>3+</sup>. This feature is evident from Fig. 2 where TODGA shows lower extraction for Cm<sup>3+</sup> compared to Am<sup>3+</sup> with an SF value of 2.4 at 0.5 M HNO<sub>3</sub> (Fig. 3). In the case of SO<sub>3</sub>PhBTBP, on the other hand, no selectivity was observed, which indicates that its complexation ability might be higher for Cm<sup>3+</sup> than that for Am<sup>3+</sup>, which almost exactly compensates for the selectivity obtained with TODGA in an RTIL medium. The selectivity of SO<sub>3</sub>PhBTPhen, however, has shown a reversal with respect to SO<sub>3</sub>PhBTBP and TODGA. In the presence of SO<sub>3</sub>PhBTBP, TODGA shows higher extraction of Cm<sup>3+</sup> compared to that of Am<sup>3+</sup> with an SF value of <0.5 for Am<sup>3+</sup> over Cm<sup>3+</sup> at 1 M HNO<sub>3</sub> (Fig. 3). This feature indirectly indicates that SO<sub>3</sub>PhBTPhen has a higher complexa-

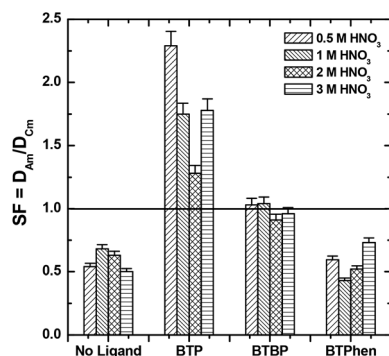


Fig. 3 Separation factor (SF) between Am<sup>3+</sup> and Cm<sup>3+</sup> by TODGA in the presence of 10 mM hydrophilic BTP ligands.

tion ability for Am<sup>3+</sup> as compared to Cm<sup>3+</sup>. A similar higher affinity for Cm<sup>3+</sup> with a hydrophobic BTPhen ligand (5-Br-CyMe4-BTPhen) was seen earlier, where an SF value of >6 has been reported for Am<sup>3+</sup> over Cm<sup>3+</sup> at lower nitric acid concentrations.<sup>29</sup> The  $D_M$  values were, however, >1 for both the metal ions which is not a practical value for their mutual separation. Kaufholz *et al.*<sup>48</sup> studied the Am<sup>3+</sup>/Cm<sup>3+</sup> separation with a hydrophilic BTPhen derivative, where they observed an SF value ( $D_{Cm}/D_{Am}$ ) in the range of 2–3 with  $D_{Am} < 1 < D_{Cm}$  in the acidity range of 0.6–0.7 M HNO<sub>3</sub>. However,  $D_{Am}$  was >1 at 1 M HNO<sub>3</sub>. The separation behaviours of Am<sup>3+</sup> and Cm<sup>3+</sup> with hydrophobic and hydrophilic BTP, BTBP and BTPhen with TODGA (as a complexing agent) in molecular diluents or ionic liquids are compared in Table 1. If we carefully go through the literature reports, it is interesting to note that the hydrophobic BTP derivatives show selectivity towards Cm<sup>3+</sup> over Am<sup>3+</sup> with an SF value ( $D_{Cm}/D_{Am}$ ) of 1.5.<sup>26,49</sup> The hydrophobic BTBP derivatives, on the other hand, show selectivity towards Am<sup>3+</sup> over Cm<sup>3+</sup> (ref. 12 and 28) and this selectivity for Am<sup>3+</sup> is further enhanced in the case of the hydrophobic BTPhen derivatives.<sup>29</sup> Afsar *et al.*, however, reported a change in the selectivity with time for the hydrophobic BTPhen derivatives due to the different extraction kinetics of Am<sup>3+</sup> and Cm<sup>3+</sup>, in which they could achieve an SF value ( $D_{Am}/D_{Cm}$ ) of 7 at a particular acidity of the aqueous phase and the time of equilibration.<sup>50</sup> Similarly, if we look into the hydrophilic BTP, BTBP

and BTPhen derivatives, analogous trends in their selectivity were observed. No selectivity was achieved in the presence of SO<sub>3</sub>PhBTP as the aqueous complexant when the extraction was carried out using TODGA in *n*-dodecane,<sup>27</sup> which is because of the cancellation of selectivity by TODGA in the organic phase and SO<sub>3</sub>PhBTP in the aqueous phase. In the present work, however, we could achieve an SF value ( $D_{Am}/D_{Cm}$ ) > 2, which is due to a significant change in the complexation of TODGA in the RTIL medium as compared to that in the molecular diluents. In the presence of hydrophilic SO<sub>3</sub>PhBTBP and SO<sub>3</sub>PhBTPphen as the aqueous complexing agents, on the other hand, TODGA in the molecular diluents selectively extracts Cm<sup>3+</sup> over Am<sup>3+</sup> and this selectivity is higher in the case of SO<sub>3</sub>PhBTPphen<sup>48,51</sup> which is in line with our observation for the extraction with TODGA in an RTIL medium.

Based on these observations, it can be concluded that BTP shows a higher affinity for Cm<sup>3+</sup> over Am<sup>3+</sup> and this selectivity is reversed when we opt for BTPhen derivatives irrespective of their substitution. The BTBP derivatives, however, show an intermediate behaviour with very mild selectivity towards Am<sup>3+</sup> over Cm<sup>3+</sup>. To gain more insights into this reversal behaviour, DFT studies were performed (*vide infra*).

### 3.2. DFT studies

**3.2.1. Geometrical structure of the Am<sup>3+</sup> and Cm<sup>3+</sup> complexes.** In order to understand the effect of ligand denticity and rigidity of the ligands on the separation behaviour of Am<sup>3+</sup> and Cm<sup>3+</sup>, the geometries of their complexes with bare BTP, BTBP and BTPhen derivatives were optimized to avoid the convergence difficulties. The Cartesian coordinates of the optimized structures of the free ligand molecules and their Am<sup>3+</sup> and Cm<sup>3+</sup> complexes are provided in the ESI (Table S1 in ESI†). Fig. 4 shows the torsional angles ( $\tau_1$ ,  $\tau_2$  and  $\tau_3$ ) which indicate the co-planarity of the coordinating donor atoms of these ligands. In the case of BTP, the magnitude of the torsional angles decreases upon complexation (Table 2), which indicates that the coordinating 'N' atoms are more coplanar in the complex as compared to the free ligand and this co-planarity is marginally higher in the Cm<sup>3+</sup> complex as compared to that in the Am<sup>3+</sup> complex. In the case of BTBP and BTPhen, on the other hand, the torsional angles decrease upon complexa-

Table 1 Comparison of the separation behaviour of Am<sup>3+</sup> and Cm<sup>3+</sup> employing different hydrophobic BTP, BTBP and BTPhen derivatives and TODGA in molecular diluents or RTIL in the presence of hydrophilic BTP, BTBP, and BTPhen derivatives as complexing agents in an aq. phase

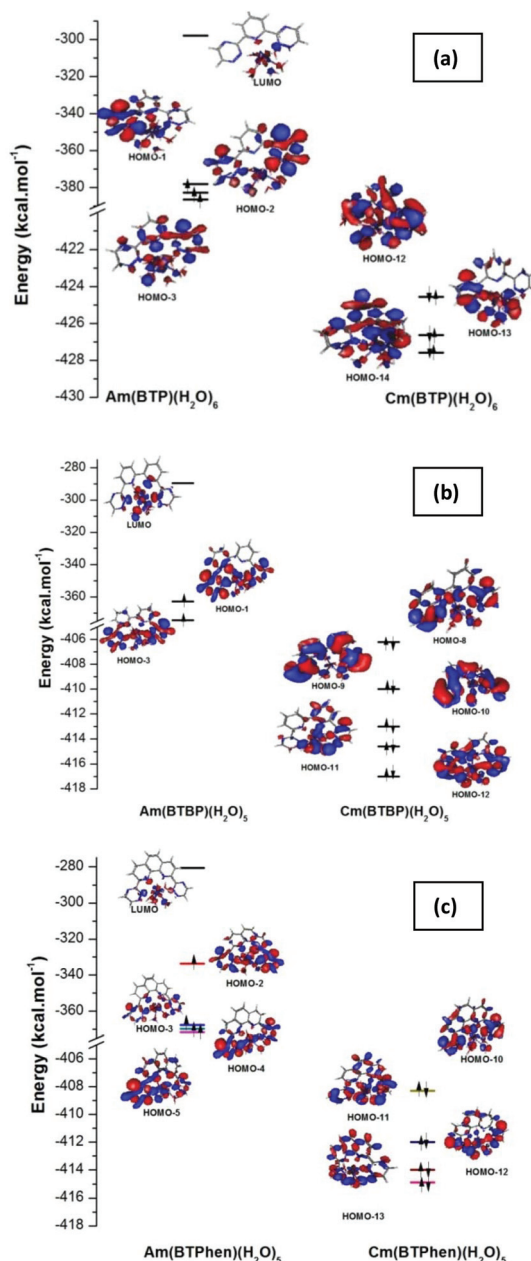
Experimental conditions				
Org. phase	Aq. phase	$D_{Am}$	SF = $D_{Am}/D_{Cm}$	Ref.
0.2 M TODGA in dodecane	18 mM SO <sub>3</sub> PhBTP, 1 M HNO <sub>3</sub>	2	~1	27
10 mM CyMe4BTBP + 0.25 M DMDOHEMA in octanol	1 M HNO <sub>3</sub> and mg L <sup>-1</sup> Lns	7	~1.6	28
CyMe4BTPphen in octanol	1 M HNO <sub>3</sub>	>100	~1	29
5-Br-CyMe4BTPphen in octanol	0.1 M HNO <sub>3</sub>	>100	7	
5-(4-Hydroxy-phenyl) CyMe4-BTPphen in octanol	1 M HNO <sub>3</sub>	>100	5	
0.2 M TODGA in TPH	10 mM SO <sub>3</sub> PhBTBP, 1 M HNO <sub>3</sub>	~1.3	0.41	48
5 mM TODGA in C <sub>4</sub> mim-Tf <sub>2</sub> N	10 mM SO <sub>3</sub> PhBTP, 1 M HNO <sub>3</sub>	0.7	1.75	p.w.
	10 mM SO <sub>3</sub> PhBTBP, 1 M HNO <sub>3</sub>	1.33	1.04	
	10 mM SO <sub>3</sub> PhBTPphen, 1 M HNO <sub>3</sub>	0.4	0.42	





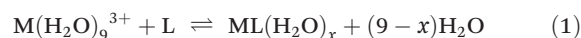
**Table 3** Mayer's bond order, M–N bond distances and natural charges on the metal ions in the Am<sup>3+</sup> and Cm<sup>3+</sup> complexes of BTP, BTBP and BTPhen

Ligand	Q <sub>Am</sub>		Am–N <sub>py</sub>		Am–N <sub>tz</sub>		Q <sub>Cm</sub>		Cm–N <sub>py</sub>		Cm–N <sub>tz</sub>
BTP	1.922	MBO	0.201		0.171	0.153	2.050	MBO	0.187		0.156
		d <sub>M–N</sub>	2.640		2.615	2.659		d <sub>M–N</sub>	2.625		2.613
BTBP	1.884	MBO	0.190	0.218	0.153	0.180	1.925	MBO	0.203	0.225	0.160
		d <sub>M–N</sub>	2.615	2.641	2.618	2.654		d <sub>M–N</sub>	2.582	2.597	2.626
BTPhen	1.891	MBO	0.193	0.207	0.152	0.167	1.931	MBO	0.206	0.220	0.151
		d <sub>M–N</sub>	2.612	2.638	2.647	2.657		d <sub>M–N</sub>	2.587	2.601	2.647

**Fig. 6** MOs of the Am<sup>3+</sup> and Cm<sup>3+</sup> complexes with metal–ligand interactions. (a) Interaction with BTP, (b) interaction with BTBP, and (c) interaction with BTPhen ligands.

the metal based orbitals could only be observed in the deep seated MOs (HOMO–12, HOMO–13 and HOMO–14), suggesting a very negligible contribution of covalence to the metal–ligand bonding. This is reflected in the higher ligand to metal charge transfer in the Am<sup>3+</sup> complex leading to a lower positive charge on americium (1.922) as compared to that on curium (2.050). Similar to BTP, in the cases of both BTBP and BTPhen, a higher covalence was noticed in the Am<sup>3+</sup> complex as compared to that in Cm<sup>3+</sup>. In spite of the higher covalence in the metal–ligand bonds in the Am<sup>3+</sup> complex a marginally higher affinity of the BTP derivatives towards Cm<sup>3+</sup> could be due to the dominance of the electrostatic interactions in their bonding. In the cases of BTBP and BTPhen, a  $\sigma$  type bonding interaction was observed between the metal-based orbitals and the triazinyl 'N' atoms (Fig. 6) and similar kinds of metal–ligand bonding interactions were observed only in the deep seated orbitals in the Cm<sup>3+</sup> complexes. This higher covalence in the Am<sup>3+</sup> complex leads to the selectivity of the BTBP and BTPhen derivatives towards Am<sup>3+</sup> over Cm<sup>3+</sup>.

**3.2.3. Energetics of the Am<sup>3+</sup> and Cm<sup>3+</sup> complexation.** In order to understand the comparison of the complexation of Am<sup>3+</sup> and Cm<sup>3+</sup>, the complexation energies ( $\Delta E_{\text{comp}}$ ) for the following equilibrium are calculated and listed in Table 4.



For a particular metal ion, the complexation energy for the equilibrium reaction (1) is expected to be more favourable in the case of the tetradentate ligand BTBP as compared to that in BTP. In the case of BTPhen, the  $\Delta E_{\text{comp}}$  values become further negative as compared to those in BTBP due to the pre-organized structure of BTPhen. However, when one compares the complexation of Am<sup>3+</sup> *vis-à-vis* Cm<sup>3+</sup>, the complexation energies for all the ligands are found to be favourable for Cm<sup>3+</sup> over Am<sup>3+</sup> due to the smaller ionic radius of Cm<sup>3+</sup>. This

**Table 4** Complexation energies ( $\Delta E_{\text{comp}}$ ) of the Am<sup>3+</sup>/Cm<sup>3+</sup> complexes (kJ mol<sup>−1</sup>)

Ligand	M <sup>3+</sup>	$\Delta E_{\text{comp}}$	$\Delta\Delta E_{\text{Cm-Am}}$	$\Delta\Delta E_{\text{Cm-Am}} - \Delta\Delta E_{\text{TMDGA}}$
BTP	Am <sup>3+</sup>	−187.4	−52.0	−20.0
	Cm <sup>3+</sup>	−239.4		
BTBP	Am <sup>3+</sup>	−256.2	−36.3	−4.3
	Cm <sup>3+</sup>	−292.5		
BTPhen	Am <sup>3+</sup>	−275.6	−24.7	7.3
	Cm <sup>3+</sup>	−300.2		

suggests that the complexation of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  with these ligands is mainly governed by the ionic interactions. If we compare the selectivity between  $\text{Cm}^{3+}$  and  $\text{Am}^{3+}$ , which is indicated by the difference in their complexation energies ( $\Delta\Delta E_{\text{Cm-Am}}$ ), BTP shows a higher selectivity towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  than the other two ligands, *viz.* BTBP and BTPPhen. In order to explain our experimental observation, we need to consider the competition of TODGA for the complexation of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  and for the computational simplicity the methyl derivative (TMDGA) was considered in the place of the octyl derivative (TODGA). Considering the complexation energy ( $\Delta E_{\text{TMDGA}}$ ) for the following equilibrium, TODGA is selective towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  by  $-32.0 \text{ kJ mol}^{-1}$  ( $\Delta\Delta E_{\text{TMDGA}}$ ). Therefore, even if one considers the competition by TMDGA, BTP remains selective towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  as reflected in the difference between the  $\Delta\Delta E_{\text{Cm-Am}}$  and  $\Delta\Delta E_{\text{TMDGA}}$  values and, therefore,  $\text{Am}^{3+}$  is selectively extracted in the organic phase with TODGA. In the case of BTPPhen, on the other hand,  $\text{Cm}^{3+}$  is extracted selectively with TODGA as the selectivity of TMDGA for  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  is observed to be higher than that of BTPPhen ( $\Delta\Delta E_{\text{Cm-Am}} = -24.7 \text{ kJ mol}^{-1}$ ). BTBP, however, shows comparable selectivity to TMDGA from  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  and therefore, no selectivity is observed in the solvent extraction study employing the BTBP derivative.

## 4. Conclusions

Separation studies of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  were performed by using a TODGA/ $\text{C}_4\text{mim-NTf}_2$  in nitric acid medium containing three different hydrophilic 'N' donor ligands, *viz.*  $\text{SO}_3\text{PhBTP}$ ,  $\text{SO}_3\text{PhBTBP}$  and  $\text{SO}_3\text{PhBTPPhen}$ . The results showed that in the case of  $\text{SO}_3\text{PhBTP}$ ,  $\text{Am}^{3+}$  was selectively extracted over  $\text{Cm}^{3+}$  with an  $\text{SF}_{(\text{Am/Cm})}$  value of 2.5 and  $\text{SO}_3\text{PhBTPPhen}$ , on the other hand, showed selectivity towards  $\text{Cm}^{3+}$  over  $\text{Am}^{3+}$  with an  $\text{SF}_{(\text{Am/Cm})}$  value of  $<0.5$ .  $\text{SO}_3\text{PhBTBP}$ , however, did not show any selectivity between  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ . The DFT studies indicated that the metal–ligand interactions in the complexes of the BTP, BTBP and BTPPhen derivatives are mainly governed by the ionic interactions. However, a higher degree of covalence in the M–N bonds is observed in the  $\text{Am}^{3+}$  complexes as compared to that in the  $\text{Cm}^{3+}$  complexes. The reversal of selectivity was explained in the light of DFT based calculations considering the competitive complexation of the BTP, BTBP or BTPPhen derivatives with the diglycolamide ligand.

## Conflicts of interest

The authors have no conflicts of interest to declare.

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