PAPER

Ligand structure and diluent nature in defining improved Am³⁺ and Cm³⁺ separation using diglycolamides: a combined solvent extraction and DFT study†

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Separation of Am³⁺ and Cm³⁺ is one of the most challenging yet unavoidable steps in the back end of the nuclear cycle. Various ligands evaluated for Am/Cm separation have their own merits and demerits, and not a single ligand has been uniquely proposed for this purpose. In the present work, we evaluated *N,N, N′,N′*-tetra-*n*-octyldiglycolamide (TODGA) *vis-à-vis N,N,N′,N′*-tetra-2-ethylhexyldiglycolamide (T2EHDGA) in combination with a hydrophilic 2,6-bis(1,2,4-triazinyl)pyridine (SO₃PhBTP) derivative in the aqueous phase for the separation of Am³⁺ and Cm³⁺ from nitric acid medium. The results showed that marginal selectivity for Am³⁺ over Cm³⁺ was observed with T2EHDGA in the presence of SO₃PhBTP, which was attributed to the difference in the entropy change for their extraction from both the temperature-dependent liquid–liquid extraction and computational studies.

Introduction

Safe management of long-lived radiotoxic elements is very important and crucial for the sustainability of nuclear power as an alternative low-carbon emission-based power program.[1,2] Minor actinides, *viz.* Am, Cm and Np, are mainly responsible for the long-term radiotoxicity of nuclear waste.[1] Unlike Am and Cm, Np shows multiple oxidation states, which is commonly exploited for the separation of this long-lived radioactive element.[3,4] Am and Cm, on the other hand, exhibit +3 as the most stable oxidation state with very close ionic radii,[5] which makes their mutual separation most difficult in the back end of the nuclear fuel cycle.[6,7] The strategy for the long-term safe management of these radiotoxic elements is to vitrify and bury them in deep geological repositories in suitable geological host formations so that they can be isolated from the biosphere.[6] Am is the most dominant heat generating radionuclide over 100 years that is responsible for affecting the integrity of the host matrix and may lead to the release of these radioisotopes in the biosphere in the long run. It is, therefore, proposed to transmute the Am isotopes in accelerator-driven subcritical systems or the reactors with a fast neutron spectrum.[6] Two options are known to be available for the transmutation process, *viz.* homogeneous and hetero-

geneous recycling.[8,9] In the case of homogeneous transmutation, all the major and minor actinides are co-extracted in a group separation method, and the separation of the individual actinide elements, *viz.* Am/Cm separation, is not attempted.[6,8] In the case of heterogeneous recycling, on the other hand, high Am-loaded targets are incorporated in the core for transmutation[6,9] where the separation of Am from Cm is a prerequisite due to the high neutron and heat emission of Cm isotopes, which makes the target preparation and other steps for the transmutation more cumbersome.[6] Two different strategies have been explored for the separation of Am and Cm, *viz.* selective oxidation of Am³⁺ followed by its separation using conventional ligands[6,10] and direct separation of Am³⁺ and Cm³⁺ employing a combination of ligands.[6] The selectivity achieved is much lower in this separation strategy of Am³⁺ and Cm³⁺. Controlling the higher oxidation state of Am is tedious; therefore, the direct separation strategy is preferred because of its ease of operation.[6] Various combinations of ligands are evaluated in different processes for the separation of Am³⁺ and Cm³⁺. In the Lanthaniden Und Curium Americium Trennung (LUCA) process, a synergistic mixture of bis(chlorophenyl) dithiophosphinic acid and tris-2-ethylhexylphosphate (TEHP) is employed for the selective extraction of Am³⁺ over Cm³⁺ where the maximum separation factor (S.F.) value of 8 is reported, and the selectivity is attributed to the difference in the entropy of complexation of these two metal ions.[6,11] As a particular ligand does not show impressive selectivity between Am³⁺ and Cm³⁺, the cooperative effect of the selectivity of two ligands with solubility in two phases (one is lipophilic while

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the other one is hydrophilic) is exploited for improving the selectivity of the overall process.[12] A combination of lipophilic malonamide (DMDOHEMA) and di-2-ethyl phosphoric acid (D2EHPA), along with a hydrophilic N,N,N',N'-tetraethyl diglycolamide (TEDGA), is used in the EXAm (EXtraction of Americium) process for Am/Cm separation,[13] and a separation factor (S.F. = D_{Am}/D_{Cm}) value of 2.5 is reported with this combination of ligands.[14] While studying the mechanism of the extraction process, it is observed that the metal ions are extracted as the heteroleptic complex, where the hydrophilic TEDGA (Fig. 1) is partitioned into the organic phase with the extracted complex, and this leads to the loss of the ligand from the aqueous phase.[14] The selectivity is further enhanced when the lipophilic nitrilotriacetamide (NTA) derivatives are chosen as the organic extractant in place of DMDOHEMA and D2EHPA; the major drawback of this extraction system is the decreasing extraction efficiency with the increasing aqueous phase acidity.[15–17] This issue is resolved by replacing the NTA derivative with the alkyl diamide amine (ADAAM) derivative, where the extraction efficiency increases up to 1 M HNO_3 and decreases drastically beyond this acidity.[15,18] The hydrophilic sulphonated bis-triazinyl bipyridine (BTBP) or phenanthroline (BTPhen) derivatives in combination with N,N,N',N'-tetraoctyl diglycolamide (TODGA) in the organic phase is evaluated for the separation of Am(III) and Cm(III), where cooperative effect of Cm^{3+} selectivity of TODGA in the organic phase and Am^{3+} selectivity of suphonated BTBP or BTPhen derivatives in aqueous phase is exploited.[19,20] We have reported a reversal of selectivity using sulphonated BTP (SO_3PhBTP), which is marginally selective for Cm^{3+} over Am^{3+}.[21] Different pyridine-based ligands with different functionalities evaluated for the Am^{3+}/Cm^{3+} separation are shown in Table 1. Unlike TODGA, the branched alkyl DGA derivatives show marginally higher affinity for Am^{3+} over Eu^{3+}; moreover, the extraction efficiency of a branched alkyl DGA, viz. N,N,N',N'-tetra (sec-butyl) diglycolamide (TsBDGA), decreases monotonically along the lanthanide series.[22] Branched alkyl DGA ligands in combination with the suphonated BTP ligand in the aqueous phase are expected to
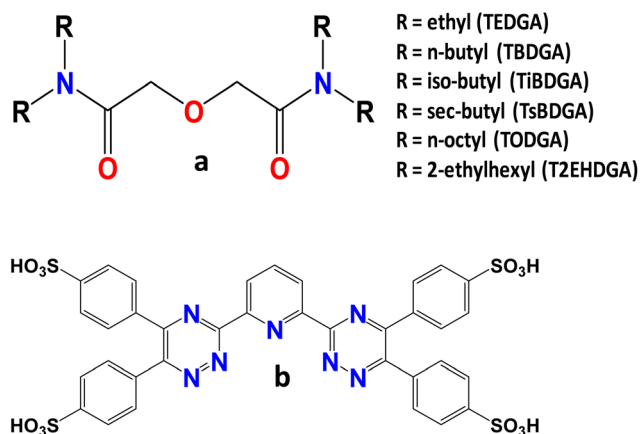
Table 1 Different 'N'-donor heterocyclic ligands evaluated for the Am^{3+}/Cm^{3+} separation

R	Backbone		
n-Pentyl	—	C_5BTBP	—
(dimethyl-triazine bicyclic)	CA-BTP	—	—
(CyMe4 triazine)	CyMe4BTP	CyMe4BTBP	CyMe4BTPhen
(Ph2P=O)	Ph2PyPO	—	—
(tBuPhP=O)	tBuPhPyPO	—	—

show selective extraction of Am^{3+} over Cm^{3+}. The insolubility of TsBDGA in the n-dodecane medium forced us to choose an alternative branched alkyl DGA derivative for the selective Am^{3+} extraction. N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA) has been studied extensively for actinide partitioning and possesses suitable properties from a process engineering point of view.[23–25] We, therefore, have chosen a combination of T2EHDGA and SO_3PhBTP for the separation studies of Am^{3+} and Cm^{3+}, and for the purpose of comparison similar experiments were performed with TODGA as well.

Experimental

Reagents and chemicals

$N,N,N'N'$-tetraoctyl diglycolamide (TODGA) and $N,N,N'N'$-tetra-2ethylhexyl diglycolamide (T2EHDGA) are synthesized at Thermax India Ltd using established procedures.[26] The detailed synthesis procedure of the hydrophilic 'N' donor heteropolycyclic ligand, SO_3PhBTP (Table 1) is provided in the ESI (Fig. S1–S14†). The purities of these ligands were confirmed by ^{1}H-NMR, FT-IR and mass spectrometry (HR-MS). The actinide tracers, ^{241}Am and ^{244}Cm were used from the laboratory stock solutions after confirming their radiochemical purities by alpha spectrometry. Both ^{241}Am and ^{244}Cm 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 (usually 0.5 mL) of the aqueous phase, containing the radiotracer of interest in 3 M HNO_3, and the organic phase, containing 0.1 M DGAs in n-dodecane, were equili-

Fig. 1 Schematic structure of (a) DGA ligands evaluated for Am^{3+}/Cm^{3+} separation and (b) SO_3PhBTP of the aqueous complexant used in this work.

R = ethyl (TEDGA)
R = n-butyl (TBDGA)
R = iso-butyl (TiBDGA)
R = sec-butyl (TsBDGA)
R = n-octyl (TODGA)
R = 2-ethylhexyl (T2EHDGA)

brated 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 minutes, followed by a radiometric assay of the separated aliquots (usually, 100 μL) removed 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.

Computational studies

In order to lower the computational cost, n-butyl (TBDGA) and iso-butyl (TiBDGA) derivatives of the diglycolamides were chosen as representative model ligands for TODGA and T2EHDGA, respectively. Geometries of the free ligands and their complexes with Am^{3+} and Cm^{3+} were optimized using def-SV(P) basis sets for all the atoms as implemented in the TURBOMOLE-7.2.1 suites of the program.[27] Geometry optimization of the Am^{3+} and Cm^{3+} complexes was carried out using 60 electron effective core potential (ECP) along with the corresponding def-SV(P) basis sets for the valence electrons.[28–31] The geometry optimization was done using the GGA functional BP86.[32,33] The single point energies of the free ligands and the complexes were, however, calculated using the hybrid functional B3LYP[34] and valence triple zeta (def-TZVP) basis sets[35] as implemented in the TURBOMOLE-7.2.1 package. All the calculations are performed in the gas phase because the complexes of both the metal ions (Am^{3+} and Cm^{3+} having very close ionic potential) have the same metal–ligand stoichiometries in the case of both DGA derivatives. Therefore, no difference is expected in the relative trends in their complexation ability with the incorporation of the solvent effect. Coordinates of the optimized structures of the free ligands and their Am^{3+} and Cm^{3+} complexes are provided in the ESI.†

Results and discussion

Liquid–liquid extraction studies

Effect of nitric acid concentration. Extraction studies of Am^{3+} and Cm^{3+} were carried out by varying the aqueous phase nitric acid concentration in the range of 0.5–2.5 M in the presence of 5 mM SO_3PhBTP at a fixed TODGA and T2EHDGA concentration of 0.2 M in n-dodecane (Fig. 2). The extraction of both metal ions increased monotonically with increasing nitric acid concentrations in the case of both DGA derivatives. Therefore, a distribution ratio of 2.5 M HNO_3 was reported at a DGA concentration of 0.05 M. Increasing extraction with increasing nitric acid concentration is the combined effect of increasing the extraction efficiency of these DGA derivatives and weaker complexation ability of the SO_3PhBTP present in the aqueous phase. In the case of TODGA, no difference in the distribution ratio values was observed throughout the acidity range studied with an S.F. value close to 1. In the case of T2EHDGA, however, Am^{3+} was extracted with marginally higher selectivity over Cm^{3+} with S.F. (D_{Am}/D_{Eu}) value in the range of 1.5–2.0 in the acidity range of 0.5–2.0 M with the highest S.F. value obtained at 1 M HNO_3. Extraction of both metal ions was, however, low at 0.5 and 1.0 M HNO_3 with D values less than 1, whereas at 2.0 M HNO_3, the D values were too high and could not be found suitable because of their mutual separation. Subsequent studies were, therefore, carried out at 1.5 M HNO_3 where the D values were close to 1, and by tuning the other experimental conditions, suitable conditions for their mutual separation could be achieved. To compare the selectivity of T2EHDGA in the absence of SO_3PhBTP, extraction studies of both Am^{3+} and Cm^{3+} were carried out from 1.5 M HNO_3 at varying T2EHDGA concentration, and the highest S.F. of 1.13 was achieved at a T2EHDGA concentration of 0.2 M (Fig. S15 in ESI†). This clearly indicates that there is marginal
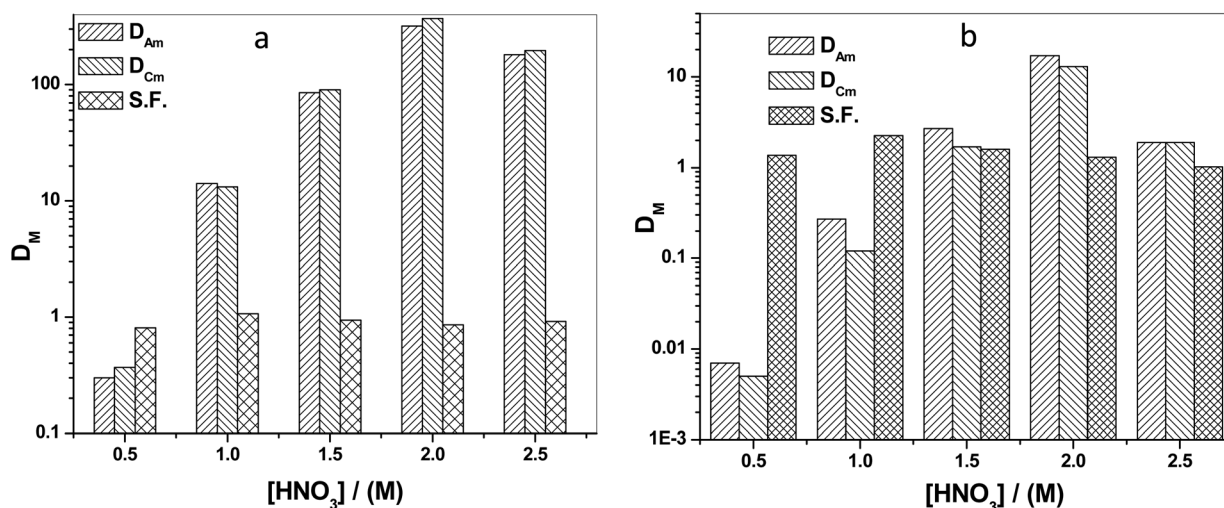

Fig. 2 Effect of nitric acid concentration on the extraction behaviour of Am(III) and Cm(III); (a) TODGA (0.2 M, 0.05 M for 2.5 M HNO_3) in n-dodecane, 0.005 M SO_3PhBTP in varying HNO_3 medium; (b) T2EHDGA (0.2 M, 0.05 M for 2.5 M HNO_3), 0.005 M SO_3PhBTP in varying HNO_3 medium.

enhancement of selectivity using T2EHDGA in the presence of SO$_3$PhBTP in the aqueous phase.

Effect of diluents. Organic diluents play a significant role in controlling the extraction behavior of the metal ions.[36,37] It is, therefore, of interest to evaluate different diluents for the extraction of Am^{3+} and Cm^{3+} with the DGA derivatives in the presence of SO$_3$PhBTP in the aqueous phase. Besides the common aliphatic hydrocarbon, n-dodecane, a series of aromatic hydrocarbon solvents was chosen as the organic diluents for the Am^{3+}/Cm^{3+} separation study. In the case of both TODGA and T2EHDGA, the extraction efficiency increased in the following order toluene: < tBu-benzene < Tri-iPr-Benzene < n-dodecane. This clearly suggests that increasing the extractability of both extractants increases as the proportion of aliphatic carbon atoms in the diluent molecule increases. The dielectric constant values change from 2.38 for toluene to 2.012 for n-dodecane; the extracted efficiency increases significantly when the diluent is changed from toluene to n-dodecane, which indicates that the polarity and other properties of the diluents play a major role in controlling the extraction behaviour in the present case. The solubility parameters, however, decrease from toluene to n-dodecane, suggesting higher solvency of toluene compared to n-dodecane,[38] which leads to higher ligand solvation of the ligand molecules in the toluene medium compared to that in the n-dodecane. Therefore, the complexation of the ligand with the metal ions is less energy expensive in the n-dodecane medium compared to that in the toluene medium, and this can result in higher extraction in the n-dodecane medium as observed from the solvent extraction study. Among the aromatic diluents, increasing alkyl substitutions in the benzene ring favoured the extraction of both metal ions (Fig. 3). Despite the highest S.F. value in the solvesso-100, n-dodecane was chosen for further studies considering the most suitable extraction efficiency in this medium.

Effects of DGA and SO$_3$PhBTP concentrations. To understand the extraction behavior of any metal ion, it is essential to identify the species extracted in the organic phase. The distribution ratio of both metal ions was, therefore, measured as a function ligand (DGA in the organic and SO$_3$PhBTP in the aqueous phase) concentration at a fixed HNO$_3$ concentration of 1.5 M in the presence of 0.007 M SO$_3$PhBTP (Fig. 4a). However, the noninteger slope values probably explained based on the extraction of mixed species, viz. the slope value of 2.62–2.78 in the case of DGA variation suggest the extraction of 1 : 2 complex along with the 1 : 3 complexes. SO$_3$PhBTP variation experiments, however, show slope values in the range of 1.69–1.96, suggesting a small contribution of 1 : 1 complexes along with their 1 : 2 complexes (Fig. 4b), which agrees with the literature report.[39] Stability constant values for the 1 : 2 complexes of Am^{3+} and Cm^{3+} with SO$_3$PhBTP were also determined from the intercept of the plot of $\log[D_0/(D-1)]$ vs. $\log$[SO$_3$PhBTP] (Fig. S16†). Details of the calculations are provided in the ESI.† The results clearly show that only the 1 : 2 complexes with $\log \beta$ values of 6.15 ± 0.09 and 6.45 ± 0.15 were observed for Am^{3+} and Cm^{3+}, respectively, in the SO$_3$PhBTP concentration range studied, which is comparable with the stability constant value reported in the literature for the 1 : 2 complex of Cm^{3+}.[40] Table 2 shows different solvent systems involving 'N' donor heteropolycyclic and DGA-based ligands and their performance for the Am^{3+}/Cm^{3+} separation. Tetradentate bistriazinyl bipyridine (BTBP) or phenanthroline (BTPhen) derivatives always showed a preference for Am^{3+} over Cm^{3+}, which was exploited for the selective Am^{3+} extraction with improved selectivity by employing aqueous soluble Cm^{3+} selective DGA derivative (TEDGA). Similarly, hydrophilic BTBP or BTPhen derivatives (SO$_3$PhBTBP or SO$_3$PhBTPhen), being Am^{3+} selective, were chosen as the aqueous complexant in combination with TODGA as the lipophilic extract for the selective extraction of Cm^{3+}.[19,20] However, selective Cm^{3+} extraction was performed using hydrophobic DGA ligands
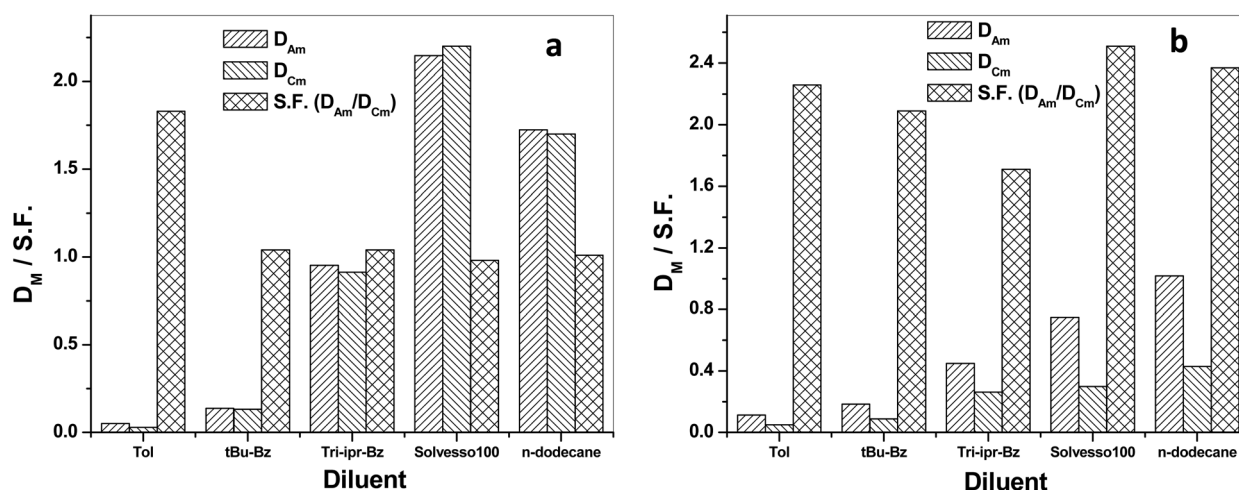

Fig. 3 Effect of diluents on the extraction behaviour of Am(III) and Cm(III); (a) 0.2 M TODGA, 0.007 M SO$_3$PhBTP; 1 M HNO$_3$; (b) 0.2 M T2EHDGA, 0.007 M SO$_3$PhBTP; 1.5 M HNO$_3$.
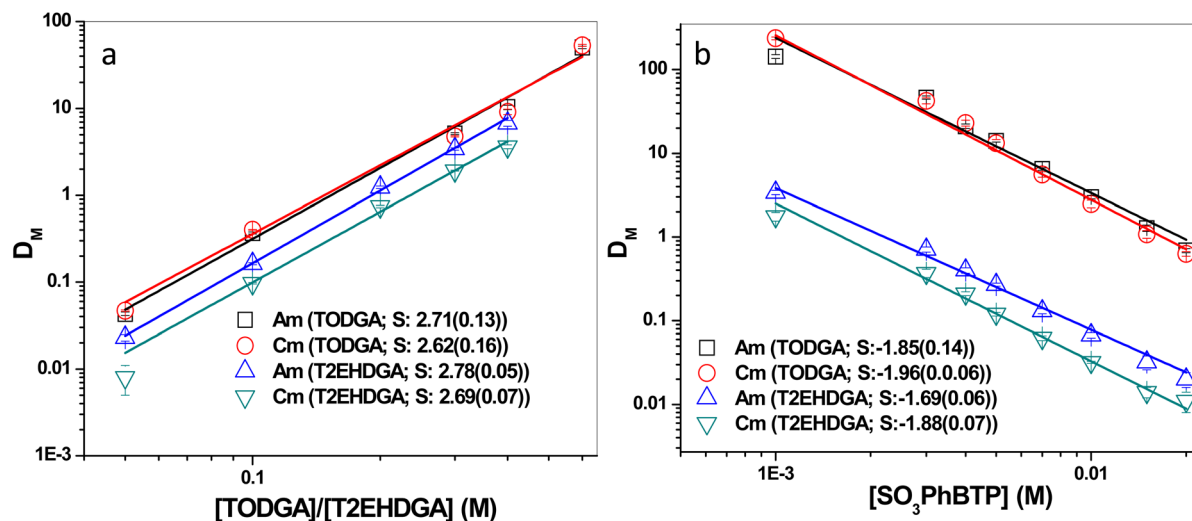
Fig. 4 (a) Effect of DGA concentration on the extraction behaviour of Am(III) and Cm(III) (Org. phase TODGA or T2EHDGA in *n*-dodecane; Aq. phase: 1 M HNO_3 (for TODGA) and 1.5 M HNO_3 (for T2EHDGA) containing 0.007 M SO_3PhBTP). (b) Effect of SO_3PhBTP concentration on the extraction behaviour of Am(III) and Cm(III) (Org. phase 0.2 M TODGA or T2EHDGA in *n*-dodecane; Aq. phase: 1.5 M HNO_3 containing SO_3PhBTP).

Table 2 Comparison of various DGA-based systems evaluated for Am^{3+}/Cm^{3+} separation studies

Lig. system	Aq. phase	Selective for & D	S.F.	Ref.
5 mM C5BTBP in cyclohexanone	0.5 M HNO_3 + 0.5 M $NaNO_3$	Am^{3+} ($D_{Am} \sim 30$)	1.8	41
30 mM CA-BTP in TPH/1-octanol	0.1 M HNO_3 + 1.7 M NH_4NO_3	Cm^{3+} ($D_{Cm} \sim 7$)	1.5	42
10 mM CyMe4BTPhen in [A336][NO_3]	17.5 mM TEDGA in 1 M HNO_3	Am^{3+} ($D_{Am} = 3.48$)	3.9	43
1 mM *t*BuPhPyPO in nitrobenzene	1 M HNO_3	Am^{3+} ($D_{Am} < 0.2$)	1.3	44
1 mM Ph_2PyPO in nitrobenzene	1 M HNO_3	Am^{3+} ($D_{Am} > 30$)	3.5	44
0.2 M TODGA in 5% octanol/TPH	20 mM SO_3PhBTPhen in 0.01–1 M HNO_3	Cm^{3+} ($D_{Cm} < 1$ at <0.5 M HNO_3; >1 at >0.5 M HNO_3)	2.4–4.5	19
0.2 M TODGA in 5% octanol/Exxsol D80	20 mM SO_3PhBTBP in 1 M HNO_3	Cm^{3+} ($D_{Cm} \sim 6$)	$\sim$2	20
0.2 M TODGA in 5% octanol/TPH	20 mM SO_3PhBTP in 1 M HNO_3	No selectivity	$\sim$1	39
0.2 M T2EHDGA in *n*-dodecane	7 mM SO_3PhBTP in 1.5 M HNO_3	Am^{3+} ($D_{Am} = 1.08$)	2.4	p.w.
0.2 M TODGA in *n*-dodecane	7 mM SO_3PhBTP in 1.5 M HNO_3	No selectivity	$\sim$1	p.w.
20 mM TODGA in octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{Cm} \sim 0.8$)	1.2	14
20 mM TnBDGA in octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{Cm} \sim 4$)	1.5	14
20 mM TiBDGA in octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{Cm} \sim 1.5$)	1.3	14
20 mM TsBDGA in octanol/TPH (40/60)	1 M HNO_3	Cm^{3+} ($D_{Cm} \sim 50$)	1.1	14

(TODGA) in the presence of Am^{3+} selective hydrophilic BTBP or BTPhen derivatives taken in the aqueous phase.

Role of temperature

To gain a deeper understanding of the separation behaviour of Am^{3+} and Cm^{3+} using these two DGA derivatives, temperature-dependent extraction studies were carried out in the absence and presence of SO_3PhBTP in the aqueous phase. Decreasing extraction with increasing temperature was observed for all the systems (Fig. 5), suggesting the exothermic nature of the extraction process in both the absence and presence of SO_3PhBTP in the aqueous phase irrespective of branching in the alkyl chain of the DGA ligands. The extraction constant values (K_{ex}) were calculated as per the equations mentioned in the ESI† at different temperature values plotted against the inverse of temperature in the Kelvin scale ($1000/T$) (Fig. 6a and b). The enthalpy (ΔH), Gibb's free energy (ΔG) and entropy

(ΔS) of the extraction of both the metal ions with TODGA and T2EHDGA in the absence and presence were calculated using vant Hoff's equation, as described in the ESI,† and the results are tabulated in Table 3. The results show that the enthalpy of the extraction of both the metal ions by the DGA ligands (TODGA and T2EHDGA) in the absence of SO_3PhBTP (in the aqueous phase) falls in the range of -22 to -26 kJ mol^{-1}, whereas in the presence of SO_3PhBTP (in the aqueous phase), the enthalpy of extraction reduced significantly to fall in the range of -16 to -19 kJ mol^{-1}. This reduction in the extraction enthalpy could be attributed to the competition from SO_3PhBTP for complexation with the metal ions, which ultimately makes the extraction of Am^{3+} and Cm^{3+} by the DGA ligands enthalpically less favored. Kajan *et al.* reported enthalpy values of >-100 kJ mol^{-1} for the extraction of both Am^{3+} and Eu^{3+} from 4 M HNO_3 medium by TODGA.[45] Lower exothermicity in this study can be attributed to the low acidity
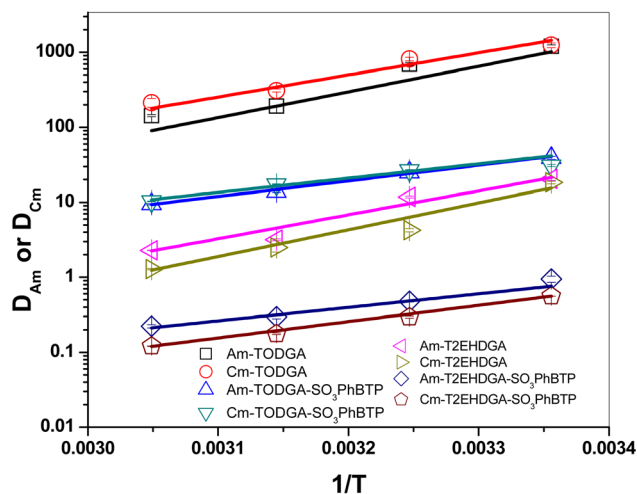
Fig. 5 Effect of temperature on the extraction of Am^{3+} and Cm^{3+} by TODGA or T2EHDGA in the absence and presence of SO_3PhBTP in the aqueous phase (Org. phase: 0.2 M TODGA or T2EHDGA in n-dodecane; Aq. phase: 1M HNO_3 in the absence or presence of 0.007 M SO_3PhBTP).

Table 3 Thermodynamic parameters for the extraction of Am^{3+} and Cm^{3+} by TODGA or T2EHDGA in the absence or presence of SO_3PhBTP in the aqueous phase (Org. phase: 0.2 M TODGA or T2EHDGA in n-dodecane; Aq. phase: 7×10^{-3} M SO_3PhBTP in 1 M HNO_3)

System	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	$\Delta\Delta G$
Am/TODGA	-22.8 ± 0.6	51.5 ± 0.4	-38.2 ± 0.5	0.09
Cm/TODGA	-24.2 ± 0.4	47.2 ± 0.6	-38.3 ± 0.8	
Am/TODGA/SO$_3$PhBTP	-16.9 ± 0.7	51.5 ± 0.9	-32.2 ± 0.6	-0.59
Cm/TODGA/SO$_3$PhBTP	-16.5 ± 0.5	50.7 ± 0.5	-31.7 ± 0.4	
Am/T2EHDGA	-25.6 ± 0.6	8.5 ± 0.6	-28.1 ± 0.7	-0.25
Cm/T2EHDGA	-25.5 ± 0.5	7.9 ± 0.3	-27.8 ± 0.5	
Am/T2EHDGA/SO$_3$PhBTP	-17.84	17.38	-23.02	-1.29
Cm/T2EHDGA/SO$_3$PhBTP	-18.75	10.00	-21.73	

ence of SO_3PhBTP in the aqueous phase, and this was due to the entropy effect where the extraction of Am^{3+} was much more entropy favoured compared to that of Cm^{3+}, leading to more selectivity for Am^{3+} over Cm^{3+}.

Computational studies

As the representative of TODGA and T2EHDGA, the n-butyl and iso-butyl derivatives of DGA were chosen to reduce the computational cost without losing much difference in their relative bonding features and energetics. Structures of the free ligands and their Am^{3+}/Cm^{3+} complexes with a metal-to-ligand ratio of 1 : 3 observed from the solvent extraction studies are shown in Fig. 7 and S17.† Different bond distances in both the ligand molecules are found to be very similar except for the distances between the amidic 'N' and alkyl 'C' atoms ($d_{N-CH_2(alkyl)}$), which are found to be marginally longer in the case of TiBDGA compared to those in the case of TBDGA, which is the effect of branching in the β carbon atom in the alkyl chain. The same feature is also noticed in their complexes with both Am^{3+} and Cm^{3+} ions, where ($d_{N-CH_2(alkyl)}$)

of the aqueous phase (1 M HNO_3), where more energy is required for the dehydration of the metal ions. All the extraction processes in this work show positive entropy changes. In the absence of SO_3PhBTP in the aqueous phase, the extraction by TODGA was found to be more entropy favoured compared to that by T2EHDGA in the case of both metal ions. This suggests that the branching in the alkyl chain in the DGA ligands leads to more steric hindrance in the 1 : 3 metal complex, which results in less entropy-favoured extraction in the case of T2EHDGA. The selectivity between Am^{3+} and Cm^{3+} can be explained by the difference in the change in their respective Gibb's free energy values ($\Delta\Delta G$). This $\Delta\Delta G$ value was found to be highest in the case of T2EHDGA in the pres-
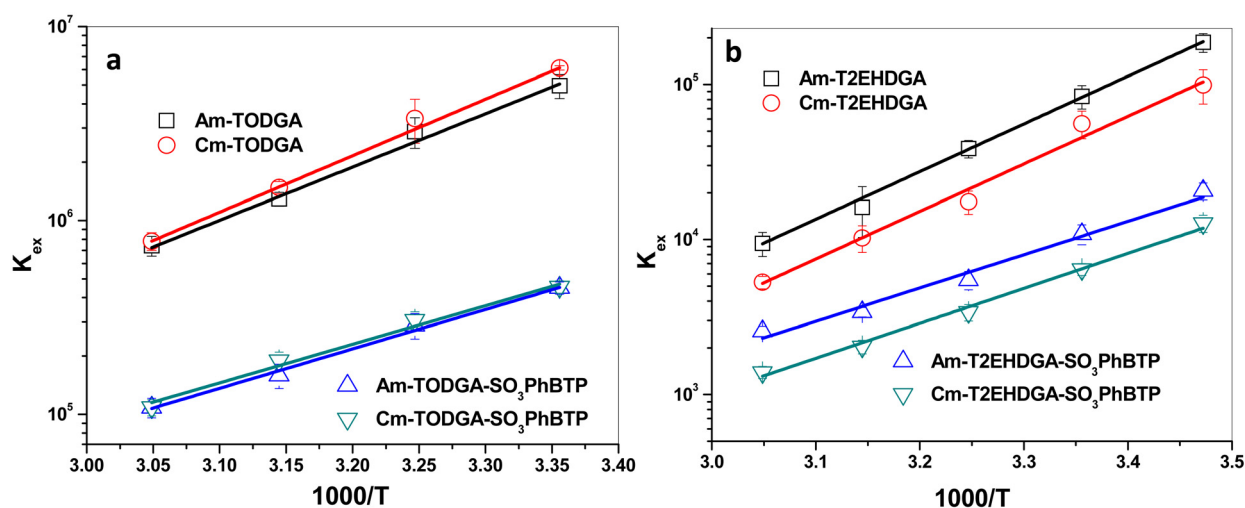

Fig. 6 Effect of temperature on the extraction constant (K_{ex}) of Am^{3+} and Cm^{3+} by TODGA (a) or T2EHDGA (b) in the absence and presence of SO_3PhBTP in the aqueous phase (Org. phase: 0.2 M TODGA or T2EHDGA in n-dodecane; Aq. phase: 1 M HNO_3 in the absence or presence of 0.007 M SO_3PhBTP).
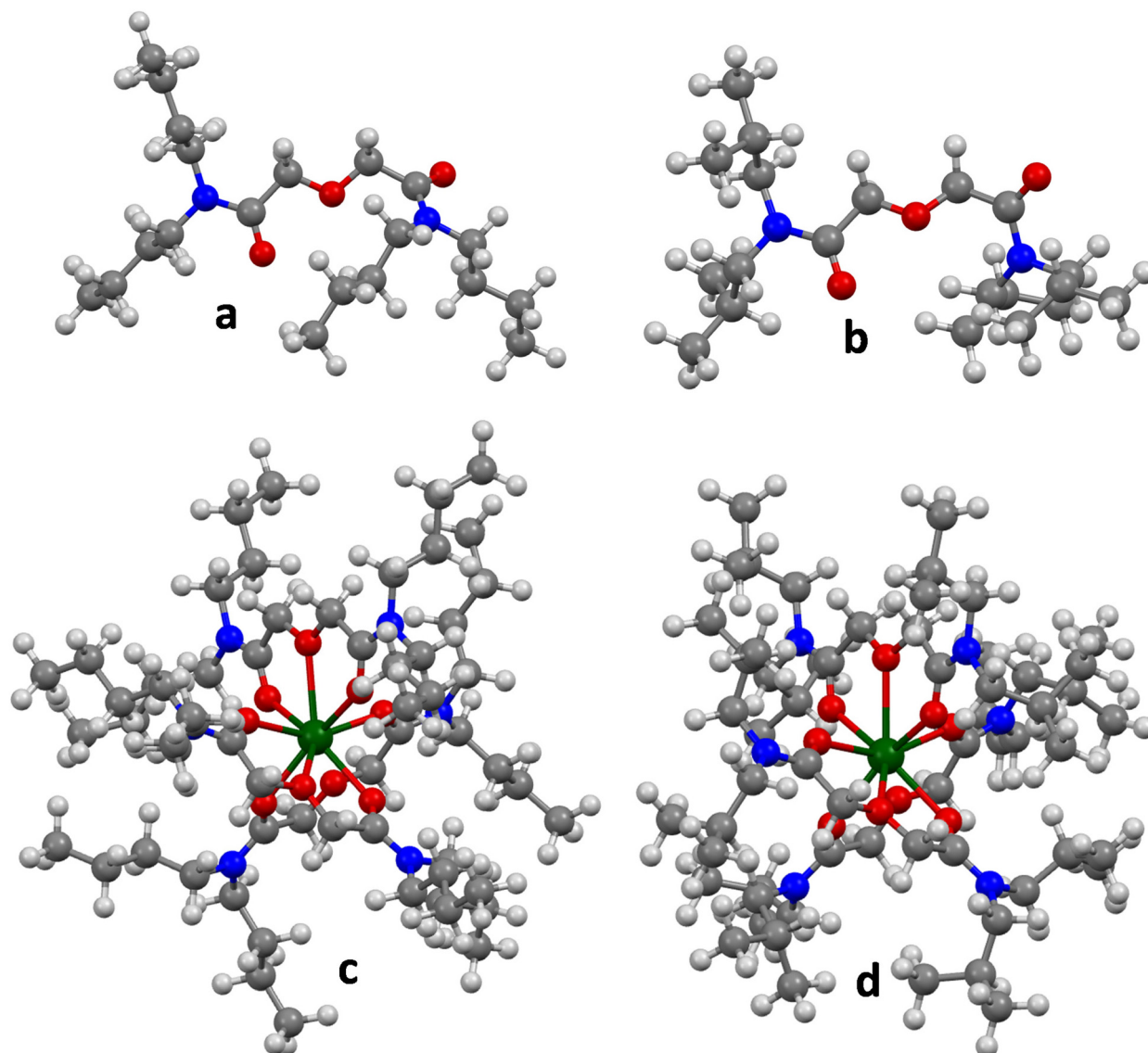
Fig. 7 Optimized structures of TBDGA (a) and TiBDGA (b) and their Am(III)/Cm(III) complexes (TBDGA complex (c); TiBDGA complex (d)) at the BP86/SVP level of theory (Green: Am/Cm; Red: Oxygen; Blue: Nitrogen; Dark grey: Carbon; Light grey: Hydrogen).

values are found to be higher in the case of the TiBDGA complexes compared to that in the TBDGA complexes (Table 4). The bond distances between the central metal ion and the amidic 'O' atoms ($d_{M-O(amide)}$) were found to be similar in the Am^{3+} and Cm^{3+} complexes. However, in the case of the TiBDGA complexes, the $d_{M-O(amide)}$ values were found to be higher compared to those in the case of TBDGA complexes for both metal ions. The distances between the metal ion and

Table 4 Different bond distances (Å) in the free ligands and their Am^{3+}/Cm^{3+} complexes obtained at the BP86/def-SVP level of theory

Ligand System	TBDGA			TiBDGA		
	L	Am(L)$_3$$^{3+}$	Cm(L)$_3$$^{3+}$		Am(L)$_3$$^{3+}$	Cm(L)$_3$$^{3+}$
$d_{M-O(amide)}$	—	2.434 ± 0.016	2.432 ± 0.004	—	2.442 ± 0.015	2.439 ± 0.006
$d_{M-O(ether)}$	—	2.638 ± 0.010	2.624 ± 0.001	—	2.630 ± 0.012	2.626 ± 0.008
$d_{C=O(amide)}$	1.233 ± 0.004	1.264 ± 0.001	1.264 ± 0.001	1.233 ± 0.004	1.264 ± 0.001	1.264 ± 0.001
$d_{C-O(ether)}$	1.408 ± 0.009	1.421 ± 0.002	1.421 ± 0.001	1.409 ± 0.009	1.421 ± 0.002	1.421 ± 0.001
$d_{C-N(amide)}$	1.379 ± 0.004	1.342 ± 0.001	1.342 ± 0.001	1.379 ± 0.003	1.343 ± 0.001	1.343 ± 0.001
$d_{N-CH_2(alkyl)}$	1.467 ± 0.003	1.479 ± 0.001	1.479 ± 0.001	1.470 ± 0.002	1.482 ± 0.001	1.481 ± 0.001

Table 5 Analysis of natural charges in the Am^{3+} and Cm^{3+} complexes of nBuDGA and iBuDGA and energetics of the complexation (complexation energies calculated as per eqn (1)[a] and (2)[b] determined by single point calculations at the B3LYP/def-TZVP level of theory on the geometry optimized structure at the BP86/def-SVP level of theory

Complex	q_M	Δq_L	Nat. electronic config. (An)	Complexation energy (ΔE) in kJ mol^{-1}	$\Delta\Delta E_{(Cm-Am)}$
Am-TBDGA	1.961	−0.346	$7s^{0.08}6d^{0.38}7d^{0.02}5f^{6.03}$	−604.2[a]	−31.3[a]
				−256.7[b]	
Cm-TBDGA	2.006	−0.331	$7s^{0.09}6d^{0.38}7d^{0.02}5f^{6.99}$	−635.5[a]	−2.5[b]
				−259.2[b]	
Am-TiBDGA	1.966	−0.345	$7s^{0.08}6d^{0.37}7d^{0.02}5f^{6.03}$	−580.3[a]	−32.4[a]
				−233.0[b]	
Cm-TiBDGA	2.009	−0.330	$7s^{0.09}6d^{0.38}7d^{0.02}5f^{6.99}$	−612.7[a]	−2.5[b]
				−235.5[b]	

ethereal 'O' atoms ($d_{M-O(ether)}$) were found to be marginally higher in the Am^{3+} complexes compared to those in the Cm^{3+} complexes in the case of both DGA ligands. This is, probably, an indication of the higher ionic radius of Am^{3+} compared to that of Cm^{3+}.[5] To further understand the bonding features in the complexes, natural charges were calculated using natural population analysis.[46,47] The results showed higher ligand-to-metal electron transfer (Δq_L) in the case of Am^{3+} complexes of both DGA derivatives. Lower charge transfer in the case of Cm^{3+} complexes could be attributed to the half-filled electronic configuration of the 'f' orbitals of Cm^{3+}, which makes them reluctant to accept further electrons, as depicted in Table 5. Higher ligand-to-metal charge transfer in the case of Am^{3+} complexes compared to that in the case of the Cm^{3+} complexes has been well reported in the literature.[48] There is no difference in the extent of change transfer in the complexes of the two DGA derivatives (TBDGA and TiBDGA) with a particular metal ion (Am^{3+} or Cm^{3+}) (Table 5). This clearly suggests that there is no significant difference in the bonding features of these two DGA derivatives. Interaction energies for complexation can provide further details on the bonding and relative selectivity of the ligand molecules.[49,50] In this work, therefore, two general chemical reactions (eqn (1) and (2)) were considered in the absence and presence of competition from bis-triazinyl pyridine (BTP). The coordination sites of the SO_3PhBTP are well reported through the three 'N' atoms (one from pyridine and two from two triazine rings) without the direct involvement of any of the suplphonic acid or phenyl group in the bonding. Simple BTP units were considered for the complexation to reduce the computational cost. The complexation energies were calculated for the following complexation equilibria:

$$M(H_2O)_9{}^{3+} + 3L = ML_3{}^{3+} + 9H_2O \tag{1}$$

$$M(BTP)_2(H_2O)_3{}^{3+} + 3L = ML_3{}^{3+} + 2BTP + 3H_2O \tag{2}$$
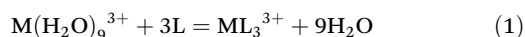
where M^{3+} is Am^{3+} or Cm^{3+} and L is TBDGA or TiBDGA. The complexation energies (ΔE) were calculated as the difference in the total internal energies of the products to those of the reactants. The results suggest that the complexation energies are lower for TiBDGA compared to TBDGA for both metal ions, which is reflected in the lower extraction capability of the branched DGA (T2EHDGA) ligand compared to that of TODGA,

as evident from the solvent extraction studies. The differences in the complexation energies of Cm^{3+} to that of Am^{3+} complexes ($\Delta\Delta E$) were found to be less negative in the presence of competition from BTP, which can be attributed to the higher affinity of BTP towards Cm^{3+} over Am^{3+}, as reported in the literature.[21] Among the complexes of the two metal ions, Cm^{3+} forms stronger complexes than Am^{3+} with both the DGA ligands, and $\Delta\Delta E$ values were found to be the same for both ligands. This suggests that in the absence of BTP, both the DGA ligands should be selective towards Cm^{3+} over Am^{3+}, and the selectivity would be lower in the presence of the competition from BTP. From the trends in the ΔE values, no difference in extraction selectivity is expected when one incorporates branching at the β carbon atom of the alkyl chain of the DGA ligands. However, the selectivity for Am^{3+} over Cm^{3+} in the case of T2EHDGA in the presence of SO_3PhBTP as the aqueous complexant can be attributed to the difference in the entropy factor responsible for the extraction, as observed in the temperature-dependent extraction studies.

Conclusions

TODGA and its analogous extractant with branching at the β-carbon atom, *i.e.*, T2EHDGA were evaluated for the separation of Am^{3+} and Cm^{3+} from nitric acid medium in the presence and absence of a 'N' donor aqueous complexant, SO_3PhBTP. A reversal of extraction selectivity was observed when we switched over from TODGA to T2EHDGA in the presence of SO_3PhBTP in the aqueous phase. The results showed that among the various diluents studied, n-dodecane was found to be most suitable, where an S.F. value of 2.4 was achieved for Am^{3+} over Cm^{3+} using 0.2 M T2EHDGA in n-dodecane from 1.5 M HNO_3 medium in the presence of 7 mM SO_3PhBTP. In the case of both the DGA ligands, both the metal ions are extracted as a 1:3 complex, while in the aqueous phase, both the metal ions were present as their 1:2 complexes with SO_3PhBTP for which the stability constant values were also determined. Temperature-dependent solvent extraction studies indicated no significant difference in the enthalpy of extraction in the case of the two DGA derivatives. The Am^{3+} selectivity of T2EHDGA in the presence of SO_3PhBTP in the aqueous phase could be attributed to the difference in

the entropy change for the extraction of these two metal ions in the case of the two DGA ligands. This observation of no enthalpy-driven selectivity was corroborated by computational studies. Further studies with more branching in the α or β carbon atoms of the alkyl chain in the DGA ligands in the combination of the BTP, BTBP or BTPhen derivatives, which are hydrophilic such as SO_3PhBTP, $SO_3PhBTBP$ and $SO_3PhBTPhen$ as the aqueous complexants, will be interesting for the separation of Am^{3+} and Cm^{3+}, which will be taken up in the future.

Conflicts of interest

There are no conflcts to declare.

Acknowledgements

References

1 L. Koch, *J. Less-Common Met.*, 1986, **122**, 371–382.
2 P. A. Baisden and G. R. Choppin, *Radiochemistry and Nuclear Chemistry*, 2007, pp. 1–63.
3 R. Isaacson and B. Judson, *Ind. Eng. Chem. Process Des. Dev.*, 1964, **3**, 296–301.
4 G. Uchiyama, S. Fujine, S. Hotoku and M. Maeda, *Nucl. Technol.*, 1993, **102**, 341–352.
5 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751–767.
6 P. Zsabka, A. Wilden, K. Van Hecke, G. Modolo, M. Verwerft and T. Cardinaels, *J. Nucl. Mater.*, 2023, **581**, 154445.
7 P. Matveev, P. K. Mohapatra, S. N. Kalmykov and V. Petrov, *Solvent Extr. Ion Exch.*, 2020, 1–35.
8 T. L. Authen, J.-M. Adnet, S. Bourg, M. Carrott, C. Ekberg, H. Galán, A. Geist, P. Guilbaud, M. Miguirditchian, G. Modolo, C. Rhodes, A. Wilden and R. Taylor, *Sep. Sci. Technol.*, 2022, **57**, 1724–1744.
9 A. Geist, J.-M. Adnet, S. Bourg, C. Ekberg, H. Galán, P. Guilbaud, M. Miguirditchian, G. Modolo, C. Rhodes and R. Taylor, *Sep. Sci. Technol.*, 2021, **56**, 1866–1881.
10 Z. Wang, X. Dong, Q. Yan, J. Chen and C. Xu, *Anal. Chem.*, 2022, **94**, 7743–7746.
11 G. Modolo, P. Kluxen and A. Geist, *Radiochim. Acta*, 2010, **98**, 193–201.
12 M. P. Jensen, R. Chiarizia, J. S. Ulicki, B. D. Spindler, D. J. Murphy, M. M. Hossain, A. Roca-Sabio, A. de Blas and T. Rodríguez-Blas, *Solvent Extr. Ion Exch.*, 2015, **33**, 329–345.
13 C. Rostaing, C. Poinssot, D. Warin, P. Baron and B. Lorraina, *Proc. Chem.*, 2012, **7**, 367–373.
14 S. Chapron, C. Marie, G. Arrachart, M. Miguirditchian and S. Pellet-Rostaing, *Solvent Extr. Ion Exch.*, 2015, **33**, 236–248.
15 H. Suzuki, Y. Tsubata and T. Matsumura, *Anal. Sci.*, 2017, **33**, 239–242.
16 Y. Ban, H. Suzuki, S. Hotoku, N. Tsutsui, Y. Tsubata and T. Matsumura, *Solvent Extr. Ion Exch.*, 2019, **37**, 489–499.
17 Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu and Y. Morita, *Solvent Extr. Ion Exch.*, 2014, **32**, 179–188.
18 Y. Sasaki, M. Kaneko, Y. Ban and H. Suzuki, *J. Nucl. Sci. Technol.*, 2023, 1–11.
19 P. Kaufholz, G. Modolo, A. Wilden, F. Sadowski, D. Bosbach, C. Wagner, A. Geist, P. J. Panak, F. W. Lewis and L. M. Harwood, *Solvent Extr. Ion Exch.*, 2016, **34**, 126–140.
20 C. Wagner, U. Müllich, A. Geist and P. J. Panak, *Solvent Extr. Ion Exch.*, 2016, **34**, 103–113.
21 A. Bhattacharyya, S. A. Ansari, N. S. Karthikeyan, C. Ravichandran, B. Venkatachalapathy, T. S. Rao, H. Seshadri and P. K. Mohapatra, *Dalton Trans.*, 2021, **50**, 7783–7790.
22 A. Bhattacharyya, A. S. Kanekar, R. J. M. Egberink, W. Verboom, J. Huskens and P. K. Mohapatra, *New J. Chem.*, 2022, **46**, 18543–18550.
23 R. Gujar, S. Ansari, M. Murali, P. Mohapatra and V. Manchanda, *J. Radioanal. Nucl. Chem.*, 2010, **284**, 377–385.
24 R. B. Gujar, S. A. Ansari, P. K. Mohapatra and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2010, **28**, 350–366.
25 R. B. Gujar, S. A. Ansari, D. R. Prabhu, D. R. Raut, P. N. Pathak, A. Sengupta, S. K. Thulasidas, P. K. Mohapatra and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2010, **28**, 764–777.
26 S. Guoxin, L. Min, C. Yu, Y. Meilong and Y. Shaohong, *Solvent Extr. Ion Exch.*, 2010, **28**, 482–494.
27 TURBOMOLE V7.0 a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, TURBOMOLE GmbH, since 2007; available from https://www.turbomole.com.
28 K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119–124.
29 M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1989, **90**, 1730–1734.
30 W. Küchle, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1994, **100**, 7535–7542.
31 X. Cao, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2003, **118**, 487–496.
32 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
33 J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **33**, 8822.
34 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785.
35 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
36 Y. Marcus, *Solvent Extr. Ion Exch.*, 1989, **7**, 567–575.
37 Y. Cui, Y.-q. Wang, M.-p. Pang, L.-n. Zhang, H.-f. Zhou, Q.-y. Dang and G.-x. Sun, *Hydrometallurgy*, 2015, **152**, 1–6.

38 F. Wang, T. J. Threatt and F. M. Vargas, *Fluid Phase Equilib.*, 2016, **430**, 19–32.

39 A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden and T. Zevaco, *Solvent Extr. Ion Exch.*, 2012, **30**, 433–444.

40 Ł. Steczek, M. Rejnis, J. Narbutt, M.-C. Charbonnel and P. Moisy, *J. Radioanal. Nucl. Chem.*, 2016, **309**, 891–897.

41 M. Nilsson, C. Ekberg, M. Foreman, M. Hudson, J. O. Liljenzin, G. Modolo and G. Skarnemark, *Solvent Extr. Ion Exch.*, 2006, **24**, 823–843.

42 S. Trumm, A. Geist, P. J. Panak and T. Fanghänel, *Solvent Extr. Ion Exch.*, 2011, **29**, 213–229.

43 P. Zsabka, K. V. Hecke, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans and T. Cardinaels, *Solvent Extr. Ion Exch.*, 2020, **38**, 194–211.

44 P. Matveev, N. Borisova, N. Andreadi, G. Zakirova, V. Petrov, E. Belova, S. Kalmykov and B. Myasoedov, *Dalton Trans.*, 2019, **48**, 2554–2559.

45 I. Kajan, M. Florianová, C. Ekberg and A. V. Matyskin, *RSC Adv.*, 2021, **11**, 36707–36718.

46 A. E. Clark, J. L. Sonnenberg, P. J. Hay and R. L. Martin, *J. Chem. Phys.*, 2004, **121**, 2563–2570.

47 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.

48 Y. Liu, C.-Z. Wang, Q.-Y. Wu, J.-H. Lan, Z.-F. Chai, Q. Liu and W.-Q. Shi, *Inorg. Chem.*, 2021, **60**, 10267–10279.

49 L. Rulíšek and Z. Havlas, *J. Am. Chem. Soc.*, 2000, **122**, 10428–10439.

50 L. Rulíšek and Z. Havlas, *J. Phys. Chem. A*, 2002, **106**, 3855–3866.