

Complexation of novel diglycolamide functionalized calix[4]arenes: Unusual extraction behaviour, transport, and fluorescence studies†

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Three diglycolamide functionalized calix[4]arenes (calix[4]-nDGA) were synthesized and evaluated for their extraction behaviour towards lanthanide/actinide ions. Exceptionally high D_{Am} and D_{Pu} values indicate these radiotoxic elements can be selectively removed from nuclear waste solutions. Transport and laser induced fluorescence studies indicated strong complexation of the trivalent metal ions with the calix[4]-4DGA ligand.

Diglycolamide (DGA) extractants have been reported to be the most promising reagents for 'actinide partitioning', a key step in high level waste remediation for the mitigation of the radiotoxic hazards of long-lived radionuclides.¹ The extraction property of diglycolamides was also reported to be unusual as compared to the common extractants for 'actinide partitioning' such as CMPO, DIDPA, and TRPO.² While these extractants mentioned above extract the actinide ions in the order $Pu^{4+} > UO_2^{2+} > Am^{3+}$, the diglycolamides extract in the order: $Am^{3+} > Pu^{4+} > UO_2^{2+}$.¹ This is rather unusual since the ionic potential of the trivalent actinide ion is much lower than that of the hexavalent or the tetravalent actinide ions and is explained on the basis of a reverse micelle mechanism, which has been supported by small angle neutron scattering³ and dynamic light scattering data.⁴ The proposed mechanism involves extraction of the metal ion into the core of the reverse micelle, which contains four units of the diglycolamide at 3 M HNO_3 and the number of DGA molecules in the reverse micelle depended on the feed acidity. Zhu *et al.*⁵ have studied the extraction of about 75 elements with TODGA and reported a unique selectivity based on the cation size. The reverse micelle formation is highly dependent on the diluent properties and hence, the extraction behaviour changes drastically with increasing diluent polarity.^{1a,3}

Our earlier studies with DGA-based tripodal ligands have shown exceptional extraction and transport properties.^{6,7} Ligands

mounted on calixarenes have shown significant enhancement in the complexation ability.⁸ Moreover, if the functional groups are appended onto a calixarene framework, the energy spent on bringing the ligands together for complexation is saved and the reaction becomes favourable.⁹ It was of interest, therefore, to synthesize DGA ligands mounted on a framework such as a calix[4]arene so that the diluent dependence can be discounted. The present paper deals with studies on the extraction of lanthanide and actinide ions with three novel calix[4]arene-DGA extractants (L_I , L_{II} , L_{III}) synthesized for the first time (see Fig. 1).¹⁰ Flat sheet supported liquid membrane transport studies as well as the fluorescence spectral behaviour of their Eu^{3+} complexes are also reported. The solvent extraction studies were carried out using mM concentrations of the extractants and a reasonably high extraction of Am^{3+} , Pu^{3+} , and Pu^{4+} was observed as compared to the distribution ratio (D) values expected for a diglycolamide extractant (Table 1).^{1,7,11}

Exceptionally high distribution ratio values were obtained with the tetravalent and trivalent actinide and lanthanide ions compared to reagents such as TODGA (where D values of the actinide ions were significantly lower, Table 1), while the hexavalent uranyl ion and Cs^+ and Sr^{2+} ions were practically unextracted. The higher extraction of the tetravalent as compared to the trivalent actinide ions is unusual for the DGA-based extractants and possibly implies a different complex formation mechanism. Nevertheless, the results indicate L_I can be used for the selective extraction of Am and Pu from nuclear waste solutions at about a 100 times lower extractant inventory. It was reported that TODGA extracts metal ions *via* a reverse micelle mechanism which may be responsible for the unusual extraction behaviour^{3a,5} while the higher extraction of Pu^{4+} as compared to Am^{3+} is as per the ionic potential trend. Though Cs^+ ion extraction was reported to be insignificant with the much studied DGA extractants such as TODGA and T2EHDGA, those reagents extract Sr^{2+} ion to a significant extent¹² making it necessary to search for a suitable decontamination step.¹³ Ligands L_{I-III} appear unique as they no longer show the preference for trivalent metal ions as displayed with TODGA and T2EHDGA, while at the same time Cs^+ and Sr^{2+} are not extracted to any significant extent making them potent for minor actinide partitioning. Ligand L_I is particularly interesting as it shows very high distribution ratio for the tetravalent and trivalent actinide (lanthanide) ions. Another unique feature is the relative non-extractability of the UO_2^{2+} ion, which is extracted to a

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† Electronic supplementary information (ESI) available: Solvent extraction data, transport data and fluorescence spectral data, synthesis of the reagents, *etc.*
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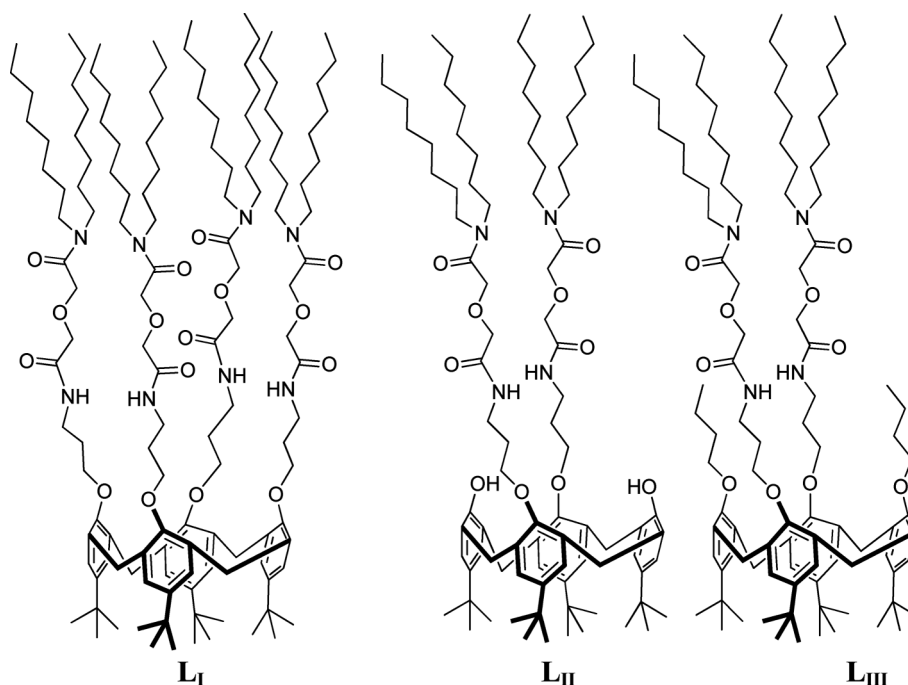


Fig. 1 Structural formulae of the three novel calix[4]arene-DGA extractants **L_I**, **L_{II}**, and **L_{III}**.

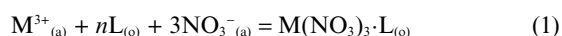
Table 1 Distribution data of some important actinide and fission product element ions relevant from the waste management point of view^a

Ligand ^b	Distribution coefficient						
	Am ³⁺	Pu ^{3+,c}	Pu ^{4+,d}	UO ₂ ²⁺	Eu ³⁺	Cs ⁺	Sr ²⁺
C-4-DGA (L_I)	26.5 ± 1.4	30.4 ± 0.8	67.9 ± 1.4	0.17 ± 0.01	155 ± 1.72	<0.001	0.023
C-2-DGA (L_{II})	1.06 ± 0.01	1.67 ± 0.00	6.86 ± 0.25	0.05 ± 0.01	5.28 ± 0.02	<0.001	<0.001
C-2-DGA-2-Bu (L_{III})	0.04 ± 0.01	0.29 ± 0.01	1.12 ± 0.10	0.04 ± 0.01	0.28 ± 0.01	<0.001	<0.001
TODGA	0.09 ± 0.01	0.03 ± 0.01	0.35 ± 0.03	<0.01	2.01 ± 0.02	<0.001	<0.001

^a Diluent: n-dodecane; Feed: 3 M HNO₃. ^b Concentration of the extractant: 3 × 10⁻³ M. ^c A mixture of hydrazine hydrate and hydroxylammonium nitrate was used as the reducing agent. ^d NaNO₂ was used as the holding oxidant.

relatively higher extent by the DGAs.¹ The insignificant extraction of the uranyl ion is probably due to the presence of the axial 'O' atoms and the stereochemical restrictions associated with the simultaneous complexation of the four DGA units. One of the proposed steps prior to minor actinide partitioning is the recovery of U, which can otherwise lead to significant hold up of the extractant as well as cause serious problems such as 'third phase formation', which can affect the hydrodynamics in plant scale operations. The present results show insignificant U extraction, making any prior U recovery step redundant. Moreover, extraction of PuO₂²⁺ was also found to be much lower (*D*-value with **L_I** is 1.06) as compared to both Pu³⁺ and Pu⁴⁺, suggesting that prior oxidation of Pu to the hexavalent state can be done to suppress Pu extraction.

The species extracted by these ligands were ascertained by a series of solvent extraction studies using a variety of diluents and n-dodecane resulted in fairly good *D*-values. The slopes of the linear regression fit lines of the log *D* vs log[**L_I**] plots are ~1 for Eu³⁺, while it changes to close to 2 when the ligands **L_{II}** and **L_{III}** were used for extraction.[†] The general extraction equilibrium is presented as eqn(1):



For all three ligands, Eu³⁺ was extracted to a greater extent than Am³⁺, which is in line with the observation for other DGA extractants.¹ However, the separation factor (*D_{Eu}*/*D_{Am}*) value with n-dodecane as the diluent (5.85) was somewhat lower than that reported with TODGA (9).^{1a} It was rather surprising that the more organophilic **L_{III}** resulted in lower extraction of the metal ions as compared to **L_{II}**, containing hydrophilic OH groups. This may be attributed to steric factors due to the presence of the *n*-butoxy groups, while forming the ML₂ type species.

Another interesting feature of the calix-DGA extractants was noticed during the flat sheet supported liquid membrane studies. While the extraction and stripping of Am³⁺ was satisfactory using **L_I** as the extractant and 3 M HNO₃ and 0.01 M HNO₃ as the feed and strip solutions, respectively the transport of the metal ion was negligible. On the other hand, when 0.01 M EDTA (pH 2) was used as the strip solution in the receiver phase, fast mass transfer resulting in ~90% Am³⁺ transport in 6 h was noticed (Fig. 2). The transport rates were drastically lower than those reported with tripodal DGA ligands with comparable extractant concentration.⁷ Though the slower transport rates in the present case can be partly attributed to the larger molar volume of the Am³⁺-**L_I** complex, it can also be due to slow kinetics of the metal ion release with either

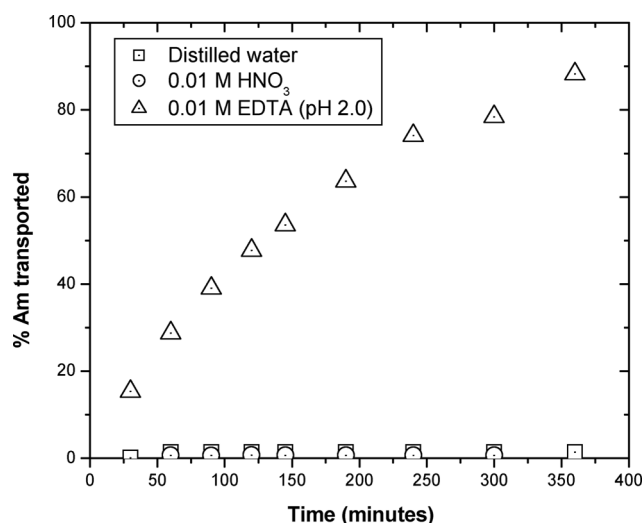


Fig. 2 Transport profiles of Am^{3+} using 1.13×10^{-3} M L_1 in n-dodecane as the carrier solvent. Feed: 3 M HNO_3 . Receiver: As indicated.

distilled water or 0.01 M HNO_3 as the strip solution in the receiver phase. On the other hand, EDTA can facilitate the decomplexation reaction due to its high stability constant with the actinide ion.¹⁴ Faster mass transfer with EDTA was also reported in our earlier work containing tripodal DGA as the carrier extractant.⁷

Laser induced fluorescence spectral studies were also carried out¹⁵ using 1×10^{-5} M Eu nitrate solution in 3 M HNO_3 diluted with acetonitrile (1 : 5). Emission spectra of Eu^{3+} for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (617 nm, electric dipole), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (592 nm, magnetic dipole) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (690 nm, electric dipole) indicated a significant enhancement in the fluorescence intensity in the presence of a comparable concentration of L_1 (Fig. 3). On the other hand, while a 10 times higher concentration of L_{II} showed a higher fluorescence efficiency than only the Eu^{3+} ion, very little change was seen when L_{III} was used as the complexing agent.[†] Moreover, lifetime data indicated formation of 1 : 1 complex species with L_1 , while the formation of 1 : 2 species was observed with both L_{II} as well as L_{III} (Table 2). Though the lifetime of Eu^{3+} in the absence of the ligands was 173–184 μs , it increased to about 1.7 ms in the presence of L_1 . Appearance of additional peaks at 617 and 700 nm indicates a strong interaction with the DGA moieties similar to that observed with TODGA in an earlier publication.¹⁶ Fluorimetric titration studies indicated the formation of 1 : 1 species even in the presence of a 20 times excess of the ligand.[†] On the other hand, fluorescence studies with L_{II} pointed to three different types of species, one decaying with a lifetime of 183 μs , and the other two decaying at 565 and 1500 μs , respectively. While the species with the lifetime of 183 μs represents a predominant nitrate and aquo complex of

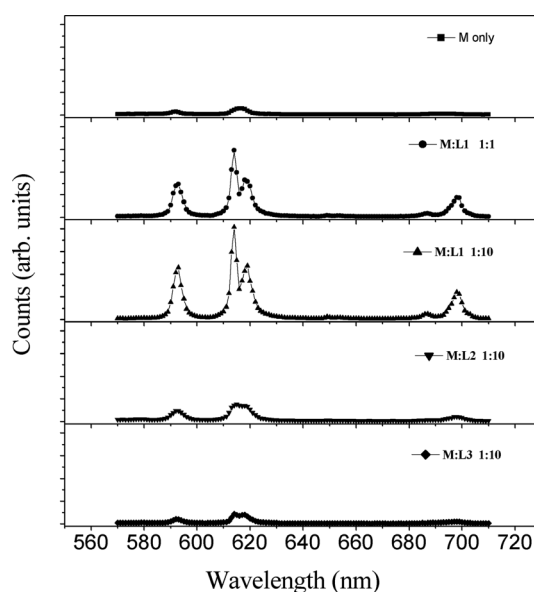


Fig. 3 Emission spectra of Eu^{3+} with the calix-DGA extractants in acetonitrile : water (5 : 1).

Eu^{3+} with about 6 water molecules¹⁷ and 3 nitrate ions and L_{II} being non-coordinating, that with a lifetime of 565 μs suggests the formation of an intermediate containing about 2 water molecules and 3 nitrate ions in the inner co-ordination sphere and a possible interaction by four donor atoms of the extractant molecule. The third species with a lifetime of 1500 μs assumes the absence of water molecules; it is possibly coordinated by 9 donor atoms from L_{II} with the ethereal 'O' atom also coordinating. With increasing ligand concentration, the fraction of the third species increased. Finally, with L_{III} , only two types of species were formed with lifetimes of 184 μs (7%) and 565 μs (93%) indicating that complete removal of inner sphere water molecules was not possible. Though solvent extraction data indicated 1 : 2 species formation with L_{III} , the results from laser induced fluorescence studies showed a weak complexation with the presence of 1–2 water molecules, which may be responsible for the poor partitioning of the complex towards the organic phase.

In conclusion, appending the calix[4]arene framework with four DGA moieties enhances the complexation ability of the ligand enormously by 'co-operative phenomena' resulting from entropic stabilization.⁷ In addition, the calix[4]-nDGA ligands exhibit a different complexation behaviour than the TODGA ligand. Very interestingly, by suitably changing the oxidation state of Pu to the +6 state, trivalent Am can be preferentially extracted from a mixture of Am, Pu, and U. The preparation of Am

Table 2 Emission lifetimes of the complexes of Eu^{3+} with the three calix[4]-nDGA ligands

Ligand	Decay time (in μs)	Inference
No ligand	173–184	6 water; 3 nitrate
L_1	$T_1 = 1700$ (100%)	Coordination by at least 9 donor atoms, no water, no nitrate
L_{II}	$T_1 = 183$ (13%) $T_2 = 565$ (58%) $T_3 = 1500$ (29%)	6 water; 3 nitrate 2 water, 3 nitrate, coordination by one ligand with 4 to 6 donor atoms Coordination by at least 9 donor atoms, no water, no nitrate
L_{III}	$T_1 = 184$ (7%) $T_2 = 565$ (93%)	6 water; 3 nitrate 2 water, 3 nitrate, coordination by one ligand with four 4 to 6 donor atoms

selective membranes may lead to the development of sensors for Am.

Notes and references

‡ The figure includes data with a 1 : 1 M : L ratio for comparison purposes.

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- Calix[4]arene 4-DGA (L_I) and Calix[4]arene-2-DGA (L_{II}) were prepared by reaction of the corresponding known tetrakis (aminopropoxy)-calix[4]arene and bis(aminopropoxy)calix[4]arene, respectively, with *p*-nitrophenol activated DGA in the presence of triethylamine as a base in refluxing chloroform. 1,3-Dibutoxycalix[4]arene 2-DGA (L_{III}) was synthesized by the reaction of 1,3-dibutoxycalix[4]arene with *N*-(3-bromopropyl)phthalimide to produce 1,3-dibutoxy-2,4-bis(phthalimidopropoxy)calix[4]arene which was subsequently converted to L_{III} . The formation of the calix[4]arene DGA ligands L_I – L_{III} was confirmed by the NMR data, the glycolic methylenes show singlets at δ 4.09 and 4.27, 4.11 and 4.16, 4.08 and 4.24, respectively. The ESI mass spectra exhibit distinct $M + H$ peaks. The detailed synthesis protocol will be published shortly.
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