



Radiation stability of diglycolamide functionalized calix[4]arenes in ionic liquid: Solvent extraction, EPR and GC–MS studies



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ABSTRACT

Ionic liquid-based solvent systems containing diglycolamide-functionalized calix[4]arenes (C4DGAs) are efficient for actinide ion extraction from nitric acid feeds. Therefore, the radiolytic stability of three C4DGAs (wide-rim, narrow-rim and both side DGA-functionalized calix[4]arenes) and TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) (used for comparison purpose), was evaluated by exposing their solutions in an ionic liquid as well as a 95:5 mixture of *n*-dodecane + isodecanol to gamma radiation up to an absorbed dose of 1000 kGy. Liquid–liquid extraction studies were carried out using ²⁴¹Am as a radiotracer. Apart from a decrease in the D_{Am} values, ascribed to radiolytic degradation, FT-IR, EPR and GC–MS studies were carried out to characterize the degraded species. The different extractants are less sensitive to radiolytic degradation in the ionic liquid than in the molecular diluent.

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1. Introduction

Diglycolamides (DGAs) are considered to be the most efficient extractants for actinides from acidic feed solutions, thereby making them strong candidates for ‘actinide partitioning’ runs for the processing of high level radioactive waste emanating from spent nuclear fuel reprocessing [1,2]. Out of the DGA ligands investigated, while the lower homologs have a significant aqueous solubility, the higher homologs, despite their higher lipophilicity, display lower metal ion extraction capabilities [3]. In view of this, the tetraoctyl substituted DGA extractants, i.e., TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) and T2EHDGA (*N,N,N',N'*-tetra-2-ethylhexyl diglycolamide) show optimum extraction properties and consequently, have been extensively investigated [4–10]. Recent studies with multiply DGA-functionalized extractants such as T-DGA (tripodal diglycolamide) and C4DGAs (diglycolamide-functionalized calix[4]arenes) have been quite promising and significantly higher extraction and separation efficiencies are reported [11–15]. This is attributed to a co-operative complexation mechanism resulting in the formation of a highly organophilic species, which is favourably partitioned toward the organic phase. However, application of these exotic extractants for actual radioac-

tive waste processing is not possible without a detailed evaluation of the sustainability of the solvent system, which is to a large extent dependent on their radiolytic stability.

Room temperature ionic liquid (RTIL) based solvent systems have been suggested as possible green alternative to the presently used solvent systems based on molecular diluents, which are volatile and inflammable [16–20]. One of the major advantages of RTIL-based solvents is a very high manifestation of the metal ion extraction even with a very small concentration of the extractant [21]. TODGA-based solvents in RTILs have shown not only very high distribution coefficient values, but the selectivities are also quite spectacular [22]. We have studied the extraction of actinide ions using C4DGAs dissolved in ionic liquids and the found selectivities were good enough for the separation of actinide ions [23]. As mentioned above, the application of the RTIL-based solvent systems containing C4DGAs to actual radioactive waste processing is only possible when their radiolytic stability is satisfactory.

Radiolysis of diglycolamide extractants such as TODGA [24–27] and T2EHDGA [28,29] has been thoroughly investigated by different research groups. Aromatic diluents such as benzene are found to be more radiation resistant as compared to aliphatic diluents such as *n*-dodecane [30]. On the other hand, while undiluted extractants are more stable [29], the DGA solutions, particularly those involving methyl substitution adjacent to the ether oxygen atom, when contacted with nitric acid, are found to be more susceptible to radiolysis [31]. The most abundant products are formed

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from the rupture of the ether linkages and the N–C_{carbonyl} bond and about eight different products have been identified by GC–MC [26].

Ionic liquids have varying degrees of stability after exposure to radiation, though in general, they are not very stable [32] and the degradation is usually facilitated through the anionic part of the ionic liquid. While [C_nmim][PF₆] or [C_nmim][NTf₂] (1-alkyl-3-methylimidazolium hexafluorophosphate and bis(trifluoromethane)sulfonamide, respectively) type ionic liquids degrade to form acidic products such as HF, which seriously affects the extraction efficiency of the solvent [33], analogous ionic liquids with chloride and nitrate anions are much more stable [34]. A sulfonyl imide anion-based ionic liquid is reported to be quite resistant to radiolysis [35]. Though the C4DGAs are highly promising for actinide ion extraction, the actual use of their solutions in ionic liquids for actinide ion separation requires testing of their long-term reusability, which indirectly means their radiolytic stability. This is because all actinide ions emit high LET (linear energy transfer) alpha particles, which may cause significant radiolytic damage. However, as exposure to the equivalent γ radiation can show the similar effect, it was decided to carry out radiolytic degradation studies using a ⁶⁰Co irradiator (vide infra). Not only the ‘green’ aspect of ionic liquids makes them a hot topic nowadays, but the ionic liquid-based solvent systems also show encouraging and

interesting extraction and separation properties of actinides compared to molecular diluent-based systems.

In view of these, it was of interest to investigate the radiolytic stability of ionic liquid-based solvents containing several DGA-functionalized (wide-rim (L_I), narrow-rim (L_{II}) and both side (L_{III}), Fig. 1) calix[4]arenes (C4DGAs). Though partly such studies have been performed by us previously [36], a comparative evaluation with respect to corresponding molecular diluent-based solvent systems, inclusive the parent TODGA itself, is lacking. Additionally, studies were carried out to identify the degradation products, involving techniques such as EPR, FT-IR, and GC–MS. To our best knowledge, this is the first comparative report on the radiolytic degradation of C4DGAs with a molecular diluent and an ionic liquid.

2. Experimental

2.1. Materials

The DGA-functionalized calix[4]arenes (C4DGAs, Fig. 1) were synthesized following a reported procedure [13]. The ionic liquid [C₈mim][NTf₂] (>99%), procured from IoliTec, Germany, was used after drying to limit the moisture content to <0.1%. Molecular diluents, *n*-dodecane (Lancaster, UK) and isodecanol (SRL, Mumbai), were used as received. Suprapur[®] nitric acid (Merck, Germany) and MilliQ water (Millipore) were used for preparing the aqueous feed solutions for the solvent extraction studies. All other reagents were of AR grade.

²⁴¹Am was used from laboratory stock solutions after purification (from its decay product ²³⁷Np) by first adding ca. 100 μ L of 0.01 M hydroxylamine hydrochloride at 1 M HNO₃ (to reduce Np to its +4 state) and subsequently contacting with 0.2 M TTA (2-thenoyltrifluoro acetone). The aqueous phase was evaporated to dryness and a few drops of mixture of concentrated HNO₃ and HClO₄ (5:1 ratio) was added to destroy the organic impurities. Alpha spectrometry of the purified ²⁴¹Am stock was carried out to rule out the presence of the impurities. The radiochemical purity of ²⁴¹Am was found to be >99.99%. For all subsequent measurements, assaying of ²⁴¹Am was done by gamma ray counting using a NaI(Tl) scintillation counter (Para Electronics, India) interfaced to a multi-channel analyzer (ECIL, India).

2.2. Instrumentation

2.2.1. EPR Spectrometer

A Bruker-EMX (EMM1843) spectrometer was used for recording EPR spectra at X-band frequency operated at 9.5 GHz with 100 kHz field modulation. The ‘g’ values were evaluated relative to a small single crystal of BDPA (1,3-bisdiphenylene-2-phenylallyl) with *g* = 2.0028 and a line width of 0.63 G. BDPA is an ideal sample for calibrating the phase and the field modulation amplitude of the single channel of the spectrometer. The viscous samples of the ligands in ionic liquids were transferred to quartz tubes which were degassed to remove O₂ as well as N₂ followed by sealing. These tubes were irradiated at liquid nitrogen temperature (77 K) to quench all the radicals generated during irradiation. The EPR parameters for different irradiated samples (C4DGA in [C₈mim][NTf₂]) were precisely determined from the calculated spectra, which were obtained with the Bruker WINEPR SimFonia program based on the perturbation theory [37]. The theoretical EPR signals were calculated using the spin Hamiltonian

$$H = \beta g H S + D[S_z^2 - 1/3(S(S+1))] + E(S_x^2 - S_y^2) \quad (1)$$

where *H* is the applied field, β is the Bohr magneton, *S_x*, *S_y* and *S_z* are the components of spin along three mutually perpendicular

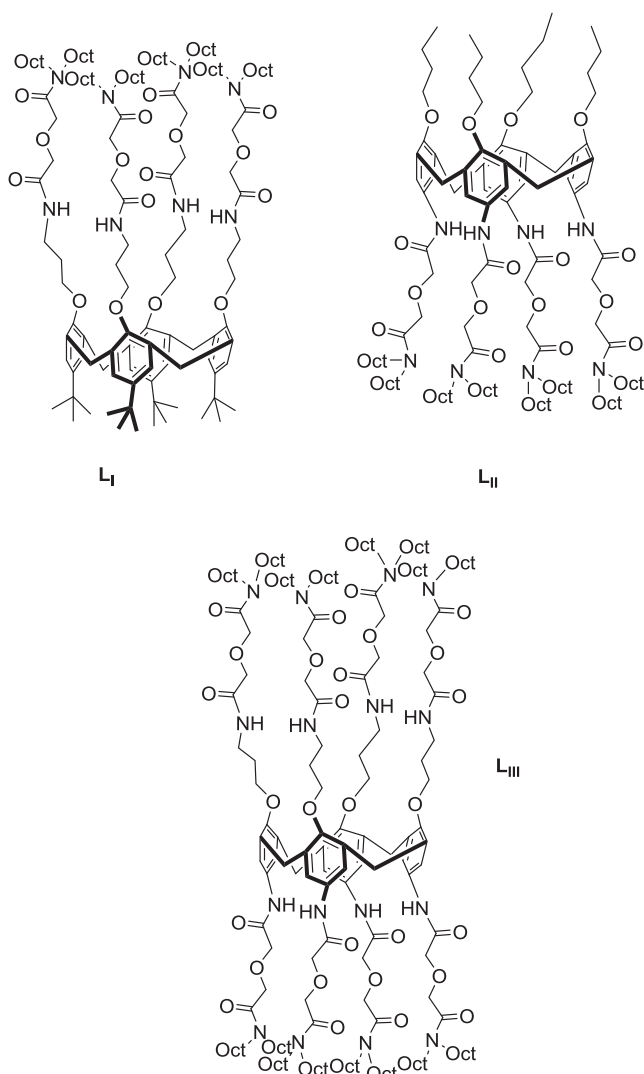


Fig. 1. Structural formulae of the C4DGA ligands L_I, L_{II}, and L_{III}.

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