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Diglycolamide-functionalized dendrimers: Studies on Americium(III) pertraction from radioactive waste

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ABSTRACT

Diglycolamide (DGA)-functionalized poly(propylene imine) diaminobutane dendrimers were evaluated as the carrier in supported liquid membranes (SLMs) for selective recovery of trivalent actinides over uranium. The 0, 1st, and 2nd generation dendrimers with 2, 4, and 8 DGA moieties, termed as **L_I**, **L_{II}**, and **L_{III}**, respectively, gave D_{Am} values of 0.11 ± 0.02, 41.9 ± 3.21 and 109.4 ± 6.22 in solvent extraction studies using 1 mmol/L ligand solutions in a diluent mixture of 95% *n*-dodecane + 5% *iso*-decanol. SLM studies using polytetrafluoroethylene flat sheet membrane filters impregnated with 1 mmol solutions of **L_{II}** and **L_{III}** suggested quantitative mass transfer of Pu^{4+}, Am^{3+}, and Eu^{3+} from 3 mol/L HNO_3 in about 5 h. Various diffusional parameters affecting SLM transport have been calculated for better understanding the transport data. The stability of the SLM was also studied over a period of five days.

1. Introduction

Global acceptability of the nuclear energy as an alternative source of energy can be increased enormously if public concerns regarding the hazards associated with the radioactive wastes can be mitigated in an efficient manner [1]. The radioactive waste remediation is proposed to be efficiently handled by a strategy called 'Partitioning & Transmutation', which dwells upon selective separation of the minor actinides (such as Am, Cm, and Np) from the high level waste (Table 1), followed by their transmutation in high flux reactors or accelerator driven sub-critical systems [2–8]. The minor actinide separation can be taken up conveniently using actinide selective extractants such as CMPO (carbamoyl methylene phosphine oxide), trialkyl phosphine oxides, DIDPA (di-*iso*-decyl phosphoric acid) or malonamides [9,10]. However, the most efficient separation of the minor actinides has been accomplished using diglycolamide (DGA) extractants [11]. Amongst the DGA extractants, TODGA (*N,N,N′,N′*-tetra-*n*-octyl diglycolamide) [12–14] and T2EHDGA (*N,N,N′,N′*-tetra-2-ethylhexyl diglycolamide) [15,16] have been studied extensively for the separation of minor actinides, and have been tested in hot runs in several laboratories [17–19]. The major features of the DGA-based extractants include a drastic change in the general extraction trend of the actinide ions from $Pu^{4+} > UO_2^{2+} > Am^{3+}$ to $Am^{3+} > Pu^{4+} > UO_2^{2+}$ favoring better extraction of minor actinides over uranium.

The extraction efficiency of DGA extractants was reported to increase manifold when multiple DGA-containing extractants such as tripodal DGA (T-DGA) [20–22], DGA-functionalized calix[4]arenes [23–25], and pillar[5]arenes [26] were used. Furthermore, the extraction of UO_2^{2+} decreased significantly with these extractants translating into a high selectivity of Am^{3+} in the presence of a large excess of UO_2^{2+} ions. In view of this, another class of multiply DGA–functionalized extractants, namely DGA-dendrimers (Fig. 1), was recently synthesized by us and evaluated for the complexation of trivalent actinides and lanthanides [27]. These DGA-dendrimers are a special class of ligands prepared by grafting DGA moieties onto the propylene imine-diaminobutane (PPI-DAB) skeleton. In view of the novelty of these ligands and their exceptionally high metal ion extraction efficiency, a thorough investigation on radioactive waste processing is warranted.

Liquid membrane-based separation methods are known to be 'green' alternatives to solvent extraction-based separation methods in view of high ligand inventory and generation of large amounts of secondary waste in the latter case [28–30]. In contrast, liquid membrane-based separation methods offer numerous advantages over conventional solvent extraction such as simultaneous extraction and stripping, generation of low volume

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Table 1
Composition of a typical high level waste of pressurized heavy water reactor origin. Acidity: ~3 mol/L HNO_3; Spent fuel burn up of ~6500 MWd/Te and 3 years cooling; Volume of waste is 800 L/tonne of spent fuel.

Element	Concentration (g/L)	Element	Concentration (g/L)
Na	5.50	Pd	0.03
K	0.22	Mo	0.14
Cr	0.12	Ba	0.06
Mn	0.43	Y	0.06
Fe	0.72	La	0.18
Sr	0.03	Ce	0.06
Cs	0.22	Pr	0.09
Zr	0.09	Nd	0.12
Ru	0.04	Sm	0.09

of volatile organic carbons and low operating cost, etc. The supported liquid membrane (SLM) technique has been evaluated successfully for the selective removal of radiotoxic elements from radioactive waste solutions [31–34]. Here the selectivity is achieved by selective complexation of the target metal with a ligand (known as carrier), followed by mass transfer of the metal-ligand complex across the membrane from the feed phase to the receiver phase. Such transport processes are, therefore, referred to as "carrier facilitated transport" processes. It is worth evaluating the transport of minor actinides from radioactive waste solutions using these novel DGA-dendrimers (Fig. 1).

The present study involves the investigation of three DGA-functionalized dendrimers, namely, zero generation ($\mathbf{L_I}$), 1st generation ($\mathbf{L_{II}}$), and 2nd generation ($\mathbf{L_{III}}$) (Fig. 1) as the carrier in SLMs for separation of Am^{3+} ion from dilute nitric acid feed solutions. Batch solvent extraction studies were performed to investigate the selectivity of the ligands for Am^{3+} over other metal ions present in the radioactive waste, *viz.* high level waste (HLW). Solvent extraction data were also obtained to optimize different parameters for efficient transport of Am^{3+} in SLMs. Various diffusional parameters affecting SLM transport were calculated for a better understanding of the transport data. Finally, the stability of the SLM was studied over a period of five days. Though we have previously reported liquid membrane transport studies involving DGA-functionalized calix[4]arenes, the dendrimers are of great interest to study in view of their less flexible conformation compared to the calixarenes as well as their special 'tree like' structure. To our knowledge, this is the first report on the transport behavior of actinides using DGA – functionalized dendrimers.

2. Experimental section

2.1. Materials

The DGA-dendrimers ($\mathbf{L_I}$-$\mathbf{L_{III}}$, Fig. 1) were synthesized by reaction of 1,4-diaminobutane or the appropriate PPI-DAB dendrimers with *p*-nitrophenyl-activated DGA in refluxing toluene as described recently [27]. The ligands were characterized by ^1H NMR and HR-MS to ascertain their purities. *n*-Dodecane (99%) and *iso*-decanol (99%) were procured from Lancaster, UK and SD Fine Chem, Mumbai, respectively. Polytetrafluoroethylene (PTFE) membranes (pore size: 0.45 μm; porosity: 72%; diameter: 47 mm; thickness: 85 μm) were purchased from Sartorius, Germany. All the other reagents were of AR grade and were used without further purification. All the solutions were prepared using Milli Q deionized water (18.2 M Ω cm).

^{241}Am from laboratory stock was used after purification (from its decay product, ^{237}Np) using the HTTA (2-thenoyltrifluoroacetone) extraction method and checking its radiochemical purity by alpha as well as gamma ray spectroscopy [35]. ^{233}U was purified from its daughter products using a reported method [36], while Pu (mainly ^{239}Pu) was purified from its decay products (mainly ^{241}Am) by the HTTA extraction method [37]. The oxidation state of Pu (taken in 1 mol/L HNO_3) was adjusted to the +4 state by adding a few drops of 5 mmol/L $NaNO_2$ followed by selective extraction of Pu^{4+} by 0.5 mol/L HTTA in xylene. ^{239}Np was prepared by neutron activation of ^{238}U followed by its purification as described earlier [38]. The neptunium valency was adjusted to the +4 state by the addition of hydroxylamine hydrochloride and ferrous sulphamate (at 1 mol/L HNO_3) followed

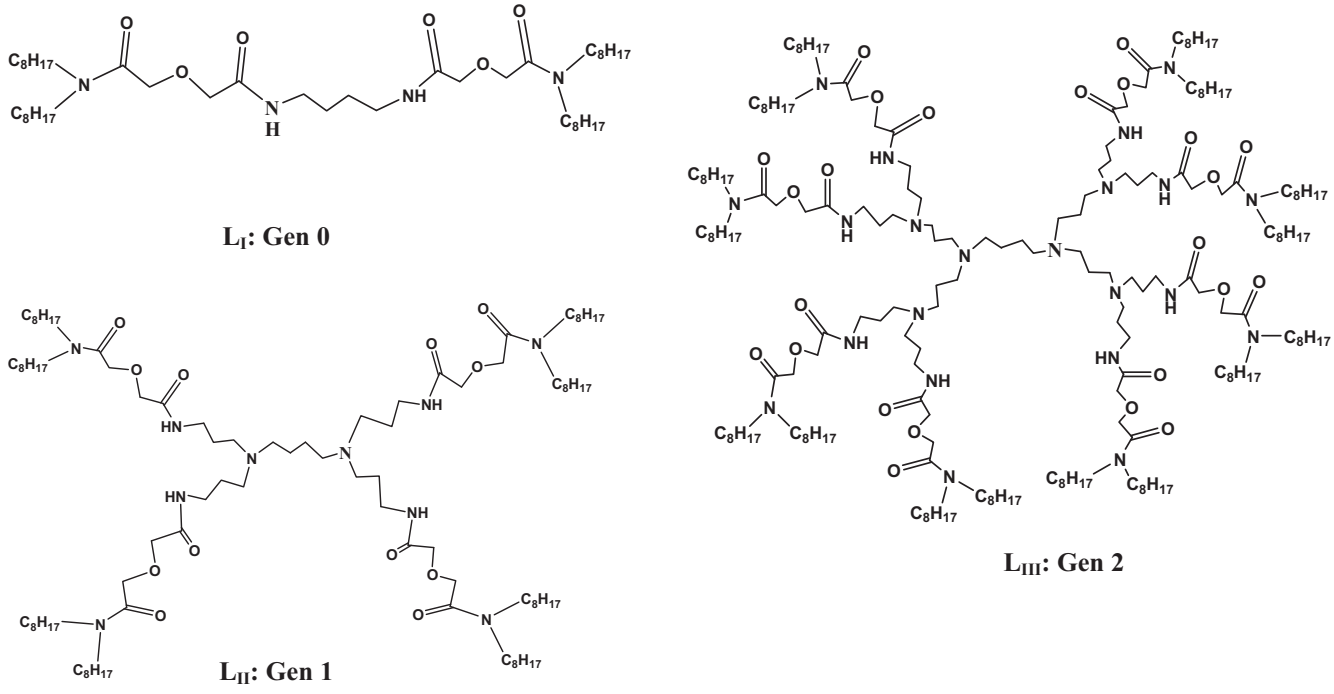

Fig. 1. Structures of the DGA-functionalized PPI-DAB dendrimers $\mathbf{L_{I-III}}$.