



Multi-podant diglycolamides and room temperature ionic liquid impregnated resins: An excellent combination for extraction chromatography of actinides



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ABSTRACT

Extraction chromatography resins, prepared by impregnating two multi-podant diglycolamide ligands, viz. diglycolamide-functionalized calix[4]arene (C4DGA) and tripodal diglycolamide (T-DGA) dissolved in the room temperature ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (RTIL: C₄mim Tf₂N) on Chromosorb-W (an inert solid support), gave excellent results for the removal of trivalent actinides from acidic waste solutions. Distribution coefficient measurements on several metal ions showed selective sorption of Am(III) over hexavalent uranyl ions and other fission product elements such as strontium and cesium. The sorbed metal ions could be efficiently desorbed with a complexing solution containing guanidine carbonate and EDTA buffer. The sorption of Am(III) on both resins followed pseudo-second order rate kinetics with rate constants of 1.37×10^{-6} and 6.88×10^{-7} g/cpm min for T-DGA and C4DGA resins, respectively. The metal sorption on both resins indicated the Langmuir monolayer chemisorption phenomenon with Eu(III) sorption capacities of 4.83 ± 0.21 and 0.52 ± 0.05 mg per g of T-DGA and C4DGA resins, respectively. The results of column studies show that these resins are of interest for a possible application for the recovery of hazardous trivalent actinides from dilute aqueous solutions.

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1. Introduction

Due to increasing global energy demands and limited fossil fuel reserves, there is a consensus evolving on the possible use of nuclear energy in a big way. This requires not only the setting up of a large number of reactors, but also a great deal of money and man power will be invested in developing fool proof waste management technologies. Increasing nuclear power production has also a risk of occasional accidents such as Chernobyl and Fukushima Daiichi, which adds risks of radionuclide contamination of the environment [1,2]. Monitoring actinides in environmental samples such as soil, sand, and ground water has always been a challenging task and conventional techniques such as solvent extraction, ion exchange or precipitation are not very promising. Recently, solid phase extraction (SPE) based separation methods have been reported to be highly efficient for actinide ion separation/pre-concentration from environmental samples [3–5]. Out of the SPE methods, extraction chromatography (XC) is suggested to be highly efficient in view of

having advantages over both solvent extraction and ion-exchange [6,7]. In XC resins, an extractant dissolved in a suitable diluent (similar to the solvent extraction based separation methods) is filled in the pores of the solid support material which stays inside the pores due to capillary forces. Therefore, selective extraction, experienced in solvent extraction based separation methods, can be made possible in XC by using a suitable extractant.

Extraction of minor actinide ions such as Am(III) is not possible from acidic feed solutions using conventional extractants such as TBP (tributyl phosphate) or D2EHPA (di(2-ethylhexyl) phosphoric acid) [8]. Tailor made selective extractants such as TODGA (N,N,N',N'-tetra-n-octyl diglycolamide) are found to be highly promising for minor actinide extraction [9–12] and have been used for the preparation of XC resins [13–15]. We have recently reported that multiply diglycolamide (DGA) –functionalized extractants such as T-DGA (a tripodal diglycolamide ligand with three DGA arms; Fig. 1a) and C4DGA (calix[4]arene appended with four DGA pendant arms; Fig. 1b) are far superior to TODGA with respect to Am(III) ion extraction [16–18]. In view of this, a XC resin was developed and was found to be very efficient for the extraction of the actinide ions from nitric acid feeds [19].

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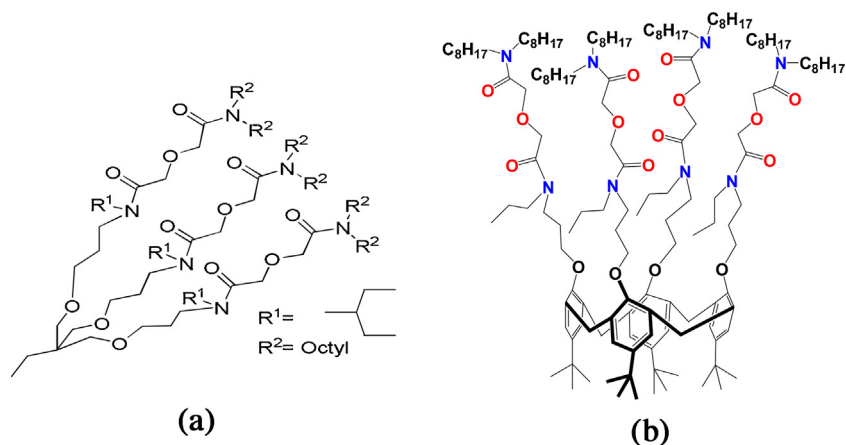


Fig. 1. (a) Tripodal-diglycolamide (T-DGA), and (b) diglycolamide-functionalized calix[4]arene (C4DGA).

Room temperature ionic liquids (RTIL) are reported to be an alternative diluent to the conventional molecular diluents, the metal ion extraction properties being improved spectacularly [20–24]. Our recent efforts to employ TODGA, C4DGA, and T-DGA for the extraction of Am(III) ion were highly encouraging as the metal ion extraction increased manifold in RTIL medium [25–27]. Furthermore, XC resins containing RTIL have shown to enhance metal ion extraction to a very large extent, though there were stripping issues [28–30]. An XC resin containing TODGA (10% TODGA) in RTIL has been reported to enhance the K_d values for Am(III) ion extraction to >15,000 as compared to only ca. 7000 with an analogous XC resin containing molecular diluents and as high as 47% TODGA [30].

In view of these, it is of interest to prepare XC resins containing T-DGA and C4DGA in a RTIL, namely 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ($C_4\text{mim}\cdot\text{Tf}_2\text{N}$) and to evaluate their performance for the extraction of Am(III) ion from acidic feeds. Apart from characterization of the XC resins by thermogravimetric and BET analysis, the surface morphology was analyzed by SEM. The uptake of Am(III) ion was studied by both batch and column chromatography modes, while sorption isotherm studies were also carried out. To our best knowledge, this is the first report on SPE studies on Am(III) ion extraction using multiply DGA-functionalized XC resins containing a RTIL.

2. Materials and methods

2.1. Chemicals and radionuclides

The tripodal diglycolamide (T-DGA, Fig. 1a) was synthesized by reacting the corresponding tripodal amine and *p*-nitrophenyl-activated diglycolamide. Similarly, the diglycolamide-functionalized calix[4]arene, in cone conformation, (C4DGA, Fig. 1b) was obtained by reacting tetrakis(aminopropoxy)calix[4]arene with *p*-nitrophenyl-activated *N,N*-di-*n*-octyl diglycolamide in the presence of triethylamine. The detailed synthesis procedures for T-DGA [16] C4DGA [17] and have been described earlier. The synthesized products were characterized by NMR, HPLC, and ESI-MS. The ionic liquid, $C_4\text{mim}\cdot\text{Tf}_2\text{N}$ (>99%), was purchased from Iolitec, Germany and used as received. The solid support, Chromosorb-W (dimethyl dichlorosilane treated acid washed celite diatomaceous silica, mesh size 60–80) was procured from John Manville. The support was washed thoroughly with distilled water, ethanol, and acetone and dried completely to remove any adsorbed impurity before its use. ^{241}Am , $^{152,154}\text{Eu}$, ^{244}Cm , Pu (mainly ^{239}Pu), ^{233}U and ^{137}Cs

tracers were used from the laboratory stock after confirming their radiochemical purities by alpha-spectroscopy and gamma-spectroscopy. Radiotracer, $^{85,89}\text{Sr}$ was obtained from Board of Radiation and Isotope Technology (BRIT), Mumbai and was used after ensuring its radiochemical purity. A stock solution of Eu(III) was prepared by dissolving Spec pure Eu_2O_3 (>99.99%) in nitric acid solution. All other chemicals used were AR grade and were used as received.

2.2. Preparation of resins

The extraction chromatographic resins were prepared by impregnating either C4DGA/ $C_4\text{mim}\cdot\text{Tf}_2\text{N}$ or T-DGA/ $C_4\text{mim}\cdot\text{Tf}_2\text{N}$ ligand solutions on Chromosorb-W. The ligand solutions were prepared by dissolving known weights of C4DGA or T-DGA in an equal amount of $C_4\text{mim}\cdot\text{Tf}_2\text{N}$ (1:1 w/w). These ligand solutions (0.2 g each) were equilibrated with 0.8 g of solid support (Chromosorb-w) in a sufficient quantity of methanol (25 mL). The slurry, containing the ligand solution and the solid support, was equilibrated for 24 h in a mechanical shaker followed by careful solvent removal by flushing nitrogen gas with gentle stirring. The resultant material was vacuum dried to constant weight. The loading of ligand on the solid support was estimated from the weight gain of the support after the impregnation and was found to be 10% w/w for both resins.

2.3. Batch sorption studies

The distribution of metal ions on the resin was determined by equilibrating a known quantity of resin (~10 mg) with 1 mL of an aqueous solution containing the required metal ions in stoppered glass tubes in a thermostated water bath maintained at $25 \pm 0.1^\circ\text{C}$. The equilibration was done for 3 h, unless specified otherwise. After equilibration, the tubes were centrifuged and suitable aliquots of the aqueous phase were removed and centrifuged a second time to remove any resin particle. Suitable aliquots from the aqueous phase were removed before and after equilibration for assaying radiometrically. Assay of ^{241}Am , $^{152,154}\text{Eu}$, $^{85,89}\text{Sr}$, and ^{137}Cs was carried out by gamma counting in a well type NaI(Tl) scintillation counter interphased with a multichannel analyzer. Alpha counting for ^{233}U , ^{244}Cm , and ^{239}Pu was carried out by a liquid scintillation counter employing a toluene-based scintillator containing 10% (v/v) HD2EHP (0.7% (w/v) 2,5-diphenyloxazole (PPO), and 0.03%

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