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Polymer inclusion membrane containing a diglycolamide-functionalized calix[4]arene for actinide ion uptake and transport

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ABSTRACT

Cellulose triacetate (CTA) -based polymer inclusion membranes (PIM) containing a diglycolamide-functionalized calix[4]arene (C4DGA) as the carrier extractant and 2-nitrophenyl octyl ether (NPOE) as the plasticizer were evaluated for the separation of actinides such as Am³⁺, Pu⁴⁺, UO₂²⁺, and Th⁴⁺ from dilute acidic feeds. The optimized PIM composition was found to be 6.5% C4DGA, 67.7% NPOE, and 25.8% CTA. The PIM of optimized composition was characterized physically by different techniques, viz., thermogravimetry, X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, and transmission infrared mapping microscopy (TIMM). The feeds in the batch uptake as well as transport studies involved solutions of the actinide tracer in the required oxidation state in 1 M HNO₃, while the receiver solutions used in the transport studies contained a 1 M *alpha*-hydroxy-*iso*-butyric acid (AHIBA) solution at pH 3.0. The uptake efficiency followed the order: Am³⁺ > Pu⁴⁺ > Th⁴⁺ >> UO₂²⁺, while the transport efficiency order was: Pu⁴⁺ > Am³⁺ > Th⁴⁺ with no detectable transport of the UO₂²⁺ ion. The effective diffusion coefficient (D_{eff}) was determined from time-lag experiments, while the permeability coefficient (P) values were obtained from the transport studies and compared with those reported for TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) and T2EHDGA (*N,N,N',N'*-tetra-2-ethylhexyl diglycolamide) containing PIMs. The reusability of the PIMs was assessed by successive uptake and stripping studies, while the stability of the PIMs was assessed by carrying out continuous transport studies over a period of time.

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1. Introduction

There is a growing risk of environmental contamination with radionuclides such as actinides due to increasing nuclear fuel cycle activity associated with the ever increasing number of nuclear reactors in the world [1]. This is not only due to the possibility of escape of the radionuclides from the underground radioactive waste burial sites, but also because of stray incidents of accidents such as Chernobyl and Fukushima Daiichi. So, there is a long term radiation hazard due to the presence of long lived actinides in the environment. Thus, an efficient separation method for the removal of actinides from a variety of samples, such as soil, rock, food, air, biological samples, etc, is required. However, the separation of actinides, particularly those of minor actinides (Am, Cm, Np), is a challenging task [2] and generally requires custom made extractants. Out of the different extractants proposed [3–6],

diglycolamide ligands, such as *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (T2EHDGA) have proven to be very promising for the removal of minor actinides from acidic feed solutions [7–9]. It has been proven from small angle neutron scattering and dynamic light scattering experiments that four TODGA molecules form an aggregated structure at 3 M HNO₃, which is responsible for the preferential extraction of the trivalent / tetravalent actinides over the hexavalent actinide ions [10,11]. This aggregate formation highly depends on the diluent properties and hence the extraction behavior of the actinides changes drastically with diluents polarity. In order to mimic the effectiveness of the TODGA-based aggregation independent of diluent polarity, derivatives of diglycolamides were synthesized where four diglycolamide (DGA) units, each containing two *n*-octyl groups at the outer amide group, were appended at the lower rim of the calix[4]arene skeleton [12–14]. The four preorganized DGA groups enhance the complexation ability of the ligand by a co-operative complexation mechanism resulting from entropy stabilization [15]. DGA-functionalized calix

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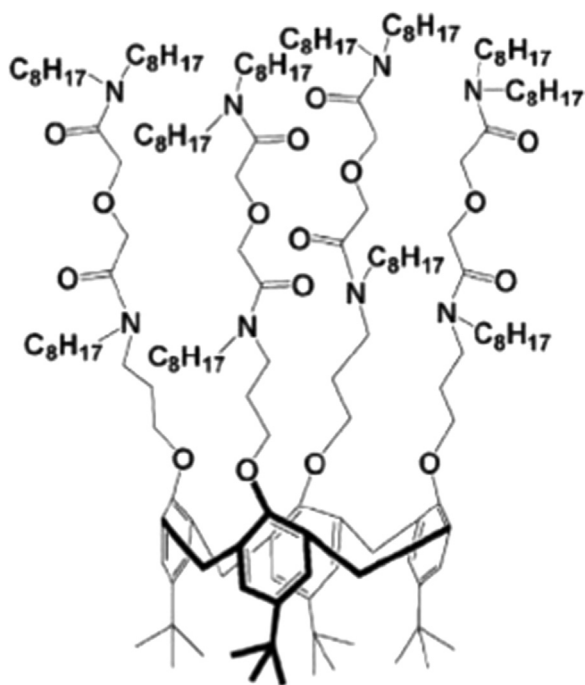


Fig. 1. Structure of the DGA-functionalized calix[4]arene ligand (C4DGA).

[4]arene C4DGA (Fig. 1), having an additional *n*-octyl group at the other amide moiety, extracts tri- and tetravalent actinides with greater efficiency than TODGA [16]. For example, the distribution ratios for Am^{3+} at 1.0×10^{-3} M extractant concentration and 3 M HNO_3 as feed acidity are < 0.1 and 300 for TODGA and C4DGA, respectively.

Liquid membrane-based separations, such as supported liquid membrane (SLM), have the advantage of lower inventory of ligand making it possible to employ expensive tailor-made ligands such as C4DGA for separation studies. Other advantages of the SLM-based separations include simultaneous extraction and stripping, continuous flow, possibility to achieve a high volume reduction factor, and easy scale up possibility [17–19]. However, one of the major drawbacks of SLMs is the possible loss of carrier extractant from the membrane due to leaching of the carrier with time, which reduces their long term stability [20]. There are ongoing attempts to increase the lifetime of the membranes by fixing the carrier inside the polymeric matrices, which is known as a polymer inclusion membrane (PIM) [21–24]. Though it is generally accepted that PIMs have higher stability and lower permeability than the SLMs [25], there are reports which suggest higher permeability for PIMs as compared to the SLMs [26]. Furthermore, the stability of the PIMs can be affected based on the nature of the polymer and feed conditions used. For example, CTA based PIMs undergo extensive hydrolysis when moderate to high concentrations of HNO_3 are used [27].

We have carried out extensive studies on the separation of actinides from acidic feed solutions employing various diglycolamide-containing PIMs [28–32]. The promising extraction ability of the DGA-functionalized calix[4]arene C4DGA towards the actinides prompted us to use it as the carrier extractant in PIMs to separate actinides from acidic feed solutions. Though we have reported SLM transport studies on actinide ion separations using C4DGA, this is the first report on a PIM containing a DGA-functionalized calix[4]arene for actinide ion uptake and transport. The studies included in this paper are PIM preparation and characterization using techniques such as transmission infrared mapping microscopy (TIMM), X-ray diffraction (XRD), thermogravimetry (TGA), and Fourier transform infrared spectroscopy (FT-IR) followed by

uptake and transport studies involving actinide ions such as Am^{3+} , Pu^{4+} , UO_2^{2+} , and Th^{4+} from dilute HNO_3 feeds.

2. Experimental

2.1. Reagents

C4DGA (Fig. 1) was synthesized and characterized as described [12]. Cellulose triacetate (CTA) (Alfa Biochem), 2-nitrophenyl *n*-octyl ether (NPOE) (Fluka), dichloromethane (Merck), and *alpha*-hydroxy-*iso*-butyric acid (AHIBA) (Aldrich) were used as obtained. Dilute nitric acid solution (1 M HNO_3), prepared from suprapur nitric acid (Merck), was standardized volumetrically using phenolphthalein (Merck) indicator. All the other reagents were of AR grade.

2.2. Radiotracers

^{241}Am , Pu (mainly ^{239}Pu), and ^{233}U were obtained from laboratory stocks after checking their radiochemical purities (Supporting Information) by alpha spectrometry as well as by gamma ray spectrometry (for ^{241}Am). ^{234}Th was milked from ^{238}U (natural U) following a reported method [33] as detailed in the Supporting Information. The typical concentrations of the radiotracers used in the present studies were $\sim 10^{-7}$ M for Am, $\sim 10^{-6}$ M for Pu and U, and $\sim 10^{-11}$ M for Th. Liquid scintillation counting was done for assaying ^{239}Pu and ^{233}U , whereas gamma ray spectrometry was done for assaying ^{241}Am and ^{234}Th . The oxidation state of Pu was adjusted to +4 by a reported method (Supporting Information) in which tetravalent Pu was extracted into TTA (2-thenoyltrifluoroacetone) in xylene and subsequently stripped in the presence of 8 M HNO_3 [34].

2.3. Equipments

Liquid scintillation counting was carried out using an automated counting system (Hidex, Finland), which used a toluene-based scintillator cocktail (SRL, Mumbai), whereas gamma ray spectrometry was done using a NaI(Tl) counter (Para Electronics) coupled to a multi-channel analyzer (ECIL, India). The thickness of the PIM was measured using a Mututoya digital micrometer. The scanning for Fourier transform infrared (FT-IR) spectra of the desired PIMs were carried out in the $4000\text{--}650\text{ cm}^{-1}$ range using a Perkin Elmer Spectrum 400 spectrometer. The micro homogeneity of the PIM was determined from a TIMM plot using a Perkin Elmer instrument, spotlight 300 in the wavelength range of 4000 cm^{-1} to 750 cm^{-1} , resolution 4 cm^{-1} , coupled to a mercury-cadmium telluride detector. A portion of an area of $150\text{ }\mu\text{m} \times 193\text{ }\mu\text{m}$ of the PIM was chosen for mapping with 16 scans per pixel. XRD of the sample was carried out in the range of $10\text{--}40^\circ$ at a scanning speed of $1^\circ/\text{min}$ using a Cu target and Xe-proportional detector (GBC scientific equipment). Weight loss of a small piece of the PIM was recorded in the temperature range of $25\text{--}600^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ using a high resolution thermogravimetric analyzer (Setaram Setsys Evolution) under a constant flow (100 mL/min) of high purity (99.995%) argon gas.

2.4. Membrane preparation

The PIM was prepared following a literature method [35] by taking the required amount of CTA solution in dichloromethane (DCM) (1.62% CTA), plasticizer (NPOE) and carrier (C4DGA), dissolved in dichloromethane and homogenized for about 5 min by ultrasonication, followed by pouring the entire lot into a flat bottom glass Petri dish (90 mm of diameter) and allowing complete

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