Polymer inclusion membrane containing a tripodal diglycolamide (T-DGA): Characterization and sorption isotherm studies

B.N. Mahanty[a], P.K. Mohapatra[b,*], D.R. Raut[b], D.K. Das[a], P.G. Behere[a], Md. Afzal[a], W. Verboom[c]

[a] Advanced Fuel Fabrication Facility, Bhabha Atomic Research Centre, Tarapur 401502, India
[b] Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India
[c] Laboratory of Molecular Nanofabrication, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT

Polymer inclusion membranes (PIMs) of the composition, 25.6% T-DGA (tripodal diglycolamide), 53.9% NPOE (2-nitrophenyloctyl ether), and 20.5% CTA (cellulose triacetate) were prepared and characterized using thermogravimetric analysis, X-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission infrared mapping microscopy (TIMM) using Fourier transform infrared (FT-IR) spectroscopy. Uptake of Am^{3+} was found to be higher than that of Eu^{3+} and >82% uptake of Am^{3+} was seen with the PIM of the composition mentioned above. The batch sorption study of Eu^{3+} (used as a surrogate of Am^{3+}) by this PIM was investigated in 1 M HNO_3 and the data were fitted with different conventional kinetic and isotherm model equations. The sorption followed pseudo-second order (H_o) kinetic model suggesting a two-step uptake process, a fast chemical reaction followed by a slow diffusion process. The experimental data were best fitted with a three-parameter model, i.e., the Redlich-Peterson isotherm model. A comparison is made with results obtained with T2EHDGA-based PIMs reported earlier.

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1. Introduction

Monitoring of actinides is a mandatory norm especially after accidental release of radionuclides into the environment by unfortunate events such as Chernobyl and Fukushima. The actinides to be monitored not only include the major ones such as uranium and plutonium, but also highly radiotoxic minor actinides such as americium. The analytical methodology for this purpose includes separation, pre-concentration, and estimation using radiometric methods. The most efficient methods for separation and pre-concentration are solid phase extraction [1] and membrane-based methods [2]. Solid phase extraction methods involve batch- or column-based methods, which are highly dependent on the particle size. On the other hand, liquid membrane-based methods involve high throughput techniques such as hollow fiber contactors [3,4]. The major disadvantages of liquid membrane-based separation/pre-concentration methods include the liquid membrane stability, which can be alleviated by employing polymer inclusion membranes (PIM). A PIM is a sort of composite membrane constituting of a base polymer (such as cellulose triacetate (CTA) and polyvinylchloride (PVC)), a plasticizer, and an actinide specific ligand, which can complex the metal ions from the PIM-aqueous feed interface facilitating the pre-concentration process [5]. While the base polymer is known to be the skeleton of the PIM, the role of the plasticizer is to prevent entanglement of the polymer strands and also to create a semi-fluid medium for metal-ligand complex diffusion [6]. This results in a faster mass transport in PIMs as compared to solid membranes, but gives rise to a slower mass transport than in liquid membranes. The presence of a plasticizer also imparts some sort of flexibility to the otherwise rigid 'fixed-site jumping' mechanism [7–9], so well adapted to PIM-based transport systems with lower than expected percolation threshold values [10].

Minor actinide uptakes by PIMs have been thoroughly investigated using diglycolamide (DGA) extractants such as TODGA (N,N,N',N'-tetraoctyl diglycolamide) and T2EHDGA (N,N,N',N'-tetra-2-ethylhexyl diglycolamide) [11–14]. We have recently used a multiple-DGA functionalized tripodal extractant with octyl groups (Fig. 1), referred hereafter as T-DGA, for the uptake and transport of actinide ions such as Am^{3+}, Pu^{4+}, Th^{4+}, and UO_2^{2+} from acidic feeds such as 1 M HNO_3 [15,16]. The extraction of actinide ions was found to be far more efficient using T-DGA as compared to
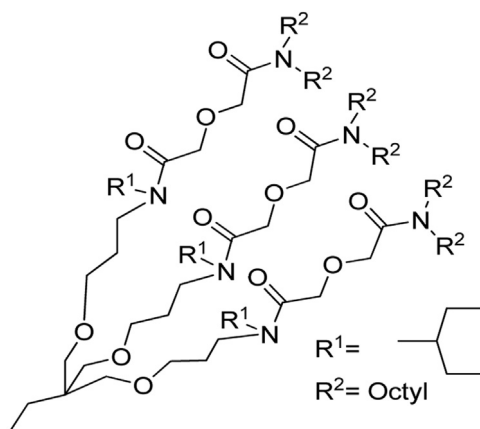
Fig. 1. Structure of T-DGA molecule.

TODGA which was attributed to a cooperative complexation mechanism operative in the former ligand. In these studies, the transport of Am^{3+} was significantly higher than that of the other actinide ions. Furthermore, a significant fraction of the pre-concentrated actinide ions was found to be held up in the PIM raising curiosities about the sorption mechanism. We have reported very good efficiency for Am^{3+} uptake using TODGA containing PIMs [12]. Hence, it was of interest to investigate the Am^{3+} uptake behaviour of PIMs containing T-DGA. The present work has the additional objective of understanding the mechanism of sorption of the trivalent actinide ions (especially that involving Am^{3+} which is an important radionuclide in the back end of the nuclear fuel cycle) in PIMs containing T-DGA as the carrier extractant. However, in view of large radiation exposure from mg quantities of Am, required for these studies, Eu^{3+}, a trivalent lanthanide ion with very similar chemical behavior to that of Am^{3+}, was used as a surrogate.

The present paper gives a detailed investigation on the physical and chemical characterization of the T-DGA-containing PIMs using techniques such as X-ray diffraction (XRD), thermogravimetric analysis, scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FT-IR), and transmission infrared mapping microscopy (TIMM), etc. Sorption isotherm studies were carried out to understand the kinetics and mechanism of metal ion uptake. The kinetic modeling of the sorption data was used to predict the uptake mechanism.

2. Experimental

2.1. Reagents

The synthesis and characterization of T-DGA is reported previously [17] and the extractant was characterized by NMR and HR-MS. CTA (Alfa Biochem) and NPOE (Aldrich) were used without any further purification. Eu_2O_3 (99.99%, Aldrich) was used for the preparation of feed solutions containing Eu carrier and the acidity of the feed was adjusted using Suprapur nitric acid (Merck) and MilliQ (Millipore) water. All acid-base titrations were carried out using an AR grade NaOH (BDH) solution using potassium hydrogen phthalate (Merck) as the primary standard and phenolphthalein (Merck) as the indicator. All the other reagents were of AR grade.

2.2. Radiotracers

^{152}Eu was procured from the Board of Radiation and Isotope Technology (BRIT) and was used after confirming its radiochemical purity by gamma ray spectrometry using an HPGe detector (Canberra) coupled to a multi-channel analyzer. For all subsequent studies, ^{152}Eu was assayed by gamma counting using a well type NaI(Tl) counter (Para Electronics) coupled to a multi-channel analyzer (ECIL, India). The counting statistics error was limited to <1% by long time counting.

2.3. Membrane preparation

PIMs were prepared following a literature method of Sugiura et al., [18] in which a mixture of CTA (0.08 g), NPOE (0.210 g), and T-DGA (0.08 g) was first homogenized by adding 5 mL of dichloroethane followed by ultrasonification for 10 min resulting in a clear solution. Subsequently, the homogeneous solution was poured into a flat bottom glass Petri dish (90 mm of diameter) and was allowed to dry by very slow evaporation over 2 d at room temperature. A few drops of water were swirled over the dried PIM, which helped in the subsequent peeling off of the PIM from the Petri dish surface. The PIM was transparent and of good mechanical strength and its thickness was measured by a Mututoya digital micrometer and was found to be uniform within error limits of ±5%.

2.4. Membrane characterization

The PIMs were characterized by a host of techniques, viz. thermogravimetry (TG-DTA), XRD, FT-IR, SEM, and AFM. The TG-DTA analysis of the PIM was carried out using a SETARAM SETSYS evolution thermal analyzer. The heating rate was kept at 10 °C/min and the flow rate of ultra pure argon was 100 mL/min. The resolution of the microbalance is ±0.04 μg. SEM studies were carried out with a JSM 840 Scanning Electron Microscope (SEM) from JEOL, Japan, with a 1000–5000 times magnification of the membrane surface. The samples were prepared by following conventional methods mounting the PIM on a carbon tape on top of a stub and both sides of the dry membrane were coated with gold using a Polaron E5100 sputter coater. The topographic AFM images of the samples were taken with an Asylum MFP-3D classic AFM instrument using an AC 160 TS-R3 silicon cantilever probe in tapping mode (AC mode).

FT-IR spectra were recorded using a PerkinElmer instrument and transmission infrared mapping microscopy (TIMM) measurements were subsequently performed by choosing the right frequency. TIMM studies were carried out in the wavelength range of 4000–750 cm^{-1}, with a resolution of 4 cm^{-1}, coupled with a mercury-cadmium telluride detector. The mapping was carried out in the area of 150 μm x 193 μm of the PIM with 16 scans per pixel. The membrane made of CTA was taken as the blank. The distribution