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A comparative evaluation of the liquid–liquid extraction and pertraction efficiency of a both-side diglycolamide-functionalized calix[4]arene with analogous upper and lower-rim calixarenes for actinide separations

P.K. Mohapatra [a,*], D.R. Rout [a], M. Iqbal [b], J. Huskens [b], W. Verboom [b]

[a] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] 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

A lower-rim (**L-I**), an upper-rim (**L-II**), and a both-side (**L-III**) diglycolamide-functionalized calix[4]arene were evaluated for the extraction of actinide ions such as UO_2^{2+}, Pu^{4+}, and Am^{3+} and fission product element ions such as Eu^{3+}, Cs^{+}, and Sr^{2+} from dilute nitric acid feed solutions. Conditions for quantitative extraction and stripping were found out and the kinetics of it were investigated for the extraction of Am^{3+}. Though the actinide ions were generally extracted efficiently, UO_2^{2+} was poorly extracted.

Supported liquid membrane (SLM) studies were carried out using the diglycolamide-functionalized calix[4]arenes under varying feed acidities and carrier extractant concentrations and the results compared with that of TODGA under identical conditions. A 0.01 M EDTA solution (pH 3.0) was found to yield quantitative transport of Am(III) using the extractants **L-I–L-III**. The transport efficiency of the carrier solvent system was $Eu^{3+} > Pu^{4+} > Am^{3+} \gg UO_2^{2+}$. Diffusion coefficient values were both calculated by the Wilke-Chang equation and determined by the lag-time method. The SLM showed a poor stability, which did not improve by strip dispersion efforts.

1. Introduction

Solvent extraction (SX) methods using diglycolamide-based extractants are proposed for actinide partitioning from high level waste solutions for the mitigation of long-term hazards of the minor actinide elements such as Am, Cm, and Np, which have very long half-lives [1–4]. Out of the diglycolamides, TODGA (*N*,*N*,*N*′,*N*′-tetra-*n*-octyl diglycolamide) and T2EHDGA (*N*,*N*,*N*′,*N*′-tetra-2-ethylhexyl diglycolamide) have been extensively studied and counter-current extraction studies with promising results have been carried out [5–8]. These diglycolamides (DGA's) have been reported to display size selective extraction of metal ions [9] which was based on reverse micelle formation with 4 DGA molecules at 3 M HNO_3 [10]. This reverse micelle formation is dependent on the diluent characteristics. We have recently reported the synthesis of DGA-functionalized calix[4]arenes and investigated the extraction of actinides with highly encouraging results [11,12]. Though the DGA-functionalized calix[4]arenes have shown promise for actinide extraction, they have not been tested for large scale processing. However, some of the disadvantages of the SX methods are third phase formation, phase entrainment, phase disengagement limitations, etc. Also, due to the growing concerns for the environment, alternatives to the SX methods are required with low volatile organic carbon (VOC) content.

One of the most known alternatives to the SX technique is liquid membrane-based separations, which have near insignificant VOC inventory as in supported liquid membranes (SLM) [13–15]. The advantages of the SLM-based separation methods include a lesser amount of secondary waste, selective transport of target metal ions from a mixture of contaminants, simultaneous extraction and stripping possibility, no third phase limitations (due to non-dispersive mass transfer and simultaneous stripping), ease of operation, easy scale up, etc., apart from the low solvent inventory already mentioned. We extensively studied SLM-containing diglycolamides such as TODGA and T2EHDGA with quite promising reports [16–19]. The transport of actinides using DGA-functionalized calix[4]arenes using SLMs was also investigated [20,21]. We have recently reported on the exceptional extraction capabilities of an octa-diglycolamide-functionalized calix[4]arenes (functionalized at both the sides of the

Abbreviations: ESEM, Environmental scanning electron microscope; HLW, High level waste; PTFE, Polytetrafluoroethylene; SLM, Supported Liquid Membrane; SX, Solvent extraction; TODGA, *N*,*N*,*N*′,*N*′-tetra-*n*-octyl diglycolamide; VOC, Volatile organic compounds

* Corresponding author. Tel.: +91 22 25594576; fax: +91 22 25505151.
E-mail address: mpatra@barc.gov.in (P.K. Mohapatra).

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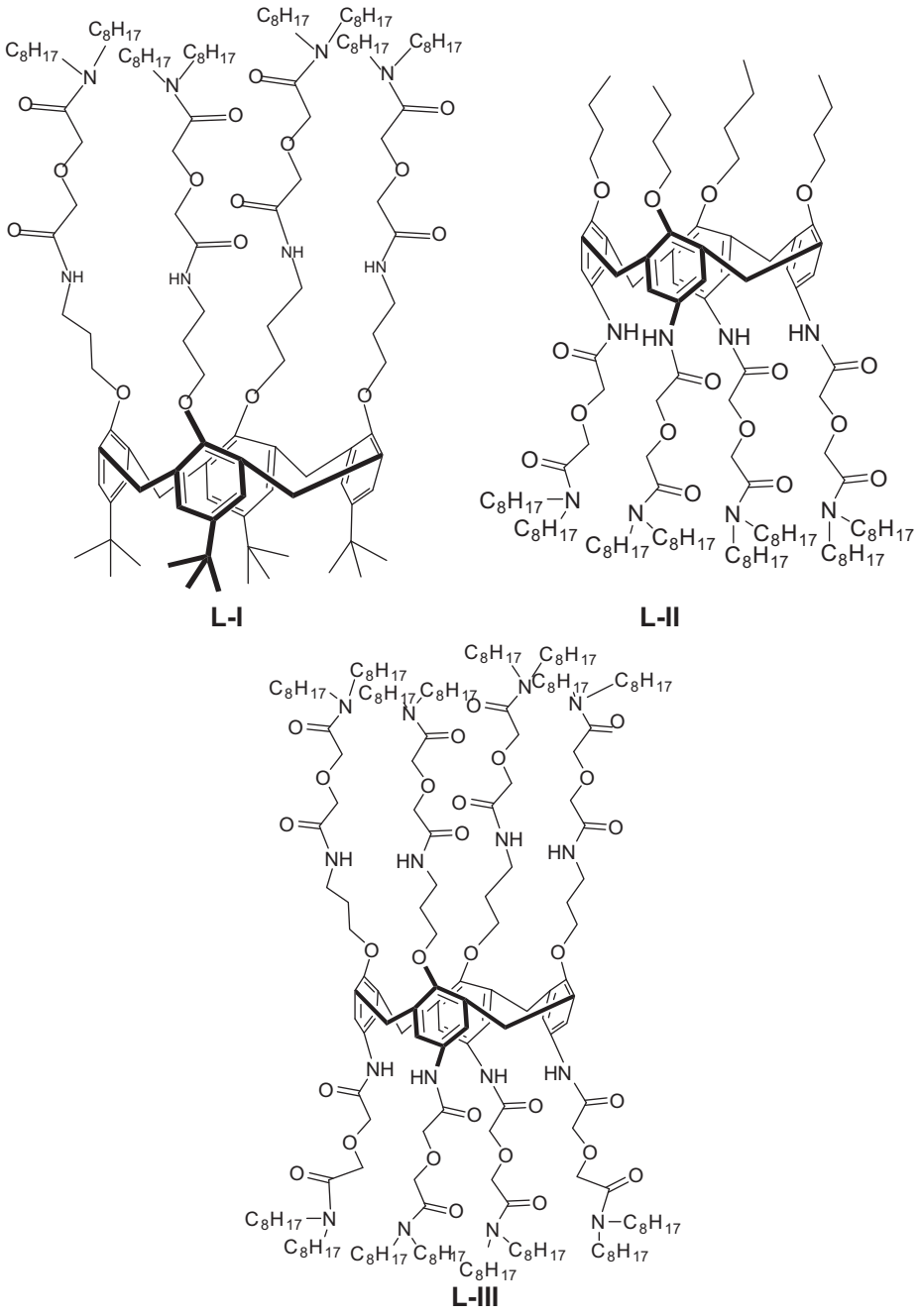

Fig. 1. Structural formulae of diglycolamide-functionalized extractants **L-I**–**L-III**.

calix[4]arenes) platform [22]. This inspired us to attempt to understand the transport properties of actinides using this DGA-functionalized calix[4]arenes (**L-III**) as the carrier extractant in the pores of flat-sheet PTFE membranes. For comparison, the lower rim (**L-I**) as well as upper rim (**L-II**) functionalized-calixarenes are also studied (Fig. 1). The present work deals with the solvent extraction as well as SLM transport studies as a function of varying nitric acid concentration. In addition, the diffusion coefficient values are also computed experimentally.

2. Experimental

2.1. Materials

Ligands, **L-I**, **L-II** and **L-III** were synthesized as reported in a previous publication [11]. The ligands were characterized by HPLC, NMR, IR, and ESI-MS analysis. Polytetrafluoroethylene (PTFE) membrane filters were obtained from Sartorius, Germany, and were characterized for membrane thickness, porosity, and tortuosity. Thickness and porosities of the PTFE filters were measured using a Mitutoyo Digital micrometer and an Electroscan 2020 environmental scanning electron microscope (ESEM), respectively. While the membrane thickness was measured to be 80 μm, the average porosity of the membrane filters was 64% and its pore size was 0.45 μm. AR grade 1-octanol and *n*-dodecane were procured from Merck (India) at a purity level of $>99\%$ and were used as received. ^{241}Am was purified using an ion-exchange procedure [23] and its radiochemical purity was checked using alpha as well as gamma ray spectrometry. Suprapur nitric acid (Merck) and MilliQ water were used for the preparation of standard acid solutions, which were standardized prior to use. All other reagents were of AR grade.