



Unusual transport behaviour of actinide ions with a novel calix[4]arene-tetra-diglycolamide (C4DGA) extractant as the carrier

P.K. Mohapatra^{a,*}, M. Iqbal^b, D.R. Raut^a, J. Huskens^b, W. Verboom^b

^a Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^b Laboratory of Molecular Nanofabrication, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 7 December 2011

Received in revised form 5 April 2012

Accepted 10 April 2012

Available online 18 April 2012

Keywords:

Calix[4]arene diglycolamide

Actinides

TODGA

Solvent extraction

Liquid membrane

ABSTRACT

A calix[4]arene appended with four diglycolamide moieties containing *n*-octyl groups (C4DGA) was evaluated for the transport of actinide ions such as UO_2^{2+} , Pu^{4+} , Pu^{3+} , and Am^{3+} from acidic feed solutions across PTFE flat sheet supported liquid membranes. The supported liquid membrane (SLM) studies were carried out with C4DGA under varying feed acidities, carrier extractant concentrations, and membrane pore sizes. While low pH solutions resulted in no Am^{3+} transport, quantitative transport of the metal ion was observed when 0.01 M EDTA solution (pH 3.0) was used as the strippant in the receiver phase. The transport efficiency of the carrier solvent system was $\text{Pu}^{4+} > \text{Am}^{3+} > \text{Pu}^{3+} \gg \text{UO}_2^{2+}$, which is not in line with those observed for diglycolamide extractants, where Am^{3+} was extracted to a much higher extent than other actinide ions. The results were compared with those reported earlier for TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide) and tripodal diglycolamide (T-DGA) under identical conditions. Eu^{3+} transport rates were found out to be significantly higher than those observed with Am^{3+} . The selectivity factors of the C4DGA extractant were compared with those of other DGA-based extractants reported earlier. The diffusion coefficient for the $\text{Am(III)}\text{-C4DGA}$ complex was obtained experimentally using the lag time method. The stability studies indicated significant deterioration of the liquid membrane with time even after only 3 days of operation.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The growing energy demands and limited reserve of fossil fuel has made nuclear energy as one of the viable alternative energy sources. However, one of the major disadvantages of nuclear energy programme is the formation of a host of radioactive isotopes generated during the fission/activation taking place during the irradiation of the fissile/fertile elements in the nuclear reactors. The management of the radioactive waste is, thus, one of the most challenging tasks for separation scientist working in the back end of the nuclear fuel cycle. Though most of the radioactivity of the HLW (high level waste emanating from the PUREX cycle) decays in about 5 years of cooling, the long lived minor actinides (mostly Am and Cm) are of concern and need to be separated prior to the vitrification of the HLW in glass blocks. The emerging strategy for radioactive waste management is the P&T or 'Partitioning & Transmutation' which involves selective separation of trivalent minor actinides and their subsequent transmutation in high flux reactors or accelerator driven sub-critical systems.

Out of the extractants used for 'minor actinide partitioning', a strategy proposed for the mitigation of the long term hazards of high level waste (HLW), those containing diglycolamide (DGA) functional groups have been found to be the most acceptable, not only due to their high distribution coefficient values shown for trivalent actinides such as Am and Cm, but also from the point of view of their complete incinerability and innocuous nature of their degradation products [1–3]. Out of the DGA-based extractants, TODGA (*N,N,N',N'*-tetraoctyl diglycolamide, Fig. 1) has been the most efficient and extracts the actinide ions in the trend: $\text{Am}^{3+} > \text{Pu}^{4+} \gg \text{UO}_2^{2+}$, which is rather unusual considering the ionic potential of these ions and their complexation tendencies which follow the order: $\text{Pu}^{4+} > \text{UO}_2^{2+} > \text{Am}^{3+}$ [4]. This has been attributed to the aggregation behaviour of TODGA in non-polar diluents leading to reverse micelle formation [5], which apparently facilitates Am^{3+} extraction to a much greater extent than Pu^{4+} and UO_2^{2+} . Small angle neutron scattering data have indicated the aggregation number as four suggesting participation of four TODGA units in the reverse micelle formation in *n*-dodecane medium, which has also independently been proven from solvent extraction studies [5,6]. It was also noted that the number of TODGA molecules in the extracted species decreased to about two when polar diluents were used [7]. Therefore, it was of interest to synthesize and evaluate extractants containing four TODGA units. It was speculated that

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

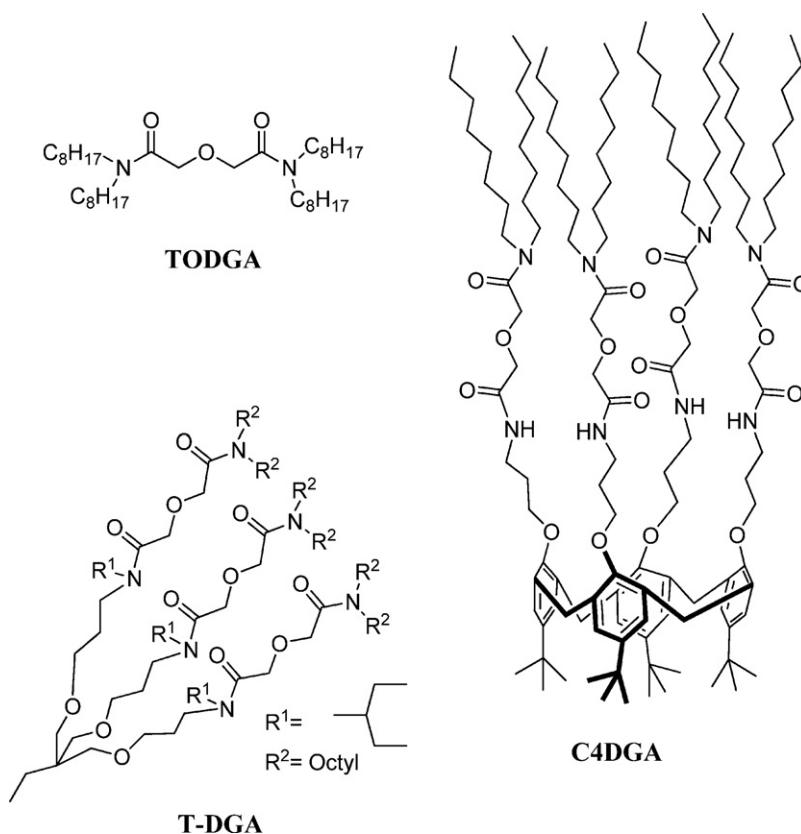


Fig. 1. Structural formulae of TODGA, T-DGA, and C4DGA.

such an extractant would make the effect of organic diluent redundant. A novel extractant was prepared consisting of a calix[4]arene molecular platform on to which four diglycolamide moieties were appended with two *n*-octyl groups in each DGA moiety so as to mimic the TODGA aggregate (C4DGA, Fig. 1).

Large scale process applications using extractants such as a diglycolamide functionalized calix[4]arene can be rather expensive. The ligand inventory can be significantly brought down, thereby reducing the cost of operation, using liquid membrane (LM) based separation methods as alternative separation technique. Moreover, LM techniques have some more advantages over solvent extraction methods, such as alleviation of problems such as third phase formation, phase separation limitations, and phase entrainment [8–11]. Furthermore, liquid membrane-based separation methods involve simultaneous extraction and stripping. We have extensively investigated the transport behaviour of various actinide elements using supported liquid membrane (SLM) based methods using TODGA as the extractant and the results were quite promising [12–16]. However, for efficient transport of the actinide ions, the diluent plays an important role and *n*-dodecane is preferred as it favours reverse micelle formation.

The objective of the present work was to evaluate the newly synthesized DGA-functionalized calix[4]arene which can offer four DGA moieties, thereby providing the same effect as the reverse micelle forming TODGA. Moreover, the presence of four DGA moieties may lead to even better complexation and hence more efficient extraction and transport properties with much lower ligand inventory, due to the ‘cooperative’ complexation phenomena.

The present work deals with the extraction as well as transport behaviour of Am(III) using C4DGA (Fig. 1) in *n*-dodecane. The extraction behaviour of the actinide ions was studied from nitric acid feed conditions using this extractant and the results were compared with those observed previously with TODGA

and a tripodal diglycolamide (T-DGA, Fig. 1 [17]), which also has multiple DGA moieties. Furthermore, liquid membrane transport studies were performed under varying feed acidities, carrier extractant concentrations, and membrane pore size. The calculated diffusion parameters are compared with those obtained experimentally. This is the first ever report on the detailed SLM transport study of actinides using the exotic ligand C4DGA as the extractant.

2. Experimental

2.1. Materials

2.1.1. General

PTFE membranes used in the present study were procured from Sartorius, Germany. The membrane thickness was measured using a Mitutoyo Digital micrometer, while porosities of the membranes were measured by an Electroscan 2020 environmental scanning electron microscope (ESEM) as reported in an earlier publication [18]. The membranes with pore sizes of 0.2, 0.45, 1.2, and 5.0 μm were found to have porosities of 51, 64, 74, and 84%, respectively, and the corresponding effective areas were calculated as 2.50, 3.14, 3.63, and 4.12 cm^2 , respectively. All reagents were of AR grade and were used without further purification. ^{241}Am , Pu (mainly ^{239}Pu), and ^{233}U tracers were purified prior to their use by ion-exchange methods [19], while $^{152,154}\text{Eu}$ tracer was purchased from Board of Radiation and Isotope Technology (BRIT), Mumbai. Assaying of ^{241}Am and $^{152,154}\text{Eu}$ was done by gamma counting using a NaI(Tl) scintillation counter, while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting.

2.1.2. Synthesis of C4DGA

The synthesis of C4DGA was performed as summarized in Scheme 1.

2.1.2.1. *p*-Nitrophenol activated DGA (2). A solution of *N,N*-dioctylglycolic acid (**1**) (2.00 g, 5.6 mmol), *p*-nitrophenol (0.81 g, 5.7 mmol), and *N,N*-dicyclohexylcarbodiimide or DCC (1.22 g, 5.8 mmol) in pyridine (60 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane, filtered and the filtrate was washed with 4% NaHCO₃ solution (2 × 50 mL). The organic layer was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂:MeOH, 98:2) to afford *p*-nitrophenol activated DGA (**2**) (2.16 g, 81%) as a light yellow oil. ¹H NMR (CDCl₃): δ 0.81–0.93 (m, 6H, CH₃), 1.14–1.38 (m, 20H, CH₃(CH₂)₅), 1.45–1.60 (m, 4H, NCH₂CH₂), 3.18 and 3.31 (t, 2H, *J* = 7.5 Hz, NCH₂), 4.37 (s, 2H, OCH₂), 4.58 (s, 2H, OCH₂), 7.33 (d, 2H, *J* = 9.0 Hz, ArH), 8.28 (d, 2H, *J* = 9.0 Hz, ArH); ¹³C NMR (CDCl₃): δ 14.3, 22.8, 29.5, 31.9, 60.1, 68.2, 69.4, 122.5, 125.5, 126.3, 145.9, 169.1; HRMS: *m/z* 479.3130 (M+H)⁺, calculated: 479.3121.

2.1.2.2. Calix[4]arene 4-DGA (C4DGA). A mixture of tetraaminopropylcalix[4]arene (**3**, 0.45 g, 0.5 mmol) [20] and **2** (1.20 g, 2.5 mmol) and triethylamine (0.25 g, 2.5 mmol) in chloroform (50 mL) was refluxed overnight. The crude reaction mixture was successively washed with 2 M NaOH solution (3 × 50 mL), 1 M HCl (3 × 50 mL), and water (2 × 50 mL). The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography (CH₂Cl₂:MeOH, 96:4) to afford C4DGA (1.10 g, 71%) as a dense oil. ¹H NMR (CDCl₃): δ 0.81–0.93 (m, 24H, CH₃), 1.07 (s, 36H, *t*-Bu), 1.17–1.35 (m, 80H, CH₃(CH₂)₅), 1.43–1.60 (m, 16H, NCH₂CH₂), 2.25 (pentet, 8H, *J* = 6.0 Hz, OCH₂CH₂), 3.04–3.16 (m, 12H, ArCH₂Ar and NCH₂), 3.27 (t, 8H, *J* = 7.5 Hz, NCH₂), 3.46 (t, 8H, *J* = 6.0 Hz, NHCH₂), 3.89 (t, 8H, *J* = 6.0 Hz, ArOCH₂), 4.09 (s, 8H, OCH₂CO), 4.27 (s, 8H, OCH₂CO), 4.34 (d, 4H, *J* = 12.0 Hz, ArCH₂Ar), 6.75 (s, 8H, ArH), 7.97–8.07 (m, 4H, NH); ¹³C NMR (CDCl₃): δ 14.3, 22.9, 27.1, 29.5, 31.6, 32.0, 34.0, 36.7, 46.3, 47.0, 60.1, 133.9, 144.8, 153.5, 168.4, 170.0; MS: *m/z* 2234.7 (M+H)⁺, calculated: 2234.8.

2.2. Methods

2.2.1. Distribution studies

The solvent extraction studies involving Am(III) were carried out by thoroughly mixing 1 mL of the ligand solution in *n*-dodecane with an equal volume of the aqueous phase containing ²⁴¹Am (in a concentration of ~10⁻⁷ M) in 3 M HNO₃ in Pyrex glass tubes equilibrated in a thermostated water bath at 25 ± 0.1 °C for about 1 h. Subsequently, the tubes were centrifuged and the phases were separated and assayed radiometrically using a NaI(Tl) scintillation detector. The distribution ratio, *D_M*, was defined as the ratio of the activity per unit volume in the organic phase to that in the aqueous phase. The experiments were carried out in triplicate and the reported data points had a precision within ±5%.

2.2.2. Transport studies

The supported liquid membrane (SLM) studies were carried out using 0.45 μm pore size PTFE membrane filters unless otherwise mentioned. For the pore size variation studies, membranes of 0.2 μm, 0.45 μm, 1.2 μm, and 5.0 μm pore sizes were used. The porosity of the membranes were measured by ESEM as given in an earlier publication [18]. The SLM transport studies were carried out using Pyrex glass transport cells with feed/strip capacity of 25 mL. The micro porous PTFE membranes were soaked in the carrier solution (usually 1.13 × 10⁻³ M C4DGA in *n*-dodecane) 30 min prior to use and the carefully wiped membrane filters were planted

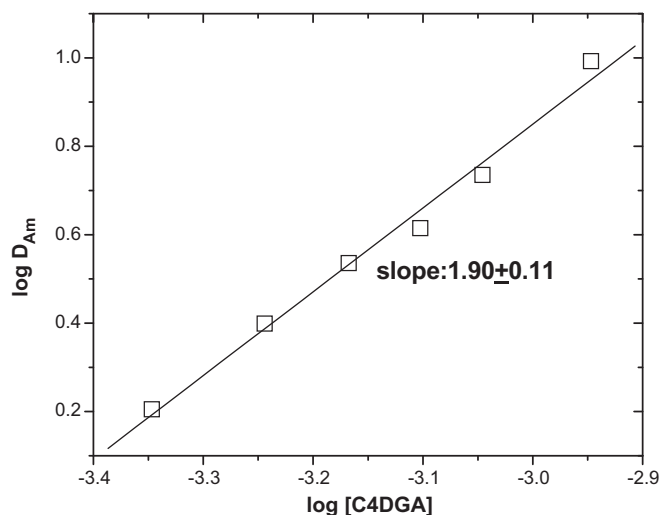


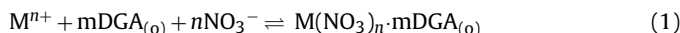
Fig. 2. Plot showing the variation of Am³⁺ extraction as a function of C4DGA concentration. Aqueous phase: 3 M HNO₃.

in between the two compartments containing the feed and receiver solutions, which were stirred at 200 rpm using synchronous motors which was reported to be the optimum speed [18]. Usually, the feed compartment contained ²⁴¹Am tracer in dilute nitric acid, while the strip solution used in the receiver compartment was 0.01 M EDTA solution (pH 3.0). An assay of the radiotracer was made as described above from the feed as well as the receiver compartment at different time intervals to calculate the permeability coefficients (*P*) and the cumulative percent transport (%*T*) data. The transport studies were carried out at ambient temperature (24 ± 1 °C). The material balance in these studies was found to be within ±5%.

3. Results and discussion

3.1. Solvent extraction studies

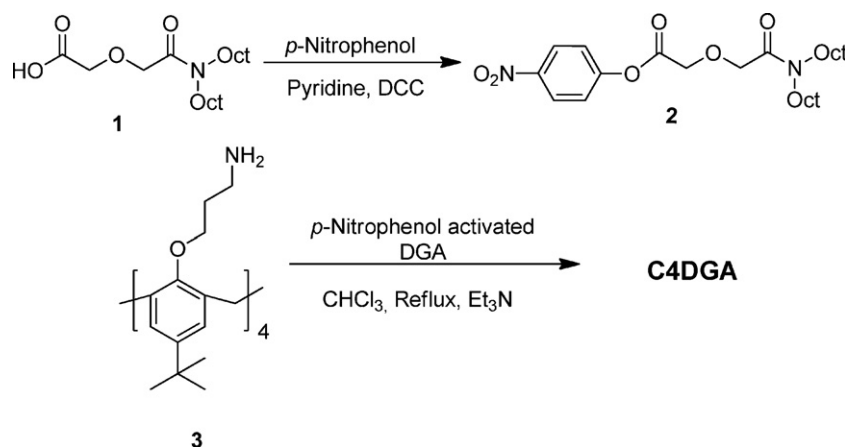
The extraction of actinide ions using a diglycolamide (DGA) extractant is given by the general extraction equilibrium [7]:



where the species with the subscript '(o)' indicate those present in the organic phase, while those without any subscript are those in the aqueous phase. It has been reported that the number of DGA molecules associated with the extracted species depends on a variety of factors such as the nature of metal ion, the nature of the substituent in the DGA compound, the nature of the diluent, and even the feed acidity [6,7]. For 3–4 M HNO₃ as the feed, usually 4 extractant molecules are associated when TODGA is used for Am³⁺ extraction [6,7]. In the present case, C4DGA has four DGA moieties appended to the calix[4]arene frame and hence it is expected that only one C4DGA extractant molecule should be associated in the extracted species. However, the ligand concentration variation experiments carried out using 3 M HNO₃ as the aqueous feed indicated a dependence of 1.90 ± 0.11 in the log *D* vs. log [C4DGA] plot (Fig. 2). Accordingly, the extraction of Am³⁺ using C4DGA can be given by the extraction equilibrium:



Extraction and stripping kinetics studies were also carried out and the data are shown in Fig. 3. About 20 min was sufficient for attaining equilibrium in the forward extraction studies, and the same amount of time was required in the stripping studies as well when 0.01 M EDTA was used as the strippant. Relatively slower extraction rates (as compared to those reported with TODGA [21])



Scheme 1. Synthesis of C4DGA.

suggested kinetic control of reorientation of the ligating sites from a pre-organized structure prior to the complexation reaction. On the other hand, the stripping reaction was even slower due to extra-stability of the complex due to simultaneous bonding to eight DGA functional groups, probably leading to a very rigid configuration. Similar behaviour in a multiple DGA functionalized tripodal diglycolamide extractant was reported by us previously [17].

3.2. Transport studies

The transport of metal ions across a supported liquid membrane using a carrier extractant involves three simple steps effecting the overall mass transfer from the feed to the receiver phase, viz. extraction of the metal ion at the membrane–feed interface, diffusion of the metal–carrier complex across the length of the membrane and finally, stripping of the metal ion at the membrane–receiver interface. For an effective mass transfer, the rates of these steps should be reasonably fast. Moreover, the aqueous diffusion layers in the feed and the receiver phases should be practically non-existent. This can be achieved by high speed stirring of the aqueous phases. Under conditions of rapid extraction and stripping kinetics, the transport rate practically depends on the diffusion rate of the metal–carrier complex. The transport of

the metal ion can be quantified by a simple model developed by Danesi [22], where the permeability co-efficient (P) is correlated with the rate of change of the metal ion concentration in the feed phase. P can be experimentally determined from the concentration of the metal ions at different time intervals using the following equation:

$$\ln \left(\frac{C_{f,t}}{C_{f,0}} \right) = - \left(\frac{Q}{V_f} \right) P \cdot t \quad (3)$$

where Q is expressed as the product of the geometrical surface area (A) and the porosity (ϵ). The geometric surface area of the membrane was 4.94 cm^2 , while the effective surface area was 3.14 cm^2 for supports of $0.45 \mu\text{m}$ pore size. The cumulative percent transport ($\%T$) at a given time is determined by the following equation

$$\%T = 100 \cdot \left(\frac{C_{f,0} - C_{f,t}}{C_{f,0}} \right) \quad (4)$$

This equation is valid under the assumption that the metal ion trapped in the membrane phase is negligible. The mass balance of the feed and receiver phase was checked and found to account for almost entire amount of the metal ion while the membrane phase had negligible amount of the transported ion.

3.2.1. Transport of actinides

Fig. 4 shows the transport of Am^{3+} using $1.13 \times 10^{-3} \text{ M}$ C4DGA in n -dodecane as a function of time. While the feed composition was 3 M HNO_3 , the receiver phase consisted of 0.01 M HNO_3 similar to our previous studies with TODGA as well as tripodal diglycolamide (T-DGA) as the extractant [12,17]. It is surprising to note that Am(III) transport was negligible under these experimental conditions. On the other hand, when 0.01 M EDTA at $\text{pH } 3.0$ was used as the strippant in the receiver phase, transport of Am(III) was observed (Fig. 4). Our previous studies with a tripodal diglycolamide (T-DGA), containing three pendent DGA arms as compared to the four DGA arms present in C4DGA, also showed that EDTA was a more suitable strippant as compared to 0.01 M HNO_3 [17]. The possible reason could be unfavourable thermodynamic parameters (may be of entropic origin) responsible for the stripping reaction.

The transport behaviour of other selected actinides such as UO_2^{2+} , Pu^{3+} , and Pu^{4+} was also investigated and the transport profiles are presented in Fig. 5. Interestingly, the transport rates of Pu^{4+} was even higher than those observed for Am^{3+} , while those for UO_2^{2+} ions were insignificant over a period of 6 h ($\sim 6\%$). On the other hand, though the Pu^{3+} and Am^{3+} transport were significantly higher than those of UO_2^{2+} ion, they were lower compared

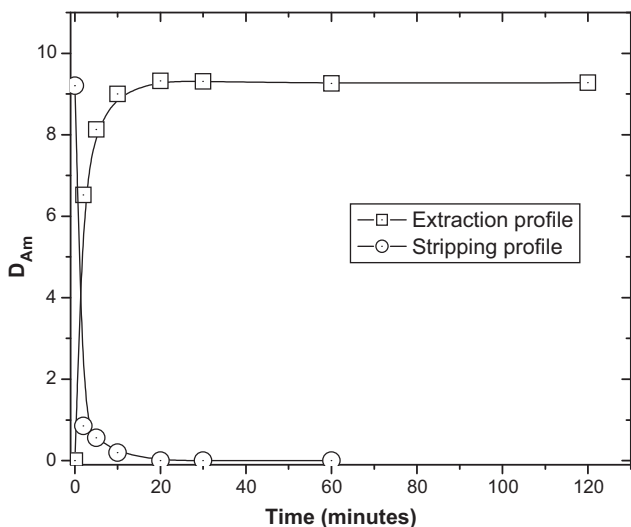


Fig. 3. Extraction and stripping profiles of Am^{3+} using $1.0 \times 10^{-3} \text{ M}$ C4DGA. Feed for the extraction studies was 3 M HNO_3 while the strippant used was 0.01 M EDTA at $\text{pH } 3.0$.

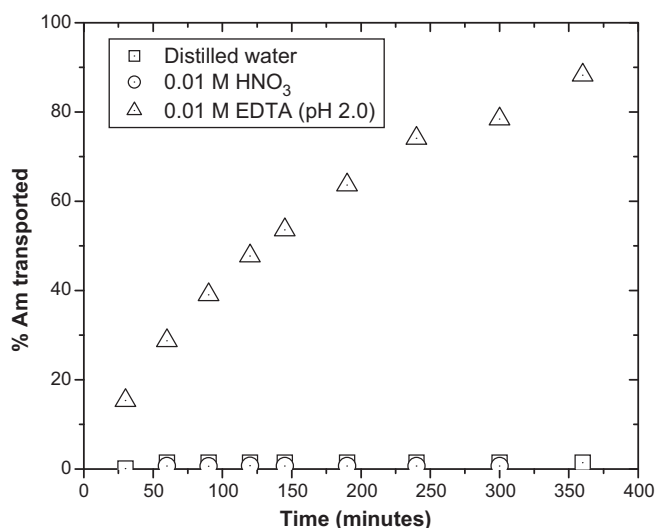


Fig. 4. Transport profiles of Am^{3+} from 3 M HNO_3 feed solutions with 0.01 M HNO_3 and 0.01 M EDTA at pH 3.0 as the strippants in the receiver phase.

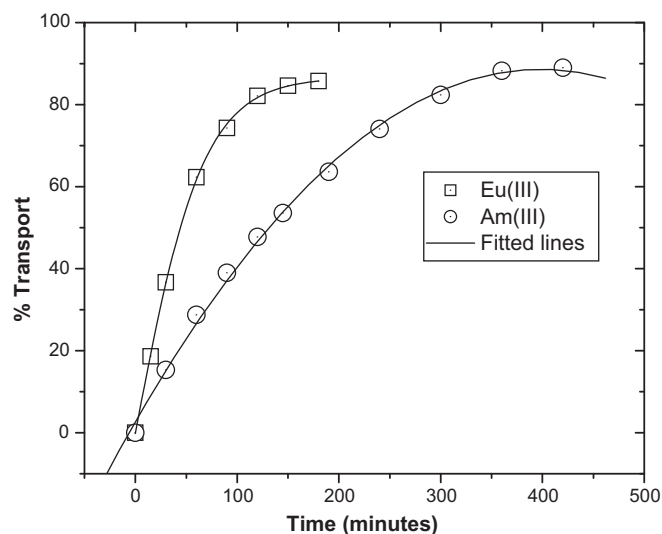


Fig. 6. Transport profiles of Am^{3+} and Eu^{3+} with time using 1.13×10^{-3} M C4DGA in *n*-dodecane as the carrier solvent. Feed: 3 M HNO_3 ; receiver: 0.01 M EDTA solution (pH 3.0).

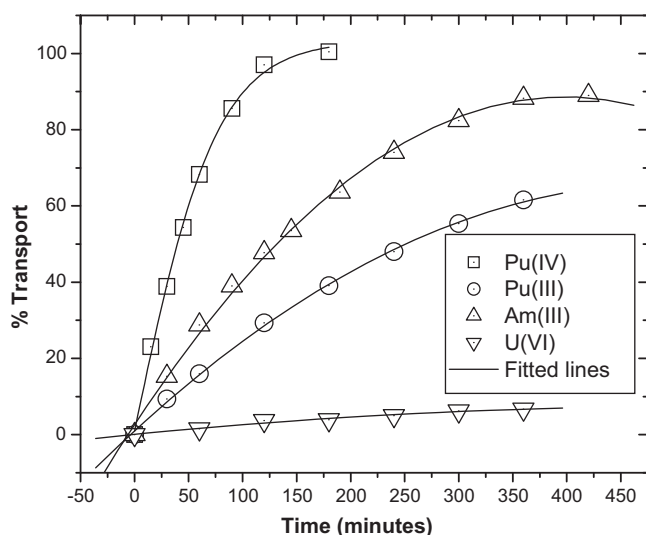


Fig. 5. Transport profiles of several actinide ions with 1.13×10^{-3} M C4DGA in *n*-dodecane as the carrier solvent. Feed: 3 M HNO_3 ; receiver: 0.01 M EDTA solution (pH 3.0).

to the Pu^{4+} ion transport rates. This behaviour is rather unusual for diglycolamide based extractants. Previous reports have shown that trivalent actinide ions have been most efficiently transported with diglycolamide extractants, while in the present study the trend is: $\text{Pu}^{4+} > \text{Am}^{3+} > \text{Pu}^{3+} \gg \text{UO}_2^{2+}$. The %T data along with the

permeability coefficient values for the actinides are listed in Table 1. For comparison purposes, the P values for the T-DGA transport system are also given. Interestingly, the P values are much lower for UO_2^{2+} and those of Pu^{3+} are of the same order for both T-DGA and C4DGA, while that for Pu^{4+} with C4DGA is about one order of magnitude higher than that with T-DGA. On the other hand, the P value for Am^{3+} transport with C4DGA is one order of magnitude lower as compared to that reported for T-DGA. This unusual trend of metal ion transport using diglycolamide extractants cannot be explained on the basis of the reverse micelle mechanism suggested by Jensen et al. [5]. Apparently, the ionic potential (charge to radius ratio) of the metal ions plays a significant role in the present case, which may also explain the higher transport rates observed with Am^{3+} as compared to that with Pu^{3+} . However, the UO_2^{2+} transport is not fitting into this explanation, as UO_2^{2+} has a greater ionic potential than Am^{3+} . It could be explained on the basis of the unusual stereochemical requirements of the uranyl ion and the strain experienced by the C4DGA ligand to form a complex with it. Such poor transport rates were also obtained in our studies with the T-DGA extractant [17]. An advantage of the poor transport rates of U is that the actinide elements such as Am (present in the +3 state) and Pu (can be easily converted to the +4 state) can be selectively separated by the SLM method using C4DGA without any significant transport of U. The high level waste contains a significant amount of U (about 6–20 g/L [14]) from the losses during the PUREX cycle. Moreover, a high U concentration can lead to saturation of the organic phase, thus seriously affecting the transport rates of other actinides such as Pu and Am. Thus, prior removal of U is usually suggested as one

Table 1
Permeability data of different actinide ions and Eu^{3+} using C4DGA as the carrier extractant. Feed: 3 M HNO_3 ; receiver: 0.01 M EDTA (pH 3.0); carrier solvent: 1.13×10^{-3} M C4DGA in *n*-dodecane.

Metal ion	%T (2 h)	$P_{\text{C4DGA}} (\text{cm/s}) \times 10^{3,a}$	Selectivity coefficient	$P_{\text{T-DGA}} (\text{cm/s}) \times 10^{3,b}$	Selectivity coefficient	$P_{\text{TODGA}} (\text{cm/s}) \times 10^{3,c}$	Selectivity coefficient
Am^{3+}	47.3	0.504 ± 0.017	–	2.39 ± 0.07	–	3.67 ± 0.06	–
Eu^{3+}	82.5	1.88 ± 0.09	0.27	–	–	3.64 ± 0.15	1.01
Pu^{3+}	29.4	0.346 ± 0.022	1.45	0.86 ± 0.17	2.77	2.24 ± 0.01^d	1.64
Pu^{4+}	97.1	1.47 ± 0.14	0.343	0.12 ± 0.04	19.9	1.52 ± 0.03	2.41
UO_2^{2+}	3.68	$(2.01 \pm 0.07) \times 10^{-2}$	25.2	$(6.09 \pm 0.71) \times 10^{-2}$	39.2	0.94 ± 0.01	3.90

^a Present work.

^b Data taken from Ref. [17].

^c Data taken from Ref. [12].

^d Data taken from Ref. [23].

of the mandatory requirements prior to the ‘actinide partitioning’ step. However, the present study indicates that prior removal of U is not a requirement if C4DGA is used as the extractant. The comparative transport data of the actinide ions are also listed in Table 1, in which the permeability coefficients (P) and the cumulative percentage transport after 2 h are presented. These data indicate poor transport of U from 3 M HNO_3 feed conditions.

Selectivity coefficients, defined as the ratio of the permeability coefficients of Am^{3+} to that of other actinide ions, are also listed in Table 1. The selectivity coefficient for Pu^{3+} was comparable those of C4DGA and TODGA as the extractants, while that with T-DGA was nearly double, suggesting favourable transport of Am^{3+} vis-à-vis Pu^{3+} with T-DGA as the carrier. On the other hand, the selectivity coefficient for Pu^{4+} is highly favourable with respect to C4DGA (Table 1). While an opposite trend was reported for both TODGA and T-DGA, highly favourable Am^{3+} transport vis-à-vis Pu^{4+} transport was reported for T-DGA. As discussed in the previous paragraph, selectivities with respect to uranyl ion are favourable for the multiple functionalized ligands such as C4DGA and T-DGA (Table 1).

3.2.2. Transport of Eu^{3+} ion

The transport profile of Eu^{3+} ion is presented in Fig. 6 and for comparison purposes the transport profile of Am^{3+} ion is also presented in it. Interestingly, the transport rate of Eu^{3+} is much faster than of Am^{3+} and it saturates after 85% of Eu transported which took about 150 min. On the other hand, in the same time interval about 55% Am^{3+} transport was noticed. This is in sharp contrast to the transport behaviour of Eu^{3+} vis-à-vis Am^{3+} reported earlier with TODGA as the carrier extractant [13]. Accordingly, the selectivity coefficient for Eu^{3+} is nearly comparable to that observed for Pu^{4+} , which also implies much faster transport rates than those for Am^{3+} . Though the reverse micellar mechanism is the reason for the comparable transport of Eu^{3+} and Am^{3+} with TODGA as the carrier extractant [5], difference in the complex species may be the reason for the difference in the transport rates. Am^{3+} forms a 1:2 complex with C4DGA, while the formation of 1:1 species for Eu^{3+} was observed recently [24].

3.2.3. Effect of the feed acidity

As indicated by the extraction equilibrium, the extraction of Am^{3+} is influenced by the feed phase nitrate concentration. Therefore, an increase in the nitric acid concentration will enhance the transport rates of the actinide ion. However, the only factor affecting the transport rates with increasing acidity is the co-transport of nitric acid into the receiver compartment. Previously, we reported a significant decrease in the transport rates of Am^{3+} when CMPO+TBP were used as the extractants as these ligands co-transport large concentrations of nitric acid causing reverse transport after a certain time [25,26]. The transport profiles of Am^{3+} as a function of the feed nitric acid concentration are presented in Fig. 7. Interestingly, a monotonous increase in Am^{3+} transport rates was observed when the feed phase acidity was gradually changed from 1 M to 6 M HNO_3 (Fig. 7). This is in sharp contrast to the earlier reports on Am^{3+} transport using TODGA and T-DGA, where maximum transport rates were seen at 2 M and 4 M HNO_3 , respectively, and the transport rates were significantly low at 6 M HNO_3 . The P values are listed in Table 2 and they exhibit a continuous increase with increasing feed acidity. The monotonous increase in the P values up to 6 M HNO_3 in the present case is attributed to negligible nitric acid co-transport (<0.1%), which in turn is attributed to unfavourable complexation of H^+ ions with C4DGA due to the pre-organization of the ligating sites.

3.2.4. Effect of C4DGA concentration

As indicated in Eqn. (2), an increase in the carrier concentration should increase the extraction of Am^{3+} at the feed–membrane

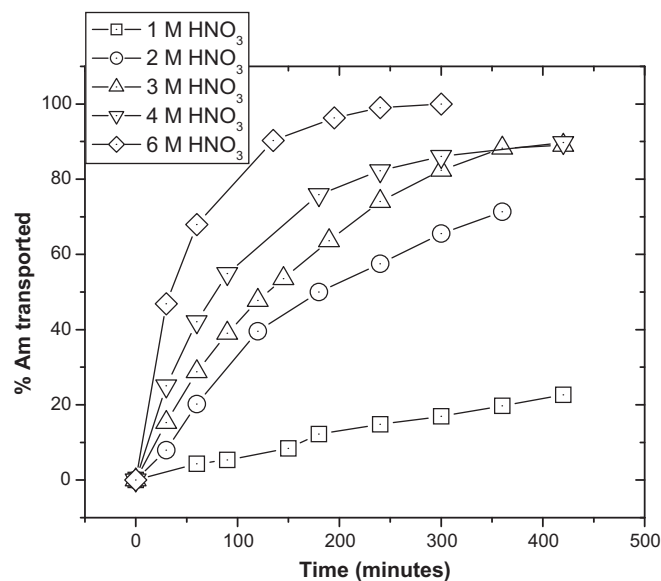


Fig. 7. Transport profiles of Am^{3+} with varying feed acidity. Carrier: 1.13×10^{-3} M C4DGA in n -dodecane; receiver: 0.01 M EDTA solution (pH 3.0).

Table 2

Transport data of Am(III) using C4DGA in n -dodecane as the carrier solvent.

$[\text{HNO}_3]$ (M) ^a	$P \times 10^4$ (cm/s)	$[\text{C4DGA}] \times 10^4$ (M) ^b	$P \times 10^3$ (cm/s)
1	0.59 ± 0.08	2.5	0.34 ± 0.04
2	3.50 ± 0.23	5.0	2.86 ± 0.03
3	5.04 ± 0.17	11.3	5.04 ± 0.17
4	8.56 ± 0.31		
6	20.6 ± 1.32		

^a $[\text{C4DGA}] = 1.13 \times 10^{-3}$ M; receiver phase: 0.01 M EDTA at pH 3.0.

^b Feed: 3 M HNO_3 ; receiver phase: 0.01 M EDTA at pH 3.0.

interface and hence may have a positive influence on the metal ion transport. The extraction profiles with varying C4DGA concentration are presented in Fig. 8 and as expected the transport rates have significantly improved on changing the extractant concentration from 2.5×10^{-4} M to 5.0×10^{-4} M. The %Am transport has increased about four times on doubling the C4DGA concentration (%Am transport with 2.5×10^{-4} M C4DGA and 5.0×10^{-4} M C4DGA

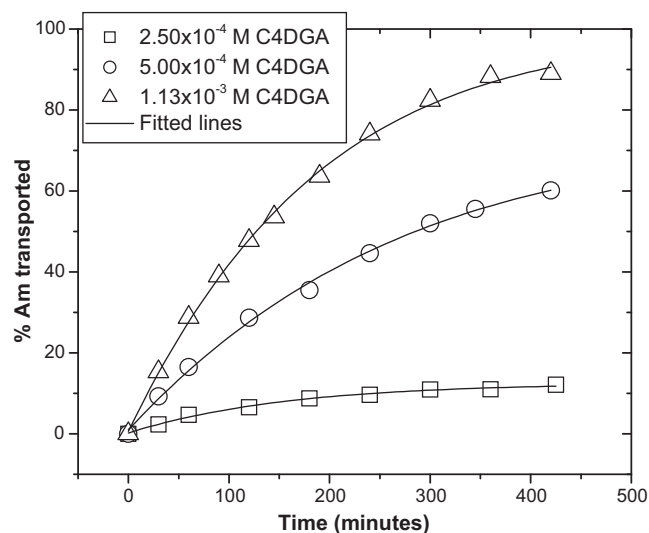


Fig. 8. Transport profiles of Am^{3+} with varying C4DGA concentration. Feed: 3 M HNO_3 ; receiver: 0.01 M EDTA solution (pH 3.0).

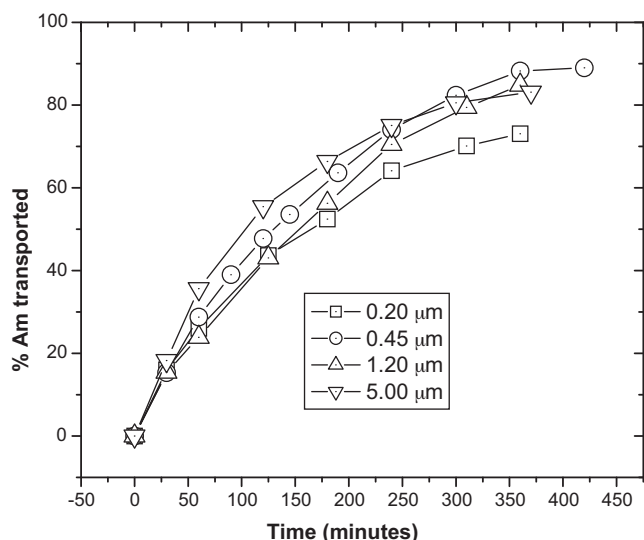


Fig. 9. Effect of membrane pore size on Am^{3+} transport behaviour. Carrier: 1.13×10^{-3} M C4DGA in *n*-dodecane; Feed: 3 M HNO_3 ; receiver: 0.01 M EDTA solution (pH 3.0).

were 6.5% and >28% after 2 h). This is rather remarkable considering the fact that the $\text{Am}(\text{III})$ extraction has a dependence of ~ 1 with the carrier extractant concentration (vide supra). On increasing the extractant concentration further to 1.13×10^{-3} M, the %Am transport was only 47.3% (after 2 h), suggesting that there is no linear dependence of mass transfer with carrier concentration. This can again be attributed to kinetic factors, possibly to the stripping reaction at the membrane-strip interface. The permeability coefficient values are calculated and listed in Table 2.

3.2.5. Effect of membrane pore size

There are only very few reports on the effect of membrane pore size on the metal ion transport. For metal ion transport in an SLM system, the permeability co-efficient (P) value is directly proportional to the membrane pore size [27] as can be seen from Eq. (5):

$$P = \frac{\varepsilon R^2}{\tau 2d_o} \quad (5)$$

where R is the membrane pore radius, τ is the tortuosity factor, ε is the membrane porosity, and d_o is the membrane thickness. Eq. (5) suggests that with increasing pore size of the membrane the permeability coefficient should increase, which is perhaps a consequence of the less hindrance experienced by the diffusing species. On the other hand, the Laplace's equation suggests that the minimum trans-membrane pressure (p) required to eject the carrier molecules from the membrane pores is given as:

$$p = \left(\frac{2\gamma}{R} \right) \cos \theta \quad (6)$$

where R is the pore radius, γ is the interfacial tension between solvent and water, and θ is the contact angle. With increasing pore size, the possibility of the carrier molecules getting ejected out of the pores becomes more favourable. This effect can lead to a decrease in carrier content in the pores and hence is reflected in a lowering in the transport rate. In many cases, this effect is prominent and a decrease in the permeability coefficient is observed with increasing membrane pore size [28]. The results of the transport studies using varying pore size of the PTFE filters containing 1.13×10^{-3} M C4DGA in *n*-dodecane as the carrier solvent are presented in Fig. 9. Though the trend is not very clear, it is apparent that the transport rate is the lowest with a 0.2 μm membrane and is highest with

Table 3

Permeability data with membranes of varying pore sizes.

Pore size	$P_{\text{C4DGA}} \times 10^4$ (cm/s) ^a	$P_{\text{TODGA}} \times 10^4$ (cm/s) ^b
0.2	4.11 ± 0.09	20.4
0.45	5.04 ± 0.17	13.68
1.2	4.71 ± 0.16	12.33
5.0	5.40 ± 0.19	9.17

^a [C4DGA] = 1.13×10^{-3} M; feed: 3 M HNO_3 ; receiver phase: 0.01 M EDTA at pH 3.0.

^b [TODGA] = 0.1 M in *n*-dodecane; feed: 1 M HNO_3 ; receiver phase: 0.01 M HNO_3 .

those of 5.0 μm pore size. This is not the case in our earlier studies. For comparison purposes, the P values for the C4DGA system are listed together with those obtained for the TODGA system in Table 3. Whereas a clear decreasing trend with increasing membrane pore size was noted for the TODGA system, a near constancy in the P values with a marginal increase with increasing pore size was obtained in the present transport system containing C4DGA as the carrier extractant. This could be attributed to the large volume of the metal-carrier complex in the present system. A similar increasing trend with increasing pore size was also observed for higher molar volume complexes [29].

3.2.6. Calculation of membrane diffusion coefficient

The transport rate of $\text{Am}(\text{III})$ using C4DGA is significantly slower than that of TODGA ($\sim 62\%$ in 3 h vs. $>98\%$ in 3 h with TODGA [12]) and even than that of the analogous multi-functional T-DGA as the extractant ($>96\%$ [17]). This may be attributed to the slow diffusion of the bulky $\text{Am}(\text{III})$ -C4DGA complex in the membrane phase, which has a dynamic viscosity of 1.34 mPa.s. As the viscosity of the medium is lower compared to that used in the TODGA system ($\eta = 1.604$ mPa.s), the slow transport rate could be mainly ascribed to the higher molar volume of the complex and may be to some extent to the kinetic factors responsible during complexation/de-complexation due to the pre-organized structure of the free ligand. However, comparison with the TODGA transport system [12] which also contained four diglycolamide moieties in the extracted species, suggested definite role of the complexation/de-complexation kinetics. The size of the diffusing complex is inversely proportional to its diffusion rate suggesting that bulkier metal-carrier complexes result in slower transport rates as indicated by the Wilke-Chang equation [30]:

$$D_o = 7.4 \times 10^{-8} \frac{(\chi^{0.5} M^{0.5} T)}{(\eta V_m^{0.6})} \quad (7)$$

where D_o , M , χ and η are the diffusion coefficient of the complex, molecular weight of the complex, solvent association parameter and the viscosity of the solvent, respectively, V_m the molar volume of the complex and T is the temperature. The diffusion coefficient calculated from Wilke-Chang equation is 5.79×10^{-6} cm²/s. On the other hand, the effective diffusion coefficient (D_{eff}) of the complex can be calculated from lag-time (t_{lag} , the time required for the complex to be detected in the receiver phase from the start of the experiment) measurements involving the metal carrier complex from the following expression [31]:

$$D_{\text{eff}} = \frac{d_o^2 \varepsilon}{6t_{\text{lag}}} \quad (8)$$

where ε is the membrane porosity and d_o is the membrane thickness. Using 1.13×10^{-3} M C4DGA as the carrier extractant for a 0.45 μm pore size PTFE membrane of 65 μm thickness, the lag time was experimentally determined to be about 180 s and the D_{eff} value was calculated to be 2.82×10^{-8} cm²/s. This is about two orders of magnitude lower compared to that obtained by the Wilke-Chang equation suggesting that the diffusion coefficient (Table 4) calculated by the lag-time

Table 4
Diffusion coefficient data for Am³⁺ transport using various DGA based extractants.

Transport system	Diffusion coefficient (cm ² /s)	Method	Remarks
Am ³⁺ -C4DGA	2.82×10^{-8}	Lag-time	Present work
Am ³⁺ -C4DGA	5.79×10^{-6}	Wilke-Chang	Present work
Am ³⁺ -T-DGA	3.28×10^{-6}	Lag-time	Ref. [17]
Am ³⁺ -TODGA	1.51×10^{-6}	Danesi's method	Ref. [22]

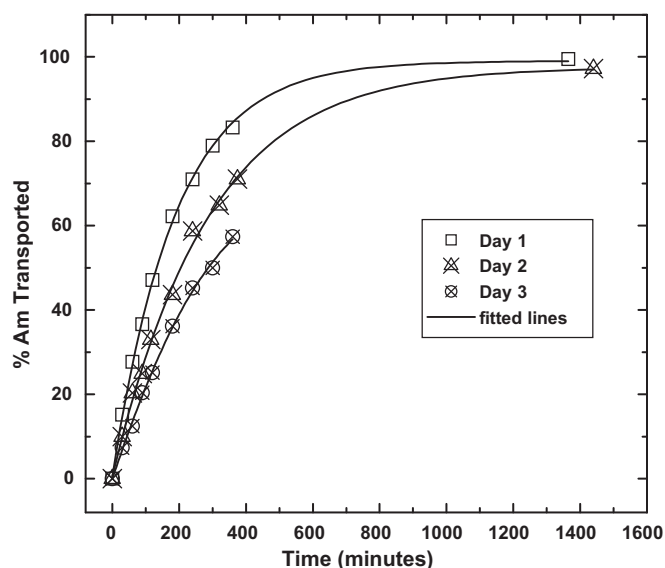


Fig. 10. Am³⁺ transport profiles as a function of number of days of operation. Feed: 3 M HNO₃; receiver: 0.01 M EDTA solution (pH 3.0); carrier solvent: 1.13×10^{-3} M C4DGA in *n*-dodecane.

method is not purely correct considering the metal-carrier complex diffusion and has significant contribution from the kinetic factors associated with the complexation/de-complexation reactions.

3.2.7. Membrane stability

The membrane stability studies were carried out using the SLM containing 1.13×10^{-3} M C4DGA in *n*-dodecane as the carrier extractant while using 3 M HNO₃ as the feed and 0.01 M EDTA in pH 3.0 solution as the receiver phase. The results of the Am(III) transport studies using the same SLM as a function of days of operation are presented in Fig. 10. As indicated in the figure, the transport rates declined with increasing days of operation suggesting significant degradation of the membrane. Though the %Am transport data after about 24 h of operation were more or less comparable as seen from the first day (99.5%) and second day (97.4%) transport profiles, during the initial period of the profiles there was noticeable lower transport (27.8% vs. 20.3% after 1 h, for the first and second day studies, respectively) was seen. This was reflected in lower *P* values obtained in the second day ($P: (4.17 \pm 0.07) \times 10^{-4}$ cm/s) as compared to that obtained during the studies carried out in the first day ($P: (5.76 \pm 0.09) \times 10^{-4}$ cm/s). Studies carried out during the third day indicated further decrease in the Am transport (Fig. 10) and a *P* value of $(2.18 \pm 0.06) \times 10^{-4}$ cm/s was obtained suggesting significant deterioration of the SLM. This behaviour was in sharp contrast to the highly stable SLM observed when TODGA in *n*-dodecane was used as the carrier solvent [12].

4. Conclusions

The present study clearly demonstrates that C4DGA, in which four DGA moieties are brought together on a calix[4]arene

Abbreviations

C4DGA	calix[4]arene tetra-diglycolamide
CMPO	carbamoyl methyl phosphine oxide
EDTA	ethylene diamine- <i>N,N,N',N'</i> -tetraacetic acid
HLW	high level waste
PUREX	plutonium uranium extraction
PTFE	polytetrafluoroethylene
SLM	supported liquid membrane
TBP	tri- <i>n</i> -butyl phosphate
T-DGA	tripodal diglycolamide
TODGA	tetra- <i>n</i> -octyl diglycolamide

Symbols

<i>A</i>	geometrical surface area
<i>C_{f,t}</i>	concentration of metal ion in aqueous feed at time <i>t</i>
<i>C_{f,0}</i>	initial metal ion concentration (at <i>t</i> =0)
<i>D</i>	distribution ratio of Am
<i>D₀</i>	diffusion coefficient of the metal-carrier complex
<i>D_{eff}</i>	effective diffusion coefficient of the metal-carrier complex
<i>d₀</i>	membrane thickness
<i>Q</i>	effective surface area
<i>R</i>	membrane pore radius
% <i>T</i>	cumulative percent transport
<i>t_{lag}</i>	lag time for the metal ion as detected in the receiver phase
<i>V_f</i>	aqueous feed volume

Greek letters

ε	porosity of the membrane
τ	tortuosity factor
γ	interfacial tension between solvent and water
θ	contact angle

platform to discount the diluent dependent aggregation responsible for favourable actinide extraction, is a significantly superior extractant for the extraction of trivalent actinides such as Am³⁺ than TODGA. The transport behaviour shows, however, an entirely different trend than those of TODGA and the tripodal diglycolamide, reported earlier. The transport behaviour follows the pattern as that of most other extractants where a micellar mechanism is not operating to a large extent. The unusual transport behaviour of Am³⁺ with respect to Eu³⁺, with nearly the same ionic potential, can be attributed to different extracted species. Overall, the C4DGA ligand is capable to transport actinides in a very efficient manner as only milli-molar concentrations of the reagent are required for quantitative metal ion transport. Moreover, C4DGA is of importance for applications, since it suppresses the hexavalent actinide ion (actinyl ion) transport, making a prior removal of U from HLW redundant. The synthesis and evaluation of C4DGA extractants with different alkyl groups, replacement of -NH for -NR groups, and varying spacer length between the calix[4]arene and the DGA group is under investigation. In view of the poor stability of the SLM it is proposed to carry out studies under strip dispersion conditions [32].

Acknowledgement

P.K.M. and D.R. are thankful to Dr. A. Goswami, Head, Radiochemistry Division for his keen interest in this work.

References

- [1] S.A. Ansari, P.N. Pathak, P.K. Mohapatra, V.K. Manchanda, Chemistry of Diglycolamides-Promising extractants for actinide partitioning, *Chem. Rev.* 112 (2012) 1751–1772.
- [2] J.N. Mathur, M.S. Murali, K.L. Nash, Actinide partitioning – a review, *Solvent Extr. Ion Exch.* 19 (2001) 357–390.
- [3] A.P. Paiva, P. Malik, Recent advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes, *J. Radioanal. Nucl. Chem.* 261 (2004) 485–496.
- [4] Z.-X. Zhu, Y. Sasaki, H. Suzuki, T. Kimura, Cumulative study on solvent extraction of elements by *NNN',N'*-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into *n*-dodecane, *Anal. Chim. Acta* 527 (2004) 163–168.
- [5] M.P. Jensen, T. Yaita, R. Chiarizia, Reverse-micelle formation in the partitioning of trivalent f-element cations by biphasic systems containing a tetraalkyl diglycolamide, *Langmuir* 23 (2007) 4765–4774.
- [6] Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3 -*n*-dodecane system, *Solvent Extr. Ion Exch.* 19 (2001) 91–103.
- [7] S. Panja, P.K. Mohapatra, S.C. Tripathi, P.M. Gandhi, P. Janardan, Role of organic diluents on Am(III) extraction and transport behaviour using *NNN',N'*-tetraoctyl-3-oxapentanediamide as the extractant, *J. Membr. Sci.* 403–404 (2012) 71–77.
- [8] L. Boyadzhiev, Z. Lazarova, in: R.D. Noble, S.A. Stern (Eds.), *Membrane Separations Technology: Principles and Applications*, Elsevier Science B.V., 1995, pp. 283–300.
- [9] P.K. Mohapatra, V.K. Manchanda, Liquid membrane based separations of actinides and fission products, *Indian J. Chem.* 42A (2003) 2925–2939.
- [10] L.A.J. Chrisstoffels, F. de Jong, D.N. Reinhoudt, in: R.A. Bartsch, J.D. Way (Eds.), *Chemical Separations with Liquid Membranes*, ACS Symposium Series Number 642, ACS, Washington, DC, 1996, pp. 1–10.
- [11] N.M. Kocherginsky, Q. Yang, L. Seelam, Recent advances in supported liquid membrane technology, *Sep. Purif. Technol.* 53 (2007) 171–177.
- [12] S.A. Ansari, P.K. Mohapatra, D.R. Prabhu, V.K. Manchanda, Transport of Americium(III) through a supported liquid membrane containing *NNN',N'*-tetraoctyl-3-oxapentane diamide (TODGA) in *n*-dodecane as the carrier, *J. Membr. Sci.* 282 (2006) 133–141.
- [13] S.A. Ansari, P.K. Mohapatra, D.R. Prabhu, V.K. Manchanda, Evaluation of *NNN',N'*-tetraoctyl-3-oxapentane-diamide (TODGA) as a mobile carrier in remediation of nuclear waste using supported liquid membrane, *J. Membr. Sci.* 298 (2007) 169–174.
- [14] S. Panja, P.K. Mohapatra, S.C. Tripathi, V.K. Manchanda, Studies on uranium(VI) pertraction across a *NNN',N'*-tetraoctyldiglycolamide (TODGA) supported liquid membrane, *J. Membr. Sci.* 337 (2009) 274–281.
- [15] S. Panja, P.K. Mohapatra, P. Kandwal, S.C. Tripathi, V.K. Manchanda, Pertraction of plutonium in the +4 oxidation state through a supported liquid membrane containing TODGA as the carrier, *Desalination* 262 (2010) 57–63.
- [16] S. Panja, P.K. Mohapatra, A. Dakshinamoorthy, V.K. Manchanda, Transport of thorium(IV) across a supported liquid membrane containing TODGA as the carrier, *Sep. Sci. Technol.* 46 (2011) 94–104.
- [17] P.K. Mohapatra, M. Iqbal, D.R. Raut, W. Verboom, J. Huskens, V.K. Manchanda, Evaluation of a novel tripodal diglycolamide for actinide extraction: solvent extraction and SLM transport studies, *J. Membr. Sci.* 375 (2011) 141–149.
- [18] S. Sriram, P.K. Mohapatra, A.K. Pandey, V.K. Manchanda, L.P. Badhka, Facilitated transport of americium(III) from nitric acid media using dimethyldibutyl-tetradecyl-1,3-malonamide, *J. Membr. Sci.* 177 (2000) 163–175.
- [19] P.K. Mohapatra, Ph.D. Thesis, University of Bombay, 1993.
- [20] S. Barbosa, A.G. Carrera, S.E. Matthews, F. Arnaud-Neu, V. Böhmer, J. Dozol, H. Rouquette, M.J. Schwing-Weill, *J. Chem. Soc. Perkin Trans. 2* (1999) 719–723.
- [21] S. Panja, P.K. Mohapatra, S.C. Tripathi, G.D. Dhekane, P.M. Gandhi, P. Janardan, Liquid–liquid extraction and pertraction behavior of Am(III) and Sr(II) with diglycolamide carrier extractants, *J. Membr. Sci.* 399–400 (2012) 28–36.
- [22] P.R. Danesi, Separation of metal species by supported liquid membranes, *Sep. Sci. Technol.* 19 (1985) 857–894.
- [23] S. Panja, P.K. Mohapatra, S.C. Tripathi, V.K. Manchanda, Controlled pertraction of plutonium(III) under reducing conditions from acidic feeds using TODGA as the carrier extractant, *Sep. Sci. Technol.* 46 (2011) 94–104.
- [24] P.K. Mohapatra, M. Iqbal, D.R. Raut, W. Verboom, J. Huskens, S.V. Godbole, Complexation of novel diglycolamide functionalized calix[4]arenes: Unusual extraction behaviour, transport, and fluorescence studies, *Dalton Trans* 1 (4) (2012) 360–363.
- [25] A.K. Dinkar, P.K. Mohapatra, A. Dakshinamoorthy, V.K. Manchanda, Transport of americium(III) across SLM containing CMPO as the carrier extractant, *Des. Water Treat.* 12 (2009) 73–78.
- [26] S.A. Ansari, P.K. Mohapatra, D.R. Raut, B. Rajeswari, M. Kumar, V.K. Manchanda, Performance of some extractants used for 'actinide partitioning' in a comparative hollow fibre supported liquid membrane transport study using simulated high level nuclear waste, *J. Membr. Sci.* 337 (2009) 304–309.
- [27] V.G.J. Rodgers, S.F. Oppenheim, R. Datta, Correlation of permeability and solute uptake in membranes of arbitrary pore morphology, *AIChE J.* 41 (1995) 1826–1829.
- [28] D.S. Lakshmi, P.K. Mohapatra, D. Mohan, V.K. Manchanda, Uranium transport using a PTFE flat-sheet membrane containing alamine 336 in toluene as the carrier, *Desalination* 163 (2004) 13–18.
- [29] P.K. Mohapatra, D.S. Lakshmi, D. Mohan, V.K. Manchanda, Uranium transport using a PTFE flat-sheet membrane containing aliquat 336 in toluene as the carrier, *Sep. Purif. Tech.* 51 (2006) 24–30.
- [30] C.R. Wilke, P. Chang, Correlation of diffusion coefficients in dilute solutions, *AIChE J.* 1 (1955) 264–270.
- [31] J. Crank, *The Mathematics of Diffusion*, 2nd edn., Oxford University Press Inc., New York, 1975, p. 414.
- [32] W.S. Winston Ho, Removal and recovery of metals and other materials by supported liquid membranes with strip dispersion, *Ann. N. Y. Acad. Sci.* 984 (2003) 97–122.