Carrier mediated transport of actinides using hexa-*n*-hexylnitrilotriacetamide (HHNTA)

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ABSTRACT

Solutions of *N,N,N',N'',N'''*-hexa-*n*-hexylnitrilotriacetamide (HHNTA) in 20 % isodecanol-80 % *n*-dodecane (v/v) were employed for the supported liquid membrane (SLM) transport of U(VI), Np(IV), and Pu(IV) from nitric acid feed solutions using PTFE (polytetrafluoroethylene) flat sheet membranes. Preliminary transport studies revealed poor transport of U(VI) when compared with that of the tetravalent ions Np(IV) and Pu(IV) which may find application for their separation from acidic radioactive feeds. In view of this, all subsequent studies were carried out using Np(IV) and Pu(IV). The SLM studies performed with 0.08 M HHNTA as the carrier extractant indicated increased transport of the tetravalent actinide ions with increasing nitric acid and carrier extractant concentrations, while using 0.5 M HNO₃ + 0.5 M oxalic acid as the strip (or receiver) phase composition. However, while > 80 % transport of Np(IV) and Pu(IV) was obtained for a feed phase of 3 M HNO₃, a sharp decrease in the transport rate was seen at a feed acidity of 6 M HNO₃ probably due to anionic hexanitrate complex formation of the metal ions and also because of lower availability of the free ligand in the membrane phase at higher nitric acid concentrations. The membrane stability was poor suggesting the need for continuous replenishment for long term use.

1. Introduction

One of the major factors which concern the global acceptance of nuclear energy as an alternative to the conventional fossil fuel-based energy is the safe management of the radioactive wastes [1]. Spent nuclear fuel reprocessing using the PUREX (Plutonium Uranium Reduction Extraction) process leaves behind large volumes of raffinate, which, when concentrated, gives rise to high level waste (HLW) containing long-lived minor actinides (Am, Cm, Np), small fractions of the unextracted uranium and plutonium, fission products and structural materials [2]. The safe management of the HLW involves a strategy for the partitioning [3–5] of the long-lived actinides and their subsequent ‘burning’ in high flux reactors [6], now famously known as the ‘P&T’ strategy. It is now clear that the major radiotoxicity of the HLW is due to the long-lived actinides, i.e., the long-lived isotopes of U, Np, Pu, Am and Cm. Therefore, remediation of HLW necessarily involves selective

separation of these actinide elements; the better the separation efficiency, the more successful the radioactive waste management program [7].

Though extractants such as CMPO (carbamoylmethylphosphine oxide) [8], TRPO (trialkylphosphine oxide) [9] and DIDPA (diisodecyl phosphoric acid) [10] have been thoroughly evaluated for the extraction of actinide ions from HLW simulants, these are not considered for large scale applications due to the fact that large volumes of solid waste are generated. On the other hand, CHON extractants such as malonamides have been found to be quite promising [11]. The European Union has proposed actinide partitioning [12] schemes based on DMDOHEMA (*N,N'*-dimethyl-*N,N'*-di-*n*-octyl hexylethoxy malonamide), a malonamide extractant. During the turn of the century, diglycolamide extractants were proposed by Sasaki et al. [13], which turned out to be even better than the malonamides and hence, have been extensively investigated by various researchers, globally [14–16]. One of the key features of the

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diglycolamide-based extractants is their preference for trivalent lanthanides vis-à-vis the trivalent actinides. Sasaki et al. reported a separation factor ($SF = D_{Eu}/D_{Am}$) value of ca. 10, using 0.1 M TODGA (N,N,N',N' -tetra-*n*-octyldiglycolamide) as the extractant and 1 M HNO_3 as the aqueous phase [13]. The same authors reported a reversal in this selectivity using a tripodal amide of nitrilotriacetic acid, termed as NTA amide [17]. This unique feature of this class of extractants has fascinated many researchers and there are a flurry of research activities using these ligands, of late [18–20]. We have recently studied the extraction of actinide ions such as UO_2^{2+} , $Np(IV)$, $Pu(IV)$, etc. using HHNTA (N,N,N',N',N'',N'' -hexa-*n*-hexylnitrilotriacetamide) and the results are quite promising [21].

Supported liquid membrane (SLM) based separations have many advantages over solvent extraction techniques [22–24], which include low inventory of the carrier ligands, simultaneous extraction and stripping of metal ions and alleviation of tricky issues such as formation of third phase, phase entrainment, phase disengagement limitations, etc., which are often encountered with solvent extraction processes. While using rather exotic ligands such as the NTA derivatives, it is imperative to develop separation methods with very low ligand inventory and hence, SLM transport studies were taken up during this study.

The present study involves studies on the transport of $U(VI)$, $Np(IV)$ and $Pu(IV)$ from nitric acid feeds using N,N,N',N',N'',N'' -hexa-*n*-butylnitrilotriacetamide (HBNTA) and N,N,N',N',N'',N'' -hexa-*n*-hexylnitrilotriacetamide (HHNTA) in a mixture of isodecanol and *n*-dodecane (Fig. 1) across PTFE (polytetrafluoroethylene) flat sheet supports. To the best of our knowledge, it is the first report on the use of these two NTA ligands as carrier ligands in SLM for the separation of any of the actinide ions from acidic feed solutions.

2. Experimental

2.1. Chemicals

The NTA ligands were synthesized as reported before [25] and were characterized using elemental analysis, 1H NMR and HR-MS and the purity was >95 %. The diluents, *n*-dodecane (Lancaster, UK, purity >99 %), isodecanol (SRL, Mumbai, purity >99 %) and xylene (Merck, Germany) were used as received. Dilute nitric acid solutions used in this study were prepared using Suprapur nitric acid (Merck, Germany) and MilliQ water (Millipore, USA) and the solutions were standardized by NaOH solution (Merck) using phenolphthalein (Fluka) as the indicator. All the other chemicals were of AR grade.

2.2. Membranes

PTFE (polytetrafluoroethylene) membranes (diameter: 47 mm, thickness: 80 μm , pore size: 0.45 μm , porosity: 64 %) were purchased from Sartorius, Germany. The pore size and the thickness of the membranes were confirmed from Hg porosimetry measurements and using a Mututoya digital micrometer, respectively.

2.3. Radiotracers

Freshly purified Pu (^{239}Pu mainly) [26] and ^{233}U [27] were taken from laboratory stock solutions after checking their radiochemical purities. The oxidation state of Pu was adjusted to +4 by the standard

Fig. 1. Structural formulae of N,N,N',N',N'',N'' -hexa-*n*-alkylnitrilotriacetamides.

recommended procedure using TTA (2-thenoyltrifluoroacetone) extraction. A few drops of a $NaNO_2$ (0.05 M) solution were added to a beaker containing Pu radiotracer taken in ca. 1 mL of 1 M HNO_3 . The solution was contacted with an equal volume of 0.5 M HTTA in xylene which resulted in quantitative extraction of the converted Pu(IV) leaving behind Pu(III) and Pu(VI) in the aqueous phase [26]. The loaded organic phase was stripped using 8 M HNO_3 and the separated aqueous phase was washed three times with barren xylene to remove the dissolved TTA. The aqueous stock solution of Pu(IV), free from any organic impurity, was used as the stock solution for all subsequent studies. The purity of the Pu stock was checked by alpha and gamma ray spectrometry which indicated a pure solution of Pu without any ^{241}Am .

The ^{239}Np radiotracer was obtained as per a reported procedure [28]. About 2 mg of uranyl nitrate hexahydrate (obtained from the Uranium Extraction Division, BARC) was irradiated in the Dhruva reactor (BARC, Mumbai) at a thermal neutron flux of 1×10^{13} n/cm²/s. The irradiated product was dissolved in 1 M nitric acid containing a mixture of ferrous sulfamate (0.005 M) and hydroxylamine (0.25 M) and was subsequently contacted with 0.5 M HTTA in xylene. The extract contained Np(IV), which was stripped by 8 M HNO_3 . The valency of Pu (IV) and Np(IV) was confirmed from slope analysis of the linear fitting plots of the log of D_{Pu} (or D_{Np}) with log of [HTTA] in xylene [29]. The concentration of ^{239}Np , ^{233}U and Pu used in the following studies was approximately 10^{-12} M, 10^{-5} M and 10^{-6} M, respectively.

2.4. Distribution studies

The liquid-liquid extraction studies were carried out by contacting equal volumes (usually 1 mL) of the organic and aqueous phases, which contained the extractant and the radiotracer, respectively, in leak tight stoppered Pyrex glass tubes (10 mL capacity) using a vortex shaker at 25 ± 0.1 °C for about one hour. The tubes were subsequently centrifuged and suitable aliquots (usually 0.1 mL) of the organic and aqueous phases were removed for radiometric assay. ^{233}U and Pu were assayed in a liquid scintillation counter (Hidex, Finland) using an Ultima Gold scintillator, whereas ^{239}Np was assayed by a well type NaI(Tl) scintillation counter (Para electronics) coupled to a multichannel analyzer (ECIL, India). The distribution ratio (D_M) of the metal ion was determined using the following formula,

$$D_M = \frac{\text{Activity of the metal ion in the organic phase per unit volume}}{\text{Activity of the metal ion in the aqueous phase per unit volume}} \quad (1)$$

All the experiments were performed in duplicate and the reproducibility in the D values was found to be within $\pm 2\%$.

2.5. Supported liquid membrane transport studies

The supported liquid membrane (SLM) studies were carried out in a two-compartment Pyrex transport cell (each cell volume is 20 mL, geometrical surface area: 4.90 cm²) containing a PTFE membrane whose pores were filled with the ligand solution by overnight dipping in a Petri dish containing the extractant solution. Subsequently, the membrane was taken out of the solution and was wiped gently with a tissue paper to remove the excess organic liquid present on the surface of the membrane. The membrane was clamped in between the two transport cells containing two small magnetic bars and with the provision of a sampling port each one on the transport cell. Subsequently, both cells with the membrane present in between were fixed with the help of parafilm. The feed phase contained the actinide ion in nitric acid medium, whereas the strip (or receiver) phase contained the stripping solution, and both phases were uniformly stirred (stirring speed: 200 rpm) with the help of a precisely controlled magnetic stirrer. Fixed volumes of samples were pipetted out (50–100 μL) through the sampling ports one each in the source (or feed) and the receiver (or strip) phases at regular time intervals to assay by alpha or gamma ray counting (vide supra). The transport percentage of the metal ion into the receiver phase (%T) and

the percentage metal ion remained in the source phase (%R) at a given time were calculated using the following formulae:

$$\% T = 100 \times C_{r,t}/C_0 \quad (2)$$

$$\% R = 100 \times C_{f,t}/C_0 \quad (3)$$

where C_0 is the metal ion concentration at the start of the experiment ($t = 0$) in the feed phase, $C_{r,t}$ and $C_{f,t}$ are the metal ion concentrations at time t in the strip and feed phases, respectively. The permeability coefficient (P) of the metal ion was calculated using the following formula [30]:

$$\ln \frac{C_{f,t}}{C_0} = -P \left(\frac{A}{V} \right) t \quad (4)$$

Where $C_{f,t}$, C_0 and t have the same meanings as stated above, whereas P , A and V are the permeability coefficient (cm s^{-1}), effective surface area of the transport cell (3.14 cm^2), which was obtained by multiplying the exposed surface area (4.90 cm^2) with the porosity (64 %) of the membrane, and the volume of the transport cell (20 mL), respectively. The permeability coefficient (P) values were obtained from the slope of the straight line fitting the plot $\ln (C_{f,t}/C_0)$ vs. time. All the SLM studies were carried out at room temperature (ca. 24°C) under ambient conditions.

3. Results and discussion

3.1. Solvent extraction studies

The extraction of a metal ion, M^{n+} , by a neutral donor ligand, L , is given by the following equation:

where 'n' units of the nitrate ions are used as the counter anion to get a charge-neutralized species, while 'y' units of the extractants are required for obtaining a lipophilic extractable species. The supported liquid membrane transport of a metal ion is a combination of the extraction from the feed (or source) phase into the membrane phase ($M(\text{NO}_3)_n \cdot yL_{\text{org}}$) followed by its back extraction into the strip (or receiver) phase. For the facile transport of metal ions across the supported liquid membranes, it is required that both the extraction as well as back extraction kinetics should be rapid. As shown in Fig. 2, the attainment of the extraction equilibrium for Pu(IV), Np(IV) and UO_2^{2+} ion is accomplished in about 5–10 min using HHNTA as the carrier extractant for feed conditions of 3 M HNO_3 for the tetravalent ions and pH 2 for the uranyl ion. In view of the rapidly decreasing extraction of the uranyl ion with increasing HNO_3 concentration [21], it was decided to carry out the extraction of the metal ion from much lower acidity as compared to that employed for the extraction of Np(IV) and Pu(IV).

Fig. 2. Kinetics of extraction (filled symbols) and stripping (empty symbols) of actinide ions using 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v). Aqueous phase for extraction: pH 2 for U(VI) and 3 M HNO_3 for Pu(IV) and Np(IV). Aqueous phase for stripping: 1 M Na_2CO_3 for U(VI) and 0.5 M HNO_3 + 0.5 M oxalic acid for Np(IV) and Pu(IV).

It is quite obvious that the stripping of the metal ions from the organic extract requires different conditions. While UO_2^{2+} ion could be back extracted using 1 M Na_2CO_3 , a mixture of 0.5 M HNO_3 + 0.5 M oxalic acid was used for the stripping of Np(IV) and Pu(IV) from the organic extract (0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v)). Sodium carbonate was used to strip U(VI) as it forms a very strong $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex [31]. For tetra-valent actinide ions, a mixture of 0.5 M oxalic acid and 0.5 M HNO_3 was reported to be quite efficient [32].

3.2. Supported liquid membrane studies

Transport studies of UO_2^{2+} , Np(IV) and Pu(IV) were carried out using SLM with HHNTA as the carrier ligand. For comparison purpose, some experiments were also carried out using HBNTA as the extractant under identical experimental conditions. The studies were carried out to determine the effect of the feed acid concentration and the carrier ligand concentration in the membrane on the transport efficiency of the metal ions. The permeability coefficients of the metal ions were also determined for a comparative assessment of the transport results.

The transport of UO_2^{2+} ion was carried out at pH 2, while that of Np(IV) and Pu(IV) at nitric acid concentrations $> 0.5 \text{ M}$ in view of possible hydrolysis of the tetravalent ions [33]. However, as the HLW contains 3–4 M HNO_3 , it was thought of interest to carry out the transport studies of the tetravalent actinides at a feed nitric acid concentration of 3 M. The comparative transport data are presented in Fig. 3, which shows negligible ($< 2\%$) transport of UO_2^{2+} ion over a period of 5 h. In view of this, all subsequent studies were limited to Pu(IV) and in some cases Np(IV). The slow transport of the uranyl ion can be attributed to poor diffusion of the uranyl ion complex which formed much more bulky complexes as compared to the tetravalent ions. The solvent extraction data for UO_2^{2+} ion [21] indicated a mixture of ML_2 and ML_3 type species at pH 2.0 in 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v) in sharp contrast to the ML type species with Np(IV) and Pu(IV) at 3 M HNO_3 suggesting formation of bulkier diffusing species for the uranyl ion. It is well known that the diffusion of the complex is very important in the mass transfer and while a species may be very well extracted in a solvent extraction study, but poor transport may happen in the SLM study based on the slow diffusion of the extracted complex [22]. In summary, as the results are not very encouraging, it was decided not to further investigate the uranyl ion transport behavior. However, these observations can be considered interesting if one considers to separate U(VI) from Pu(IV) and Np(IV) from acidic feeds as in radioactive wastes.

At first, the transport of Pu(IV) was studied using both 0.08 M HBNTA and HHNTA in the diluent mixture of 20 % isodecanol + 80 % *n*-dodecane (v/v). To get a better picture of the transport rates, 0.5 M

Fig. 3. Transport of actinide ions (Square: U(VI); Circle: Np(IV); Triangle: Pu(IV); filled symbols: Strip phase; open symbols: Feed phase) across PTFE flat sheet SLM with 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v) in the membrane.

HNO_3 was used as the feed solution (using 3 M HNO_3 as the feed may result in very high transport rates, thereby making it difficult to compare the transport data). The strip compartment contained 0.5 M HNO_3 + 0.5 M oxalic acid as the strip solution for both the ligands. The transport profiles are plotted in Fig. 4, which suggested significantly higher transport of Pu(IV) with HHNTA vis-à-vis HBNTA. While about 5% Pu(IV) transport was observed in 5 h with HBNTA, about 40 % Pu(IV) was transported with HHNTA in the same time period. This is attributed to the lower extractability of the former ligand as reported in our earlier publication [21]. In view of this, our subsequent studies involved only HHNTA as the carrier extractant.

3.2.1. Effect of feed nitric acid concentration

According to Eq. (5), an increase in the nitrate ion concentration in the feed phase would shift the equilibrium towards the forward direction and thereby facilitating the extraction of the metal-ligand complex into the membrane phase which eventually increases the transport efficiency of the metal ion across the flat sheet membrane. We have reported that the extraction of Np(IV) and Pu(IV) with 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v) increased with increasing concentration of nitric acid [21]. This prompted us to investigate the effect of the feed phase nitric acid concentration on the transport of Np(IV) and Pu(IV) keeping the membrane- and stripping phase compositions fixed. Therefore, the nitric acid concentration in the feed phase containing the actinide ion was varied from 0.5 M to 6 M, keeping the carrier extractant as 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v) and the strip phase as 0.5 M HNO_3 + 0.5 M oxalic acid. The results of the transport of Pu(IV) at four different feed conditions, viz. 0.5 M, 1 M, 3 M and 6 M HNO_3 , are given in Fig. 5. It shows that the transport order changes with varying feed strength as $3\text{ M} > 6\text{ M} > 1\text{ M} > 0.5\text{ M}$. While it is expected that the D_{Pu} values should increase with increasing feed nitric acid concentration, the Pu^{4+} ions present at lower acidities are partially converted to the $\text{Pu}(\text{NO}_3)_6^{2-}$ species at 6 M HNO_3 [34], which may be responsible for the lower extraction of the metal ion leading to a lower transport. Additionally, there may be HHNTA• HNO_3 type adduct formation, which decreases the free ligand concentration in the membrane resulting in lower transport of Pu(IV) at 6 M HNO_3 .

Analogous studies were carried out with Np(IV) using 0.5 M, 1 M and 3 M HNO_3 as the feed solutions and the transport profiles are plotted in Fig. 6. As the ^{239}Np radiotracer was used in these studies, which implies about a million times lower concentration as compared to that of Pu, transport studies at 6 M HNO_3 were purposefully not carried out. This would definitely form almost quantitative formation of the hexanitrate anionic species, $\text{Np}(\text{NO}_3)_6^{2-}$, thereby resulting in poor transport of the metal ion. Such an observation has been made in our recent study on the

transport of Np(IV) ions with tripodal diglycolamide ligands [35]. The permeability coefficients were obtained by linear fitting of the $\ln(C_t/C_0)$ vs time plots. A representative plots obtained for Pu(IV) and Np(IV) transport from 1 M HNO_3 feed solutions is presented in Fig. 7.

The transport parameters (P values) along with the %transport data are presented in Table 1 for making a comparative assessment. From the figures and Table 1, it can be surmised that at a given time and nitric acid concentration, the transport of Pu(IV) is always higher than that of Np(IV), which is in accordance to their extraction trend using HHNTA (vide supra). The transport of the actinide ion increased with a nitric acid concentration up to 3 M, followed by a decreasing trend at 6 M HNO_3 . For example, the transport percentage of Pu(IV) to the strip phase at 4 h was 35.7, 39.3, 85.9 and 67.4 at 0.5, 1, 3 and 6 M HNO_3 , respectively.

Table 1 exhibits that the transport percentages of Np(IV) at 0.5 M and 3 M HNO_3 were 22.2 and 82.3, respectively, after 4 h. The increasing trend in the transport up to 3 M HNO_3 for a given metal ion can again be attributed to the increasing extraction of the metal ion with increasing nitric acid concentration. The increased concentration of acid in the strip phase, due to the co-transport of HNO_3 , also decreases the efficiency of the metal ion stripping from the membrane phase.

3.2.2. Transport mechanism

The transport of a given metal ion from the feed phase into the strip phase basically involves three steps. In the first step, the metal ion is extracted into the membrane phase containing the carrier ligand, which is very similar to the extraction of a metal ion from the aqueous phase to the organic phase. The second step involves the transport (or diffusion) of the metal-ligand complex through the membrane phase, which is a diffusion process and in the final step, the stripping of a metal ion is done into the strip phase, which is similar to the back extraction of a metal ion from the organic phase to the aqueous phase in solvent extraction studies. The transport mechanism of Pu is schematically depicted in Fig. 8. The metal ion concentration profiles are presented as thick lines. Effective transport means efficient extraction at the feed-membrane interface and efficient stripping at the membrane-strip interface. As seen from Fig. 8, efficient extraction is represented as a sharp fall in the metal ion concentration at the aqueous diffusion layer-1 and a concomitant sharp increase in the metal ion concentration in the membrane phase. An analogous profile is shown at the aqueous diffusion layer-2, where an efficient stripping indicates a sharp fall of the metal ion concentration at the extreme right side of the membrane phase just adjacent to the aqueous diffusion layer-2. This results in a concomitant sharp rise in the metal ion concentration at the left side of the aqueous diffusion layer-2. Subsequently, the metal ion concentration flattens out just after the diffusion layer due to stirring of the strip phase. For efficient transport to occur, the extraction of the metal ion into the membrane phase should be very high at a fast kinetics. Simultaneously, the back extraction into the strip phase should be efficient with a good kinetics. Finally, as the diffusion in the aqueous phases (feed and the strip phases) are considered fast, the diffusion in the membrane phase holds the key and it depends on the viscosity of the carrier solvent. In the present case, the extractant concentration was very low (0.08 M) suggesting that the viscosity of the carrier solvent was close to that of the diluent, i.e., ca. 2.

The permeability coefficients values were determined for Np(IV) and Pu(IV) at different feed nitric acid concentrations. The data given in Table 1 indicate a higher P value of Pu(IV) than of Np(IV) at a given nitric acid concentration; the P values increased with increasing nitric acid concentrations. For example, the P values of Np(IV) at 0.5 M and 3 M HNO_3 are $(0.09 \pm 0.01) \times 10^{-3} \text{ cm s}^{-1}$ and $(0.61 \pm 0.03) \times 10^{-3} \text{ cm s}^{-1}$, respectively, whereas those of Pu(IV) at 0.5 M, 3 M and 6 M are $(0.14 \pm 0.01) \times 10^{-3} \text{ cm s}^{-1}$, $(0.73 \pm 0.04) \times 10^{-3} \text{ cm s}^{-1}$ and $(0.52 \pm 0.03) \times 10^{-3} \text{ cm s}^{-1}$, respectively. A significant decrease in the P value of Pu(IV) was observed at 6 M HNO_3 . As we are not aware of an analogous transport system in literature, the results of Pu(IV) transport by TODGA as the carrier extractant were used for comparison. Panja

Fig. 4. Transport of Pu(IV) across PTFE a flat sheet SLM with different carrier ligands (0.08 M HHNTA/HBNTA in 20 % isodecanol-80 % *n*-dodecane (v/v)); Feed phase: Pu(IV) in 0.5 M HNO_3 ; Strip phase: 0.5 M oxalic acid + 0.5 M HNO_3 .

Fig. 5. Transport of Pu(IV) from different nitric acid concentrations (a) 0.5 M HNO₃; (b) 1 M HNO₃; (c) 3 M HNO₃; (d): 6 M HNO₃ across a PTFE flat sheet supported liquid membrane; Carrier solvent: 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v); Strip phase: 0.5 M oxalic acid + 0.5 M HNO₃.

Fig. 6. Transport of Np(IV) from different nitric acid concentrations (Square: 0.5 M HNO₃; Circle: 1 M HNO₃; Triangle: 3 M HNO₃; filled symbols: Strip phase; open symbols: Feed phase) across a PTFE flat sheet supported liquid membrane, carrier ligand: 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v); Strip phase: 0.5 M oxalic acid + 0.5 M HNO₃.

et al. [36] reported a P value of Pu(IV) with 0.1 M TODGA in *n*-dodecane as $(2.11 \pm 0.04) \times 10^{-3} \text{ cm s}^{-1}$, using 3 M HNO₃ as source phase and 0.1 M oxalic acid in the strip phase, which is higher than that of Pu(IV) transport with HHNTA as the carrier ligand.

3.2.3. Effect of carrier ligand concentration

The carrier ligand in the membrane phase plays a major role in the transport of a metal ion from the feed phase to the strip phase by forming a hydrophobic complex at the feed-membrane interface which gets eventually transported through the membrane. After the demetallation

of the complex at the membrane-strip interface, the metal ion is deposited in the strip compartment, while the carrier extractant (HHNTA in the present case) diffuses back to the feed phase to complete the 'ferry' action. As depicted in the metal ion distribution diagram over the three phases (feed, membrane and strip), the metal ion concentration sharply rises at the feed-membrane interface (Fig. 8) and then falls with a linear concentration gradient across the thickness of the membrane phase. Finally, the metal ion concentration at the membrane-strip phase interface approaches to near 'zero' value due to the fast diffusion of the stripped metal ion into the bulk of the strip phase (Fig. 8). The facile diffusion of the M-L complex across the membrane phase is due to the concentration gradient over the thickness of the membrane. In the absence of HHNTA in the membrane phase, the transport of Pu(IV) was negligible ($<0.1\%$). The effect of carrier ligand concentration in the membrane phase was studied by varying the HHNTA concentration from 0.08 M to 0.16 M in 20 % isodecanol-80 % *n*-dodecane (v/v) and monitoring the transport percentage of Pu(IV) in the strip phase, while maintaining the feed nitric acid concentration at 3 M HNO₃ and the strip phase as 0.5 M HNO₃ + 0.5 M oxalic acid.

It is expected that the transport of Pu(IV) would increase with increasing HHNTA concentration in the membrane phase according to Eq. (5). However, the transport percentage of Pu(IV) decreased significantly upon increasing the HHNTA concentration from 0.08 M to 0.16 M. For example, the transport percentages of Pu(IV) at 4 h were 85.9, 38.0 and 18.7 at HHNTA concentrations in the membrane phase of 0.08, 0.12 and 0.16 M, respectively (Fig. 9). The corresponding dynamic viscosities (in mPa.s) were determined to be 2.1845, 2.4304 and 2.6917, respectively. The trans-membrane transport of a metal ion is diffusion controlled and, therefore, depends on the viscosity of the medium according to the Stokes-Einstein equation (Eq. (6)), which states that the diffusion coefficient (D_0) of a species would decrease with increase of the viscosity of the medium (η) according to the following

Fig. 7. Permeability coefficient determination of (a) Np(IV) (b) Pu(IV) across PTFE flat sheet supported liquid membrane, carrier ligand: 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v); Feed phase: Metal ion in 1 M HNO₃; Strip phase: 0.5 M oxalic acid + 0.5 M HNO₃.

Table 1

Effect of feed acid concentration on the transport and permeability coefficient of metal ions; Membrane: PTFE filled in 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v); Feed: HNO₃, Volume: 20 mL; Strippant: 0.5 M HNO₃ + 0.5 M oxalic acid, Volume: 20 mL, data at 240 min.

[HNO ₃], M	% Np (IV) in Feed	% Np (IV) in Strip	$P_{Np(IV)} \times 10^3$ (cm s ⁻¹)	% Pu (IV) in Feed	% Pu (IV) in Strip	$P_{Pu(IV)} \times 10^3$ (cm s ⁻¹)
0.5	78.3	22.2	0.09 ± 0.01	67.0	35.7	0.14 ± 0.01
1.0	70.7	27.9	0.14 ± 0.00	60.6	39.3	0.22 ± 0.01
3	27.8	82.3	0.61 ± 0.03	15.2	85.9	0.73 ± 0.04^a
6	–	–	–	29.1	67.4	0.52 ± 0.03

^a 2.11 ± 0.04 with 0.1 M TODGA in *n*-dodecane [36]; ND: Not determined.

equation:

$$D_0 = \frac{KT}{6\pi\eta r} \quad (6)$$

Where K is the Boltzmann constant, T the absolute temperature, η the viscosity of the medium and ' r ' the radius of the diffusing species. Shukla and Misra have reported a significant slowing down in the transport of U

(VI) with TBP solutions with lower viscosities that those seen in the present study [37]. Therefore, with an increase in the HHNTA concentration, the transport of Pu(IV) should decrease due to an increase in the viscosity of the medium. This is also reflected in the respective P values of Pu(IV) at different HHNTA concentrations (Table 2). The P values of Pu(IV) were $(0.73 \pm 0.04) \times 10^{-3}$, $(0.36 \pm 0.05) \times 10^{-3}$ and $(0.36 \pm 0.03) \times 10^{-3}$, respectively, for HHNTA concentrations of 0.08 M, 0.12 M and 0.16 M. Thus, around 50 % decrease in the P value was observed when the concentration of HHNTA increased from 0.08 M to 0.12 M. However, further increase of the HHNTA concentration to 0.16 M would not alter the P value. This may be explained based on the following equation of the permeability coefficient (P):

$$P = \frac{D_{Pu(IV)}}{\left[D_{Pu(IV)} \left(\frac{d_a}{D_a} \right) + \left(\frac{d_0 \tau}{D_0} \right) \right]} \quad (7)$$

where $D_{Pu(IV)}$, D_a and D_0 are the distribution ratio, aqueous diffusion coefficient and membrane diffusion coefficients of Pu(IV), respectively, whereas d_a , d_0 and τ are the aqueous diffusion layer thickness, membrane thickness and tortuosity factor, respectively.

Assuming that the rate-limiting step is the diffusion of the Pu(IV)-HHNTA complex, the first term in the denominator of Eq. (7) can be

Fig. 8. Schematic presentation of the Pu(IV) ion transport from the feed to the strip side.

Fig. 9. Transport of Pu(IV) across a PTFE flat sheet supported liquid membrane phase; Feed phase: Pu(IV) in 3 M HNO₃; Strip phase: 0.5 M oxalic acid + 0.5 M HNO₃; carrier ligand: varying concentrations of HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v).

Table 2

Effect of carrier ligand concentration on the permeability coefficient of Pu(IV); Feed: 3 M HNO₃, Volume: 20 mL; Strippant: 0.5 M HNO₃ + 0.5 M oxalic acid, Volume: 20 mL; membrane: PTFE filled in carrier ligand.

[HHNTA], M in 20 % isodecanol-80 % <i>n</i> -dodecane (v/v)	Viscosity (mPa.s)	$P_{\text{Pu(IV)}} \times 10^3$ (cm s ⁻¹)
0.08	2.1845	0.73 ± 0.04
0.12	2.4304	0.36 ± 0.05
0.16	2.6917	0.36 ± 0.03^a

^a $P_{\text{Pu(IV)}}$: $(0.95 \pm 0.05) \times 10^{-3}$ cm s⁻¹; 0.15 M TODGA [36]; source phase: 3 M HNO₃.

ignored and, therefore, the equation simplifies to:

$$P = D_{\text{Pu(IV)}} \frac{D_0}{d_0 \tau} \quad (8)$$

Therefore, the P value would increase with an increase of the HHNTA concentration due to an increase of the $D_{\text{Pu(IV)}}$ value. Conversely, it would decrease due to a decrease of D_0 with an increase of the HHNTA concentration in the diffusing medium. This two opposing factors influence the overall P value of Pu(IV) transport and as a result, a constancy in the P value is seen on increasing the HHNTA concentration from 0.12 to 0.16 M in the medium. A similar decrease in the P value of Pu(IV) was also found when the concentration of TODGA, as the carrier ligand, in the membrane was increased to more than 0.10 M [36].

3.2.4. Stability of the membrane

The stability of an SLM is an important aspect when considering scaling up of the process for subsequent applications [38]. One of the ways the stability of the membrane can be quantified is by measuring the transport parameters such as the permeability coefficient (P) or the transport percentage (%T) of a given metal ion at consecutive cycles of operations. A cycle is defined as the complete operation in which the concerned metal ion is quantitatively transported from the feed side to the strip side in a given amount of time without replenishing the feed and strip volume with the respective fresh solutions. An SLM is said to be stable if the transport efficiency (as measured by %T or the P value) of the metal ion does not change significantly over several cycles of operation. Generally, an SLM shows poor stability mainly due to the loss of membrane liquid into the in-contact aqueous solutions (feed and strip phases). In addition, the trans-membrane pressure difference, wetting of support pores by the aqueous solutions or pore blockages are different causes of the instability of a membrane [38].

We found that diluents play a significant role in the stability of the membrane due to their ability to hold the solvent (membrane phase) in

the flat sheet membrane pores. This may be due to factors like diluent polarity, viscosity, interaction of the carrier with the diluent, etc. However, a clear understanding of the physical parameters on membrane stability is still lacking. Poor membrane stability was reported in the presence of polar diluents such as nitrobenzene [39], chloroform [40] and PTFS [41], however, 1-octanol [42] and 2-nitrophenyloctyl ether [43] (also polar diluents) displayed a reasonably good membrane stability. A mixture of isodecanol and *n*-dodecane as the diluent gave ample stability to the SLM used in flat sheet mode [44].

The stability of the membrane containing 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v) was investigated by measuring the transport efficiency (%T and the P values) of Np(IV) for ca. 4 h by keeping the source phase at 3 M HNO₃, whereas the strip phase contained 0.5 M HNO₃ + 0.5 M oxalic acid. In the next cycle of transport experiment, only the feed and strip phases were changed with the respective fresh solutions, while keeping the membrane phase physically intact. This process was continued for six days. It is clear from Fig. 10a and Table 3 that the transport efficiency of Np(IV) changed drastically already from day 1. The cumulative percentages of the transport values of Np(IV) at 4 h on day 1, 2, 5 and 6 were 82.3, 58.7, 37.5 and 29.0, respectively. A similar decreasing trend in the P value of Np(IV) was also observed. In order to see the role of iso-decanol content, another set of stability studies were carried out using the carrier solvent as 0.08 M HHNTA in 10 % isodecanol + 90 % *n*-dodecane (v/v). The results of this set of studies are included in Fig. 10b. However, as seen from both the figures and Table 3, the membrane stability has become worse. A similar poor stability of the membrane was also observed in our earlier publication with multiple DGA-based ligands studied in an analogous diluent mixture [45]. This poor stability of the membrane, however, could be alleviated by freshly replenishing the carrier ligand solution before the start of a new cycle.

4. Conclusions

Supported liquid membrane studies with actinide ions indicated poor U(VI) transport vis-à-vis the tetravalent actinide ions Np(IV) and Pu(IV) and a higher transport efficiency of the hexyl NTA derivative HHNTA as compared to the butyl analogue HBNTA. The poor transport of U(VI) may be utilized for the selective permeation of tetra-valent actinide ions from radioactive feeds containing a mixture of U(VI), Np(IV) and Pu(IV). Transport studies of Np(IV), Pu(IV) with HHNTA as the carrier extractant indicated more than 90 % transport of the metal ions to the strip phase after 5 h from a feed at 3 M HNO₃, which, however, decreased at 0.5 M HNO₃ and 6 M HNO₃ as the feed solutions. The decreased transport at 0.5 M HNO₃ is considered to be due to the lower extraction of the metal ion (as per Eq. (5)) in the membrane. On the other hand, the decreased transport at 6 M HNO₃ may be due to the formation of anionic species bearing the metal ions and also partly due to the lower availability of the free ligand in the membrane due to more HHNTA.HNO₃ adduct formation at a higher nitric acid concentration. The stability data point to a poor stability of the membrane over six days which, however, can be avoided by refilling the pores of the membrane with ligand solution after each cycle of experiment. Despite the rather poor stability of the membrane, one would be tempted to utilize the SLM-based separation method for large scale processing of lean radioactive wastes because of the fast mass transfer rates and low ligand inventory. For such application, of course, one may opt for the hollow fiber supported liquid membrane technique.

Transparency document

The Transparency document associated with this article can be found in the online version.

Fig. 10. Transport of Np(IV) across a PTFE flat sheet supported liquid membrane phase; Feed phase: Np(IV) in 3 M HNO_3 ; Strip phase: 0.5 M oxalic acid + 0.5 M HNO_3 ; (a) carrier ligand: 0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v); (b) carrier ligand: 0.08 M HHNTA in 10 % isodecanol-90 % *n*-dodecane (v/v).

Table 3

Stability studies by monitoring the transport of Np(IV) in six cycles using the same membrane phase (0.08 M HHNTA in 20 % isodecanol-80 % *n*-dodecane (v/v)) and fresh feed (3 M HNO_3) and strip (0.5 M HNO_3 + 0.5 M oxalic acid) solutions over 6 days. Feed and strip volumes: 20 mL; Transport data at 4 h.

Day	% Transport to the strip	$P_{\text{Np(IV)}} \times 10^3$ (cm s^{-1})	% Transport to the strip	$P_{\text{Np(IV)}} \times 10^3$ (cm s^{-1})
1	82.3	0.61 ± 0.03	68.9	0.47 ± 0.02
2	58.7	0.42 ± 0.03	15.0	0.08 ± 0.00
5	37.5	0.30 ± 0.02	–	–
6	29.0	0.22 ± 0.01	2.4	0.02 ± 0.00

^a Determined in the strip compartment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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