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Understanding the extraction mechanism, radiolytic stability and stripping behavior of thorium by ionic liquid based solvent systems: evidence of 'ion-exchange' and 'solvation' mechanism

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Abstract The extraction efficiency for thorium followed the trend: Cyanex-923 > Cyanex-272 > DHOA > TBP. In case of TBP and DHOA the extraction proceeded via 'solvation mechanism' through $Th(NO_3)_4{\cdot}2L$, while for Cyanex-923 and Cyanex-272 it proceeded via 'ion exchange' mechanism through $(Th(NO_3)_2{\cdot}2L)^{2+}$. The extraction process followed slower kinetics while change in Gibb's energy revealed the spontaneity of the process. These ionic liquid based systems were found to be radiolytically stable, highly efficient and selective for Th. Oxalic acid was found to be suitable for almost quantitative stripping of Th from extracted ionic liquid phase.

Keywords Ionic liquid · TBP · DHOA · Cyanex-272 · Cyanex-923 · Ion-exchange · Solvation

Introduction

Room temperature ionic liquid has gained world-wide acceptance as the 'green' alternative to the volatile organic compounds and finds application in the field of chemical synthesis, catalysis, electro chemistry and drug delivery [1–8]. In nuclear industry, ionic liquid based research is aiming at the processing of radioactive waste [9–12]. Apart from the 'green' aspect, the overall extraction/complexation chemistry of lanthanides and actinides differs in ionic liquids compared to that in molecular diluents [13, 14]. It is very interesting to note that ionic liquid based systems not only improve the extraction efficiency or selectivity but also the extraction mechanism, kinetics, thermodynamics and species involved in extraction show interesting features which are unconventional and definitely not the same as observed in case of molecular diluents based systems. The ionic liquid based solvent systems were found to be radiolytically more stable than the conventional solvent due to the formation of resonance stabilized (mainly imidazolium based) organic radical [15–18]. A small structural modification in either cationic or anionic part of ionic liquid led to drastic change in their physico-chemical properties and as a consequence the extraction kinetics and mechanism can be modified [19, 20]. In view of these advantages ionic liquid was chosen as diluent for the extraction of thorium in the present investigation.

To fulfil the world-wide ever increasing energy demand, nuclear energy is one of the prime sources of energy. In a country like India, the nuclear energy programme largely depends on the utilization of the vast thorium resources due to the unavailability of large amount of high quality uranium [21, 22]. Significant efforts were found in literature on the extraction and complexation of thorium using varieties of ligands in molecular diluents like dodecane, xylene etc. [23–27]. Though several literatures are available on Am^{3+}, Pu^{4+}, UO_2^{2+}, Sr^{2+}, Cs^{+} in ionic liquid [28–30], to the best of our knowledge the extraction, complexation properties of Th have not yet been explored widely [31, 32]. So there is a need to put efforts on

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development of highly efficient, selective and 'green' method for the extraction of thorium.

In view of these, phosphorous based ligands like TBP (tri-*n*-butyl phosphate), Cyanex-923 (tri-*n*-alkyl phosphine oxide) and Cyanex-272 (Bis(2,4,4-trimethyl) pentyl phosphinic acid); and non-phosphorous based ligand DHOA (di-*n*-hexyl octanamide) in C_8mimNTf$_2$ (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) were investigated for the extraction/complexation behaviour of thorium [33–35].

TBP, Cyanex-923 and Cyanex-272, having phosphorous atom in their structure, are routinely employed in nuclear industries for the extraction of uranium, plutonium and thorium. It is proposed that any ligand constituting C, H, N, O is only completely incinerable and therefore environmentally benign. The ligands containing atoms other than C, H, O, N does not meet the above criteria of being environment friendly. Since our aim was to find out an environmentally benign method for efficient and selective extraction of thorium; we were looking for both green diluent and green ligand. In view of these ionic liquid was chosen to serve the purpose of green solvent while the established ligands for actinide separation namely TBP, Cyanex-272, Cyanex-923 are not so. Therefore, a non phosphorous based ligand is only constituted of C, H, O, N atoms; Di-*n*-hexyl octanamide (DHOA) which showed potential in Lab scale experiment, was employed along with TBP, Cyanex-923 and Cyanex-272 for the present investigation. The study includes the identification of the species involved in the extraction, kinetics, radiolytic stability and stripping behaviour. Finally, these solvent systems were applied for processing of simulated high level waste solutions (SHLW) obtained from the fast breeder reactor (FBR) and research reactor (RR) [36].

Experimental

Instrument and operating conditions

The analysis was carried out using atomic emission spectroscopy (AES) with inductively colupled argon plasma as an excitation source and capacitatively coupled device (CCD) as detector system. Operating conditions and instrumental specifications are listed in Supplementary Table 1.

Reagents and standard solutions

Standard solutions for all the elements were prepared from CertiPUR® ICP solutions of individual elements (E-Merck, Darmstadt, Germany) by proper dilution. Supra- pure HNO_3 (E-Merck, Darmstadt, Germany) and quartz double distilled water were used throughout the study. Multi-point standardization was carried out using standard in the range of 0.05–500 mg/L for each analytical line after proper peak search, auto attenuation etc. For the analyses of each sample 5 replicated measurements were carried.

Th(IV) stock solution was prepared by dissolving spectra pure ThO_2. For dissolution HF–HNO_3 was used primarily. To avoid the interference from fluoride ion, it was removed by repeated evaporation to dryness and finally, the feed was adjusted to the required acidity. Xylene was procured from Prabhat Chemicals, Gujrat Mumbai, whereas oxalic acid and Na_2CO_3 were produced from Thomas Baker Chemical limited and Qualigens fine Chemicals, Mumbai, India, respectively. TBP was procured from Koch-Light Laboratories, USA. DHOA was synthesized by previously reported method and its purity was determined by ^{1}H NMR, elemental analysis and distribution coefficient measurement for UO_2^{2+} [37, 38]. C_8mimNTf$_2$ has been procured from Global Nanotech, India with purity more than 99 % and was used for extraction process without further purification. Bis(trifluoromethane)sulfanilamide lithium salt (LiNTf$_2$) has been procured from Aldrich Chemistry, USA. The structures of TBP, DHOA, Cyanex-923 Cyanex-272 and C_8mimNTf$_2$ have been shown in Fig. 1.

Method

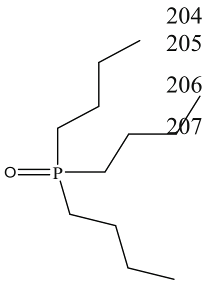
For all the experiments the 10 mg L^{-1} thorium solution was taken in the required feed acidity. Then it was allowed to be contacted with same volume (5 mL) of organic phase containing ligands of suitable concentration in ionic liquid. Then both the phase were equilibrated for 2 h in a thermostated water bath at 300 K. Then this reaction mixture was allowed for centrifugation for 2 min for complete phase separation. Finally, suitable aliquot of the aqueous phase was fed into the plasma directly for the analysis. The distribution ratio for any metal ion can be expressed as

$$D = {[\mathrm{A}]_{\mathrm{org}}}\Big/{[\mathrm{A}]_{\mathrm{aq}}}$$

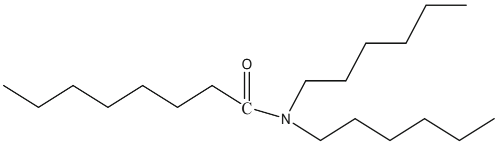
The subscripts org and aq refer to the organic and aqueous phases respectively. Since the initial concentration of thorium was known (10 mg L^{-1}), and the final concentration after solvent extraction was evaluated, the concentration of the thorium in the organic phase was calculated. All the experiments were carried out in triplicate to evaluate the reproducibility of the data.

For the stripping purpose, these thorium loaded organic phase was allowed to equilibrate for 2 h with equal volume of aqueous phase containing stripping solution at 300 K temperature. The again after complete phase separation, the aqueous phase was analyzed for thorium concentration and thus the stripping percentages were evaluated.

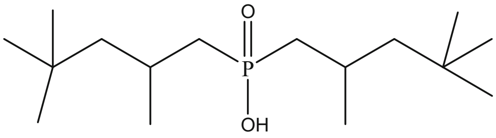
Fig. 1 Structures for TBP, DHOA, Cyanex-923, Cyanex-272 and $C_8mimNTf_2$



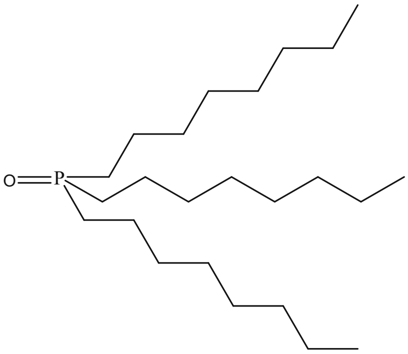
TBP (tri-*n*-butyl phosphate)



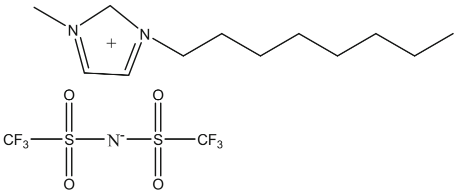
DHOA (N,N di-*n*-hexyl octanamide)



Cyanex-272
(Bis(2,4,4-trimethyl) pentyl phosphinic acid)



Cyanex-923
(tir-*n*-octyl phosphine oxide)



$C_8mimNTf_2$ (where R = 8)

Spectroscopic studies

UV–Visible spectroscopic studies were carried out using a JASCO V 530 double beam spectrophotometer using quartz cells and suitable reference solutions. The aqueous phase containing different concentration of thorium was allowed to equilibrate with 0.35 M ligand in ionic liquid for 2 h at 300 K with a phase ratio of 1. After complete phase separation, 2 mL of such aqueous phase was collected and the UV–Vis spectra were recorded for the absorbance. The blank solution showed no absorbance in the range 200–350 nm.

Results and discussion

Extraction profile of thorium at various feed acidities

The D_{Th} value was found to decrease gradually with increase in feed acidity up to 3 M HNO_3 followed by a sharp decrease both in case of Cyanex-923 and Cyanex-272, whereas for TBP and DHOA, the D_{Th} values decrease marginally up to 0.1 M HNO_3 followed by increase in D_{Th} values (Fig. 2). The decrease in D_{Th} values can be attributed to the strong competition of H^+ ion with Th^{4+} and suggesting the predominance of 'ion-exchange mechanism' while for TBP and DHOA systems beyond 0.1 M HNO_3 solvation mechanism seems to be predominating. Extraction of UO_2^{2+} using TBP in $C_8mimNTf_2$ also showed similar trend as seen in case of Th extraction by TBP or DHOA [39]. It was also reported that for most of the diglycolamide based ligands in C_8mim NTf_2 followed ion exchange mechanism for extraction of actinides throughout the feed acidity range as seen in case of Cyanex-923 and Cyanex-272 for the extraction of thorium [40–42]. It was revealed from the literature that the extraction mechanism changed from ion exchange to solvation on increasing the length of alkyl substituent in the alkyl methyl imidazolium ring of the ionic liquid for the extraction of Sr^{2+} using

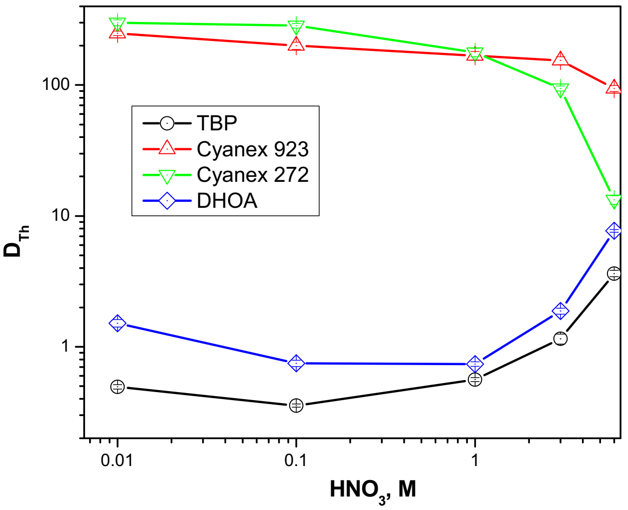


Fig. 2 Extraction profiles of Th at various feed acidity using TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 2 h, $T = 300$ K, ligand conc. = 0.35 M

crown ether in ionic liquids [43–45]. Therefore, the nature of extraction mechanism in ionic liquid based systems depends on the nature of the ligands and ionic liquids. In case of solvation mechanism the Th complex needs to be neutral in nature as suggested by Eq. (1). In case of cation exchange mechanism the overall Th complex is to be cationic in nature and will be transferred to the organic phase while to make overall charge balance equivalent amount of cations from ionic liquid phase i.e. C_8mim^+ ion will come to the aqueous phase Eq. (2). Similarly, if it proceeds through anion exchange mechanism the overall charge of the complex will be anionic and it will be transferred from aqueous phase to organic phase while equivalent amount of anion from ionic liquid medium i.e. NO_3^- will come to the aqueous phase Eq. (3). Therefore, to ascertain the nature of species which is extracted into the ionic liquid phase and the mechanism of extraction, it needs to investigate the effect of different species like NO_3^-, C_8mim^+, NTf_2^- and ligands on the extraction properties of thorium. The variation in feed acidity only gives an indication that the overall extraction mechanism of thorium is ion exchange for Cyanex-923 and Cyanex-272 while for TBP and DHOA it is solvation beyond 0.1 M HNO_3.

$$\mathrm{Th}^{+4}_{\mathrm{aq}} + 4\mathrm{NO}^{-}_{3_{\mathrm{aq}}} + n\mathrm{L}_{\mathrm{IL}} = \mathrm{Th}(\mathrm{NO}_3)_4 n\mathrm{L}_{\mathrm{IL}} \tag{1}$$

$$\begin{aligned}\mathrm{Th}^{4+}_{\mathrm{aq}} &+ m\mathrm{NO}^{-}_{3_{\mathrm{aq}}} + n\mathrm{L}_{\mathrm{IL}} + (4-m)\mathrm{C_8mim}^{+}_{\mathrm{IL}}\\ &= (\mathrm{Th}(\mathrm{NO}_3)_m n\mathrm{L})^{4-m}_{\mathrm{IL}} + (4-m)\mathrm{C_8mim}^{+}_{\mathrm{aq}}\end{aligned} \tag{2}$$

$$\begin{aligned}\mathrm{Th}^{4+}_{\mathrm{aq}} &+ m\mathrm{NO}^{-}_{3_{\mathrm{aq}}} + n\mathrm{L}_{\mathrm{IL}} + (m-4)\mathrm{NTf}^{-}_{2_{\mathrm{IL}}}\\ &= (\mathrm{Th}(\mathrm{NO}_3)_m n\mathrm{L})^{m-4}_{\mathrm{IL}} + (m-4)\mathrm{NTf}^{-}_{2_{\mathrm{aq}}}\end{aligned} \tag{3}$$

where, ‘aq’ and ‘IL’ referred to the aqueous and ionic liquid phase, ‘*m*’ and ‘*n*’ referred to the number of nitrate ion and ligand molecules attached to the thorium atom.

The D_{Th} values obtained in the present investigation were compared with the ionic liquid based systems reported in the literature [46–49] and presented in Table 1. 0.04 M TODGA in $C_n mimPF_6$ (where $n = 4, 8$) were employed for the extraction of Th [46]. The ionic liquids with PF_6^- anion were reported to be unstable in presence of even small amount of acid. There is liberation of fluoride ion in the systems leads to the interference during separation and problem of corrosion and hence not advisable [50]. Moreover, TODGA was reported to have very high *D* values for specially trivalent lanthanides and actinides and hence used for actinide partitioning [51, 52]. Application of N1923 ligand in C_8mimPF_6 showed appreciable extraction of Th only in lower feed acidity. In case of a series of amides and beta di-ketone, higher D_{Th} values were reported only from less than 1 M feed acidity. The acidity of high level waste solution encountered is mostly ~3 M HNO_3 [36, 51, 52]. Therefore it is desirable to develop extraction method from the feed of similar acidity.

Determination of metal–ligand stoichiometry

In order to examine the metal–ligand stoichiometry, the D_{Th} value was varied as a function of free ligand concentration (Fig. 3). The increase D_{Th} value on increasing the free ligand concentration primarily revealed the participation of ligand molecule into the extracted complex. The equilibrium constant for the extraction process can be expressed asFor solvation mechanism

$$k_{\mathrm{ex}} = \frac{[\mathrm{Th}(\mathrm{NO}_3)_4 \cdot n\mathrm{L}]_{\mathrm{IL}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}[\mathrm{NO}_3{}^{-}]^{4}_{\mathrm{aq}}[\mathrm{L}]^{n}_{\mathrm{IL}}} \tag{4}$$

For cation exchange mechanism

$$k_{\mathrm{ex}} = \frac{[(\mathrm{Th}(\mathrm{NO}_3)_m \cdot \mathrm{L}_n)^{(4-m)}_{\mathrm{IL}}]}{[\mathrm{Th}^{4+}_{\mathrm{aq}}]}\left(\frac{[\mathrm{C_8mim}^{+}]_{\mathrm{aq}}}{[\mathrm{C_8mim}^{+}]_{\mathrm{IL}}}\right)^{4-m}\frac{1}{[\mathrm{L}]^{n}_{\mathrm{IL}}}\frac{1}{[\mathrm{NO}_3{}^{-}]^{m}_{\mathrm{aq}}} \tag{5}$$

For anion exchange mechanism

$$k_{\mathrm{ex}} = \frac{[(\mathrm{Th}(\mathrm{NO}_3)_m \cdot \mathrm{L}_n)^{(m-4)}_{\mathrm{IL}}]}{[\mathrm{Th}^{4+}_{\mathrm{aq}}]}\left(\frac{[\mathrm{NTf}_2{}^{-}]_{\mathrm{aq}}}{[\mathrm{NTf}_2{}^{-}]_{\mathrm{IL}}}\right)^{m-4}\frac{1}{[\mathrm{L}]^{n}_{\mathrm{IL}}}\frac{1}{[\mathrm{NO}_3{}^{-}]^{m}_{\mathrm{aq}}} \tag{6}$$

If the free ligand concentration is varied at a particular feed acidity and at particular temperature then Eqs. (4), (5) and (6) can be simplified as Eq. (7), where k'_{ex} is conditional extraction constant. It is assumed that at a particular

Table 1 Comparison of D_{Th} values with the literature reported values in ionic liquid based systems

Ligand	Ionic liquid	Ligand conc	Feed acidity	D_{Th}	Comment	Reference
TBP	$C_8mimNTf_2$	0.35 M	3 M	1.15	–	Present work
Cyanex-923	$C_8mimNTf_2$			154	–	Present work
Cyanex-272	$C_8mimNTf_2$			94	–	Present work
DHOA	$C_8mimNTf_2$			1.87	–	Present work
TODGA	C_4mimPF_6	0.04 M		14	IL not stable, TODGA also extracts tri and hexavalent Ln/An	[46]
	C_8mimPF_6			18		
N1923	C_8mimPF_6	0.068 M		Negligible	IL not stable	[35]
TBDA	C_4mimPF_6	0.01 M		~3	IL not stable	[53]
	C_6mimPF_6			~3	IL not stable	[53]
	C_8mimPF_6			~2	IL not stable	[53]
MBDA	C_4mimPF_6			~1.8	IL not stable	[53]
	C_6mimPF_6			~1.6	IL not stable	[53]
	C_8mimPF_6			~1.5	IL not stable	[53]
DBEHA	C_4mimPF_6	0.2 M	0.2 M	0.85	IL not stable, low feed acidity	[47]
DBDMBA	C_4mimPF_6			6.3		
DBPA	C_4mimPF_6			3.97		
DHOA	C_4mimPF_6			7.07		
DBOA	C_4mimPF_6			13.5		
HTTA	$C_2mimNTf_2$	0.1 M	0.1 M	7.94	Low feed acidity, high ligand concentration	[48]
HTTA	$C_4mimNTf_2$			11.22		
HTTA	$C_6mimNTf_2$			12.30		
HTTA	$C_8mimNTf_2$			15.85		
DEHEHP	C_8mimPF_6	–	–	–	IL not stable	[54]

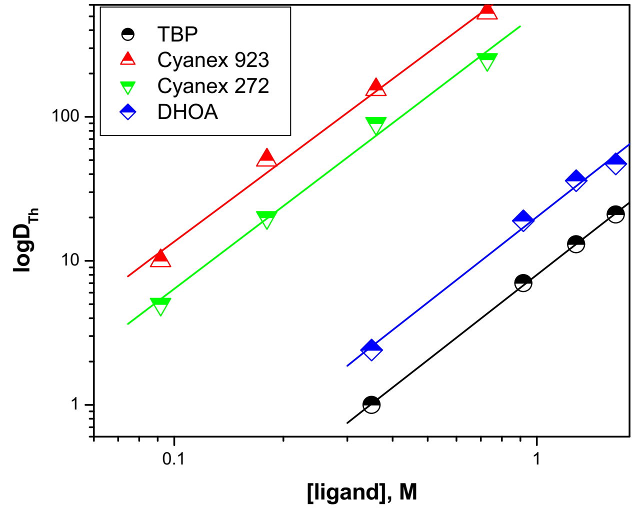


Fig. 3 Variation of D_{Th} as a function of ligand concentration using TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 2 h, $T = 300$ K, feed acidity 3 M HNO_3

temperature the partition coefficients for C_8mim^+ and NTf_2^- were constants.

$$k'_{ex} = \frac{D_{Th}}{[L]^n_{IL}} \quad (7)$$

$$\log D_{Th} = \log k'_{ex} + n \log[L]_{IL} \quad (8)$$

In accordance with Eq. (8), a plot of log D_{Th} versus log [L] gave straight line with a slope of 'n' which is nothing but the number of ligand molecule associated with a Th atom. For all the solvent systems, one Th molecule is associated with two ligand molecules which is found to be same as that observed in case of molecular diluent based systems [55]. Similar metal–ligand stoichiometry but different extraction mechanism was also reported in case of uranyl-TBP complex in molecular diluent and ionic liquid [56]. The uranyl complex of CMPO in dodecane and in ionic liquid also showed same metal–ligand stoichiometry [20].

Table 2 Determination of metal–ligand stoichiometry, conditional extraction constants, formation constants and change in Gibb's free energy

Ligand	Slope	Metal:ligand	Intercept	k'_{ex}	ΔG (kJ/mol)	k_f
TBP	1.96	1:2	0.9	7.94E+00	−5.17	1.59E+02
Cyanex-923	1.87	1:2	3.01	1.02E+03	−17.29	2.05E+04
Cyanex-272	1.91	1:2	2.72	5.25E+02	−15.62	1.05E+04
DHOA	1.97	1:2	1.3	2.00E+01	−7.47	3.99E+02

If we consider the complexation of Th^{4+} with two ligands then the conditional formation constant (k_f) can be expressed as follows [57].

$$Th^{4+}_{IL} + 2L_{IL} = (Th.2L)^{4+}_{IL} \tag{9}$$

$$k_f = \frac{[(Th \cdot 2L)^{4+}]_{IL}}{[Th^{4+}]_{IL}[L]^2_{IL}} \tag{10}$$

$$k_f = k'_{ex}\frac{[Th^{4+}]_{aq}}{[Th^{4+}]_{IL}} \tag{11}$$

$$k_f = \frac{k'_{ex}}{P_{Th}} \tag{12}$$

where, P_{Th} is the partition coefficient of thorium between 3 M HNO_3 and $C_8mimNTf_2$ (This is the distribution ratio of thorium between 3 M HNO_3 and $C_8mimNTf_2$ without ligands. The aqueous phase containg 10 mg L^{-1} of Th in 3 M HNO_3 was allowed to equilibrate with $C_8mimNTf_2$ for 2 h. After complete phase separation by centrifugation, the aqueous phase was analyzed by ICP-AES for thorium and D value for thorium was calculated using the equation shown in experimental section and this is denoted as P_{Th}). Table 2 summarized the conditional extraction constants, formation constants of thorium by TBP, DHOA, Cyanex-923, Cyanex-272 in ionic liquid. The overall 'Gibb's free energy change during the extraction can also be evaluated by the following equation

$$\Delta G = 2.303\,RT \log k'_{ex} \tag{13}$$

The k'_{ex} and k_f values were found to follow the trend Cyanex-923 > Cyanex-272 > DHOA > TBP. The extraction processes were found to be energetically favorable with the similar trend as above.

Participation of NO_3^- anion in the extraction

To ascertain the nature of extraction mechanism, it is essential to understand the participation of NO_3^- anion in the extracted species. For the extraction of Th using constant concentration of ligands and at constant temperature, Eqs. (4), (5) and (6) can be simplified as

$$k'_{ex} = \frac{D_{Th}}{[NO_3^-]^m} \tag{14}$$

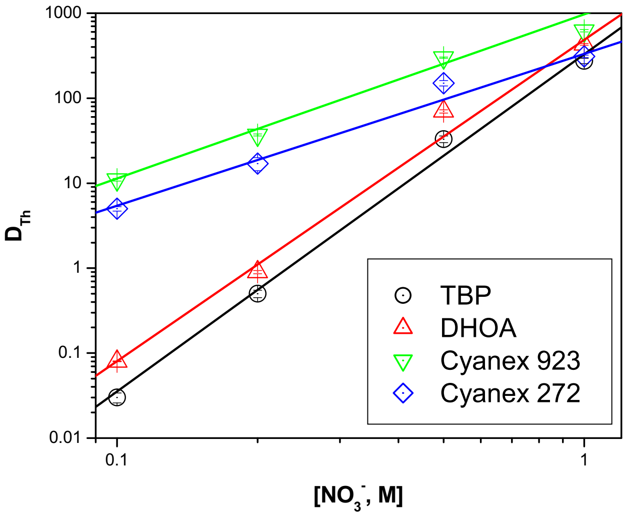


Fig. 4 Variation of D_{Th} as a function of NO_3^- concentration using 0.35 M TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 2 h, $T = 300$ K

$$\log D_{Th} = \log k'_{ex} + m\log[NO_3^-] \tag{15}$$

Figure 4 depicted the plots of log D_{Th} versus log $[NO_3^-]$ for different systems. The increase in D_{Th} values with increase in NO_3^- concentration in the aqueous phase primarily confirmed the participation of NO_3^- in the extracted Th complex. Slope values revealed the participation of four NO_3^- ion in the extracted species of TBP and DHOA, revealing the possibility of neutral extracted complex ($Th(NO_3)_4{\cdot}2L$) via solvation mechanism (provided there is no participation of NO_3^- anion). In case of Cyanex-923 and Cyanex-272, only two NO_3^- were found to participate in the extracted complex making the overall charge of the extracted species 2+ ($(Th(NO_3)_2{\cdot}2L)^{2+}$). The slope and intercept values alongwith the errors and regression coefficients were summarized in Supplementary Table 2.

Participation of NTF_2^- anion in the extracted complex

It is clear from the above studies that it is essential to understand the participation of NTF_2^- into the extracted species to ascertain the extraction mechanism. The concentration of NTF_2^- in aqueous phase was varied in the

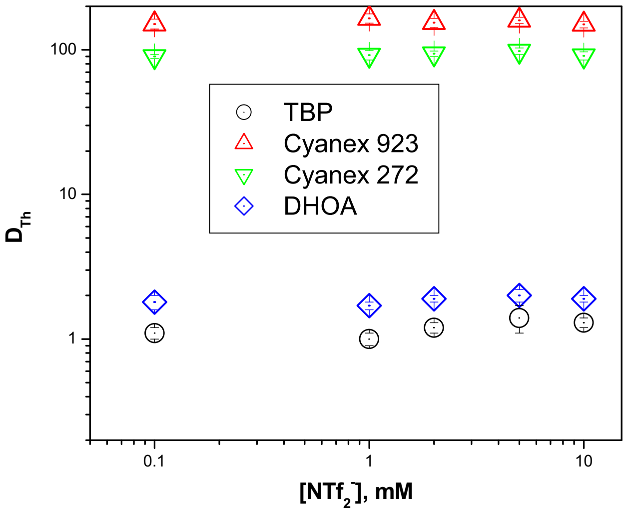


Fig. 5 Variation of D_{Th} as a function of NTf_2^- concentration in aqueous phase as $LiNTf_2$ using 0.35 M TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 2 h, $T = 300$ K, feed acidity 3 M HNO_3

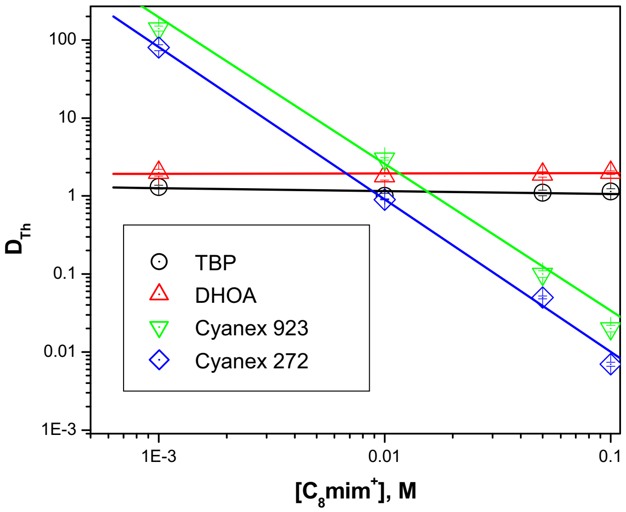


Fig. 6 Variation of D_{Th} as a function of C_8mim^+ concentration in the aqueous phase as C_8mimBr using 0.35 M TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 2 h, $T = 300$ K, feed acidity 3 M HNO_3

form of water soluble $LiNTf_2$ salt. If NTF_2^- is participating in the extracted species, then with increase in NTF_2^-concentration in the aqueous phase should favour the extraction of Th and hence increase in D_{Th} values. If the overall extraction mechanism is anion exchange, then with increase in NTF_2^- ion concentration in aqueous, D_{Th} values are expected to decrease. But no changes in D_{Th} values were observed during a vast change of NTF_2^- ion concentration in the aqueous phase in the range of 0.1–10 mM (Fig. 5). The above fact revealed that there was no participation of NTF_2^- ion in the extracted species which confirmed the extracted species of $Th(NO_3)_4{\cdot}2L$ for TBP and DHOA via salvation mechanism and $(Th(NO_3)_2{\cdot}2L)^{2+}$ for Cyanex-923 and Cyanex-272 via 'cation exchange' mechanism.

Effect of C_8mim^+ on extraction of thorium

As the above study revealed that the extraction of Th by TBP and DHOA was proposed to follow through 'solvation mechanism' while that for Cyanex-923 and Cyanex-272 followed through 'cation exchange mechanism'. To ascertain the facts a variation of D_{Th} as a function of C_8mim^+ concentration in aqueous phase was investigated (Fig. 6). In case of TBP and DHOA systems the D_{Th} values were found to remain unchanged with C_8mim^+ concentration in the aqueous phase, suggesting the non participation of C_8mim^+ in the extraction process which was expected from the solvation mechanism. In case of Cyanex-923 and Cyanex-272, on increasing C_8mim^+ concentration in the aqueous phase the D_{Th} values were found to decrease. Since in cation exchange process, Th-ligand complex in overall cationic form was exchanged from aqueous phase to organic phase by C_8mim^+ ion. This exchange process would likely to be hampered with increase in C_8mim^+ cation in aqueous phase. Hence the reverse reaction was favoured. Hence D_{Th} values were found to decrease on increasing C_8mim^+ ion concentration in aqueous phase.

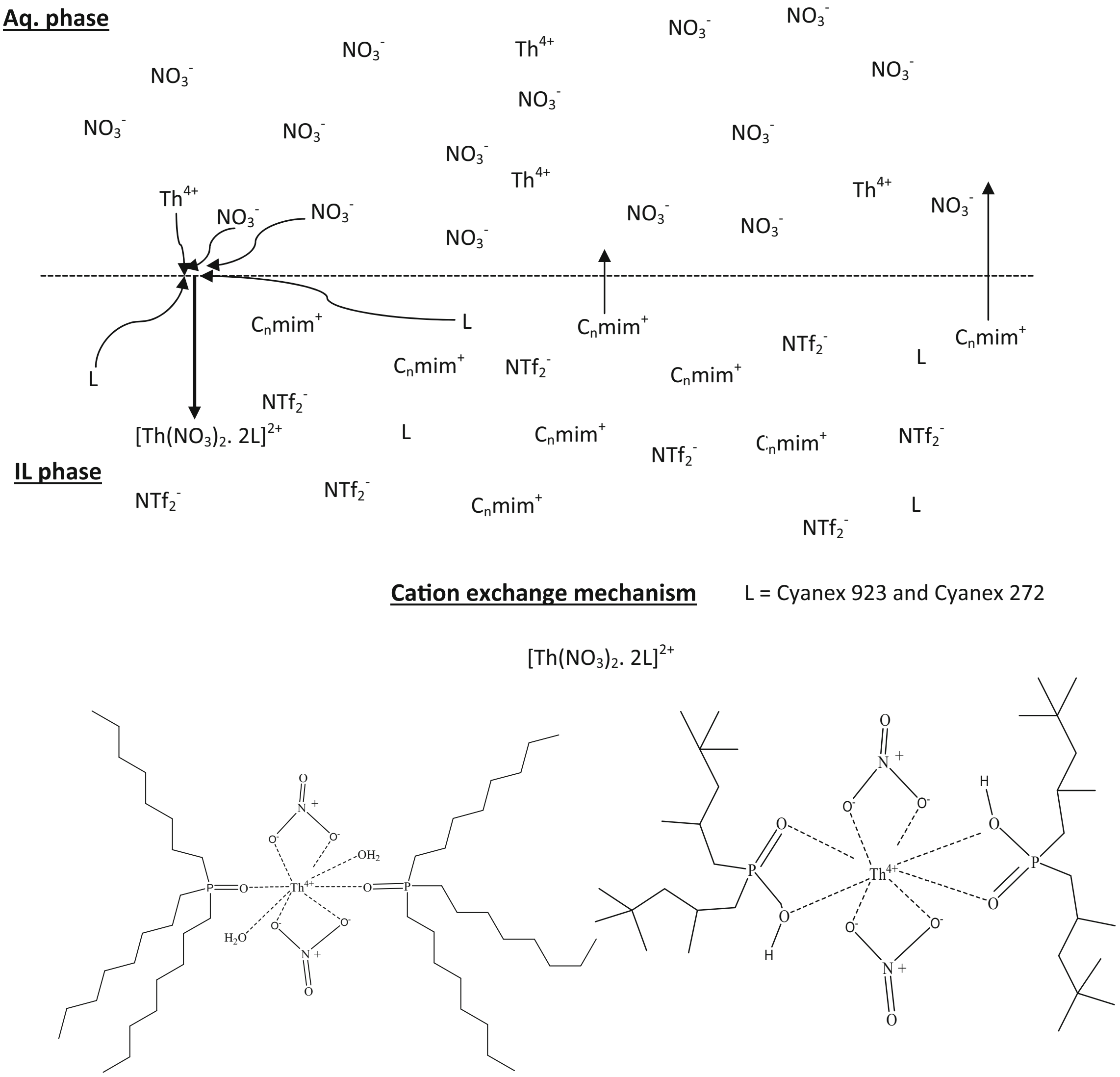
To confirm the extraction mechanism another approach has also been adopted. The aqueous phase was loaded with various concentrations of Th and after extraction, the raffinates were analyzed for UV–Vis spectroscopy to monitor the absorption due to C_8mim^+ ion. If the extraction proceeds via 'cation exchange' mechanism involving the exchange of C_8mim^+ in place of Th-extracted cationic species, then more loading of Th leads to more concentration of C_8mim^+ in the raffinate and the absorption in UV–Vis spectra should increase without changing the absorption maxima [1]. In the present investigation, it was observed that on increasing Th concentration the absorption increased for Cyanex-923 and Cyanex-272 confirming the 'cation exchange' nature of the extraction through C_8mim^+ ion (Supplementary Fig. 1). On the other hand no such observation was noticed confirming the predominance of 'solvation mechanism' for them.

Ionic liquid based all these solvent systems were found to be much more efficient than the common molecular diluents like xylene (Supplementary Table 3). At such lower ligand concentration (0.35 M), TBP and DHOA were not able to extract Th practically into xylene phase while in $C_8mimNTf_2$ more than 50 % Th can be extracted.

This fact revealed that though in both the cases the extraction proceeds through 'solvation mechanism' some additional driving force was responsible for higher extraction of Th into ionic liquid phase. For Cyanex-923 and 272, from molecular diluents to ionic liquid, the extraction mechanism changed from salvation to ion exchange which might be responsible for higher extraction efficiency of Th in ionic liquid.

Scheme 1 revealed the 'cation exchange' mechanism predominated for Cyanex-272 and Cyanex-923. In this mechanism, Th^{4+} ion from aqueous phase came to the ionic liquid phase by formation of species $[Th(NO_3)_2 \cdot 2L]^{2+}$. To maintain the overall charge balance, two C_8mim^+ ion from the ionic liquid phase came to the aqueous phase. In the above species two nitrate ion coordinated in a bidentate fashion, while Cyanex-923 coordinated through the phosphoryl oxygen in a monodentate fashion. Most probably two water molecules from the medium also coordinated to the thorium ion to fulfill the coordination saturation of 8 for tetravalent actinides. In case of Cyanex-272, there is a chance that two oxygen atoms from the ligand would coordinate to the thorium ion which removes the possibility of coordination of two water due to coordination unsaturation.

Scheme 2 represented the 'solvation mechanism' predominately operating for the TBP and DHOA. For these ligands thorium form neutral complex with two ligand molecules associated by four nitrate ions. In these case,

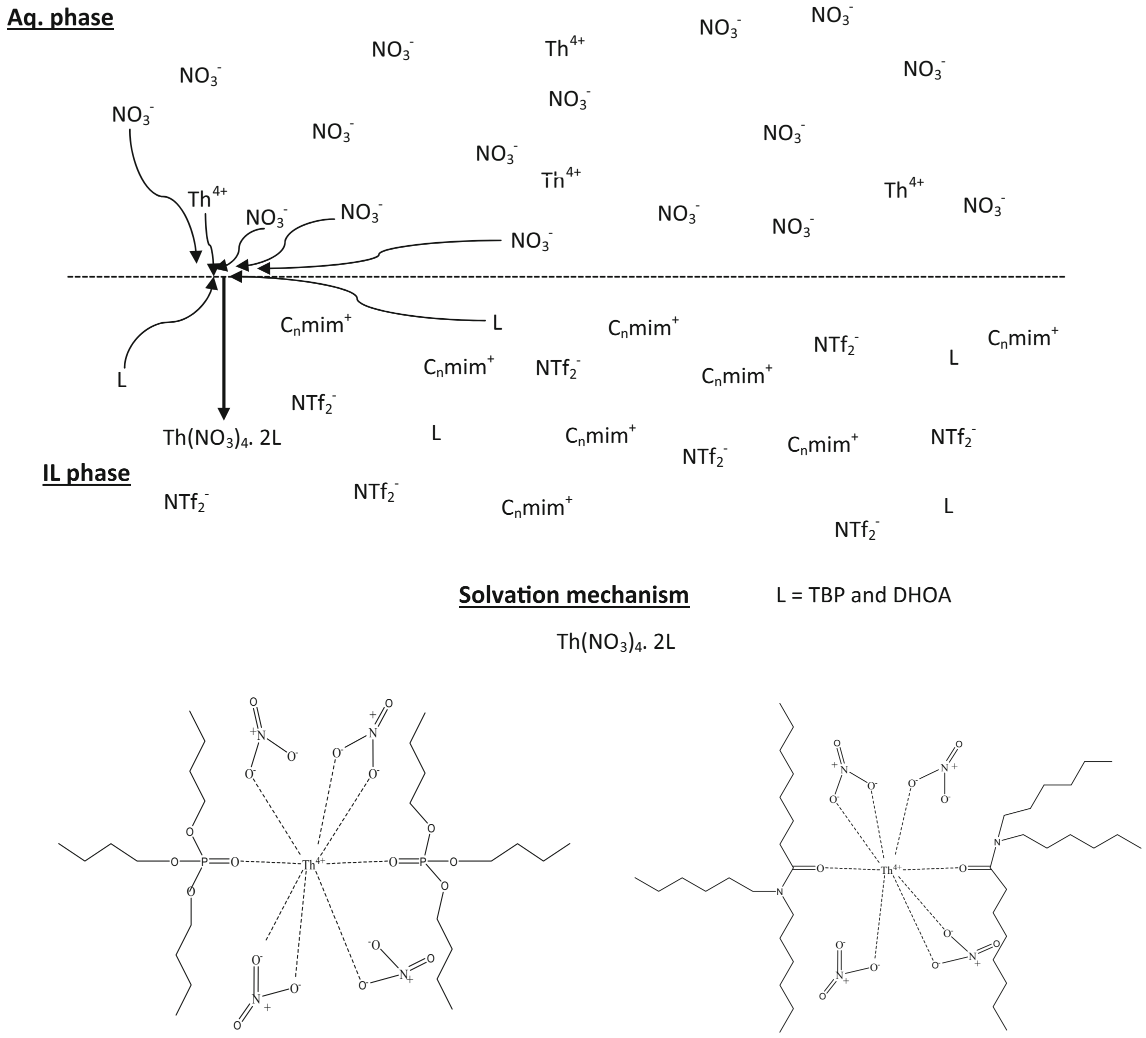


Scheme 1 Schematic of Cation exchange mechanism predominated for Cyanex-923 and Cyanex-272

two ligand molecules coordinated in a monodentate fashion. Out of four nitrate ions, two coordinated in bidentate and one coordinated in monodentate fashion to fulfill the 8 coordination numbers for the tetravalent actinides.

Extraction kinetics

The D_{Th} values were investigated as a function of equilibration time for all the solvent systems. For TBP the D_{Th} values were found to increase up to 60 mintutes followed by a plateau with D_{Th} ~1.2. The similar trend was also seen for Cyanex-923, Cyanex-272 and DHOA with D_{Th} values of ~150, 100 and 1.9 at the plateau. The investigation revealed that 60 min was required for achieving maximum D values for all the ligands in ionic liquid (while 15 min. was found to be sufficient for the extraction using molecular diluent, doecane (Supplementary Fig. 2). Since for all the solvent systems same time was required, it indicated that probably the diluent, $C_8mimNTf_2$ was playing the role for such slower kinetics of extraction. Earlier reports revealed that such slower kinetics were also observed in ionic liquid based systems due to the higher viscosity coefficient of the ionic liquid during the extraction of Am^{3+} [30]. In our previous investigation a correlation was made for methylimidazolium based ionic liquids, how the structural modification in ionic liquid led to increase in viscosity coefficient which



Scheme 2 Schematic of solvation mechanism predominated for TBP and DHOA

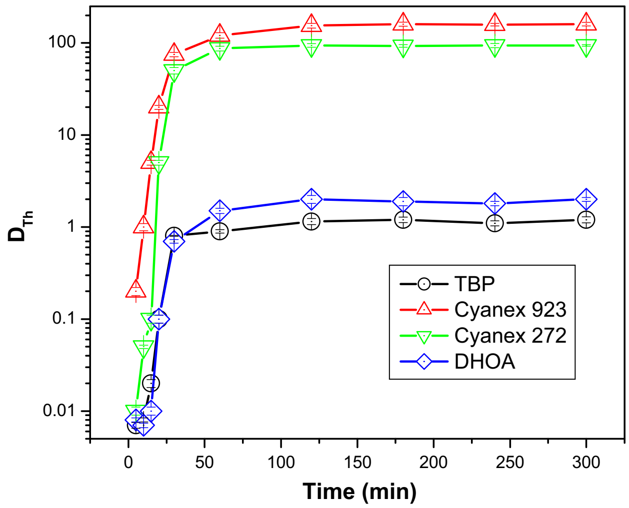


Fig. 7 The variation of D_U values as a function of imidazolium ion concentration in aqueous phase in the form of 1-Ethyl-2,3-dimethylimidazolium chloride, 300 K, Phase ratio 1, time of equilibration 2 h

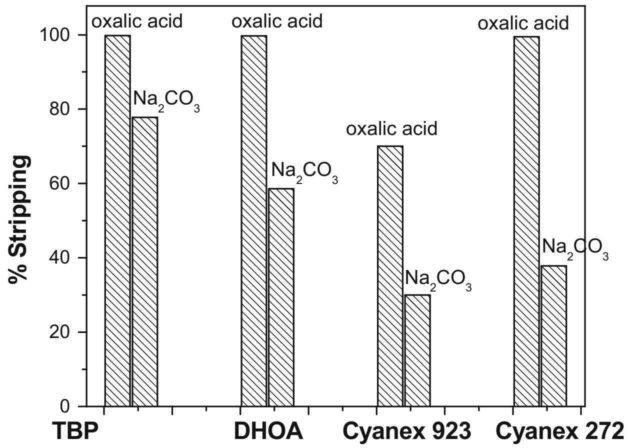


Fig. 8 Stripping of Th form extracted complexes of TBP, Cyanex-923, Cyanex-272 and DHOA in $C_8mimNTf_2$ with phase ratio 1, equilibration time 5 min, $T = 300$ K

subsequently made the extraction kinetics of Sr^{2+} even slower [13]. Figure 7 showing the extraction kinetic behavior of Th by these ionic liquid based systems attributed to the viscous nature of ionic liquid.

Stripping of Th(IV) from organic phase

With room temperature ionic liquids, the stripping of the metal ions from the ionic liquid phase is one of the major challenges. Usually, the extraction is carried out at higher acidity (3–6 M HNO_3), while the stripping is done at lower acidity (pH −2.0) for molecular diluents based systems. However, with ionic liquids as the diluent the D values at lower feed acidity are too high to back extract. Therefore, the problem of stripping of Th from ionic liquid phase was overcome by using aqueous phase complexing agents like 0.5 M Na_2CO_3 and 0.5 M oxalic acid.[15] These solutions were employed in the present study for the stripping of Th(IV) from TBP, DHOA, Cyanex-923 and Cyanex-272. The results are shown in Fig. 8, which suggest that 0.5 M oxalic acid solution are effective as strippant where close to 95 % stripping of Th was observed in a single stage in case of TBP, Cyanex-272, DHOA while in case of Cyanex-923 oxalic acid could extract nearly 75 %. On the other hand, Na_2CO_3 was not very effective as a strippant as only 80 % stripping was obtained in a single stripping case of TBP while dealing with DHOA, Cyanex-272 and Cyanex-923 stripping was nearly 60, 38 and 30 %.The results are encouraging by using oxalic acid for stripping. It was also observed that 2 contacts of oxalic acid with phase ratio were required for the quantitative back extraction of Th from ionic liquid phase containing TBP, Cyanex-272 and DHOA while for Cyanex-923, which is a stronger extractant needs 6 such contacts. Using Na_2CO_3 as strippant, 6 contacts can led to quantitative stripping of Th from TBP ionic liquid phase while even after 6 contacts, 88, 94 and 99.5 % Th were found to be back extracted into the aqueous phase from complexes of Cyanex-923, Cyanex-272 and DHOA, respectively (Supplementary Fig. 3).

Effect of Gama Irradiation on extraction of Th(IV)

Though the TBP, DHOA, Cyanex-923 and Cyanex-272 ligands are highly promising for actinide ion extraction, their actual use for actinide ion separation requires their

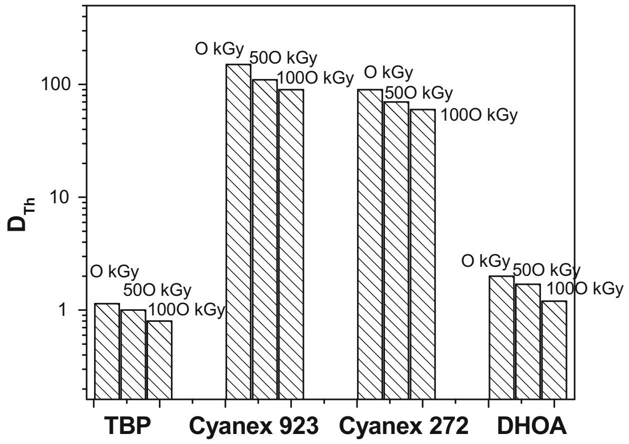


Fig. 9 Radiation stability of 0.35 M TBP, Cyanex-923, Cyanex-272 and DHOA in ionic liquid

Table 3 Analytical results obtained after extraction of simulated high level waste solution of fast breeder reactor origin by ionic liquid based solvent systems with phase ratio 1:1, at 300 K, equilibration time 2 h

Element	SHLW	TBP		Cyanex-923		Cyanex-272		DHOA	
	Fast breeder reactor (mg/L)	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M
Sr	30	29 ± 2	0.03	27 ± 2	0.11	28 ± 3	0.07	28 ± 3	0.07
Zr	5	4.0 ± 0.1	0.25	3.5 ± 0.1	0.43	3.9 ± 0.1	0.28	4.6 ± 0.03	0.09
Nb	0.1	0.09 ± 0.002	0.11	0.1 ± 0.002	–	0.1 ± 0.01	0.00	0.09 ± 0.003	0.11
Mo	150	140 ± 11	0.07	140 ± 6	0.07	142 ± 8	0.06	149 ± 2	0.007
Ru	100	97 ± 8	0.03	99 ± 7	0.01	96 ± 6	0.04	97 ± 0.2	0.03
Rh	50	47 ± 2	0.06	43 ± 3	0.16	46 ± 1	0.09	47 ± 2	0.06
Pd	5	4.9 ± 0.2	0.02	4.5 ± 0.02	0.11	4.7 ± 0. 2	0.06	4.9 ± 0.1	0.02
Ag	5	4.9 ± 0.1	0.02	4.9 ± 0.08	0.02	4.8 ± 0.3	0.04	4.8 ± 0.2	0.04
Cd	5	4.9 ± 0.3	0.02	4.9 ± 0.06	0.02	4.6 ± 0.4	0.09	4.8 ± 0.2	0.04
Ba	75	74 ± 1	0.01	72 ± 1	0.04	74 ± 4	0.01	74 ± 1	0.014
La	75	71 ± 2	0.06	74 ± 2	0.01	74 ± 5	0.01	72 ± 5	0.04
Ce	100	98 ± 4	0.02	98 ± 2	0.02	96 ± 5	0.04	96 ± 3	0.04
Pr	50	48 ± 1	0.04	47 ± 1	0.06	45 ± 4	0.11	49 ± 1	0.02
Nd	200	195 ± 9	0.03	190 ± 11	0.05	192 ± 8	0.04	196 ± 9	0.02
Sm	50	48 ± 2	0.04	49 ± 2	0.02	49 ± 2	0.02	49 ± 1	0.02
Eu	5	4.9 ± 0.1	0.02	4.9 ± 0. 4	0.02	4.8 ± 0.1	0.04	4.9 ± 0.2	0.02
Gd	5	4.6 ± 0.1	0.09	4.7 ± 0.1	0.06	4.8 ± 0.2	0.04	4.9 ± 0. 3	0.02
Dy	5	4.8 ± 0.1	0.04	4.8 ± 0.1	0.04	4.8 ± 0.3	0.04	4.7 ± 0.1	0.06
U	200	10 ± 1	19	1 ± 0.2	199	7 ± 0.2	27	20 ± 1	9.00
Cr	200	198 ± 8	0.010	199 ± 5	0.01	190 ± 10	0.05	195 ± 6	0.03
Mn	25	22 ± 1	0.14	20 ± 1	0.25	22 ± 2	0.14	23 ± 1	0.09
Fe	600	596 ± 15	0.007	588 ± 13	0.02	590 ± 10	0.02	590 ± 12	0.02
Ni	100	97 ± 2	0.03	91 ± 6	0.10	95 ± 6	0.05	96 ± 5	0.04
Na	1000	999 ± 19	0.001	1000 ± 17	–	994 ± 18	0.006	993 ± 18	0.007

prolonged reusability, which means their good radiolytic stability. This is because all actinide ions emit high LET (linear energy transfer) alpha particles, β particles and γ radiation. Therefore, a systematic study was carried out to investigate the radiolytic stability of the TBP, DHOA, Cyanex-923 and Cyanex-272 in C_8mimNTf$_2$. It was revealed that after exposing the organic phase to 500 kGy of the absorbed gamma dose, the extraction efficiency becomes 88, 85, 73, and 78 % of the original D_{Th} values (with the unirradiated ligand solution) for TBP, DHOA, Cyanex-923 and Cyanex-272, respectively. On exposure to 1000 kGy, D_{Th} values decreased to 70, 60, 60, and 67 %, respectively of the original values (Fig. 9). The results suggested that after 1000 kGy gamma exposure, TBP-ionic liquid system was the most radio resistant (D_{Th} becomes ~70 % of its original value) and the radiolytic sability of all the solvent systems were good up to 500 kGy of gamma exposure.

Application of ionic liquid based solvent systems for processing simulated high level waste solutions (SHLW) from fast breeder reactor (FBR) and research reactor (RR) origin

The main aim of developing these ionic liquid based solvent systems was to process the radioactive waste generated from different streams. The selectivity of these solvent based systems also needs to be investigated. In the present case, SHLW solutions of FBR and RR origin were contacted with these ionic liquid based systems for 2 h and the raffinate was directly fed into the plasma. All these ionic liquid based solvent systems were found to be highly selective for thorium. Only U and very small amount of Zr were found to co-extracted into the ionic liquid phase with the trend in extraction efficiency Cyanex-923 > Cyanex-272 > TBP > DHOA. Tables 3 and 4 summarized the

Table 4 Analytical results obtained after extraction of simulated high level waste solution of research reactor origin by ionic liquid based solvent systems with phase ratio 1:1, at 300 K, equilibration time 2 h

Element	SHLW	TBP		Cyanex-923		Cyanex-272		DHOA	
	Research reactor (mg/L)	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M	Raffinate after extraction (mg/L)	D_M
Sr	50	47 ± 2	0.064	49 ± 2	0.020	46 ± 2	0.087	49 ± 3	0.020
Mo	200	198 ± 8	0.010	187 ± 3	0.070	190 ± 3	0.053	196 ± 9	0.020
Ru	75	74 ± 3	0.014	72 ± 2	0.042	73 ± 3	0.027	75 ± 2	0.000
Cd	300	292 ± 9	0.027	290 ± 6	0.034	293 ± 6	0.024	298 ± 9	0.007
Ba	100	97 ± 4	0.031	90 ± 4	0.111	94 ± 4	0.064	99 ± 4	0.010
La	100	99 ± 3	0.010	91 ± 2	0.099	97 ± 3	0.031	92 ± 5	0.087
Ce	100	98 ± 2	0.020	93 ± 4	0.075	96 ± 4	0.042	96 ± 3	0.042
U	2000	254 ± 2	6.9	67 ± 2	28.8	97 ± 4	19.6	96 ± 5	5.7
Cr	400	398 ± 6	0.005	380 ± 8	0.053	389 ± 8	0.028	386 ± 9	0.036
Mn	500	499 ± 8	0.002	448 ± 6	0.116	488 ± 8	0.025	396 ± 11	0.263
Fe	1500	1490 ± 11	0.007	1470 ± 18	0.020	1480 ± 16	0.014	1491 ± 12	0.006
Ni	300	290 ± 6	0.034	295 ± 6	0.017	297 ± 5	0.010	295 ± 9	0.017
Na	5000	4977 ± 10	0.005	4958 ± 9	0.008	4970 ± 7	0.006	4995 ± 12	0.001
Mg	300	297 ± 2	0.010	292 ± 9	0.027	293 ± 9	0.024	296 ± 6	0.014
Ca	400	395 ± 6	0.013	392 ± 11	0.020	394 ± 11	0.015	393 ± 9	0.018
Al	2000	1990 ± 15	0.005	1921 ± 16	0.041	1944 ± 12	0.029	1990 ± 16	0.005

analytical results obtained after processing the SHLW of FBR and RR origins.

Conclusions

In the present investigation TBP, DHOA, Cyanex-923, Cyanex-272 in ionic liquid have been explored for the selective separation of thorium from aqueous acidic waste solution and even simulated high level waste solutions of Fast Breeder and Research reactor. The extraction process was found to be kinetically slower but energetically favourable. For all the cases the metal–ligand stoichiometry was found to 1:2 with four NO_3^- coordinated to Th for TBP and DHOA and 2 for Cyanex-923 and Cyanex-272. In case of TBP and DHOA, the extraction was found to proceed via 'solvation mechanism' while 'cation exchange' mechanism was found to be predominating for Cyanex-923 and 272. The extraction efficiency was found to follow the trend Cyanex-923 > Cyanex-272 > DHOA > TBP while stripping of thorium followed the reverse trend. Oxalic acid was found to be suitable for the quantitative back extraction of Th from ionic liquid phase. Up to 500 kGy, all the solvent systems were found to be radiolytically stable with the trend TBP > DHOA > Cyanex-272 > Cyanex-923.

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