

## **Exploring novel functionality for efficient extraction of $\text{UO}_2^{2+}$ and $\text{Th}^{4+}$ in ionic liquid: Mechanism, Speciation, Selectivity, Stability and Stripping**

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### **Abstract**

Novel ligand functionality, 5-bromo-N1, N3-bis(4,6-dimethylpyridin-2-yl)isophthalamide, was explored for highly efficient and selective separation of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  in pyridinium based ionic liquid. The comprehensive investigation revealed that, both in ionic liquid as well as in molecular diluents the extraction predominantly proceeded via 'solvation' mechanism. However, the species involved in extraction were  $\text{UO}_2(\text{NO}_3)_2$ , L and  $\text{Th}(\text{NO}_3)_4$ , L in ionic liquid, while  $\text{UO}_2(\text{NO}_3)_2$ , 2L and  $\text{Th}(\text{NO}_3)_4$ , 3L in molecular diluent. The highly viscous ionic liquid resulted the mass transfer slower during extraction. In ionic liquid based system, the extraction processes were endothermic, spontaneous and entropy driven. Ionic liquid based solvent systems exhibited high radiation stability, which was attributed to the formation of resonance-stabilized aromatic cation as well as the restricted movement of radicals in viscous ionic liquid. The aqueous solution of sodium carbonate was found to be effective for the stripping of  $\text{UO}_2^{2+}$ , while oxalic acid solution was found to be effective for  $\text{Th}^{4+}$ . The solvent systems were used for processing of simulated high level waste solutions of a Research Reactor (RR) and Fast Breeder Reactor (FBR) origin.

**Keywords:** Ionic liquid; Pyridine isophthalamide; Solvation mechanism; Endothermic, Slower kinetics

## Introduction

Ionic liquid has been proposed worldwide as 'green' alternatives to volatile organic solvent (VOS), due to the promising characteristics like low vapour pressure, wide electrochemical potential, large liquid range, high degree of chemical, and radiation stability in drastic chemical environment and extensive solubilizing capabilities of organic, inorganic and polymeric materials[1-3]. The lower charge density of the constituents ions of ionic liquid lowers the lattice energy of ionic liquid and hence, it is liquid at room temperature even though ionic in nature[4]. Due to these, a wide range of applicability of ionic liquids has been demonstrated in the field of synthesis, electrochemistry, sensor, nuclear establishment and membrane-based separation technologies[5-8]. The antimicrobial characteristics of ionic liquid / ionic liquid based materials have also drawn the attention of researchers[9, 10].

In recent years, ionic liquid has been exploited widely in membrane technology as supported ionic liquid membranes/poly ionic liquid membranes to achieve un-conventional separation[11-13]. Polymer brush has been widely used to enhance and improve the membrane performances using plasma, UV grafting, ATRP, second interfacial polymerization, etc.; among them, poly(ionic liquid) presents a good performance[14-19]. The performance improvement and improvement in anti-fouling characteristics were highly appreciated compared to conventional polymer grafting. Such grafting was also reported to bring electrical response in the ultrafiltration membrane in presence of oscillating electrical field frequency[20].

In nuclear establishment, ionic liquid is mainly used as diluent for separation of lanthanides/actinides; or it can be used for task specific applications, where the organic functionalities are covalently attached to the ionic liquid moieties and thus resulting in significant improvement in extraction efficiency and selectivity[21-24]. There were also parallel efforts going on for non-aqueous reprocessing of highly radiotoxic spent nuclear fuel materials[25, 26]. Using molten salt for reprocessing leads to a chemically drastic corrosive environment and requirement of high temperature. The substitution of these molten salts with ionic liquid for non-aqueous reprocessing is one of the reported attractive options. Application of ionic liquid as a diluent during the separation of lanthanides/actinides demonstrated some unique chemistry, which otherwise is not common [27-29]. For example, in conventional molecular diluents, the extracted species must be overall electrically neutral following 'solvation' mechanism. However, in ionic liquid both 'solvation' and 'ion exchange' mechanism can predominate involving neutral/ionic species depending upon the systems [30, 31]. In ionic liquid; both 'cation exchange' as well as 'anion exchange' mechanism has been reported[32, 33]. It was also reported that the nature of the mechanism can be tuned based on

the requirement by minimal structural modification in ionic liquid[34]. Few reports are also available in the literature to demonstrate the structure-activity relationship of some of the properties of ionic liquids[35, 36]. Apart from tuning the extraction mechanism, mostly ionic liquid based separation showed a significant improvement in extraction efficiency, selectivity, and radiation stability. The speciation in complexation was also reported to differ in ionic liquid compared to molecular diluent[37]. However, using ionic liquid in separation has its own drawback, which cannot be ignored. Still ionic liquid can provide some exciting chemistry.

Tri-n-butyl phosphate is the work horse for efficient extraction of uranium, plutonium and thorium during aqueous reprocessing of spent nuclear fuel[38]. However, it showed several drawbacks including moderate aqueous solubility, third phase formation, poor selectivity, poor radiation stability etc[39]. Moreover, ligands containing P, S based functionalities are not completely incinerable and hence, exist as radiotoxic burden to the environment. Therefore, there is always a need for ligands constituted with C, H, N, O atoms. Diglycolamide functionalized ligands have been explored for the extraction of actinides of different oxidation states[40, 41]. The D values followed the trend  $An^{3+} > An^{4+} > AnO_2^{2+} > AnO_2^+$ [23, 42]. The unusually higher D values for trivalent actinides compared to tetravalent actinides was attributed to the formation of reverse micellar aggregation[43-45]. Therefore, even though, diglycolamide functionalized ligands might extract  $Th^{4+}$ ,  $UO_2^{2+}$  from  $HNO_3$  media, but in presence of trivalent actinides/lanthanides the extraction would be very poor.

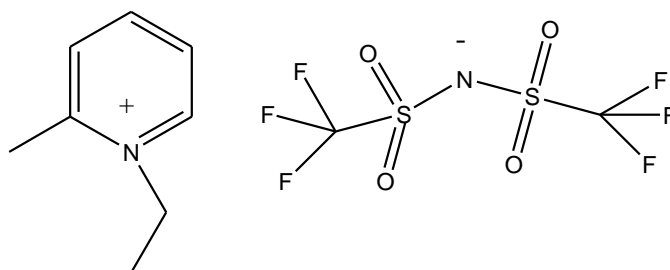
Amide based compounds have a wide range of application in the field of biology, medicine [46], coordination and supramolecular chemistry[47, 48]. Pyridine-amide based ligands form discrete molecular assemblies, which offer a wide range of applications that are often architecture-dependent [49]. Dipicolinamide and isophthalamide group-based chemical scaffolds have promising applications in the field of chemosensing. These chemical scaffolds have been developed as effective and selective chemosensors for the detection of assorted analytes ranging from cations, anions and other species, drugs and biomolecules to explosives[50, 51]. The substituted isophthalamide derivatives find applications in the medical field as they were found to mimic the key interactions in the S2-S3 regions of the enzyme active sites of 3-bound memapsin 2( $\beta$ -Secretase)[52, 53]. Amide based ligands (secondary amide, diamide, malonamide, etc) were also reported for the separation of f block elements[54-56]. In view of that, 5-bromo-N1, N3-bis(4,6-dimethylpyridin-2-yl)isophthalamide moieties, which has not yet been explored for f-block element separation was considered for the present investigation. It was also thought to be interesting that, organic phase containing 5-bromo-N1, N3-bis(4,6-dimethylpyridin-2-yl)isophthalamide as a ligand in ionic liquid to be a better candidate for understanding extraction mechanism, kinetics, speciation, and

thermodynamics. A total evaluation of this solvent system was attempted along with the comparative evaluation with the corresponding molecular diluent based system.

## Experimental

### Materials

5-Bromoisophthalic Acid, 6-Amino-2,4-lutidine, and triethylamine were purchased from TCI Chemicals. Dichloromethane and thionylchloride were purchased from SRL Chemicals. The solvents were freshly distilled before use. Estimation of U and Th was performed by using Energy Dispersive X-ray Fluorescence Spectroscopy. All the reagents used in the present investigation were of analytical grade unless otherwise mentioned. The ionic liquid, 1-Ethyl-2-methyl pyridinium bis(trifluoromethyl sulfonyl imide) and 1-ethyl-2-methyl chloride were procured from TCI Chemical Pvt Ltd., India [The structures were depicted in **Fig. 1**. Suprapure nitric acid, bis(trifluoromethane)sulfonimide lithium salt (LiNTf<sub>2</sub>), NaNO<sub>3</sub>, oxalic acid, N<sub>2</sub>CO<sub>3</sub>, *iso*-decanol and *n*-dodecane were purchased from Sigma Aldrich. Milipore water was used throughout the experiment. U and Th solutions were prepared from high purity U<sub>3</sub>O<sub>8</sub> and ThO<sub>2</sub> powders (more than 99 % purity) obtained by the intra laboratory comparison experiments involving different laboratories of the Department of Atomic Energy, India. Black U<sub>3</sub>O<sub>8</sub> powder was dissolved in conc. HNO<sub>3</sub> followed by evaporated to dryness repeatedly. Finally, the stock solution of UO<sub>2</sub><sup>2+</sup> was made in 1 M HNO<sub>3</sub>. White ThO<sub>2</sub> powder was dissolved in conc. HNO<sub>3</sub> containing a catalytic amount of HF. The repeated evaporation to dryness is essential for fluoride removal. Finally, the Th stock was prepared at 1 M HNO<sub>3</sub>. Catalytic amount of F<sup>-</sup> ion was required to dissolve ThO<sub>2</sub>. However, F<sup>-</sup> formed a strong complex with Th<sup>4+</sup> ions and hence if present would lead to interference in the complexation with the ligand molecules. This would result a considerable reduction in D values for the metal ions.



**Fig.1:** The structure of 1-Ethyl-2-methyl pyridinium bis (trifluoromethyl sulfonyl)imide

## ***Instrumentation***

EDXRF experiments were carried out on a spectrometer procured from Xenometrix (Model: EX3600SDD). NMR spectra were recorded on a Bruker Avance 300MHz spectrometer at 300.13(<sup>1</sup>H). The mass spectrum was collected on LC-MS (Shimadzu) instrument. The IR spectrum was recorded on Shimadzu IRAffinity-1, Fourier Transform Infrared Spectrophotometer. The irradiation was carried out by <sup>60</sup>Co in Food Irradiation Division GB 5000, BARC, India. For extraction experiments, used a thermostat water bath procured from Classic Scientific, Thane, India.

## ***Synthesis and characterization of ligand***

*5-Bromoisophthaloyl dichloride (L1)*: Thionyl chloride (40 mmol, 2.66mL) was added to 4-bromoisophthalic acid (2mmol, 0.490g) and the suspension was refluxed under nitrogen atmosphere for 16 h to give a clear solution. The resulting solution was dried over vacuum to yield a colorless viscous liquid[57].

*5-bromo-N1,N3-bis(4,6-dimethylpyridin-2-yl)isophthalamide(L)*: 5-Bromoisophthaloyldichloride (**L1**, 2.0 mmol) was dissolved in a dry dichloromethane (10mL) and cooled to 0°C. A solution of 6-amino-2,4-lutidine (4.0 mmol, 0.489g) and triethylamine (8.0 mmol, 1.12 mL) in dry DCM (5 mL) was added drop by drop. The resulting mixture was stirred at room temperature under a nitrogen atmosphere for 16 h then the mixture was dried over a vacuum. The residue was dissolved in dichloromethane and washed with aqueous ammonium chloride solution followed by water. The organic phase was dried in anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness yielded **L**. Purification was performed by column chromatography on silica gel with chloroform and methanol (0 to 5%) mixture as eluent and afforded 0.705g (78%) of white solid (**L**), R<sub>f</sub> = 0.42, TLC (eluent: chloroform/methanol 99:1 v/v); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.79 (s, 2H, 2×NH amide), 8.45 (s, 1H, ArH), 8.26 (s, 2H, 2× ArH), 8.01 (s, 2H, 2×Pyr.CH) 7.28 (CDCl<sub>3</sub>), 6.81 (s, 2H, 2×Pyr.CH), 2.43-2.38 (s, s, 12H, 2×2Pyr.CH<sub>3</sub>); FTIR (KBr, cm<sup>-1</sup>): 3338 (s, N-H str. amide), 3072 (C-H str. aromatic), 2918 (s, C-H str. alkane), 1691 (s, C=O str. Amide), 1624 (N-H bending) 1550-1444 (C=C str. aromatic), 1294 (C-N str. aromatic amine), 1230 (C-N str. amine), 893-738 (C-H bending aromatic), 646 (C-Br str.); MS (LC-MS) m/z (% rel.): 453 [M+H<sup>+</sup>] (34.89), 455 (31.95), 475 [M+Na<sup>+</sup>] (48.02), 477 (47.47), 927 [2M+Na<sup>+</sup>] (32.19), 929 (100), 931 (60.22). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>4</sub>O<sub>2</sub>Br: C 58; H 4.6; N 12.36. Found: C 57.6; H 4.6; N 12.12. **Fig. 2** shows the schematic presentation of the synthesis scheme for the ligand. **Fig. 3** shows FTIR and LCMS spectra of the ligand (L), while <sup>1</sup>H- NMR characterization was shown in Supporting Fig. 1.

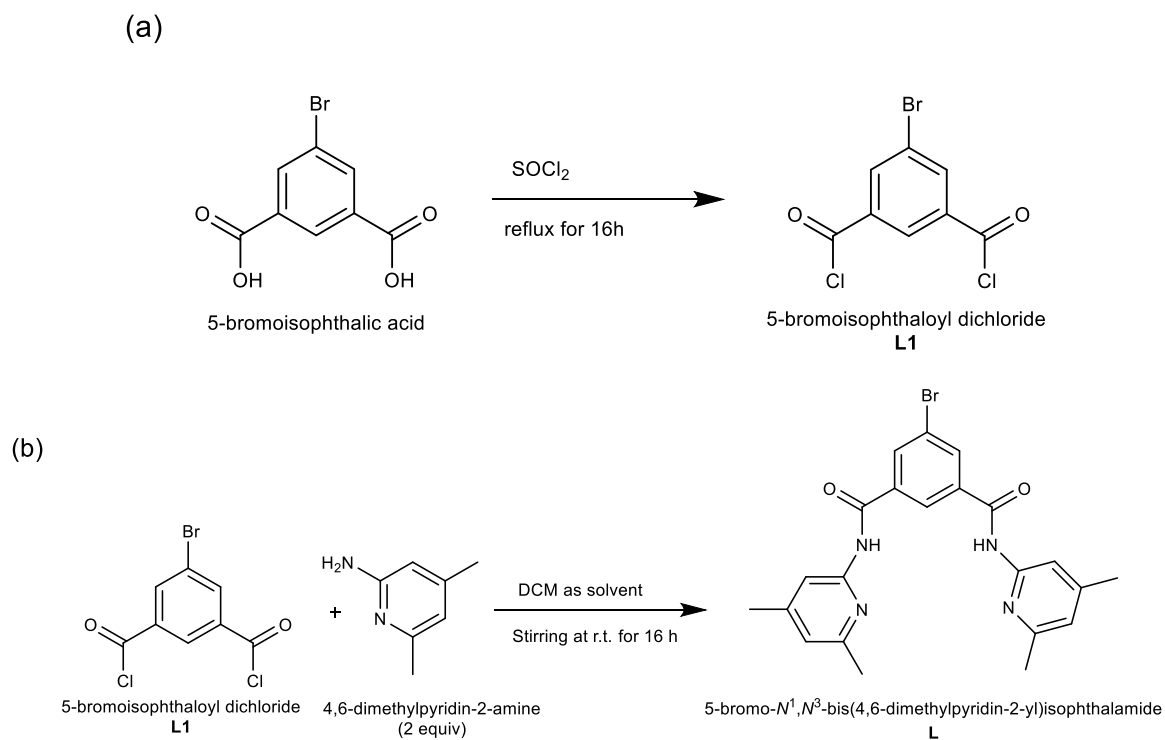
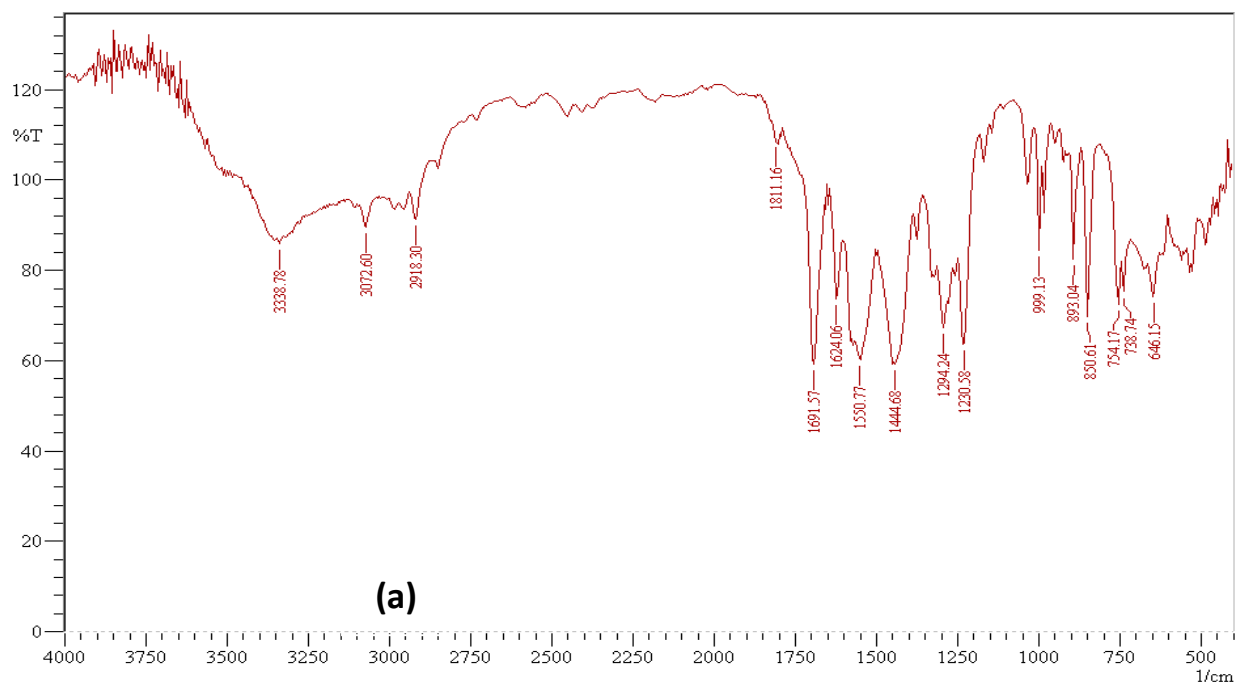
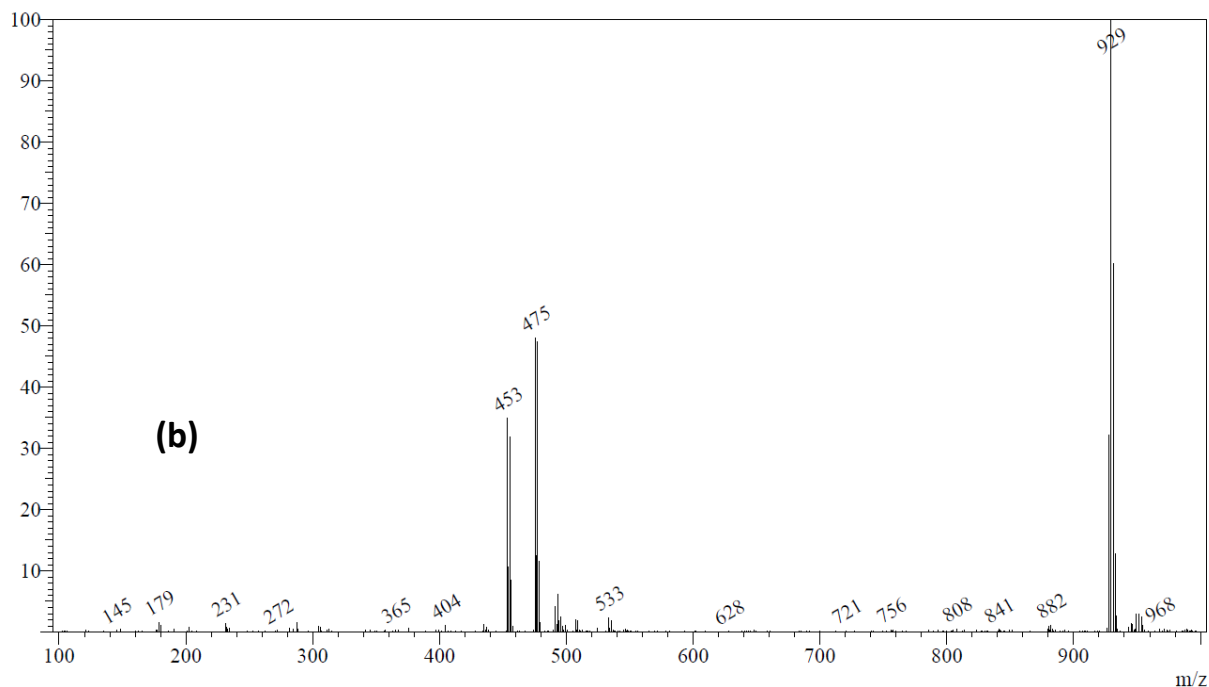


Fig.2: (a) Synthesis of 5-bromoisophthaloyl dichloride(**L1**); (b) Synthesis of 5-bromo-*N*<sup>1</sup>,*N*<sup>3</sup>-bis(4,6-dimethylpyridin-2-yl)isophthalamide (**L**)





**Fig.3:**Spectra for the characterization of ligand(L): (a)FTIR, (b) LCMS

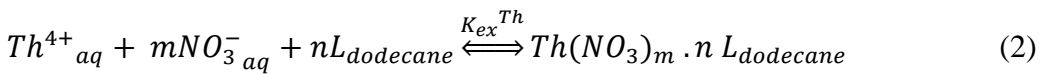
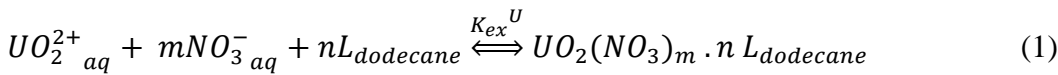
### *Separation studies*

For separation experiments, 1000 mg/L of U and Th solutions were taken as initial concentration. 1 mL of aqueous phase containing metal ion at specified feed acidity ( $\text{HNO}_3$ ) was allowed to equilibrate with 1 mL of organic phase containing ligand either in ionic liquid or in dodecane (with 10% iso-decanol as phase modifier). The equilibration time was used for three hours in most of the cases (except kinetics experiments). After that, the two phase systems were centrifuged for five minutes for complete phase separation. Then suitable aliquots were taken for estimation of U and Th. To establish the extraction profile, the aqueous phase feed acidity was varied from 0.05 M  $\text{HNO}_3$  to 6 M  $\text{HNO}_3$ . For the determination of metal-ligand stoichiometry, the aqueous feed acidity was kept 3 M  $\text{HNO}_3$ , while the ligand concentration in organic phase was varied between 0.25 mM to 2 mM. For nitrate ion variation,  $\text{NaNO}_3$  concentration was varied in the range 1 – 5 M. For variation of cationic or anionic part of ionic liquid in aqueous phase, pyridinium ion concentration in aqueous phase was varied in 0.1 mM to 10 mM in terms of pyridinium bromide, while  $\text{NTf}_2^-$  in aqueous phase was varied from 0.5 mM to 5 mM, from 3 M  $\text{HNO}_3$ . For temperature variation, the temperature was varied in the range 30°C to 60°C. For extraction kinetic experiment, the time of equilibration was found to vary 10 min to 240 min. In the case of stripping experiment, the stripping solutions, i.e. 1 mM oxalic acid, 1 mM  $\text{Na}_2\text{CO}_3$  and 0.05 M  $\text{HNO}_3$  were used to back extract. For radiolytic stability study, the organic phase was allowed to expose in a gamma radiation field of dose 50-500 kGy. The simulated high level waste (SHLW) solutions from the research reactor (RR) and Fast Breeder Reactor (FBR) were prepared using the methods reported earlier[58].

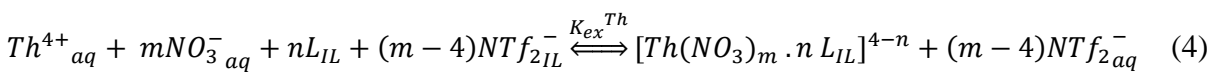
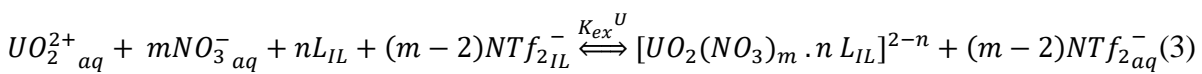
## Results and Discussion

### *Extraction profile with kinetics*

**Fig. 4(a)** shows the variation in distribution ratio value (D) for  $UO_2^{2+}$  and  $Th^{4+}$  as a function of aqueous feed acidity. The D values were found to increase with an increase in aqueous feed acidity up to 3 M  $HNO_3$ , followed by a plateau. This trend in D value profile is very common in any molecular diluent based system with neutral ligand[59] indicating the neutral extracted species predominantly following 'solvation' mechanism. In the case of ionic liquid, depending upon the nature of the ionic liquid, substituent in ionic liquid and the extracting ligand system, ion exchange as well as solvation mechanism were reported to be operative. Most of the reports in ion exchange mechanism demonstrated 'cation exchange' mechanism involving cationic extracted species. However, few reports were also available for 'anion exchange mechanism'[60]. The extraction profile in ionic liquid clearly suggested that either 'solvation' mechanism or 'anion exchange' mechanism might be operating. In case of imidazolium based ionic liquid, if the alkyl group at C3 position is very large, then the solubility of imidazolium cation into aqueous phase decreases and the extraction mechanism predominantly followed 'solvation' mechanism[34]. In the present case, pyridinium based ionic liquid was explored and the present trend was obtained. Therefore, in dodecane, the extraction mechanism can be expressed as follows

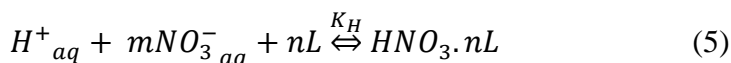


where, 'm' and 'n' are the numbers of nitrate ion and ligand atoms associated with each  $UO_2^{2+}$  and  $Th^{4+}$  during extraction. In dodecane, as the mechanism followed 'solvation' mechanism involving neutral species, then the 'm' values for  $UO_2^{2+}$  and  $Th^{4+}$  must be 2 and 4, respectively. However, further experiments were carried out to prove the participation of the number of nitrate ions. Similarly, in ionic liquid, additionally, anion exchange mechanism can be predominantly operative.  $K_{ex}^U$  and  $K_{ex}^{Th}$  are the conditional extraction constants for U and Th, respectively.



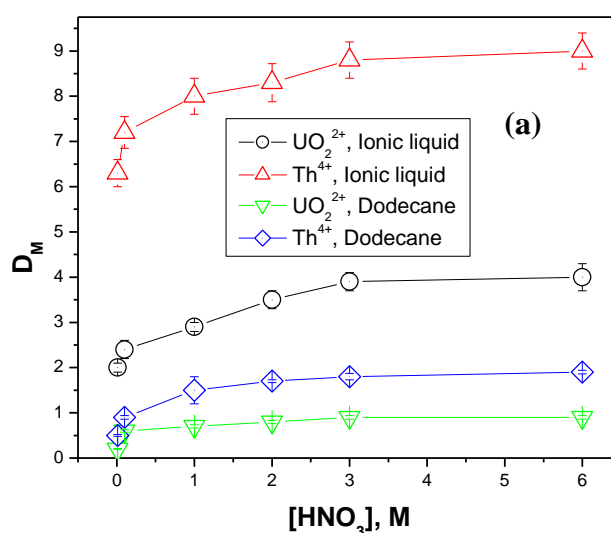


The enhancement in D value as a function of HNO<sub>3</sub> concentration is the effect of mass transfer and participation of nitrate ion in extraction. However, H<sup>+</sup> ion also competes with the metal ion, hence as a consequence, plateau was observed beyond 3 M HNO<sub>3</sub>.



The D values for Th<sup>4+</sup> were found to be more than that of UO<sub>2</sub><sup>2+</sup>, indicating the higher charge/size ratio of Th<sup>4+</sup> leading higher chemical potential and hence higher complexing ability compared to hexavalent uranyl ion[40]. In ionic liquid, the D values for metal ions were significantly higher compared to that in dodecane medium.

The time of equilibration required to achieve maximum D value is very important factor and is associated with extraction kinetics. In the case of molecular diluents based systems, the maximum D values were found to be achieved within 5 to 10 min of equilibration. However, for ionic liquid based systems, almost two hours were required for achieving maximum D values. This implies that the extraction kinetics in ionic liquid is significantly slower compared to that in molecular diluent based systems. The slower kinetics in ionic liquid was attributed to the high viscosity coefficient of the ionic liquid compared to dodecane[61]. It was reported that the mass transfer in ionic liquid became slower for the extraction of Am<sup>3+</sup> using a varieties of diglycolamide functionalized ligands[42, 44, 62]. Sengupta *et al* have also reported a comprehensive analysis on the influence of structural modification of ionic liquid on their viscosity coefficient and hence on the extraction kinetics[61]. **Fig. 4(b)** depicts the variation in D values for UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> as a function of time of equilibration.



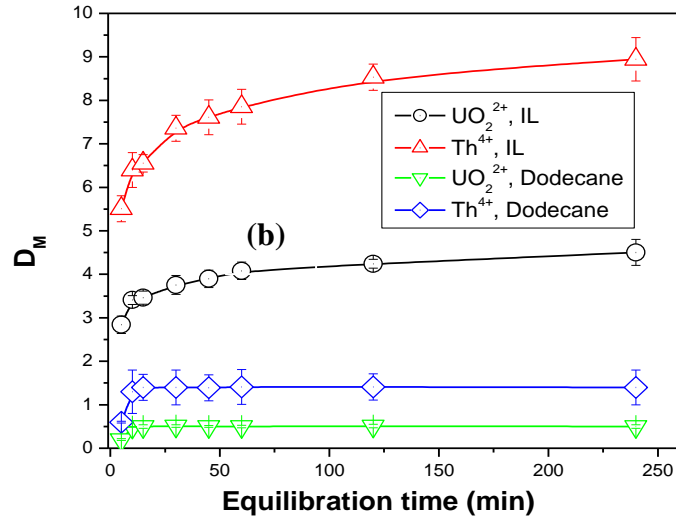


Fig. 4(a): Extraction profile of  $UO_2^{2+}$  and  $Th^{4+}$  using ligand in Ionic liquid, equilibration time: 3 hours,  $T = 300$  K, ligand concentration 1 mM, aq: org 1:1; (b) Extraction kinetics of  $UO_2^{2+}$  and  $Th^{4+}$  using ligand in Ionic liquid, ligand concentration 1 mM, Aqueous feed acidity 3 M  $HNO_3$ ,  $T = 300$  K, aq:org = 1:1

### Metal-ligand stoichiometry

To ascertain the nature of extracted species, the number of ligand molecules associated with each metal ion needs to be determined. The conditional extraction constant and the D values for metal ions can be related to each other as follows

For solvation mechanism

$$K_{ex}^U = \frac{[UO_2(NO_3)_m \cdot n L_{dodecane}]}{[UO_2^{2+}]_{aq} [NO_3^-]_{aq}^m [L_{dodecane}]^n} \quad (6)$$

$$K_{ex}^{Th} = \frac{[Th(NO_3)_m \cdot n L_{dodecane}]}{[Th^{4+}]_{aq} [NO_3^-]_{aq}^m [L_{dodecane}]^n} \quad (7)$$

$$\text{Log} D_U = \text{Log} K_{ex}^U + m \text{Log} [NO_3^-]_{aq} + n \text{Log} [L_{dodecane}] \quad (8)$$

$$\text{Log} D_{Th} = \text{Log} K_{ex}^{Th} + m \text{Log} [NO_3^-]_{aq} + n \text{Log} [L_{dodecane}] \quad (9)$$

For anion exchange mechanism

$$K_{ex}^U = \frac{[UO_2(NO_3)_m \cdot n L_{IL}]^{2-n} [NTf_2^-]_{aq}^{2-m}}{[UO_2^{2+}]_{aq} [NTf_2^-]_{IL}^{2-m} [NO_3^-]_{aq}^m [L_{IL}]^n} \quad (10)$$

$$K_{ex}^{Th} = \frac{[Th(NO_3)_m \cdot n L_{IL}]^{4-n} [NTf_2^-]_{aq}^{4-m}}{[Th^{4+}]_{aq} [NTf_2^-]_{IL}^{4-m} [NO_3^-]_{aq}^m [L_{IL}]^n} \quad (11)$$

$$\text{Log}D_U = \text{Log}K_{ex}^U + m \text{Log} [NO_3^-] + n [L_{dodecane}] + (2 - m) \log \frac{[NTf_2^-]_{aq}}{[NTf_2^-]_{IL}} \quad (12)$$

$$\text{Log}D_{Th} = \text{Log}K_{ex}^{Th} + m \text{Log} [NO_3^-] + n [L_{dodecane}] + (4 - m) \log \frac{[NTf_2^-]_{aq}}{[NTf_2^-]_{IL}} \quad (13)$$

This implies that the plot of LogD values as a function of Log[ligand] should follow a straight line with a slope 'n', which would indicate the number of ligand molecules associated with metal ion during complexation, i.e. metal-ligand stoichiometry (keeping all other experimental parameters constant). **Fig. 5** shows the variation of D as a function of ligand concentration. The D values were found to increase with an increase in ligand concentration, which primarily indicates that the ligand molecules directly influence the complexation. However, the slope values were found to vary from system to system. In ionic liquid, The straight lines for Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> were found to be parallel with slope ~ 1.01. This implied the formation of 1:1 metal-ligand complex. In dodecane, the slope for UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> was found to be ~ 1.98 and 2.97 respectively. These implied the formation of 1:2 and 1:3 metal-ligand complex, respectively. The extracted species in molecule diluents were found to be more organophilic compared to that in ionic liquids.

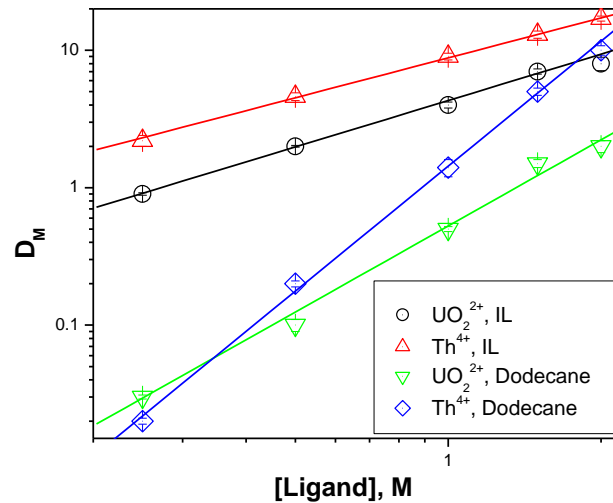


Fig. 5: Variation in distribution ratio values for UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> as a function of ligand concentration in Ionic liquid, Aqueous phase acidity 3 M HNO<sub>3</sub>, Time of equilibration 3 h, T = 300 K, aq:org = 1:1

### Participation of nitrate ion

To ascertain the nature of the species (whether cationic, anionic or neutral) participation of nitrate ions needs to be investigated. **Fig. 6** shows, how the D value varies as a function of nitrate ion concentration in the aqueous phase. By similar mathematical treatment (equation 8 and 9 for solvation mechanism and equation 12 and 13 for anion exchange mechanism), we can get a linear

relationship between  $\text{Log}D$  vs  $\text{Log}[\text{NO}_3^-]_{\text{aq}}$ . Now, for a particular ligand concentration, equilibration time and 300 K temperature, the  $\text{Log}D$  value vs  $\text{Log}[\text{NO}_3^-]_{\text{aq}}$  would be a straight line with a slope indicating the number of nitrate ion associated in extracted species. The enhancement in  $D$  value with nitrate ion concentration revealed that the nitrate ion was directly participating in complexation. The slopes of the straight lines pertaining to  $\text{UO}_2^{2+}$  in dodecane and ionic liquid were found to be 1.95 and 2.11, respectively. For  $\text{Th}^{4+}$ , the slope values for ionic liquid and dodecane were 3.91, and 3.99, respectively. This implied that four nitrate ions are participating during the extraction. It is clear that, for  $\text{UO}_2^{2+}$  the extracted species are  $\text{UO}_2(\text{NO}_3)_2, \text{L}$  and  $\text{UO}_2(\text{NO}_3)_2, 2\text{L}$  for ionic liquid and dodecane respectively, while the same for  $\text{Th}^{4+}$  are  $\text{Th}(\text{NO}_3)_4, \text{L}$  and  $\text{Th}(\text{NO}_3)_4, 3\text{L}$  respectively. This implied that a neutral extracted species were involved for extraction predominantly following 'solvation' mechanism. However, the investigations on the participation of cationic and anionic moieties of ionic liquids need to be carried out for conclusive remarks in this regard.

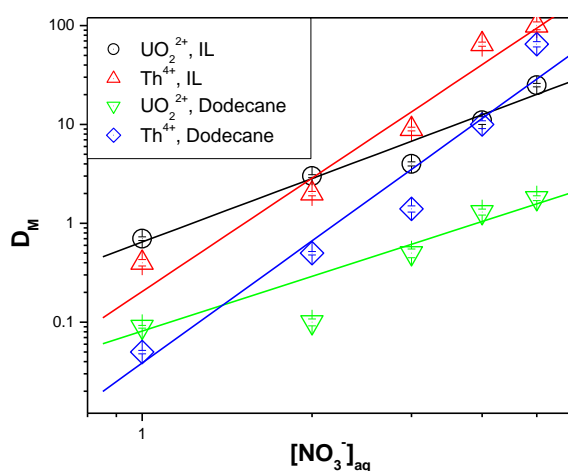


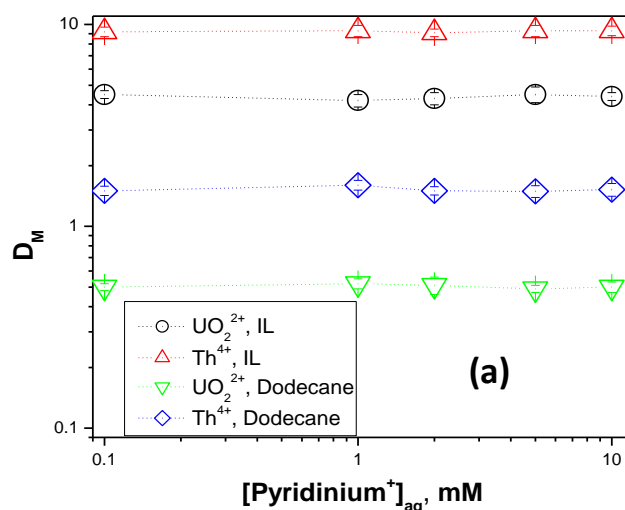
Fig. 6: Variation in distribution ratio values of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  as a function of nitrate ion concentration in aqueous phase using ligand in ionic liquid,  $T = 300 \text{ K}$ , equilibration time 3 h; aq: or = 1:1

Table 1: Speciation and mechanism for

System	$\text{UO}_2^{2+}$		$\text{Th}^{4+}$	
	IL	Molecular Diluent	IL	Molecular Diluent
Species	$\text{UO}_2(\text{NO}_3)_2, \text{L}$	$\text{UO}_2(\text{NO}_3)_2, 2\text{L}$	$\text{Th}(\text{NO}_3)_4, \text{L}$	$\text{Th}(\text{NO}_3)_4, 3\text{L}$
Mechanism	Solvation	Solvation	Solvation	Solvation
Equilibration time	2 h	10 min	2 h	10 min
$D$ (1 M $\text{HNO}_3$ )	4.5	0.5	9.2	1.6

### *Participation of cationic and anionic moieties of ionic liquid*

For further confirmation of the extraction mechanism and nature of the species, water soluble salts containing either same cation or anion of ionic liquid have been used in different concentrations and the effects on D values were monitored. In view of these, pyridinium bromide and LiNTf<sub>2</sub> water soluble salts were used. In the case of cation exchange mechanism, the pyridinium ion from ionic liquid phase should come to aqueous phase, while there would be transfer of cationic metal-ligand species to ionic liquid phase and hence, charge neutrality should be maintained. In presence of pyridinium ion in aqueous phase such exchange would be hampered and hence D value would reduce. A similar argument also holds for the NTf<sub>2</sub><sup>-</sup> anion. **Fig. 7** shows the variation in D values as a function of pyridinium ion and NTf<sub>2</sub><sup>-</sup> ion concentration. The results revealed that there was no significant change in D values with a change in pyridinium as well as NTf<sub>2</sub><sup>-</sup> ion concentration in the aqueous phase. This also confirmed that the extraction proceeded via 'solvation' mechanism involving neutral metal-ligand complex species.



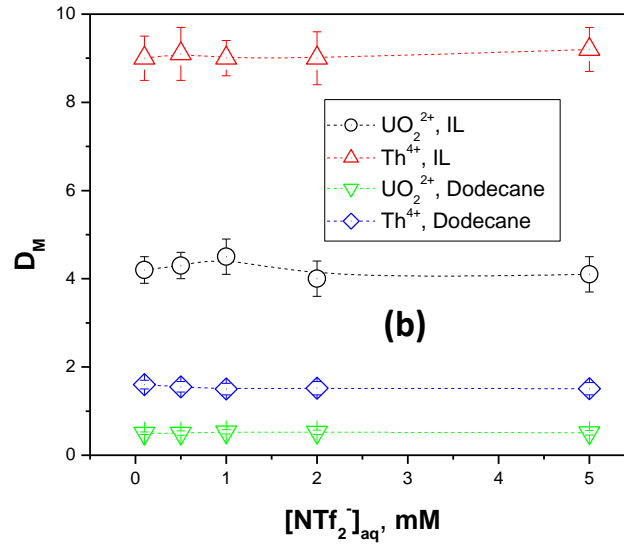


Fig. 7: Variation in distribution ratio values of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  as a function of (a) pyridinium cation concentration; (b)  $\text{NTf}_2^-$  ion concentration in aqueous phase using ligand in ionic liquid, aqueous phase acidity 3 M  $\text{HNO}_3$ ,  $T = 300$  K, time of equilibration 3 h, ligand conc. 1 mM, aq: or = 1:1

### Extraction thermodynamics

The change in energetics during extraction is one of the important aspects to be looked into for understanding the extraction process. The change in enthalpy ( $\Delta H$ ) is quantitatively linked with the conditional extraction constant ( $K'_{ex}$ ) and temperature ( $T$ ) in the following relation[60]

$$\Delta H = -2.303 R \frac{\Delta \log K'_{ex}}{\Delta \frac{1}{T}} + Constant \quad (14)$$

where,  $R$  represents the universal gas constant, and after suitable mathematical rearrangement the above expression can be written in the following form[60]

$$\Delta \log K'_{ex} = -\frac{\Delta H}{2.303R} \Delta \frac{1}{T} + Constant \quad (15)$$

Equation (15) implied that, the  $\log K'_{ex}$  vs  $\frac{1}{T}$  should possess a linear relationship [Fig. 8] with a slope value for the determination of  $\Delta H$ . The  $D$  value was found to increase with the increase in temperature, suggesting heat removal during extraction. Therefore, the process was endothermic in nature ( $\Delta H_U = 0.93 \text{ kJ mol}^{-1}$ , and  $\Delta H_{Th} = 1.11 \text{ kJ mole}^{-1}$ ). The change in Gibbs's energy ( $\Delta G$ ) for the extraction was calculated from the conditional extraction constants as follows[60]

$$\Delta G = -2.303RT \log K_{ex} \quad (16)$$

The calculated  $\Delta G$  values for  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  extraction into ionic liquid phase were  $\Delta G_U = -6.6 \text{ kJ mol}^{-1}$  and  $\Delta G_{Th} = -7.1 \text{ kJ mol}^{-1}$ , respectively. The (-) ve sign revealed that, the extraction process was spontaneous in nature, i.e. energetically favorable. At 300 K, the change in entropy was also calculated using the following equation[60]

$$\Delta G = \Delta H - T\Delta S \quad (17)$$

The  $\Delta S$  values for the ionic liquid based systems were found to be (+) ve ( $25.1 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $27.4 \text{ J K}^{-1} \text{ mol}^{-1}$  for U and Th, respectively), indicating the enhancement in entropy during extraction. The enhancement in entropy is responsible for the spontaneity of the extraction. In view of this, the extraction process can be called as an entropically driven process. This exercise was only carried out for ionic liquid system (in molecular dodecane based system 5 % iso-decanol was used as phase modifier hence high temperature experiments were not carried out).

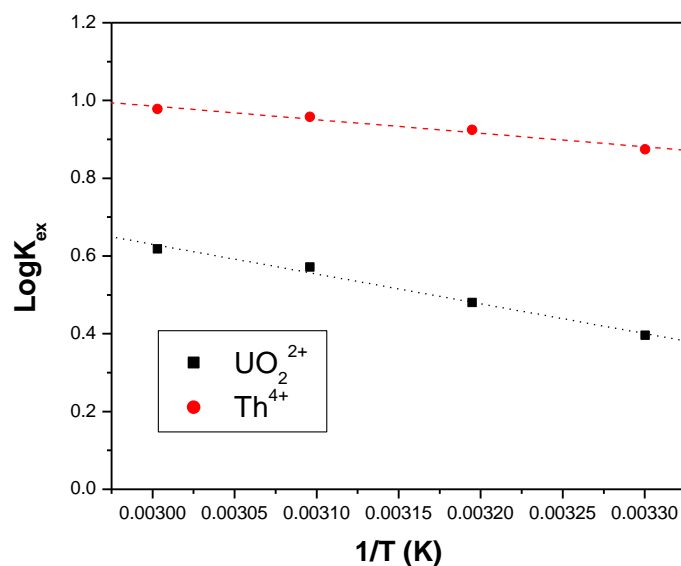


Fig. 8: Variation in conditional extraction constants of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  as a function of temperature using ligand in Ionic liquid; aqueous phase acidity 3 M  $\text{HNO}_3$ , ligand conc. 1 mM, equilibration time 3 h, aq:or 1:1

### ***Radiolytic stability***

The radiolytic stability plays a significant role to evaluate the long-term usage of the solvent systems. The radio-toxic isotopes processed using these solvent systems would continuously emit high energy particles like alpha, beta, neutron, positron etc, alongwith the high energy electromagnetic radiation

as gamma depending upon the nature of isotopes. Therefore, high energy quanta would be deposited into the solvent systems. This large energy would lead to the breaking of the weaker bonds in the systems. If the functionalities responsible for complexation with metal ion got distorted, then their extraction efficiency, as well as selectivity would also be hampered. In view of that, the organic solvent systems were allowed to expose to gamma irradiation for a definite dose. Using these irradiated solvent systems, the D values for metal ions were calculated. The deviation in D values (from unirradiated solvent systems) would suggest, how radiolytically susceptible the solvent systems are. Lesser the deviation in D values, more radioresistant the solvent systems are. **Fig. 9** shows the variation of D values for metal ions as a function of gamma dose up to 500 kGy. For ionic liquid based systems, only marginal change in D values were observed, while a significant reduction in D values were noticed for dodecane based systems. The ionic liquid based systems were also reported to be more radio-resistant compared to their molecular diluent based systems[63]. The formation of resonance stabilized organic aromatic carbocation was reported to be one of the main causes for the high degree of radiation stability of ionic liquid based systems. Moreover, the high viscosity of the ionic liquids can make the diffusion of organic radical much slower and hence lead to a reduction in the devastating effects of gamma irradiation. It was also reported that ionic liquid acted as a sink to protect the ligand functionalities[64, 65]. Our present result also corroborates the idea reported in the literature.

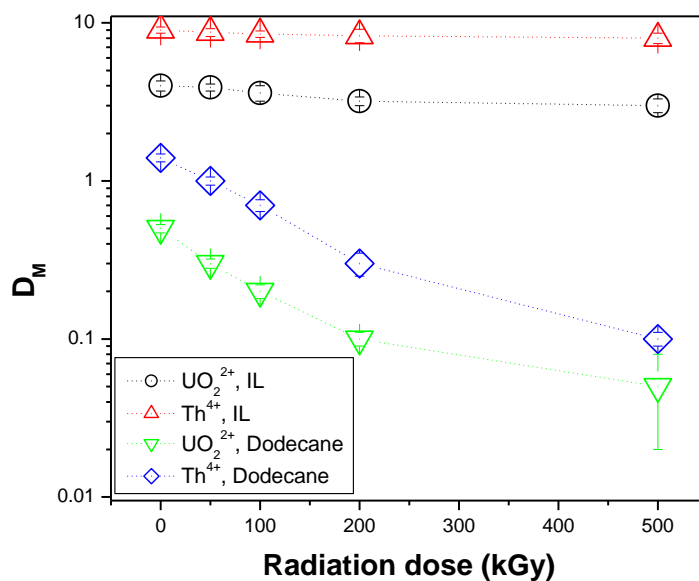


Fig. 9: The variation in D values as a function of gamma dose by which the solvent systems were irradiated, aqueous phase acidity 3 M HNO<sub>3</sub>, ligand concentration 1 mM, equilibration time 3 h, T = 300 K, aq:or = 1:1



## Stripping

The metal ion extracted to the organic phase needs to be stripped effectively to evaluate the reusability of the solvent systems. 0.05 M HNO<sub>3</sub>, 1 mM oxalic acid and 1 mM Na<sub>2</sub>CO<sub>3</sub> aqueous solution were used as stripping solutions in the present investigation. Dilute HNO<sub>3</sub> was found to be ineffective for stripping especially from the ionic liquid phase. 1 mM Na<sub>2</sub>CO<sub>3</sub> aqueous solution was found to be highly effective in stripping of UO<sub>2</sub><sup>2+</sup> from its complex form the ionic liquid as well as dodecane phase, whereas for Th<sup>4+</sup>, 1 mM oxalic acid solution served the purpose. The overall stripping ability from ionic liquid was found to be poorer in ionic liquid phase compared to that in aqueous phase, suggesting the stronger complexation in ionic liquid phase. **Fig. 10** shows the % stripping of metal ions from the ionic liquid as well as the molecular diluent phase using different stripping solutions.

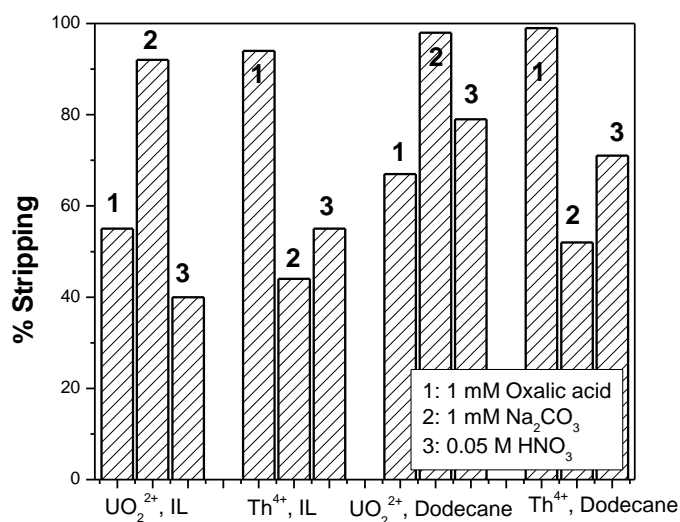


Fig. 10: The % stripping of UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> from ionic liquid and dodecane phase using dilute HNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> aqueous solution, oxalic acid aqueous solution

## Processing SHLW

**Table 1** is summarizing the analytical results obtained after processing the simulated high level waste solutions of research reactor (RR) and Fast Breeder Reactor (FBR) origin. Both ionic liquid based system, as well as dodecane based system was used for this purpose. It was found that all the rare earth elements (La, Ce, Pr, Sm, Zr, Gd, Dy, and Eu) were coextracted to a greater extent with these solvent systems. However, Fe, Cr, Ni, Sr, Ba, Nd, Mo, Ru got partially extracted. Na, Ca and

Cd were extracted to very negligible amount. The ionic liquid based system showed marginally more selectivity towards U and Th over other analytes compared to dodecane based systems.

Table 1: Analytical results obtained after processing of SHLW from RR and FBR origin

Elements	FBR						RR					
	Ionic Liquid		D	Dodecane		D	Ionic Liquid		D	Dodecane		D
	Initial (mgL <sup>-1</sup> )	Final (mgL <sup>-1</sup> )		Initial (mgL <sup>-1</sup> )	Final (mgL <sup>-1</sup> )		Initial (mgL <sup>-1</sup> )	Final (mgL <sup>-1</sup> )		Initial (mgL <sup>-1</sup> )	Final (mgL <sup>-1</sup> )	
Al	-	-	-				250	240	0.04	250	200	0.25
Ag	5	4.7	0.06	5	4.2	0.19	-	-		-		
Ba	70	68.2	0.03	70	53	0.32	100	7.26	13	100	11.5	8
Ca	-	-	-	-	-	-	400	394	0.01	400	395	0.01
Cd	5	4.8	0.04	5	4.4	0.13	300	280	0.07	300	280	0.07
Cr	-	-	-	-	-	-	400	140	2	400	122	2
Fe	-	-	-	-	-	-	1500	1000	0.5	1500	750	1
Mg	-	-	-	-	-	-	300	270	0.1	300	285	0.05
Mn	-	-	-	-	-	-	500	194	2	500	250	1
Na	-	-	-	-	-	-	500	497	0.01	500	500	-
Ni	-	-	-	-	-	-	300	101	2	300	250	0.2
Sr	30	29	0.03	30	25	0.2	50	6.94	6	50	14.1	2
Ce	200	7.1	27	200	63	2	100	2.2	44	100	5.3	18
La	75	1.1	67	75	8.1	8	100	1.1	90	100	4.5	21
Pr	50	1.5	32	50	6.3	7	-	-		-	-	-
Nd	30	1.7	16	30	5.1	5	-	-		-	-	
Sm	50	0.9	54	50	6.6	6	-	-		-	-	-
Zr	15	0.5	29	15	3.2	4	-	-		-	-	-
Ru	10	7.1	0.41	10	9.8	0.02	7.5	6.5	0.15	7.5	6.9	0.09
Mo	1.5	0.5	2	1.5	1	0.5	30	22	0.36	30	21	0.42
Pd	5	4.9	0.02	5	4.7	0.06	-	-		-	-	-
Gd	5	0.11	44	5	1.5	2	-	-		-	-	-
Dy	5	0.11	44	5	1.7	2	-	-		-	-	-
Eu	5	0.11	44	5	0.97	4	-	-		-	-	-

## Conclusions

5-bromo-N1, N3-bis(4,6-dimethylpyridin-2-yl)isophthalamide ligand was synthesized and characterized by <sup>1</sup>H-NMR, FTIR and LC-MS spectroscopic data. In combination with pyridinium based ionic liquid, the systems showed highly efficient extraction of tetra and hexavalent actinides. The mechanism of extraction predominantly followed ‘solvation’ mechanism involving neutral extracted species  $\text{UO}_2(\text{NO}_3)_2, \text{L}$  and  $\text{Th}(\text{NO}_3)_4, \text{L}$  respectively. Similarly, neutral extracted species with a predominance of ‘solvation’ mechanism was also reported in molecular diluents based systems. However, the speciation was found to be quite different [ $\text{UO}_2(\text{NO}_3)_2, 2\text{L}$  and  $\text{Th}(\text{NO}_3)_4, 3\text{L}$ ] than that of ionic liquid phase. The ionic liquid based extraction processes were evaluated to be spontaneous, and endothermic in nature. The overall entropy was found to enhance during extraction. Only marginal reduction in extraction efficiency was observed for upto 500 kGy gamma irradiated ionic liquid based solvent systems, while a significant loss in extraction efficiency was demonstrated for dodecane based systems. The viscosity driven slower extraction kinetics was observed in ionic liquid compared to molecular diluents based systems. Aqueous phase complexing agents were found to be suitable for the effective stripping of metal ions from ionic liquid phase. The selectivity of these solvent systems was investigated by processing simulated high level waste solutions from RR and FBR origins.

## Acknowledgement

The authors wish to acknowledge Dr. P.K.Pujari, Director, RC & I Group and Head, Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai, India. Dr. VelavanKathirvelu acknowledges the financial support by the Science and Engineering Research Board(SB/FT/CS-119/2014)

## Conflict of Interest

There is no conflict of interest to disclose

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