

Tuning the extraction mechanism of uranyl ion in Bicyclooctanium, Propylpyridinium, Piperidinium and Imidazolium based ionic liquids: First ever evidence of 'Cation exchange', 'Anion exchange' and 'Solvation' mechanism

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Abstract

A novel diamide ligand, 5-bromo-N1, N3-diisopropylisophthalamide has been synthesized and characterized by ¹H NMR, ¹³C NMR, and FTIR. The extraction mechanism of uranyl ion with the diamide ligand has been studied in unexplored ionic liquid families. For the same metal-ligand system; cation exchange, anion exchange, and solvation mechanism can be predominately achieved by changing the ionic liquid system. The experimental results suggest that the change in extraction mechanism is induced by the cations of the ionic liquids. In bicyclooctanium ionic liquid, the extracted species was [UO₂(NO₃)₃L₂]⁻; In piperidinium and pyridinium-based ionic liquid, the species were UO₂(NO₃)₂L and UO₂(NO₃)₂L₂ respectively. In imidazolium-based ionic liquid, the species was [UO₂(NO₃)L]⁺. Though the extraction efficiency in methylpyridinium and bicyclooctanium based ionic liquids are better, the piperidinium and imidazolium-based ionic liquids exhibited a high degree of radiological stability. The aqueous solution of sodium carbonate is found to be better in the back extraction of uranyl ions from the ionic liquids relative to EDTA and oxalic acid. However, the efficacy of back extraction differs largely on the ionic liquid system.

Keywords: Cation exchange; Anion exchange; Solvation; Speciation; Ionic liquid

Introduction

Though ionic liquid based research evolved mainly as a potential 'green' alternatives to the volatile organic diluents due to some of the advantageous properties like lower vapor pressure, high flash point, high degree of chemical, thermal and electrochemical stability; the high 'anti microbial' characteristic of some of the ionic liquids put doubts on the 'greenness'[1-6]. Some classes of ionic liquids are neither biodegradable nor completely incinerable. However, the most interesting property of ionic liquid is its tunability due to which it is widely accepted as a 'designer solvent'. It has been reported that for N3 alkyl-substituted methylimidazolium cation, the extraction mechanism depends on the length of the alkyl group. If the butyl group at the N3 position is replaced with an octyl or decyl, the extraction mechanism changes from cation exchange to solvation[7-9]. This was attributed to the ease of solubilizing ability of N3 alkyl-substituted methyl imidazolium cation in water, which reduces as the alkyl chain length increases. This also indicates that the species involved can also be modified from cationic to neutral. It was also reported in the literature that the extraction kinetics are highly dependent on the length of the alkyl groups of N3 alkyl-substituted methylimidazolium ion and even the nature of the anionic moieties of the ionic liquid[10-14]. The longer the alkyl chain length, viscous the ionic liquids are, and hence slower is the mass transfer. The ionic liquid with PF_6^- anion is more viscous compared to NTf_2^- anion and hence resulting in slower extraction kinetics. The more branched ionic liquids are more prone to radiation-induced fragmentation[15, 16]. Hence depending upon the requirement, the extraction process can be modified by modification in ionic liquids[17]. The extraction efficiency also depends on the nature of alkyl substitution in the imidazolium cations of ionic liquid. There are several attempts to design the functionalized ionic liquid for task-specific applications, where functionalities are covalently attached to the ionic liquid moieties. Carbonyl methyl phosphine oxide (CMPO), diglycolamide (DGA), trialkyl phosphine (TRPO) functionalized ionic liquids have been extensively used for the extraction of actinides[18, 19]. The extraction behavior of neodymium and other rare earth were investigated by trioctylmethylammonium dioctyl diglycolamate functionalized ionic liquid[20]. Many amino-functionalized ionic liquids have been exploited for CO₂ capture[21]. The homogeneous liquid-liquid extraction of metals by functionalized ionic liquid is another new approach reported in the literature[22].

Application of ionic liquid not only improves the efficiency/ selectivity of metal extraction; but also the speciation may differ [23, 24]. Vast research on the application of ionic liquids in the separation of metal ions, mainly f block elements is centered at imidazolium-based ionic liquids only. Recently, it has been demonstrated for the first time that a sulphoxide ligand in bicyclooctanium ionic liquid can be used for separation of f-block elements [25]. However, different families of ionic liquids

(pyridinium, piperidinium, phosphonium, octanium, etc.) are still unexplored and they may show some unique features. One such example is the extraction of Sr^{2+} by Calix crown ether using pyridinium-based ionic liquid. The extraction of Sr^{2+} predominantly follows the least common 'anion exchange' mechanism through a monoanionic complex [26]. In view of that, pyridinium, piperidinium, and bicyclooctanium families of ionic liquids are considered in the present case and are compared with the most commonly used methylimidazolium-based ionic liquid.

The success of nuclear establishment highly depends on the safe management of radiotoxic material; efficient and selective separation scheme for actinides, lanthanides, and other fission products[27-29]. The tri-n-butyl phosphate is the conventional workhorse for efficient separation schemes in PUREX and THOREX processes in nuclear establishment[30, 31]. Phosphine oxides, phosphonates, Cyanex 923, phosphinic acids, carbamoyl methyl phosphine oxide are some of the ligands explored for uranyl extraction[18, 32-35]. However, phosphate-based ligands are not completely incinerable, hence there is always a quest for new nitrogen-based ligand functionalities for the separation of uranyl ions. Secondary amides like di-n-hexyl octanamide (DHOA), diamide, glycolamides are some of the functionalities explored for efficient uranyl extraction[36-40].

In the present case, diisopropylisophthalamide in pyredinium, piperidinium, imidazolium, and bicyclooctanium based ionic liquids have been used for the extraction of UO_2^{2+} from the aqueous nitric acid feed. The investigation deals with the understanding of the extraction mechanism, species involved, etc. The radiation and chemical stability of organic phases, stripping of metal ions from organic phases have also been investigated.

Experimental

Materials and Methods

5-Bromoisophthalic acid, isopropylamine, triethylamine and the ionic liquids (Fig.1); 1-Hexyl-1,4-diaza[2,2,2]bicyclooctaniumbis(trifluoromethylsulfonyl)imide (IL1), 1-Propylpyridinium bis(trifluoromethylsulfonyl)imide (IL2), 1-Butyl-1methylpiperidinium bis(trifluoromethylsulfonyl)imide (IL3), 1-Hexyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (IL4) were procured from TCI Chemical Pvt Ltd., India. Dichloromethane and thionyl chloride were purchased from SRL Chemicals. The solvents used for the synthesis of ligand were freshly distilled before use. Nitric acid (Suprapure grade) was purchased from Sigma Aldrich. The reagents like NaNO_3 , N_2CO_3 , n-dodecane, and oxalic acid, were of analytical grade purchased from Sigma Aldrich. Deionized water was used throughout the experiment. The U

stock solutions were prepared from U_3O_8 powder by dissolving in Conc. HNO_3 followed by repeated evaporation. The stock solutions were made in 1 M HNO_3 .

NMR spectra were recorded on a Bruker Avance 400MHz spectrometer at 400 MHz (1H) and 100 MHz (^{13}C) with $SiMe_4$ as internal references. The IR spectrum was recorded on IR Affinity-1, Fourier Transform Infrared Spectrophotometer (Shimadzu). CHNS analysis of the ligand was carried out in Elementar vario MICRO cube CHNS Analyzer. The powder sample (3mg) wrapped in a small tin foil was directly dropped into the combustion tube where it was fully combusted in the presence of oxygen. The MICRO cube analyzed the CHN content (weight %) of the ligand in one single run. Energy Dispersive X-ray Fluorescence (EDXRF) Spectroscopy (Make: Xenometrix, Model: EX3600SDD) was used for the estimation of U[41-43].

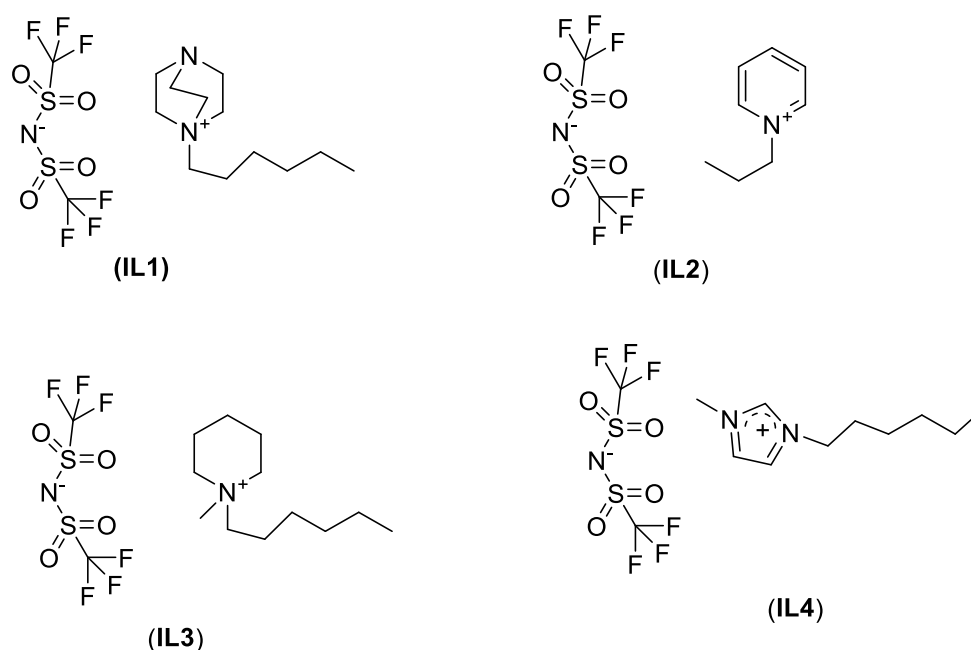


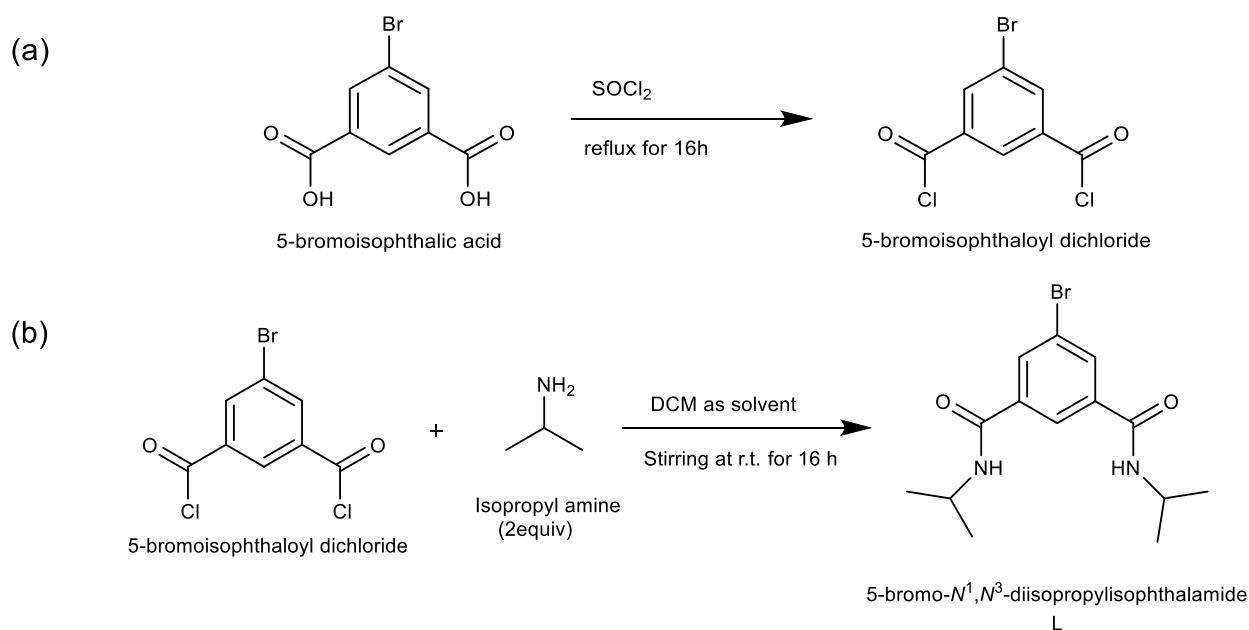
Fig. 1: The structures of the ionic liquids used in the present investigation

Synthesis and Characterization of Ligands

5-bromo-N1, N3-diisopropylisophthalamide (L): Thionyl chloride (40 mmol, 2.90 mL) and 5-bromoisophthalic acid (2 mmol, 0.490 g) were taken in a round bottom flask and refluxed under nitrogen atmosphere for 16 hr. A clear transparent solution was formed. Excess thionyl chloride was removed in a vacuum to give a colorless viscous liquid, 5-bromoisophthaloyl dichloride[9, 38]. The acid chloride was then dissolved in dry dichloromethane (10 mL) and cooled to 0° C. A solution of isopropylamine (8.0 mmol, 0.655 mL) and triethylamine (4.0 mmol, 0.56 mL) in dry dichloromethane (5 mL) was added in the acid chloride solution drop by drop. The resulting mixture was kept stirring

at room temperature under a nitrogen atmosphere for 16 hr [44]. The reaction mixture was then dried over a vacuum. The residue was dissolved in dichloromethane and washed with aqueous ammonium chloride solution followed by water. The organic layer was dried with anhydrous Na_2SO_4 and concentrated to dryness yielded ligand (L). Purification by silica gel column chromatography with petroleum ether and ethyl acetate (0 to 30%) mixture as eluent afforded 0.536 g (82%) of white solid (L), $R_f = 0.28$, TLC (eluent: petroleum ether/ethyl acetate 30:70 v/v). The ^1H NMR, ^{13}C NMR, and IR spectrum of the ligand are shown in Fig.2 - 4 respectively.

Analytical and spectroscopic data: CHNS analysis: Anal. Calcd: C 51.39; H 5.85; N 8.56. Found: C 51.62; H 5.85; N 8.50; FTIR (KBr, cm^{-1}): 3251 (s, N–H str. amide), 3078 (C–H str. aromatic), 2973 - 2874 (s, C–H str. alkyl), 1632 (s, C=O str. amide), 1551 (s, N–H bend amide) 1591 - 1462 (C=C str. aromatic), 894 - 714 (C–H bend aromatic); ^1H NMR (400 MHz, CDCl_3 , δ): 8.027 (s, 1H, ArH), 7.964 (s, 2H, 2 ArH), 7.26 (residual solvent peak), 6.206-6.190 (d, 2H, 2×NH amide), 4.300-4.249 (m, 2H, 2×CH isopropyl), 1.285-1.269 (d, 12H, 4× CH_3 isopropyl). ^{13}C NMR (100 MHz, CDCl_3 , δ): 164.52, 136.96, 132.63, 123.84, 122.97, 42.40, 22.73.



Scheme 1: (a) Synthesis of 5-bromoisophthaloyl dichloride; (b) Synthesis of 5-bromo- N^1,N^3 -diisopropylisophthalamide (L)

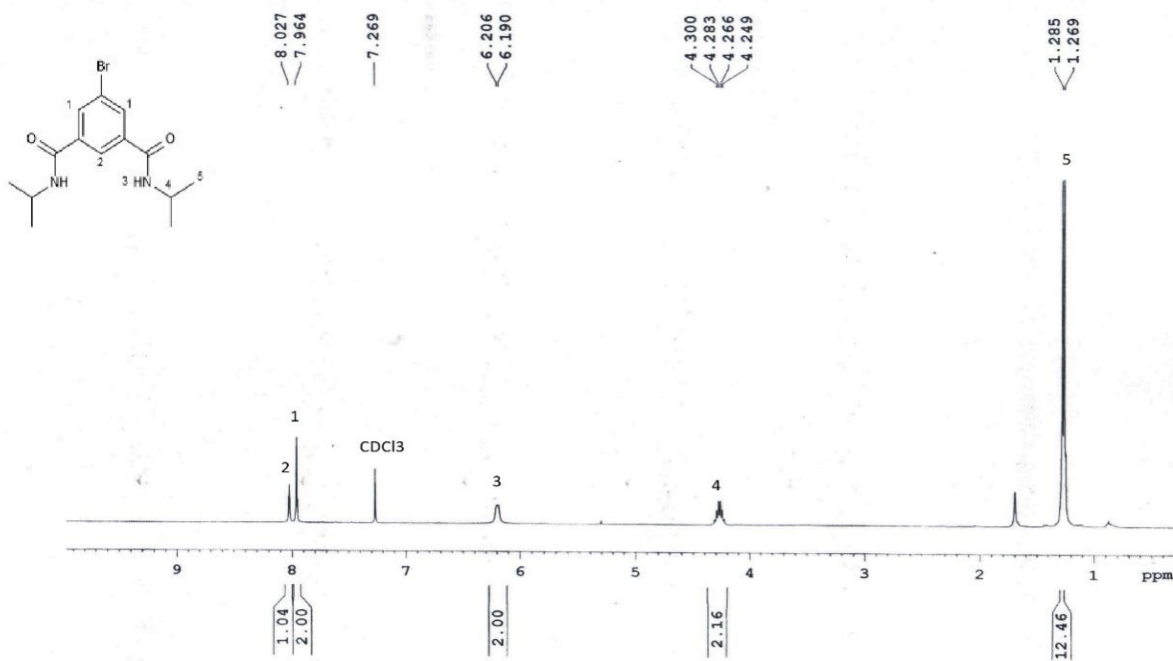


Fig.2: ^1H NMR Spectra of 5-bromo-N1, N3-diisopropylisophthalamide

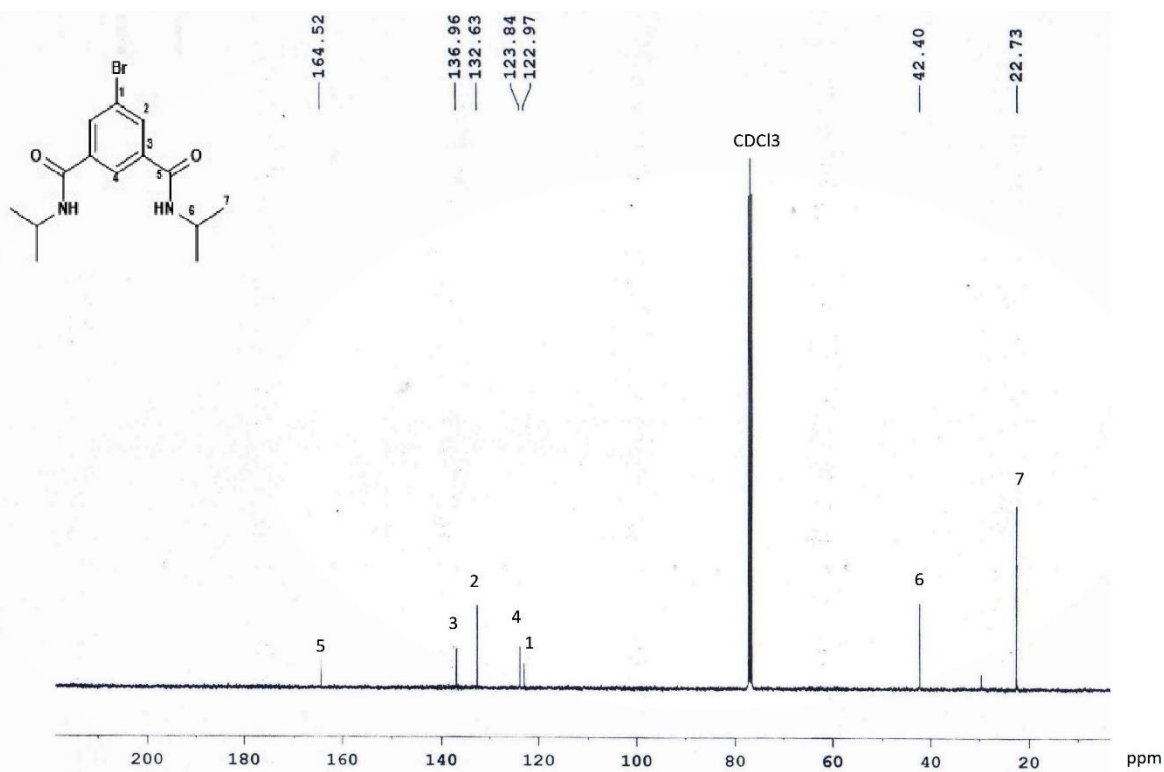


Fig. 3: ^{13}C NMR Spectra of 5-bromo-N1, N3-diisopropylisophthalamide

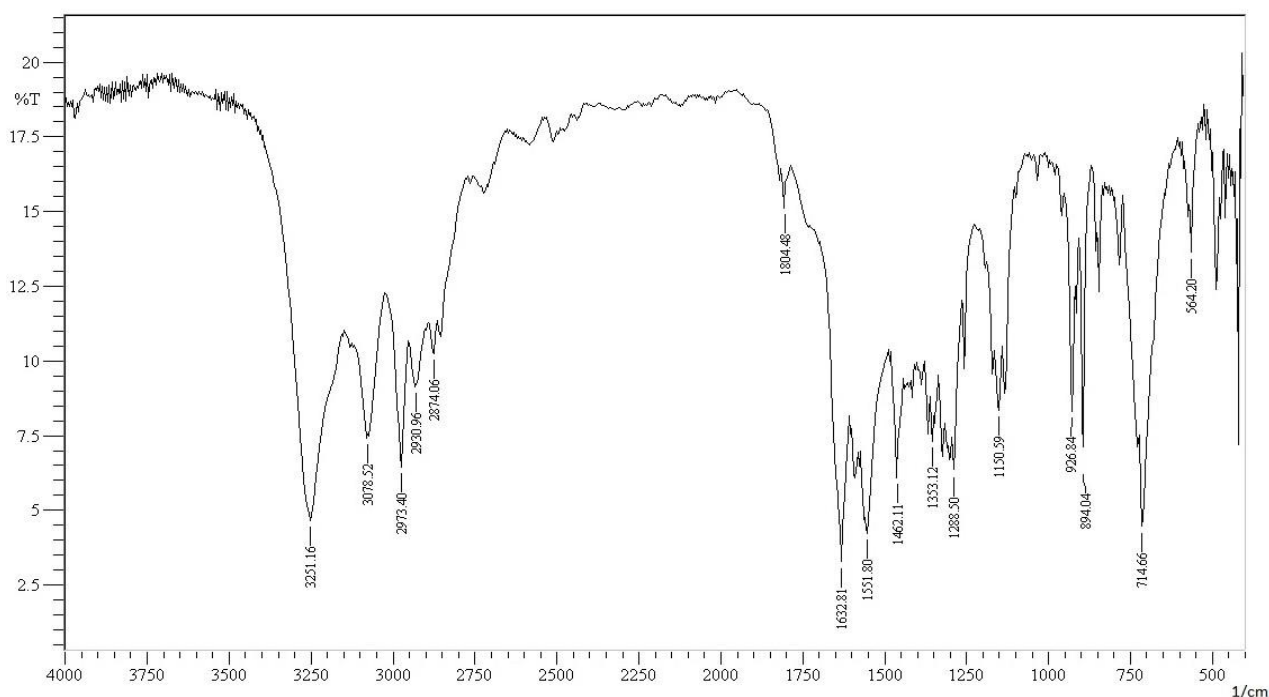


Fig. 4: FTIR Spectra of 5-bromo-N1, N3-diisopropylisophthalamide

Extraction

The extraction profile of uranyl is obtained by measuring D_U as a function of aqueous feed acidity in various ionic liquid systems at a constant ligand concentration (1 mM) and temperature (300 K). An equivalent volume of the organic (IL) and aqueous solutions were used in the extraction process. The equilibration time and the time of centrifugation were 180 min and 5 min, respectively. The Distribution ratio was calculated as follows[45]

$$D_U = \frac{[M]_{IL}}{[M]_{aq}} \quad (1)$$

Where $[M]_{IL}$, and $[M]_{aq}$ are the analytical concentrations of uranyl in ionic liquid and aqueous phase. The dependence of the D_U as a function of ligand concentration was investigated by keeping the acidity of the feed solution as a constant (1 M HNO_3). For nitrate ion variation, aqueous phase $NaNO_3$ concentration was varied keeping other parameters constant. $LiNTf_2$ salt and bromide salts of the corresponding ionic liquid cations are water-soluble and hence their concentration was varied in water to investigate their involvement in the extraction of uranyl ion by the ligand. Stripping studies were carried out in two steps. In the first step, the extraction process was done. while in the subsequent step, the stripping was carried out using sodium carbonate, oxalic acid, and ethylenediaminetetraacetic acid (EDTA). Several consecutive contacts of the stripping agent were made for achieving cumulative back

extraction of locked up uranyl from the ionic liquid phase. The % stripping was calculated as follows[46]

$$\% \text{ Stripping} = \frac{[M]_{aq}}{[M]_{IL}} \times 100 \% \quad (2)$$

For the radiation stability study, the solvent systems were irradiated with various gamma radiation doses using ^{60}Co as a source. With the irradiated solvent systems, the D values were calculated and the deviation was monitored.

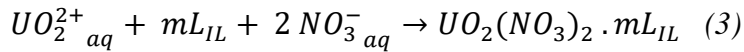
Results and discussion

Extraction profile

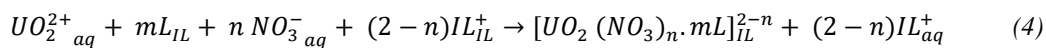
Extraction of uranyl ion has been carried out with a 1 mM concentration of ligand. The extraction profile as a function of aqueous feed acidity is shown in **Fig. 5**. In IL1, the D_U increases up to 2 M HNO_3 reaching a maximum value of ~ 12 , and remains almost constant between 2 M and 4 M HNO_3 followed by a marginal decrease. The decrease in D_U value at higher acidity is not very significant. In the case of IL2, the D_U value increases rapidly up to 1 M HNO_3 followed by a marginal increase from 1 M to 2 M HNO_3 and remained unchanged beyond 2 M HNO_3 . In the plateau region, the D_U value was ~ 20 . In IL3 based system, the trend was almost similar. The enhancement in D_U value was gradual up to 4 M HNO_3 , followed by a plateau. The maximum D_U value obtained in this case was ~ 13 . Interestingly, using IL4 as a solvent system, the trend in D_U vs aqueous feed acidity is unique compared to other ionic liquid systems, i.e. D_U value was maximum (~ 8) at 1 M HNO_3 and decreases with an increase in feed acidity. This diluent-induced difference in extraction profiles is not very common in molecular diluents. However, in ionic liquid, structural modification can bring changes in extraction properties. The above fact was verified and well-reported for imidazolium-based ionic liquids[47, 48]. In the case of methylimidazolium-based ionic liquid, it was demonstrated that if the alkyl group at the 3rd position is butyl, then there is a chance of cation exchange mechanism, where, the butyl imidazolium cation is getting exchanged with the cationic metal-ligand complex. However, for higher homologue, i.e. C_8mim^+ or $\text{C}_{10}\text{mim}^+$ ion, water solubility is very less and hence, the ion exchange mechanism is prohibited and the extraction proceeds through a solvation mechanism involving neutral metal-ligand complex. In the present case, it is quite interesting to study ionic liquids that have diverse cationic motifs. There are only a few reports that describe the extraction of metal ions in ionic liquids through the anion-exchange mechanism. One such example is the extraction of uranyl ion by tri-*n*-butyl phosphate in ionic liquid from higher aqueous feed acidity[49]. Recently anion exchange mechanism was also reported for Sr^{2+} extraction by Calix crown ether using pyridinium-based ionic liquid[26]. The increasing trend in D_U with an increase in aqueous feed acidity is an indication of either

the solvation mechanism or anion exchange mechanism. The initial enhancement in D_U with aqueous feed acidity is ascribed to the participation of nitrate ions. However, at higher feed acidity, plenty of H^+ ions are available and they compete with uranyl ion resulting in either plateau or marginal reduction in D_U values. In the case of ionic liquid IL4, the extraction profile indicates the extraction might proceed through the cation exchange mechanism.

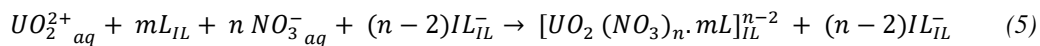
Solvation mechanism:



Cation exchange mechanism:



Anion exchange mechanism:



Where, m and n are the number of ligand molecules and nitrate ions associated with each uranyl ion in the formation of the complex. IL^+ represents the cationic part of the ionic liquid, while IL^- is the anionic part of the ionic liquid.

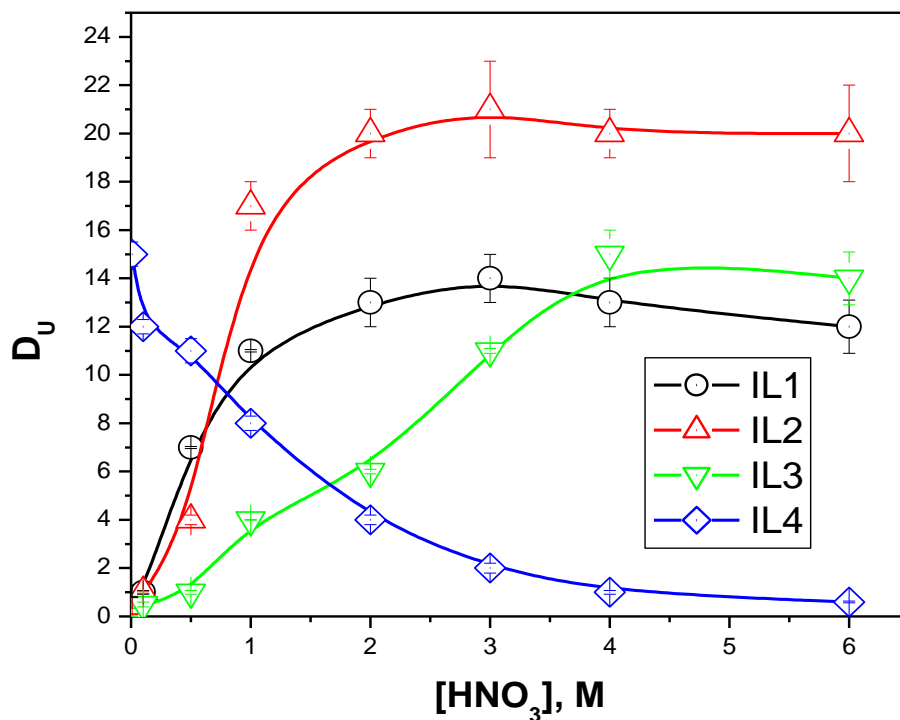


Fig. 5: The variation in D_U value as a function of aqueous feed acid concentration using 1 mM ligand in different ionic liquid

Speciation and Extraction mechanism

The equilibrium constant for the uranyl extraction can be defined as follows

$$\text{Solvation mechanism} \quad K_{ex} = \frac{[UO_2(NO_3)_2 \cdot mL_{IL}]}{[UO_2^{2+}]_{aq} [L_{IL}]^m [NO_3^-]_{aq}^2} \quad (6)$$

$$K_{ex} = \frac{D_U}{[L_{IL}]^m [NO_3^-]_{aq}^2} \quad (7)$$

Taking logarithm on both sides and rearranging, the equation takes the form

$$\text{Log} D_U = \text{Log} K_{ex} + m \text{Log} [L_{IL}] + 2 \text{Log} [NO_3^-]_{aq} \quad (8)$$

Similarly, for the cation exchange mechanism, the equilibrium constant can be written as

$$K_{ex} = \frac{[[UO_2(NO_3)_n \cdot mL]_{IL}^{2-n}] [L_{IL}^+]^{2-n}}{[UO_2^{2+}]_{aq} [L_{IL}]^m [NO_3^-]_{aq}^n [L_{IL}^+]^{2-n}} \quad (9)$$

The ratio of the concentration of cationic part of ionic liquid in both the phase is known as the partition coefficient for that species. The partition coefficient is a constant for a given temperature and also considering K_{ex} as the conditional extraction, the equation can be simplified as follows

$$K'_{ex} = \frac{[[UO_2(NO_3)_n \cdot mL]_{IL}^{2-n}]}{[UO_2^{2+}]_{aq} [L_{IL}]^m [NO_3^-]_{aq}^n} \quad (10)$$

$$\text{Log} D_U = \text{Log} K'_{ex} + m \text{Log} [L_{IL}] + n \text{Log} [NO_3^-]_{aq} \quad (11)$$

For anion exchange mechanism the K_{ex} can be written as follows

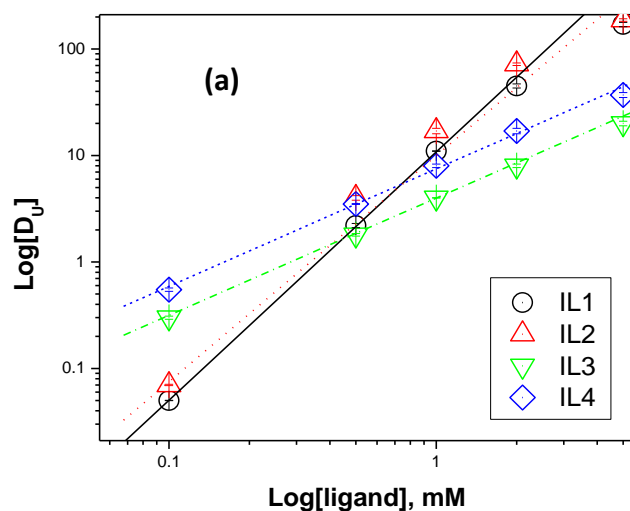
$$K_{ex} = \frac{[[UO_2(NO_3)_n \cdot mL]_{IL}^{(n-2)}] [L_{IL}^-]^{n-2}}{[UO_2^{2+}]_{aq} [L_{IL}]^m [NO_3^-]_{aq}^n [L_{IL}^-]^{n-2}} \quad (12)$$

Similarly, the partition coefficient for the anionic part of the ionic liquid is a constant for a given temperature, and hence equation can be written as

$$\text{Log} D_U = \text{Log} K'_{ex} + m \text{Log} [L_{IL}] + n \text{Log} [NO_3^-]_{aq} \quad (13)$$

Therefore, a plot of $\text{Log}(D_U)$ as a function of $\text{Log}([L])$ will be a straight line with a slope, which determines the metal-ligand stoichiometry, keeping nitrate ion in the aqueous phase constant. Similarly, a plot of $\text{Log}(D_U)$ value as a function of $\text{Log}([NO_3^-])$ would be a straight line with a slope value, which determines the number of nitrate ions associated with each metal ion in the complex. **Fig. 6(a)** shows the variation in D_U value as a function of ligand concentration. An increase in D_U value with ligand concentration indicates the direct participation of ligand molecules. For ionic liquids IL1 and IL2, the slope is evaluated as 2, while it is 1 for ionic liquids IL3 and IL4. This revealed that UO_2^{2+}

formed 1:2 complex in ionic liquid IL1 and IL2, whereas 1:1 metal-ligand complex with IL3 and IL4. **Fig. 6(b)** represented the variation in D_U value as a function of nitrate ion concentration in the aqueous phase. The slope for IL1 and IL2 were found to be 3 and 2, respectively. However, for IL3 and IL4, the slope is evaluated as 2 and 1, respectively. These results indicate that in IL1, the species is $[\text{UO}_2(\text{NO}_3)_3\text{L}_2]^-$, in IL2 the species is $\text{UO}_2(\text{NO}_3)_2\text{L}_2$, whereas in IL3 the species is $\text{UO}_2(\text{NO}_3)_2\text{L}$ and in IL4 the species involved is $[\text{UO}_2(\text{NO}_3)\text{L}]^+$. This implies that in IL4, the cation exchange mechanism predominates following cationic species, and the cationic part of the ionic liquid will be exchanged in place of the metal-ligand complex during extraction to maintain the electrical neutrality. On the other hand, in IL1, the anion exchange mechanism predominates involving anionic metal-ligand species. To maintain the charge neutrality in both phases, an equivalent amount of ionic liquid anion would get exchanged. However, for IL2 and IL3, the solvation mechanism is predominant involving a neutral metal-ligand complex. However, this has to be confirmed by further investigation on the dependence of cations or anions of ionic liquids on the extraction properties of uranyl.



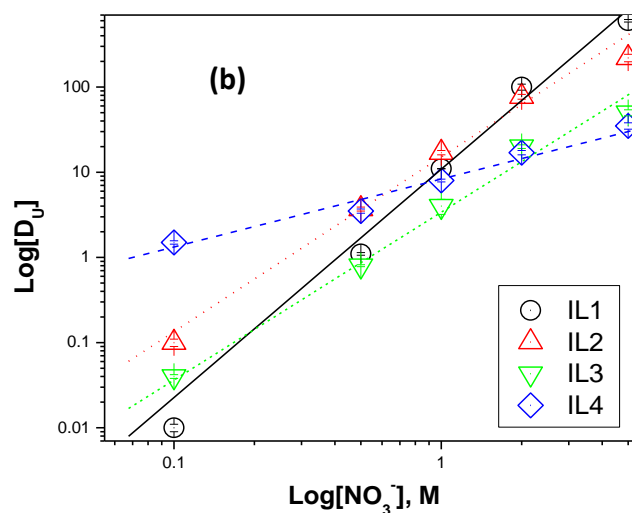


Fig. 6: The variation of D_U values as a function of (a) ligand concentration in ionic liquid phase; (b) nitrate ion concentration in the aqueous phase

To further confirm the speciation and the extraction mechanism, cation and anion dependence of ionic liquid on D_U values were monitored using the water-soluble salts of the same [Fig.7]. For example, in cation dependence experiments, the chloride salts of the corresponding ionic liquid were taken, while anion dependence was checked using Li salt of NTf_2^- anion. The chloride salts used in the present case are: 1-Hexyl-1,4-diaza[2,2,2]bicyclooctanium chloride, 1-Propylpyridinium chloride, 1-Butyl-1methylpiperidinium chloride, 1-Hexyl-3methylimidazolium chloride. In cation dependence experiments, the D_U values were independent of the concentration of ionic liquid cations in the aqueous phase for IL1, IL2, and IL3, suggesting no cation exchange mechanism involved. However, the D_U value decreases with an increase in ionic liquid cation concentration in the aqueous phase for IL4. The concentration dependence of the D_U value in IL4 confirms the participation of IL cation in the extraction process. More the initial concentration of cations in water, the equilibrium of the extraction process shifted more towards the backward direction, i.e. the extent of uranyl extraction would reduce. The slope of the linear dependence of D_U in IL4 is evaluated as -1. This implies that only one C_8mim^+ ion gets exchanged during each metal-ligand complex extraction. This also proves that a singly charged metal-ligand complex formed during extraction of uranyl with amide functionalized ligand in $\text{C}_8\text{mimNTf}_2$. On a similar note, anion dependence experiments suggested that, for IL2, IL3, and IL4, the D_U remained unchanged with an increase in the NTf_2^- ion concentration in the aqueous phase. However, for IL1, i.e. for bicyclooctanium ionic liquid, the D_U decreases with an increase in NTf_2^- ion concentration in the aqueous phase with a slope value of -1. This result confirms that, for IL2 and IL3, neither cation exchange nor anion exchange mechanism was predominant. Therefore, the extraction

proceeds through the neutral metal-ligand complex with a 'solvation' mechanism. However, for IL1, i.e. bicyclooctanium ionic liquid the extraction proceeded via mono negative U-ligand complex. To maintain the charge neutrality, one NTf_2^- anion would be transferred from the IL phase to the aqueous phase for the transfer of each U-ligand complex. In the case of IL4, C_8mim^+ cation got exchanged in place of mono positive U-ligand complex and the extraction proceeded via cation exchange mechanism. This particular case is very interesting to demonstrate that by changing the cations of the ionic liquids, the extraction species and mechanism can be changed from solvation to cation exchange or anion exchange.

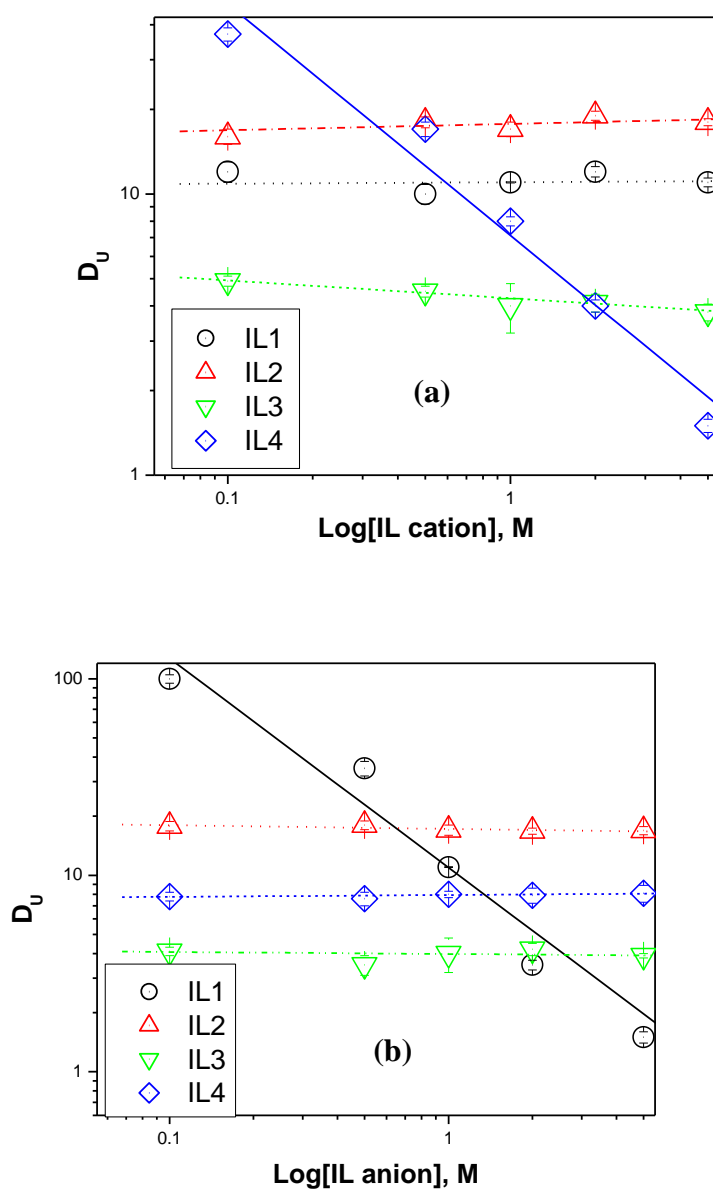


Fig.7: The dependence of D_U values on the concentration of (a) cations of ionic liquid and (b) anions of ionic liquids in the aqueous phase

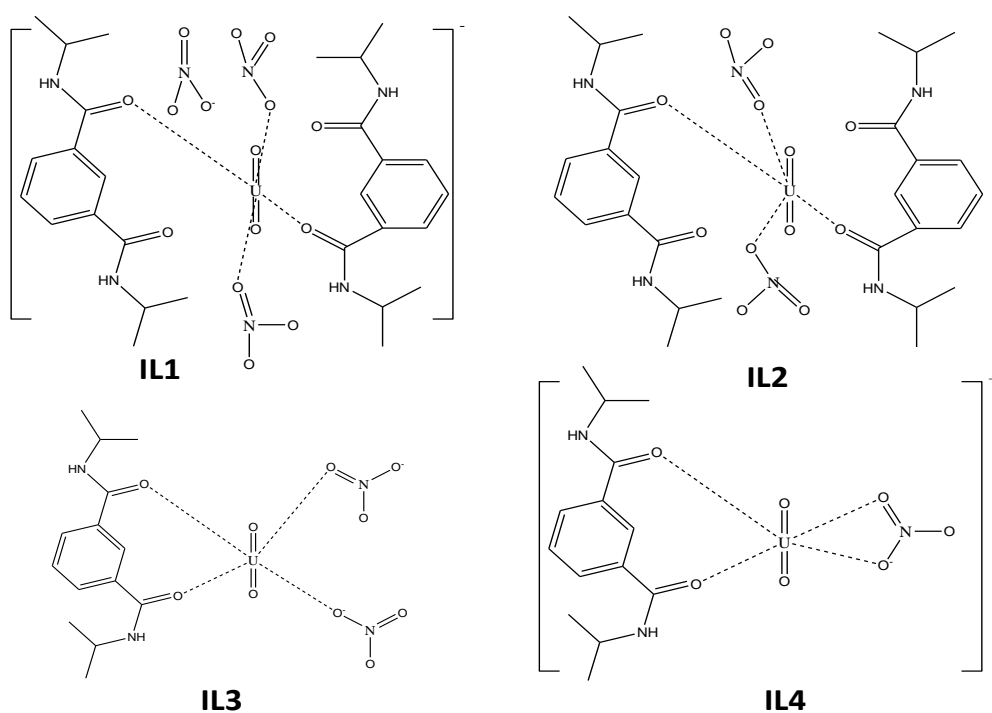


Fig. 8: The U complexes with the diamides in different ionic liquids involved in the separation

Fig. 8 depicts the most plausible uranyl-ligand complexes in different ionic liquids. In IL2 and IL3, neutral species were formed. However, the speciation and mode of coordination are quite different. In IL2, two diamides, and two nitrate ions were found to be coordinating in a monodentate fashion, whereas in IL3, one diamide was found to be coordinating through bidentate fashion, while two nitrates are in monodentate mode. In IL1, the species was found to be anionic with two ligands and three nitrates all are in the monodentate mode of coordination. However, in IL4 the species was mono positive with one diamide and one nitrate both in the bidentate mode of coordination with uranyl to satisfy the 8 coordination number.

Radiolytic stability

For long time use of the ligands, the solvent system must be radiologically stable, since this would experience lots of radiation coming out of the isotopes processed using the solvent system[50, 51]. To understand the radiolytic stability, the solvent systems were exposed to gamma rays of different dose rates, and the D_U values were evaluated. The change in D_U values in irradiated solvent compared to the unirradiated solvent would pertain to the radiological damage faced by them. From **Fig 9**, it is clear that for IL3 and IL4, the D_U values of unirradiated systems were ~ 8 and ~ 4 , respectively. On irradiation with gamma rays, no significant change in D_U values observed. This implies that these two solvent

systems were highly radiologically stable. However, IL2 showed a maximum reduction in D_U values. In the unirradiated condition, the D_U was 17, which was drastically reduced to 2 at a dose of 500 kGy. IL1 also showed similar results, i.e. unirradiated system showed D_U of 11, which reduced to ~ 3.8 after a dose of 500kGy. Therefore, high radiological stability along with the efficiency of the solvent should be considered for processing high radioactive isotopes. In view of that, IL4 might be the best solvent among the four ionic liquids.

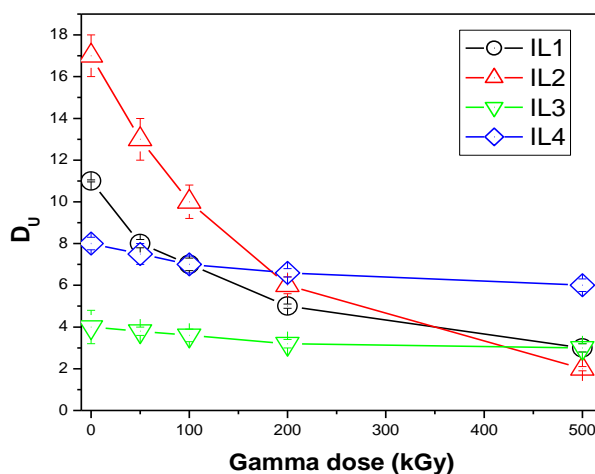


Fig. 9: The radiolytic stability of the solvent systems under the influence of gamma-ray exposure

Back extraction

The reusability of the solvent system is another important aspect to be looked into. The expectation is to have solvent systems having high extraction efficiency as well as can be regenerated very easily after extraction. In view of this, stripping behavior needs to be investigated. It is well-known fact that only dilute acid might not be sufficient to back extract the complexed uranium from ionic liquid. Several methodologies including electro-deposition have been employed for back extraction[52]. However, another well-accepted approach is to make use of the complexing agent in water[53]. The idea is to make a stronger complex of uranyl in water so that the uranium-amide complex in ionic liquid breaks up. Based on the literature, 1 mM aqueous solution of oxalic acid, sodium carbonate, and ethylenediaminetetraacetic acid have been chosen as aqueous complexing agents for back extraction.

Fig. 10(a) shows the % of stripping of uranium using the stripping solution in a single contact. The results indicate that an aqueous solution of sodium carbonate is the best out of these three stripping solutions. Using aqueous sodium carbonate as a stripping solution, the effect of a different number of contact cycles on % stripping was investigated. Four contacts of IL1 were required for about 99.5 % back extraction, while 2 contacts of IL2 and IL4 were sufficient for almost 99 % back extraction. Back

extraction from IL3 was not as satisfactory as observed in other cases. Even after five contacts, the cumulative back extraction was slightly less than 99 %. **Fig. 10 (b)** depicts the cumulative % back extraction of uranyl ion from the uranyl-diamide complex in ionic liquid.

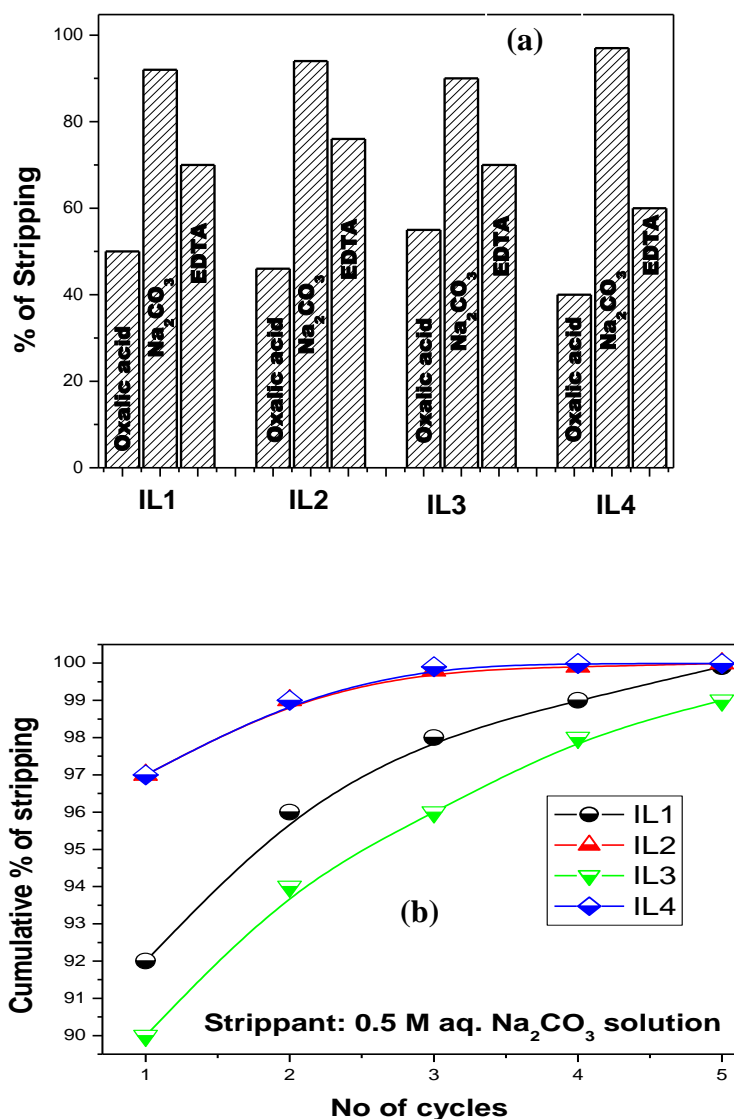


Fig. 10: (a) The stripping behavior of uranium from the uranyl-diamide complex in ionic liquid using different aqueous complexing agents; (b) Cumulative % of stripping of locked up uranium using sodium carbonate in multiple contacts

The variation of D_U values for the ionic liquids having prior contact (1 hr) with 1 M HNO_3 as a function of time is shown in Fig.11. This investigation reveals the chemical stability of the solvent systems in the presence of 1 M HNO_3 . The D values were monitored up to 72 hours i.e. 3 days of contact time. D_U value is almost independent of time from 1 hr onwards, suggesting that all the ionic

liquid based solvent systems are chemically stable. Table 1 summarizes the mechanism, speciation and other characteristics of extraction for the four ionic liquid systems used in the study.

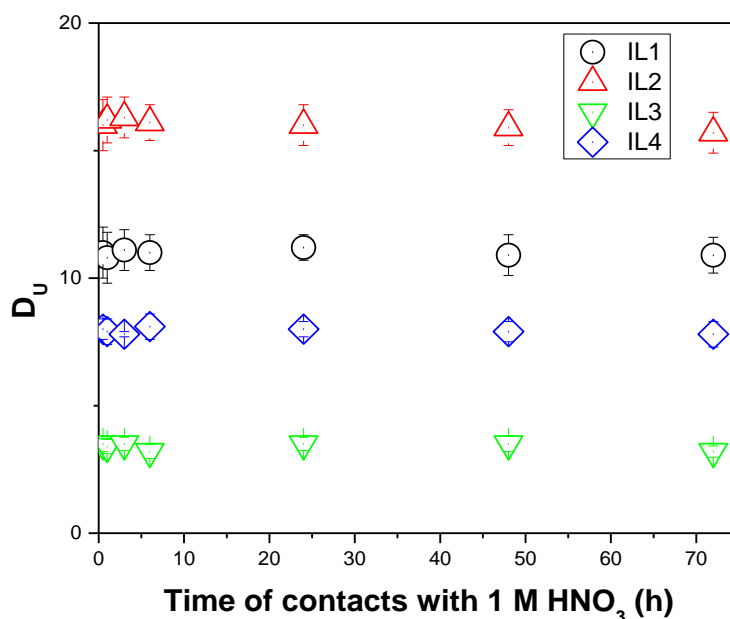


Fig. 11: The variation in D_U as a function of contact time of organic phase with 1 M HNO_3

Table 1: The extraction characteristics of the ionic liquid based solvent systems

Metal	Ligand	IL	D (1 M HNO_3)	Mechanism	Species	No of contact for stripping
UO_2^{2+}	5-bromo-N1, N3-diisopropylisophthalamide	1-Hexyl-1,4-diaza[2,2,2]bicyclooctaniumbis(trifluoromethylsulfonyl)imide	11	Anion exchange	$[UO_2(NO_3)_3L_2]^-$	4
		1-Propylpyridinium bis(trifluoromethylsulfonyl)imide	16	Solvation	$UO_2(NO_3)_2L_2$	2
		1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	3.7	Solvation	$UO_2(NO_3)_2L$	even 5 is not sufficient
		1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	8	Cation exchange	$[UO_2(NO_3)L]^+$	2

Conclusion

This manuscript describes the first-ever report of tuning the extraction mechanism of uranyl ion from cation exchange to anion exchange or solvation mechanism by changing the cationic part of the ionic liquid for the same uranyl-diamide systems. The novel diamide ligand (5-Bromo-N1, N3-diisopropylisophthalamide) was synthesized and characterized by ^1H NMR, ^{13}C NMR and FTIR spectroscopy. In imidazolium-based ionic liquid, the extraction proceeds via monocationic $[\text{UO}_2(\text{NO}_3)\text{L}]^+$ species. For pyridinium ionic liquid, the extraction proceeds via neutral $\text{UO}_2(\text{NO}_3)_2\text{L}_2$ species, whereas for piperidinium ionic liquid, neutral $\text{UO}_2(\text{NO}_3)_2\text{L}$ species is predominating. However, for bicyclooctanium ionic liquid, monoanionic complex $[\text{UO}_2(\text{NO}_3)_3\text{L}_2]^-$ was predominating. The radiation stability of pyridinium and imidazolium-based ionic liquids was more than that of the other two ionic liquid systems. An aqueous solution of sodium carbonate (1mM) back extracts the uranyl ion effectively from the ionic liquid phase compared to oxalic acid and EDTA. Four contacts of eluent are required for back extraction of uranyl from bicyclooctanium ionic liquid, whereas 2 contacts were sufficient for imidazolium and piperidinium based ionic liquid. In pyridinium-based ionic liquid, the uranyl complex was so strong, and hence can not be stripped quantitatively even after five contacts.

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Conflict of interest

There is no conflict of interest to disclose

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