



An overview of molecular extractants in room temperature ionic liquids and task specific ionic liquids for the partitioning of actinides/lanthanides

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Abstract

Solvent extraction process is applied for the extraction of actinides/lanthanides from waste water produced in nuclear industry. Various extractants have been developed for this purpose. More recently separation scientists have shown extensive interest toward ionic liquids (ILs) due to their unique properties. ILs have extensively been used as extraction medium for the recovery of rare earths and actinides or modified to task specific ionic liquids (TSILs); where ionic liquid part has been covalently attached to the extractants. This article highlights some conventional extractants, the use of these extractants in IL medium and the development of TSILs. The effect of medium on extraction efficiency has also been discussed.

Keywords Ionic liquids · Extraction · Actinides · Lanthanide · Nuclear waste

Introduction

The production of high level-waste (HLW) during the generation of electricity from nuclear resources is one of the great concerns. Almost 850 cubic meters of this HLW are annually discharged worldwide. The main constituents of this HLW are uranium (U), plutonium (Pu), minor actinides (MAs) viz. Np, Cm, Am, some lanthanides (Ln), and some other fission and corrosion products e.g. lead, technetium, zirconium, iodine and strontium. Some other elements like iron, cobalt, nickel and zinc and salts of sodium, iron and aluminium are also present. Currently the most accepted worldwide protocol for the management of HLW is vitrification in glass matrix and subsequent storage for approximately 100 years in order to allow ⁹⁰Sr and ¹³⁷Cs to decay.

After this period HWL is subsequently disposed of in deep geological repositories [1]. Due to very long half-lives of a few MAs (²⁴¹Am = 432.2 years, ²⁴³Am = 7370 years, ²³⁷Np = 2.16×10^6 years, ²³⁹Np = 2.355 days, ²³⁹Pu = 2.411×10^4 years) and some fission product these vitrified blocks are not considered favorable for such a long period from environmental as well as economic perspective. Another risk involved is leakage of long-lived α -emitting MAs to the water cycle as it happened in the past; more than three million liters of nuclear waste of very high radioactivity leaked into the surrounding soil of the Columbia Basin. Millions of years would be required to reduce the radiotoxicity of HLW equivalent to natural uranium ore without proper removal of these MAs from the spent nuclear fuel.

The treatment of such a waste of high level radioactivity therefore requires much attention. Several strategies have been employed and are being employed in order to find a safer and economically viable protocol [2, 3]. Still one of the best strategies involve the partitioning (separation) of highly radioactive isotopes. The nuclear waste consists of almost 95 wt % of residual Uranium, almost 1 wt % of the highly radiotoxic transuranium element Plutonium, and some other MAs americium, neptunium, and curium (~0.1%). These actinides contribute to only small part of the bulk called minor actinides.

Partitioning and Transmutation (P&T) strategy is main protocol being employed by several countries worldwide for

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the safe disposal of HLW. In P&T strategy first step is to completely remove these MAs from HLW and their transmutation to suitable chemical forms in high flux reactors/accelerators in second step [4–6]. Several techniques are available to separate metals like precipitation, [7, 8] electrolysis, [9] ion exchange, [10] and sorption [11, 12] etc. Solvent extraction is most widely applied in nuclear waste processing as high selectivity can be obtained in this process. Main drawbacks of solvent extraction are the loss of extraction agent and the production of large amounts of organic waste. PUREX (Plutonium URaniumEXtraction) process is employed to extract U, Np, and Pu. Ln and an along with fission and corrosion products are extracted together in DIAMEX (DIAMideEXtraction) process from the bulk of waste. SANEX (Selective ActiNideEXtraction) process is used to separate actinides and lanthanides. Hence, most widely accepted protocol for the separation of metal ions involves solvent extraction.

In this article, a brief overview of the recent literature for the separation of actinides and lanthanides from nuclear waste streams using ionic liquids is presented. Efforts are made to present the work carried out with (a) conventional ligands used in room temperature ionic liquids (RTILs) (b) Task specific ionic liquids (c) solid phase extractants used in ionic liquids. Emphasis is made to summarize only the extractants which have been used for extraction of lanthanides and actinides. In addition, a brief introduction to ligands which are being employed in molecular diluents either for coextraction of An/Ln or mutual separation of Ln/An is also provided. The complexation mechanism of ligands with the metal ions in ionic liquid medium is out of scope of this review.

Extractants for solvent extraction of An/Ln

In most processes which have been developed in the last decades, initially lanthanides and actinides are extracted together, and then mutually separated. Most common processes for co-extraction of lanthanides and actinides are Plutonium Uranium Extraction (PUREX) [13], Trans Uranium Extraction (TRUEX) [14, 15], TrialkylPhosphine Oxide (TRPO) [16], Diamide Extraction (DIAMEX) [17] and Diisodecyl Phosphoric Acid (DIDPA) [18]. The mutual separation of An(III) and Ln(III) is achieved by Selective Actinide Extraction (SANEX), (Actinide-Lanthanide Inter group Separation from Acidic media (ALINA) [19], and some other processes which involve the use of polydentate ligands containing nitrogen. The actinides are left in aqueous phase in Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes (TALSPEAK) [20] and Innovative SANEX [21] processes.

Extractants for co-extraction of An/Ln

Oxygen donor ligands are considered as hard donors and thus unable to discriminate between An(III) and Ln(III). Organophosphorus ligands, glycolamides and malonamides are commonly used for the separation of Ln(III) and An(III) from fission and corrosion products. The most commonly used organophosphorus ligands (1–6), malonamides (7–9) and glycolamides (10–12) are summarized in Table 1.

The malonamides and glycolamides are completely incinerable and the amount of secondary waste produced is negligible compared to phosphorus-containing ligands. Glycolamides show better extraction of all actinides (tri and tetra valent) [22–26]. The modified glycolamides showed different extraction behavior against HNO₃ concentration compared to glycolamides [27]. The substituents on N atom of diglycolamide compounds play a vital role in metal extraction [28]. Diglycolamides preorganized on the triphenoxymethane (commonly called trityl) platform, [29, 30] C-pivot tripodal platform, [31] as bisdiglycolamides [32] and on calix[4]arene platform have also been extensively studied [33, 34].

Extractants for mutual separation of An/Ln

Mutual separation of An(III) and Ln(III) is still a challenging issue. Nevertheless, ligands with soft donor atoms like N and S (softer donor atoms) have been developed to separate them. In this section donor ligands with N or S atoms for selective extraction of actinides are discussed.

S donor ligands

Thiophosphinic/phosphoric acids are the most common class of sulfur-based soft-donor ligands which show selectivity for An(III) over Ln(III). The list of S donor ligands used so far for the extraction of An is given in Table 2.

HDEHDTP (Bis(2-ethylhexyl)dithiophosphoric acid) was the first example showing selectivity for Am(III) over Eu(III) with a separation factor (*SF*) value of 50. It was also shown that dithio ligand CYANEX 301 exhibited a good selectivity for Am(III), compared to monothio analog CYANEX 302 [47]. Jarvinen et al. [48] achieved very high *SF* values of approx. 1000 in a single extraction step by dicyclohexyl-dithiophosphinic acid.

Bis(*o*-trifluoromethylphenyl)dithiophosphinic acid selectively extracts Am(III) with a *SF*_{Am/Eu} value of ~ 100,000 at pH 2 [49]. The CF₃ group in the ortho position has a strong electron-withdrawing inductive effect which makes the sulfur atom softer and improves

Table 1 Structure of oxygen donor ligands

Sr No	Name of Ligand	Ligand Structure
1	Tri- <i>n</i> -butylphosphate (TBP)	
2	Diamylamylphosphonate [35]	
3	Trialkylphosphine oxides [16]	
4	Bidentate neutral organophosphorus compounds (BNOPCs) [36,37]	
5	Diphenyl(diisobutylcarbamoylmethyl)phosphine (Ph ₂ iBu ₂ -CMPO) [38,39]	
6	Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) [40,41]	
7	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dibutyltetradecylmalonamide (DMDBDMA) [42]	
8	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) [43,44]	
9	Bicyclic malonamides [45]	
10	<i>N,N,N',N'</i> -tetraoctyldiglycolamide (TODGA) [46]	
11	Modified <i>N,N,N',N'</i> -tetraoctyldiglycolamide [27]	
12	Glycolamidesproganized on C-pivot platform [31]	

Table 2 Structure of sulfur donor ligands

SrNo	Ligand Name	Ligand Structure
1	Bis(2-ethylhexyl)dithiophosphoric acid (HDEHDTP)	
2	Bis(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302)	
3	Bis(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301)	
4	Dicyclohexyldithiophosphinic acid	
5	Diphenyldithiophosphinic acid	
6	Bis(trifluoromethylphenyl)dithiophosphinic acid	
7	Bis(3,5-bis(trifluoromethyl)phenyl)dithiophosphinic acid	

the *SF*. However, much lower selectivity for its oxygen analogue was observed [50]; eventually phosphinic acid analogue appeared to be much stronger complexant than its thiophosphinic acid analogue [51].

In conclusion, branched alkyl chain thiophosphinic acids are selective towards Am(III) over Eu(III) compared to straight alkyl chain thiophosphinic acids. The introduction of electron-withdrawing groups on the ortho positions of aromatic rings has a highly positive effect on the *SF* values, but negatively affects the extraction efficiency.

N-donor ligands

N-donor ligands, in general, show selectivity for An(III) due to the presence of the softer N atom. The structures of most common classes are shown in Table 3.

BTPs 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines, (Table 3) [52] are well known class of N-donors and show high *SF* values of > 100 [53]. CyMe₄-BTP and BzMe₄-BTP (Table 3) exhibited *D*_{Am} value of 500 and *SF* value of around 5000 [54].

Table 3 Structure of nitrogen donor ligands

Sr No	Ligand Name	Ligand Structure
1	2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (BTP)	
2	2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)pyridine (CyMe ₄ -BTP)	
3	and 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydro-1,2,4-triaza-anthran-3-yl)pyridine (BzMe ₄ -BTP)	
4	Bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine (CA-BTP)	
5	6,6'-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBP)	
6	CyMe ₄ -BTBP	
7	6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrofuro[3,4-e]-1,2,4-triazin-3-yl)-2,2'-bipyridine Cy5-O-Me ₄ -BTBP: X = O Cy5-S-Me ₄ -BTBP: X = S	
8	1,10-phenanthroline based bipyridine Ligand (Cy ₄ BTPhen)	
9	6,6''-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2':6',2''-terpyridine (CyMe ₄ -BTTP)	
10	te-tpyda : R ¹ = R ² = C ₂ H ₅ tb-tpyda : R ¹ = R ² = C ₄ H ₉ to-tpyda : R ¹ = R ² = C ₈ H ₁₇ dedp-tpyda : R ¹ = C ₂ H ₅ , R ² = Phenyl	

Bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine (CA-BTP; Table 3) has been considered as a new, optimized ligand for the separation of Am(III) and Cm(III) from Ln(III).

A similar class of softer *N*-donor ligands is the BTBPs (6,6'-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines; Table 3) [55]. *SF* values of more than 100 have been obtained with CyMe₄-BTBP [56].

More BTBP ligands Cy₅-O-Me₄-BTBP [6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrofuro[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine] and Cy₅-S-Me₄-BTBP [6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrothieno[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine] (Table 3), have also been studied. The *D*_{Am} and *SF* values of CyMe₄-BTBP are both significantly higher than those of Cy₅-O-Me₄-BTBP and Cy₅-S-Me₄-BTBP in cyclohexanone [57]. Cy₄BTPhen ligand (Table 3) where preorganization of the donor atoms of bipyridine is made into a rigid *cis*-locked 1,10-phenanthroline system led to a highly efficient and rapid separation of actinides from lanthanides [58].

*D*_{Am} value of 0.039 with a maximum *SF* value of 12.0 from 1 M HNO₃ was achieved using terpyridine analog of BTBP, viz. 6,6''-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2':6',2''-terpyridine (CyMe₄-BTTP) (Table 3), [59].

Amide containing terpyridine ligands have been synthesized. Solvent extraction studies with *N,N,N',N'*-tetraalkyl-6,6''-(2,2':6',2''-terpyridine)diamides and *N,N'*-diethyl-*N,N'*-diphenyl-6,6''-(2,2':6',2''-terpyridine)diamide (Table 3) showed that extraction of Np (V and VI), U(VI), Am(III), Cm(III), and Pu(IV) from 3 M HNO₃ can be done. These ligands exhibited moderate extraction and *SF* values for An(III) and Ln(III). The introduction of phenyl rings on the amidic nitrogen increased the ligand efficiency [60].

The solubility of various N donor ligands has been tuned over the recent years in a wide variety of solvents by introducing different groups. Not only N donor ligands are completely incinerable and many of them show high separation possibility from 3 M HNO₃ which is in line with the nuclear waste conditions.

Ionic liquids

Room temperature ionic liquids (RTILs) have aroused increasing interest for their promising role as alternative diluent medium in synthesis, [61] separation [62] and electrochemistry [63] as a result of their unique chemical and physical properties [64]. These solvents exhibit several properties that make them attractive as a potential basis for 'green' separation processes, like negligible vapor pressure, a wide liquid range, non-flammability, tunable viscosity and miscibility and good thermal and radiation stability. Even

minor structural variation either in cationic or anionic moieties can produce significant changes in physicochemical properties of ionic liquids. This tunability is obviously offering vast opportunities for the design of ionic liquid based separation systems and also poses formidable challenges to the separation scientists. This section summarizes the use of conventional ligands in RTILs as extraction medium and modification of these ligands to TSILs.

Conventional ligands used in RTILS

Metal-ion separation in ionic liquid systems exhibits high complexity compared to traditional solvent systems. Enhanced extraction efficiency as well as selectivity of some IL systems, compared to the traditional solvent systems, has drawn attention of researchers.

Two aspects of IL systems are of great importance. First one is that the pH dependence can be altered and the selectivity of one cation over another can be reversed compared to the traditional solvent systems. This has been demonstrated in case of TODGA while using [C₂mim][NTf₂] or isooctane as IL and conventional solvent systems respectively, for the extraction of La(III), Eu(III), and Lu(III) [65]. A reversal in the extraction efficiency occurs in the IL system in comparison to isooctane as a function of [HNO₃]. In case of IL system, extraction can be done under much less acidic conditions. TODGA prefers heavier Ln in isooctane amongst the lanthanide series whereas the lighter ones in [C_{*n*}mim][NTf₂] (Fig. 1). Similar trend was found for transition metals as well [66].

The second aspect deals with the synergistic extractions, which is an effective method for enhancing the extraction efficiency and selectivity in traditional solvent systems. Stepinski et al. [67] showed that the addition of TBP can increase the extraction of Sr(II) from acidic nitrate media into [C_{*n*}mim][NTf₂] by crown ether (DCH₁₈C₆; Fig. 1). The length of alkyl chain of IL's cation can affect the magnitude of the synergistic enhancement, which contributes to the design of IL-based synergistic systems.

Well-known classes of ligands for An(III) such as malonamide, TBP, CMPO, and TODGA and their derivatives have been investigated in combination with ionic liquids.

Organophosphorus ligands

The extraction efficiency of TBP was investigated for U(VI) in [C₄mim][PF₆] ionic liquid medium as well as in TBP/*n*-dodecane system. 1.1 M TBP/[C₄mim][PF₆] system was compared with TBP/*n*-dodecane system. Extraction of U(VI) was similar in both systems as far as HNO₃ concentration was less than 4.0 M. However, upon high HNO₃ (> 4 M)

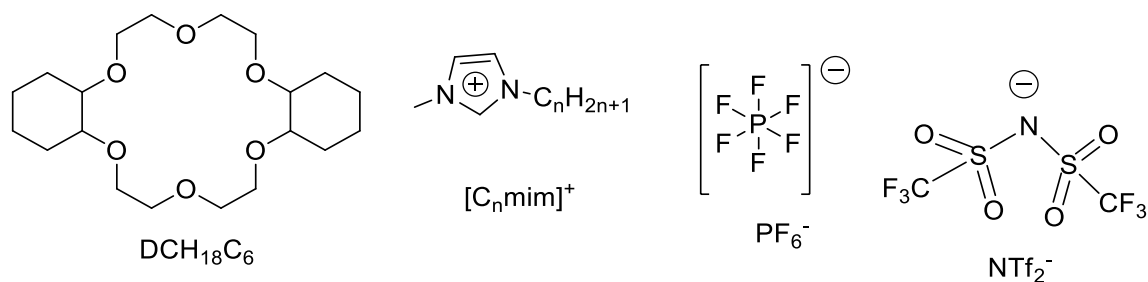


Fig. 1 Structure of DCH18C6, imidazolium, NTF2 and PF6

concentrations, enhanced U(VI) extraction was found for the TBP/[C₄mim][PF₆] [68].

Panja et al. [69] reported extraction of Pu(IV) from nitric acid medium into two diluents: *n*-dodecane and a RTIL, [C₄mim][NTf₂]. This was done using TBP as extractant. The *D* value using RTIL was > 20 while it was around 16 when *n*-dodecane was used. The analysis revealed that extraction kinetics by RTIL was slow compared to *n*-dodecane. Also the mechanism in case of lower acidity was cationic exchange, whereas at higher acidity (1 M and above) it was switched to neutral complex formation.

Rout et al. [70] observed much larger *D*_{Am} values using TBP and CMPO in [C₄mim][NTf₂] than in *n*-dodecane. By using [C₄mim][NTf₂] as a diluent, a four times lower conc. of CMPO was required for Am(III) extraction in 3–4 M HNO₃.

The extraction of Am(III), Th(IV), Pu(IV), and U(VI) was investigated by Visser et al. [71]. Distribution ratios for CMPO (CMPO and TBP) were at least an order of magnitude higher for IL [C₄mim][PF₆] compared to *n*-dodecane at ligand concentration of 0.1 M. Extraction behavior of Ce(III), Y(III), and Eu(III) was also reported by Nakashima et al. [72, 73] who studied the use of CMPO in [C₄mim][PF₆] as well as in *n*-dodecane. The efficiency of CMPO for these metals in [C₄mim][PF₆] was very high compared to *n*-dodecane.

The effect on the extraction of Am(III), U(VI), and Pu(IV), was observed by addition of ionic liquid [74]. The *D*_{Am} value increased by 126 folds on addition of 50% [C₄mim][PF₆] and 1040 folds on addition of 50% [PH₄][PF₆] to 0.1 M Ph₂iBu₂-CMPO (diphenyl(dibutyl)-carbamoylmethyl phosphine oxide). Similarly the *D* values for Pu(IV) and U(VI) increased by 135 and 272 fold, respectively, by addition of 50% [C₄mim][PF₆] to 0.001 M Ph₂iBu₂-CMPO.

Tetraphenylmethylenediphosphine dioxide, dibutyl(diethylcarbamoylmethyl)phosphine oxide and diphenyl(diethylcarbamoylmethyl)phosphine oxide were employed for the extraction of different Ln and Y nitrates. Compared with *n*-dodecane a significant increase in extraction efficiency was observed in the presence of [C₄mim][PF₆]. Rare earth elements (REEs), U(VI), and Th(IV) were

effectively recovered by a copolymer, based on macroporous styrene-divinylbenzene, impregnated with a mixture of tetraphenylmethylenediphosphine oxide and [C₄mim][PF₆] [75].

In another study Pribylova [76] and co-workers investigated the extraction of rare earth metals by adding 1–5 wt % of RTILs [C₄mim][NTf₂], [C₄mim][PF₆], and trihexyl(tetradecyl)phosphonium to a diphenyl(dibutyl)carbamoylmethylphosphine oxide (Ph₂Bu₂-CMPO) solution. It was recorded that this system increased *D*_{Am} values from nitric acid medium as high as 748, 793, and 38.8 for above RTILs respectively. The use of [C₄mim][NTf₂] made the extraction possible at a very high HNO₃ Conc. of 8 M. This renders the extraction system very important as most of the solid samples in radiochemical analysis of environmental and technological solutions are transferred to an 8 M HNO₃ solution.

The distribution of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y between aqueous HCl solutions and solutions of various carbamoyl methyl phosphine oxides (CMPOs) has been studied in the presence of the [C₄mim][NTf₂] IL [77]. The efficiency and selectivity of REE(III) extraction by CMPO solutions increased considerably in the presence of the ionic liquid in the organic phase. The *D* values were in the range of < 0.1 which increased to > 40 for various metal ions on addition of 0.1 M [C₄mim][NTf₂]. In another similar study extraction of Ln series was carried out by tetraphenylmethylenediphosphine dioxide

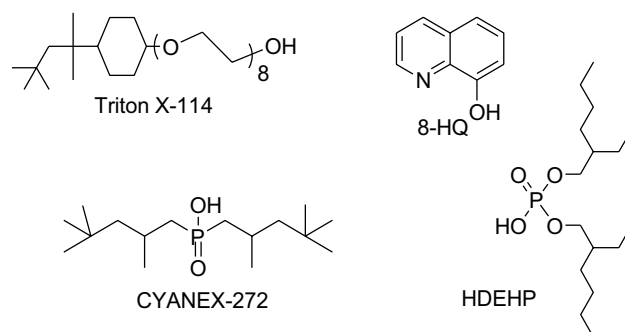


Fig. 2 Structures of Triton X-114, 8-HQ, CYANEX-272, and HDEHP

($\text{CH}_2(\text{POPh}_2)_2$) in dichloromethane and $[\text{R}_4\text{N}][\text{NTf}_2]$. A maximum D_M of > 2 was obtained at DCM:IL ratio of 1:1 [78].

The addition of ionic liquids in Triton X-114 (TX-114; Fig. 2) micellar solution using several anions viz. BF_4^- , PF_6^- , Br^- and NTf_2^- for cloud point extraction (CPE) of UO_2^{2+} and other lanthanides was also investigated [79]. The acidic extractants used were 8-hydroxyquinoline (8-HQ; Fig. 2), bis(2-ethylhexyl)phosphoric acid (HDEHP; Fig. 2), and a neutral extractant tri-octylphosphine oxide (TOPO). The addition of ionic liquid to TOPO showed significant increase in the extraction of target metal at high acidity as well as under neutral conditions. However, cloud point extraction with acidic extractants was not improved by the addition of ILs. The extraction efficiency calculated was up to 90% when $[\text{C}_4\text{mim}][\text{NTf}_2]$ was used. This study also revealed that the combination of TOPO and IL increased the separation of uranyl ions from lanthanide ions. The reason for this was the fact that TOPO micelle and NTf_2^- form a soft template for UO_2^{2+} ion thus providing a supramolecular assembly to separate UO_2^{2+} selectively and effectively.

Riano et al. [80] reported extraction of Nd(III) and Dy(III) from concentrated chloride media. Neutral molecular ligands Cyanex 923 and TBP were combined with ILs viz. trihexyl(tetradecyl)phosphonium thiocyanate ($[\text{C101}][\text{SCN}]$), $[\text{A336}][\text{SCN}]$ and their nitrate analogues $[\text{C101}][\text{NO}_3]$, $[\text{A336}][\text{NO}_3]$. Extraction study was carried out by mixing different weight percent of molecular ligands in ionic liquids as organic phase. Various parameters were studied e.g. equilibrium time, concentration of organic phase, chloride concentration, and pH of the aqueous phase. The Cyanex 923 in $[\text{C101}][\text{SCN}]$ showed increased distribution ratio of both metal ions with extraction efficiency of $> 93\%$.

The extraction of uranyl ions from nitric acid feeds by using tri-n-octyl phosphine oxide (TOPO) in several room temperature ionic liquids such as $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_6\text{mim}][\text{PF}_6]$, $[\text{C}_8\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, $[\text{C}_8\text{mim}][\text{NTf}_2]$ was also investigated [81]. According to the results, the extractions carried out with ionic liquids carrying $[\text{C}_8\text{mim}^+]$ as counter cation showed higher extraction while the ionic liquids carrying PF_6^- as counter anion showed faster extraction kinetics. The distribution ratios obtained by using $[\text{C}_n\text{mim}][\text{PF}_6]$ and $[\text{C}_n\text{mim}][\text{NTf}_2]$ were as high as 12.1 and 18.2 respectively at 0.01 M acidity and dropped to 0.01 as the acidity increased to 2 M. The observations from the extraction studies proposed a solvation mechanism for extraction. The mixture of TOPO with solutions of D2EHPA was also used for extraction of U(IV) from acidic media (both HNO_3 and H_3PO_4) in ionic liquids but there was no appreciable extraction.

The extraction of Pu(IV) and Am(III) from nitric acid medium by RTIL was investigated by Lohithakshan et al. [82] who employed an acidic extractant HDEHP (Fig. 2).

RTILs used were 1,2-dimethyl-3-propylimidazolium-bis(trifluoromethylsulphonyl)imide (DMPIIM), N-butyl-3-methylpyridinium-bis(trifluoromethylsulphonyl)imide (BMPIM), and 1-hexyl-3-methylimidazolium-bis(trifluoromethylsulphonyl)imide (HMIIM). The distribution ratios for Pu(IV) in different RTILs were in the range between 20.5 and 69 for HDEHP/BMPIM and 0.65–16.2 for HDEHP/DMPIIM at 25 °C. At 21 °C, D values of 7.2–25.2 for HDEHP/HMIIM and 1.47–19.12 for HDEHP/DMPIIM. The distribution ratios for Pu(IV) were substantial but Am(III) showed poor extraction at higher acidity of aqueous medium (1 M HNO_3) whereas at pH = 3, the extraction of Am(III) was improved. Thermodynamic parameters were also estimated by carrying out the extractions at various temperatures.

Selective extraction of Th(IV) was carried out using Cyanex-272 (Bis(2,4,4-trimethyl) pentyolphosphinic Acid; Fig. 2), Cyanex-923 (tri-n-alkyl phosphineoxide), TBP (tri-n-butyl phosphate) and DHOA (di-n-hexyloctanamide; Fig. 10) in an ionic liquid $[\text{C}_8\text{mim}][\text{NTf}_2]$ [83]. The extraction studies proposed a solvation mechanism in the case of extractants TBP and DHOA, whereas, cation exchange mechanism was found to proceed in case of Cyanex-923 and 272. The reaction was energetically favorable but kinetically slow. Oxalic acid showed good results for stripping of extracted thorium.

The extraction of Eu(III) and Th(IV) using bis(chlorophosphoryl)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine (DPO; Fig. 3) [84] was also carried out from nitric acid medium into an IL medium, $[\text{C}_6\text{mim}][\text{PF}_6]$. It was observed that Eu(III) was extracted through solvation mechanism while Th(IV) followed the pathway of ion exchange. The results revealed that the distribution ratio of Eu(III) was not appreciable as compared to Th(IV), proposing this solvent system may be selective for the extraction of Th(IV).

Another ligand system was investigated by Sharova et al. [85] for metal extraction by complexation from acidic and neutral mediums; this ligand system consists of a central nitrogen atom surrounded by tripodal platform to which three CMPO moieties are attached (tris-CMPO; Fig. 3). This extractant showed significant increase in distribution ratio

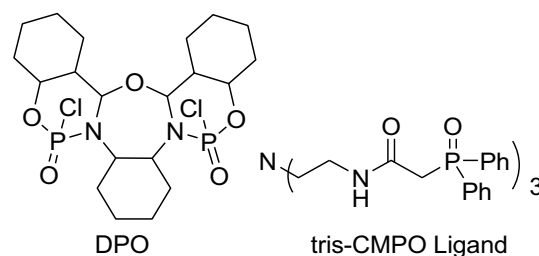


Fig. 3 Structure of tris-CMPO Ligand

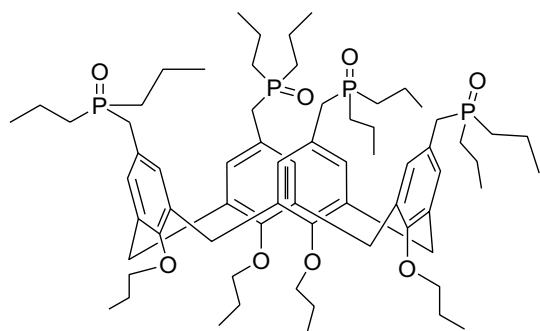


Fig. 4 Structure of phosphorylated calix[4]arenes

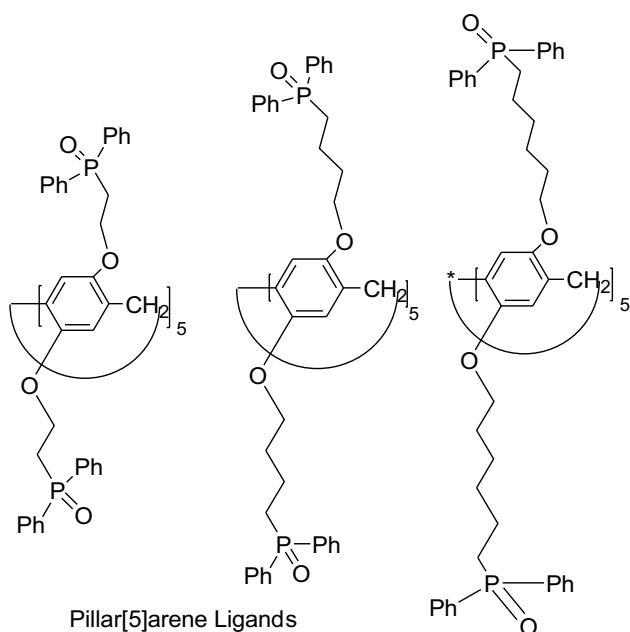


Fig. 5 Structure of Pillar[5]arene ligands

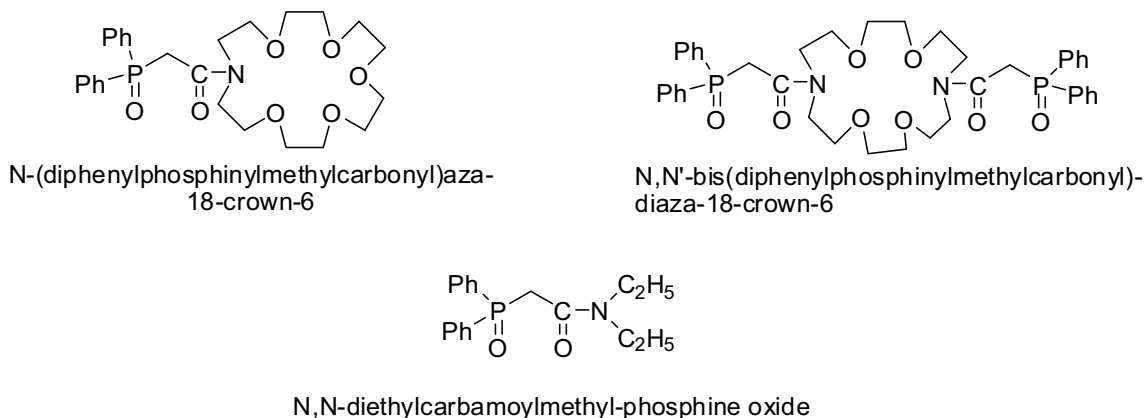


Fig. 6 Structures of CMPO derived ligands

of rare earth metals as compared to similar tripodands with one or two CMPO moieties. The system worked even better with the IL $[C_4mim][NTf_2]$ in 3 M nitric acid medium. The protonation of central nitrogen atom in the acidic media leads to effective extraction of anionic complexes.

Gorbacheva et al. [86] studied the impact of ILs on the extraction of Eu and Am using an upper rim phosphorylated calixarene, 5,11,17,23-tetrakis[dipropylphosphinylmethyl] 25,26,27,28-tetrapropoxycalix[4]arene (Fig. 4). It was shown that this calixarene can extract the metals without the ionic liquid from nitric acid medium to organic phase by forming 1:1 complex with metals. The distribution coefficients were good but the isolation of the extracted metals was insufficient thus rendering this method not suitable for extraction. The results showed that the extraction of Eu(III) and Am(III) increased by the order of twofold and 25-fold respectively when 50% ionic liquid was added.

The extraction of Am(III), Pu(IV), and U(VI) using phosphine oxide functionalized pillar[5]arenes (Fig. 5) in $[C_4mim][NTf_2]$ has recently been reported [87]. The extraction of the actinide ions followed the trend: Pu(IV) > U(VI) > Am(III) at 3 M HNO_3 . The extraction efficiency was related to spacer length. As the spacer length increased, the extraction efficiency was improved. The solvation type mechanism was observed which is not common in the extraction with ILs.

Turanov et al. [88] studied extraction of rare earth metals into an organic phase from nitric acid medium using $[C_4mim][NTf_2]$, and *N,N'*-bis(diphenylphosphinylmethylcarbonyl)-diaz-18-crown-6 as extractant and its efficiency was compared to *N*-(diphenyl-phosphinylmethylcarbonyl) aza-18-crown-6 and diphenyl-*N,N*-diethylcarbamoylmethyl-phosphine oxide (Fig. 6). The concentration of IL in organic phase, concentration of extractant and nitric acid in aqueous phase was considered during the study. The D_{Ln} with the IL was calculated to be up to 1000 as compared to D_{Ln} in some

conventional organic solvents which were up to 0.01, 0.17 and 10 for chloroform, 1,2-dichloroethane and nitrobenzene respectively. A synergistic effect due to a neutral organophosphorus ligand in the organic phase containing IL was reported. The hydrophobic nature of the ionic liquid's anion was connected to this synergistic behavior. This study demonstrates the potential applications of IL impregnated polymeric resins in the extraction of lanthanides from nitric acid medium.

Amide based ligands in ionic liquids

The extraction efficiency of DMDPhOPDA (Fig. 7) (*N,N'*-dimethyl-*N,N'*-diphenyl-1-3-oxapentanediamide for lanthanides and Y in 1,2-dichloroethane from aqueous phase containing ClO_4^- , PF_6^- , and NTf_2^- anions or by DMDPhOPDA in 1,2-dichloroethane in the presence of $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ from HNO_3 solutions was studied. The addition of HPF_6 and HNTf_2 or their salts to the aqueous HNO_3 solution led to an increase in Ln(III) extraction using DMDPhOPDA. The extraction efficiency of ILs having NTf_2^- anion is higher than those having PF_6^- anion for Ln(III). Apparently, with an increase in hydrophobicity of the IL cation a decrease in D value was observed [89].

Extraction and separation behavior of Th(IV) was investigated by Zuo et al. [90] using ILs as organic phase. They used pure $[\text{C}_8\text{mim}][\text{PF}_6]$ for separating Ce(IV) from Ln(III) and Th(IV) in HNO_3 medium. $[\text{C}_8\text{mim}][\text{PF}_6]$ exhibited a D value of 85 for Ce(IV), 15 for Th(IV) and < 1 for Ln(III). The extraction of Th(IV) with primary amine N1923 ($(\text{C}_n\text{H}_{2n+1})_2\text{CHNH}_2$ ($n = 9-11$); Fig. 8) in $[\text{C}_8\text{mim}][\text{PF}_6]$ was studied [91]. The extraction behavior was completely different from that in conventional molecular diluents (*n*-heptane and dichloromethane). Th(IV) was separated from Nd(III),

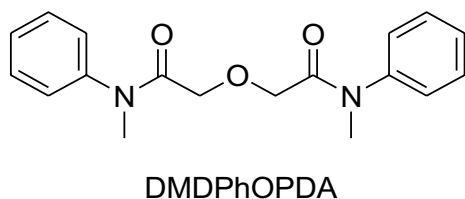
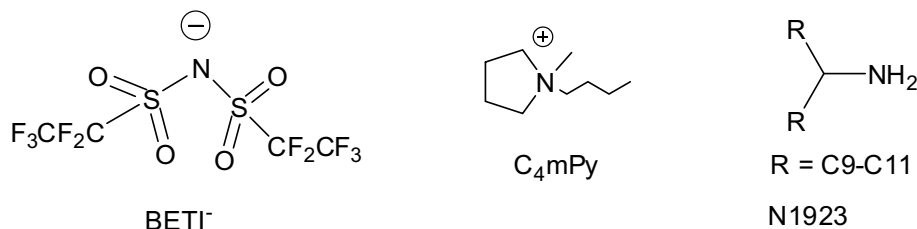


Fig. 7 Structure of DMDPhOPDA

Fig. 8 Structures of BETI, C_4mPy and N1923



Ce(III), Gd(III), La(III), and Er(III) by N1923/ $[\text{C}_8\text{mim}][\text{PF}_6]$ at lower acidity, and metal ions were stripped with citric acid, formic acid, and hydrazine hydrate.

HDEHP in $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 2, 4$) or $[\text{C}_4\text{mPy}][\text{PF}_6]$ (Fig. 8) was investigated by Yoon et al. [92] for the extraction of Ce(III), Sm(III), Dy(III), Nd(III), and Yb(III). A more than three times greater extractability of lanthanides was observed with IL system compared to *n*-hexane system. A higher distribution ratio was found for imidazolium-type IL system than for pyridinium-based IL system. Rout et al. [93] investigated the separation behavior of Am(III) and Eu(III) in HDEHDGA (bis(2-ethylhexyl)diglycolic acid) and HDEHP using $[\text{C}_8\text{mim}][\text{NTf}_2]$ as an ionic liquid. SF values of 150 and 35 were obtained for HDEHDGA and HDEHP, respectively, with 0.05 M ligand in $[\text{C}_8\text{mim}][\text{NTf}_2]$. The use of HDEHP in $[\text{C}_n\text{mim}][\text{NTf}_2]/[\text{BETI}]$ (BETI: bis(perfluoroethanesulfonyl)imide; Fig. 8) exhibited D values of 100–1500 at optimum conditions for various rare earth metal ions by leaving An(III) in the aqueous phase in comparison to that in DIPB (diisopropylbenzene), like in TALSPEAK process [94].

The extraction of Am(III), U(IV) and Pu(IV) in ionic liquid $[\text{C}_4\text{mim}][\text{NTf}_2]$ by a solution of *N,N*-dimethyl-*N,N*-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA; Table 1) using nitric acid was studied [95]. The distribution of the actinides in this system was recorded as a function of parameters such as alkyl chain length of IL, and concentration of IL, nitric acid and solution used. The results showed that extraction was significantly improved with the use of DMDOHEMA in conjunction with $[\text{C}_4\text{mim}][\text{NTf}_2]$. The extraction mechanism of metal ions depended on the nitric acid concentration. Below 4 M nitric acid, the mechanism was cation exchange, anion exchange was responsible above 4 M nitric acid. Also the separation of these metals was done and the separation factor was > 1000 for these metals from many other fission products.

Panja et al. [96] reported extraction of many actinides by using TODGA as extractant in three different ionic liquids, $[\text{C}_n\text{mim}][\text{NTf}_2]$ (where $n = 4, 6, 8$) as the diluents. The distribution ratios of these metals were comparatively high as compared to *n*-dodecane. The D value for Am(III), Pu(IV), and uranyl ion was 157, 10.6 and 5.02 in *n*-dodecane respectively where it rose to as high as 871, 588 and 7.52 when ionic liquid was used. In case of *n*-dodecane, the distribution

of these metals was lowered as the acidity increased but in case of TODGA the distribution of all the actinides was independent on pH of aqueous phase. The proposed mechanism was cation exchange in the extraction with RTILs. The nature of extracted products was also different from that of *n*-dodecane. Complexing agents such as EDTA and DTPA were used in the stripping of metals from loaded organic phase.

Mincher et al. [97] reported the extraction as well as separation of lanthanides and Am(III) in both molecular diluent and RTIL using *N,N,N',N'*-tetrabutylglycolamide (TBDGA) as extractant. The RTIL used was [C₄mim][NTf₂] which showed high extraction efficiency of Am(III) from low acidic concentration whereas the molecular diluent, 1-octanol, showed high efficiency at higher acidic concentrations. This difference was explained by the fact that RTIL extracted ionic nitrate complexes whereas neutral nitrate complexes were extracted by 1-octanol. The distribution ratio for lanthanides from RTIL was recorded up to 50–60 while the *D* value with 1-octanol reached 90. As far as the separation is concerned 1-octanol showed higher separation coefficient as compared to RTIL.

TODGA in [C_{*n*}mim][NTf₂] (where *n* = 2, 4, 6) was used to investigate the extraction behavior of Ln(III) except Pm(III). An unprecedented increase in the extraction efficiency of TODGA in IL compared to isoctane was observed. TODGA showed higher selectivity for the middle lanthanides in the IL systems, whereas, for heavier lanthanides in isoctane. The extraction behavior of [UO₂]²⁺ in aqueous solution using TBDGA (*N,N,N',N'*-tetrabutyl-3-oxapentanediamide) and MBDGA (*N,N,N',N'*-dimethyldibutyl-3-oxapentanediamide) was investigated by Shen et al. [98] in [C_{*n*}mim][PF₆] (*n* = 4, 6, 8). The extraction efficiency of TBDGA and MBDGA was considerably higher in IL systems than in chloroform, especially at lower HNO₃ concentrations (Fig. 9).

Sengupta et al. [99] also compared the efficiency of TODGA in RTIL for the extraction of Am(III) and Eu(III). TODGA showed low efficiency for Eu(III) as compared to Am(III) viz. 1:1 for Eu and TODGA as compared to 1:2 for Am and TODGA. The *D* values for Am and Eu were

32 and 11 respectively at 3 M acidity with the formation constant for Am-TODGA complex to be 4.18×10^8 whereas 3.31×10^8 for Eu-TODGA. The slow kinetics of the reaction was attributed to the high viscosity of the RTIL as compared to other molecular diluents. The formation constant and activation energy for complex formation of Am with RTIL was also measured which was comparatively higher than that of Eu explaining the difference in extraction efficiency.

The extraction of Pu(IV) from nitric acid medium was investigated [100] using TODGA and ionic liquid [C₆mim][NTf₂]. The log *D*_{Pu} increased till 6.5 M acidity then decreased. The highest value for log *D*_{Pu} obtained at 6.5 M HNO₃. The cation exchange mechanism was suggested for this process and thermodynamic parameters were calculated by monitoring the effect of extractant concentration and acidity.

The extraction of Th(IV) and UO₂²⁺ from nitric acid medium by using the extractant TODGA and the ionic liquid alkyl-3-methylimidazolium hexafluorophosphate ([C_{*n*}mim][PF₆], *n* = 6, 8) was also investigated [101]. The results showed that extraction of these metals was higher in this IL system as compared to *n*-dodecane. The *D* values for Th(IV) were around 30 with *n*-dodecane and around 55 when the ionic liquids were used. The increase in *D* values for UO₂²⁺ could also be seen as they rose from around 7–13 by using ionic liquids. The slope analysis suggested that the extraction was increased by increasing acidity of the medium. The ratio for metal ligand complex was 1:2 at lower acidity while it became 1:1 at higher acidity of aqueous phase. Stripping of the metals was also done by sodium salt of EDTA. The thermodynamic studies reported the process as exothermic.

In another study [102] the extraction of Eu(III) was carried out into ionic liquid [C₈mim][NTf₂] and TODGA as extractant. The results were compared to the *D* value obtained in *n*-dodecane by the same extractant. At lower acidity the *D* value by IL was around 1000, whereas that by *n*-dodecane was less than 0.1 but as the acidity increased the *D* value decreased to < 10. The extraction of the Eu(III) was studied as function of different parameters such as Eu(III) ion conc. in aqueous phase, nature of extractant and ionic liquid, concentration of nitric acid and TODGA and phase modifiers etc. The results showed that Eu could be extracted in ratio of 1:3 without leading to undesirable phase formation.

TODGA was used for the extraction of U(IV) in [C₄mim][NTf₂] as well as in the organic molecular diluent, 1,2-dichloroethane [103]. Results showed that the extractability was significantly enhanced when a small amount of ionic liquid was added along with the extractant. This increase in extraction can be explained by partitioning of the NTf₂⁻ anions in both aqueous and organic phases. A similar study was carried out by Boltoeva et al. [104] where extraction of U(VI) was studied using TODGA in [C₄mim]

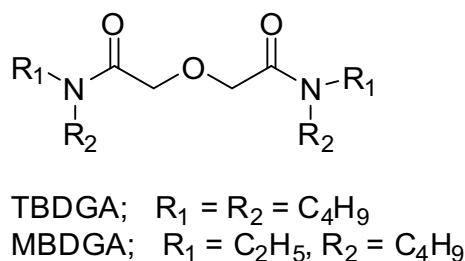


Fig. 9 Structures of TBDGA and MBDGA

[NTf₂] as well as in 1,2-dichloroethane. The study revealed completely different complexation mechanism in presence and absence of IL. The solvation mechanism was observed in dichloromethane whereas; in IL cation exchange mechanism was observed.

Extraction of Np⁴⁺ and NpO₂²⁺ ions into solutions of TODGA in the ionic liquids [C_nmim][NTf₂] (*n*=4, 8) has also been investigated [105]. The extraction of neptunium was relatively higher in [C₄mim][NTf₂] as compared to that in [C₈mim][NTf₂]. Furthermore, the extraction of Np⁴⁺ was much higher as compared to that of NpO₂²⁺ under comparable experimental conditions. The nature of the extracted species was investigated by slope analysis and cation-exchange mechanism was observed for the extraction.

The extraction of trivalent rare earth metals Pr(III), Nd(III) and Dy(III) using TODGA in ionic liquid, triethylpentyphosphonium bis(trifluoromethylsulfonyl)amide [P2225][TFSA] (Fig. 10) is also reported [106]. The results revealed a cation exchange mechanism for this process. The stoichiometry (M:TODGA) observed for metals was 1:2 for Dy, and 1:(2–3) for Pr and Nd according to slope analysis.

A monoamide *N,N*-dihexyloctanamide (DHOA; Fig. 10) in an ionic liquid, trioctylmethylammonium nitrate [107] [N1888][NO₃] was used for the extraction of Pu(IV). The extraction efficiency of this DHOA/[N1888][NTf₂] system was compared with DHOA in a conventional diluent i.e. *n*-dodecane and an IL such as [C_nmim][NTf₂]. DHOA in [N1888][NTf₂] showed excellent extractability for Pu(IV) as compared to *n*-dodecane or [C_nmim][NTf₂]. The *D* value for Pu(IV) in 0.5 M DHOA/[N1888][NTf₂] was < 1 at lower acidity but it increase to > 80 as

the acidity increased to 8 M HNO₃. DHOA was also compared with TBP but the distribution ratio of Pu(IV) was reduced in TBP.

Pathak et al. [108] studied the extraction of Pu(IV), Np(IV) and U(IV) by employing di(2-ethylhexyl)isobutyramide (D2EHIBA; Fig. 10) and different ionic liquids such as [C_nmim][NTf₂] (where *n*=4, 6, or 8). The extraction of these target metals increased gradually with the increase in acidity of the medium. The distribution ratios for U(IV) were ranging from < 10⁻³ to 0.03 and for Pu(IV), 0.002 to 2.12 when the acidity was increased up to 4 M. The extraction of these metals using the same extractant in *n*-dodecane was negligible suggesting that using RTIL can change the extraction behavior of an extractant.

In another study [109] the extraction of Th(IV) was done using *N,N*-dialkyl aliphatic amides containing different alkyl groups viz. dibutyl-3,3-dimethyl butanamide (DBDMBA), *N,N*-di-sec-butyl pentanamide (DBPA), *N,N*-dihexyloctanamide (DHOA), *N,N*-dibutyl-2-ethyl hexanamide (DBEHA) and *N,N*-dibutyloctanamide (DBOA) (Fig. 10). The solvent extraction was done from nitric acid medium into an ionic liquid, [C₄mim][PF₆]. Distribution ratios were significantly higher with the use of ionic liquid as compared to those of *n*-hexane. The *D* values ranged from 0.08 to 13.5 when the concentration of nitric acid was varied from 0.2 M to 4 M. The highest ratio was obtained by DBOA when the acidity was low, and the lowest ratio at low acidity was given by DBEHA. The extraction behavior of RTIL was also different from that in *n*-hexane in terms of kinetics, complex formation and acidity of the medium. Stripping of the extracted specie was done by supercritical carbon dioxide.

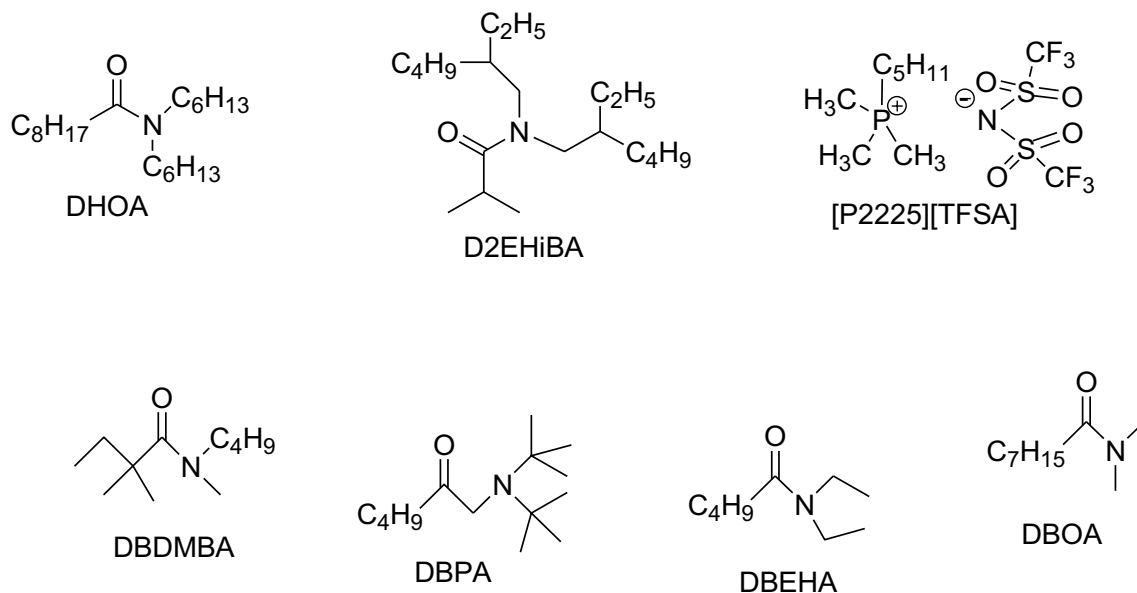


Fig. 10 Structures of various monoamide ligands

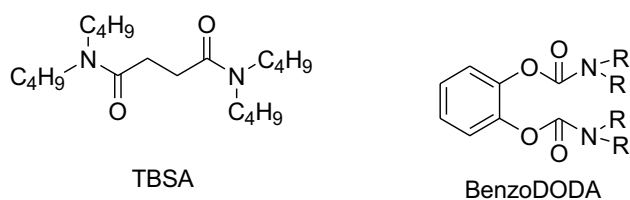


Fig. 11 Structures of BenzoDODA and TBSA

N,N,N',N'-tetrabutylsuccinamide [110] (TBSA; Fig. 11) was investigated for the extraction of Uranyl ions from nitric acid medium into an ionic liquid, $[C_4mim][NTf_2]$. At lower acidities (0.01 M HNO_3), this system showed distribution ratios 20 times larger than that obtained in common organic solvents and the D value for UO_2^{2+} is > 100 and the ratio decreased to < 0.1 when the acidity increased to 1 M HNO_3 . The efficiency was however drastically decreased when acidity of the medium increased further.

Selective extraction of Pu(IV) by bis-(2-ethylhexyl)carbamoylmethoxyphenoxy-bis-(2-ethylhexyl)acetamide (BenzoDODA; Fig. 11) was also reported [111]. The extraction was performed in RTIL $[C_nmim][NTf_2]$ as well as in *n*-dodecane as organic phases. In ionic liquid system the mechanism is cation exchange up to 3 M acidity and anionic exchange above 3 M, whereas, anion-assisted neutral complex formation mechanism was found in *n*-dodecane system. Also the mechanism involves formation of di-solvated specie in RTIL and mono-solvated specie in *n*-dodecane. The results are selective at higher pH values but the selectivity is lost at lower acidities. The distribution values for Pu(IV) in IL with BenzoDODA were around 50 and 58 for HNO_3 and HCl respectively whereas in *n*-dodecane they were < 0.01 and < 10 for HCl and HNO_3 respectively.

A tripodal diglycolamide [112] (T-DGA; Fig. 12) was used in three RTILs viz. $[C_nmim][NTf_2]$ ($n = 4, 6, 8$). These

results were then compared to extraction results of TODGA and it was found that T-DGA gave significantly higher distribution ratios. Similar trend is seen in case of conventional solvents. However, longer equilibrium time was reported for T-DGA which was due to the viscous character of RTIL and slow conformations of T-DGA during complex formation with metals. The distribution ratio for Am(III), when T-DGA was used was 1518 as compared to 208 obtained with TODGA at acidity of 0.01 M. The D_{Am} ratio decreased to 0.6 for T-DGA and 0.25 for TODGA as the acidity was increased to 3 M. Extraction of Pu^{4+} , Sr^{2+} , Cs^+ , UO_2^{2+} , Eu^{3+} and Am^{3+} was studied with this system. Stripping was done up to 99% in three stages when 0.5 M EDTA in 1 M guanidine carbonate was used. The extraction of 1:1 complexed species of Am(III) with T-DGA was reported by slope analysis.

N-pivot T-DGA ligands (Fig. 12) with several substituents on amidic nitrogen and different spacer length between central nitrogen and amide group were investigated in $[C_4mim][Tf_2N]$ for the extraction of several An(III) and Eu(III) [113]. The substituents greatly influenced the extraction efficiency. Highest D value was obtained for ligand having $R_1 = H$ and $R_2 = Octyl$ with spacer length of 2. D_{Am} was around 60 where as D_{Eu} value was 128. Low distribution for U ($D_U = 0.04$) was observed.

Diglycolamide-functionalized calix[4]arenes [114, 115] (Fig. 13) with various modifications in structure were investigated for the extraction of actinides such as UO_2^{2+} , Pu^{4+} , PuO_2^{2+} and Am^{3+} in RTIL $[C_8mim][NTf_2]$. The distribution values for Am^{3+} , Eu^{3+} , UO_2^{2+} , Pu^{4+} , PuO_2^{2+} were ranging from 9.37–748, 143–879, 0.07–0.41, 2.88–6.17, and 0.1–0.60 respectively depending upon the nature of substituent in the ligand. The formation of metal ligand complex was affected by the nature and size of substituents on the extractant calix[4]arenes (C4DGAs), the spacer length and acidity of the medium. Lower acidity favored the metal complex

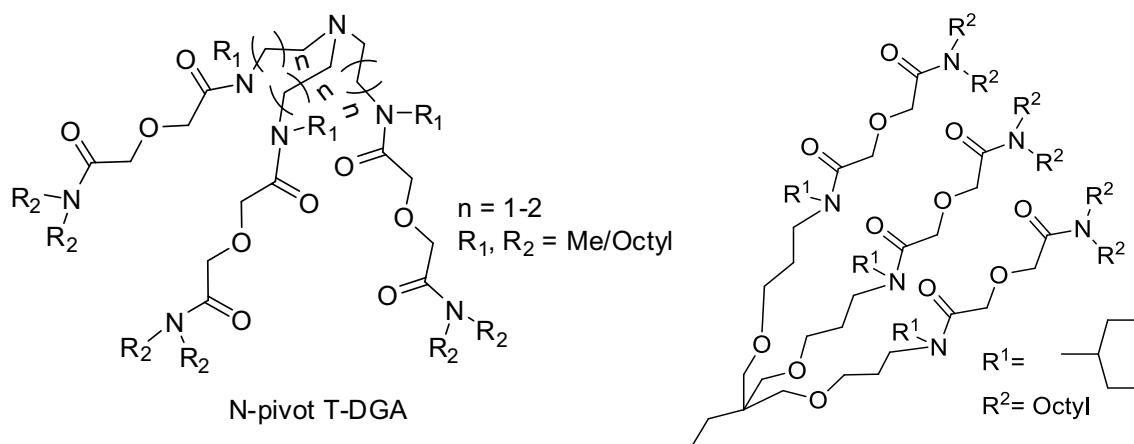
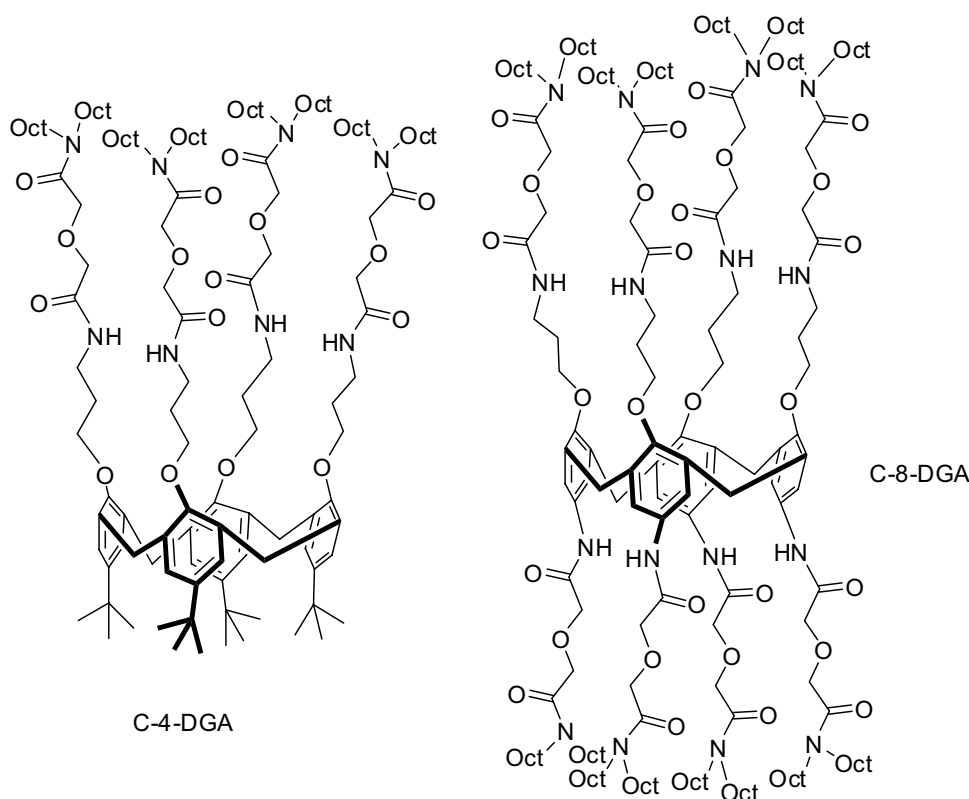


Fig. 12 Structures of *N*-pivot T-DGA and T-DGA

Fig. 13 Structures of C-4-DGA and C-8-DGA



formation whereas the high acidity caused ligand crowding at liganding site, which leads to a reduction in extraction efficiency. Again here the Am(III) showed more symmetrical complex formation with ligands as compared to Eu(III) and hence giving more extraction efficiency.

A solvent system having diglycolamides functionalized on upper and lower rims of calix[4]arene [116] (Fig. 13) in ionic liquid showed high extraction of actinides as well as independent of acid concentration.

More recently two diglycolamide based ligands, CR4-TZ-DODGA and C4-TZ-DODGA, preorganized on resorcin[4]arene cavitand and calix[4]arene platforms (Fig. 14) are reported [117]. In this study selectivity of the ligands toward light, medium and heavy lanthanide cations viz. Eu(III), La(III), and Yb(III) respectively has been studied using *N*-octyl-*N*-ethylpiperidiniumbis(trifluoromethylsulfonyl)imide ([EOPip][NTf₂]) TSIL. More than 98% of Yb(III) and Eu(III) could be extracted in comparison to 18% of La(III) under given parameters. Similar trend and efficiencies have been obtained for both ligands.

Another ionic liquid, trioctylmethylammonium nitrate ([N1888][NO₃]) utilizing *N,N,N',N'*-tetra(ethylhexyl)diglycolamide (T2EHDGA; Fig. 15), DMDOHEMA and CMPO as extractants was also reported [118]. The *D* values using these extractants were < 10 when acidity was low (< 1 M HNO₃) whereas they increased to < 100 for T2EHDGA as the acidity increased (8 M HNO₃) while the *D* values for

DMDOHEMA and CMPO did not show any appreciable increase. T2EHDGA was found to have better extraction efficiency as compared to other two extractants in this particular ionic liquid. This extraction was measured as a function of several parameters such as extractant concentration, aqueous phase acidity, temperature and isomeric forms of extractant. The isomeric forms of extractant had no significantly different effect than T2EHDGA. The analysis revealed a neutral solvation pathway. Stripping of extracted Am(III) was done using dilute nitric acid.

Dipicolinamide extractant *N,N'*-diethyl-*N,N'*-di(para)fluorophenyl-2,6-dipicolinamide (DPA; Fig. 15), [119] was investigated for the extraction of Am(III), Pu(IV) and Eu(III) from nitric acid medium into ionic liquid [C_{*n*}mim][NTf₂] (*n* = 4, 6, 8). The *D*_{Eu} and *D*_{Am} values were recorded from 0.37–9.45 and 1.22–15.5 respectively. The highest *D* value for both metals was obtained by using [C₄mim][NTf₂]. Further when chlorinated cobalt dicarbollide (CCD) was added into this system then the *D* value rose to 15.95 and 12.58 for Am(III) and Eu(III) respectively. This was an efficient solvent system as compared to conventional diluents used.

Other ligands

Several ligands with C=O, N and S donor sites have also been investigated. In a study extraction of Am(III) was done from nitric acid into 1-butyl-1-methylpyrrolidinium

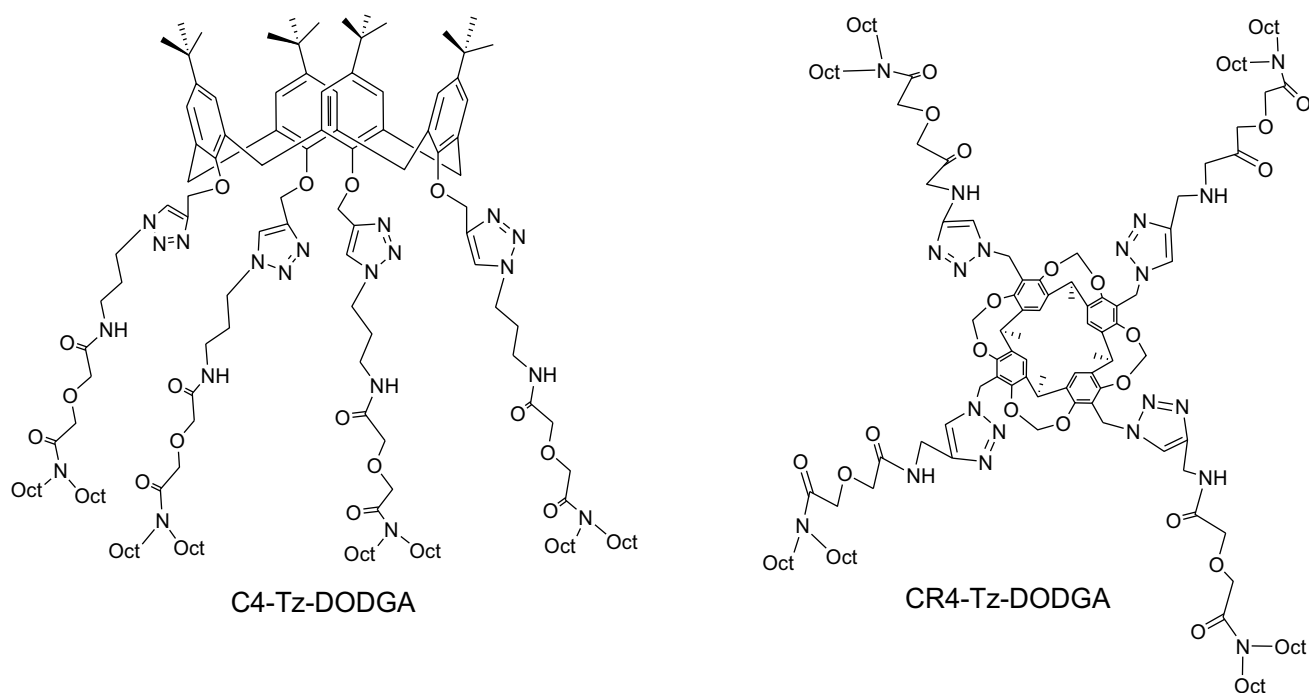


Fig. 14 Structure of C4-Tz-DODGA and CR4-Tz-DODGA

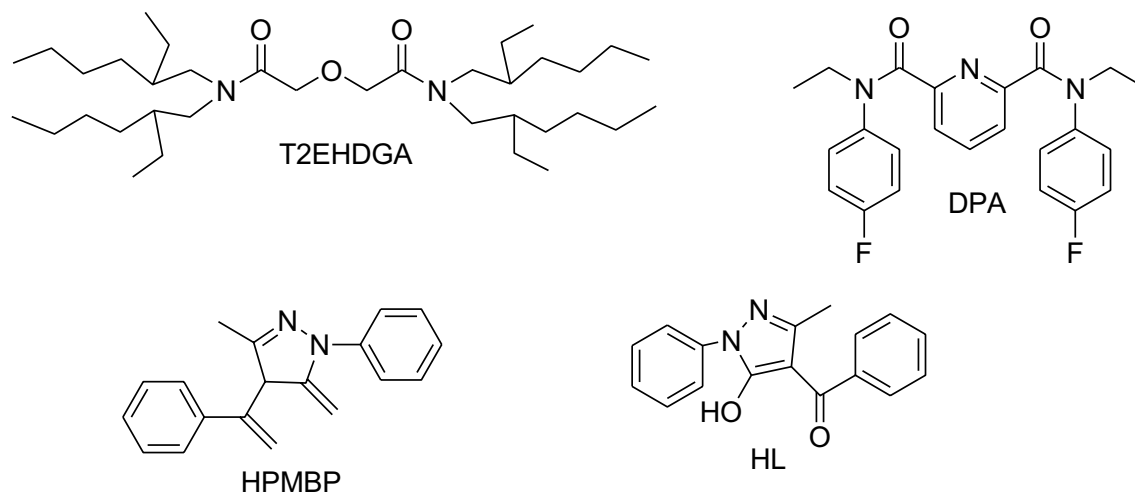


Fig. 15 Structures of T2EHDGA, DPA, HPMBP, and HL

bis(trifluoro-methanesulfonyl)imide ($[C_4\text{mpyr}][\text{NTf}_2]$) ionic liquid using benzoylpyrazolone (HPMBP; Fig. 15) solution as extractant [120]. The distribution ratio of Am(III) in this system was significantly greater than conventional diluent *n*-dodecane and any other diketone based extractant as well. HPMBP was also compared to the MPP (3-methyl-1-phenyl-2-pyrazolin-5-one) from which HPMBP was derived and HPMBP was better than MPP. The *D* value for Am(III) was < 10 at 1 M HNO_3 concentration but it rose to > 1000

when the concentration of nitric acid reached 3 M. The slope analysis suggested that the mechanism for Am(III) extraction in IL and in *n*-dodecane was different.

Extraction of Lu^{3+} , Ce^{3+} , and Eu^{3+} into four ionic liquids of imidazolium family i.e. $[C_n\text{mim}][\text{NTf}_2]$ ($n=4, 6, 8,$ and 10) was also evaluated [121]. The extractant used was 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one (HL; Fig. 15) in addition to CMPO. The studies showed that the $\log D$ values for the lanthanide ions decreased as function of

the 'n' value of IL in the order of hydrophobicity of their cations i.e. $4 > 6 > 8 > 10$. They also studied the effect of para-substituted 4-acylpyrazolone on the extractant and its synergistic effects were discussed.

Zhao et al. [122] investigated extraction of lanthanides (La^{3+} , Eu^{3+} , Lu^{3+}) using a novel extractant, 6-bis(5,6-dihexyl-1,2,4-triazin-3-yl)pyridine (*isohexyl*-BTP; Fig. 16) in ionic liquid, $[\text{C}_n\text{mim}][\text{NTf}_2]$. It was observed by slope analysis that the mechanism was cation exchange at lower acidity whereas it shifted to neutral species extraction at higher acidity. Moreover, the extractant worked better with shorter alkyl chain of the ionic liquid and lower acidity as the extraction efficiency was 80–100% when the acidity was < 0.5 M and it decreased as the acidity increased.

Bhattacharyya et al. [123] attempted to separate trivalent actinides and lanthanides by using ligands such as (bis-(5,6-dialkyl-1,2,4-triazinyl)pyridine (R-BTP; Fig. 16) at room temperature by using an ionic liquid $[\text{C}_n\text{mim}][\text{NTf}_2]$ as the diluent (where $n = 2, 3, 4, 6$ or 8). The D values for Am(III) were very high, 231 and > 2000 , when Me-BTP was used in $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$ respectively. The distribution ratios with Et-BTP were < 3 and with *n*-Pr-BTP were < 1 . A spectacular separation factor of > 3000 for Am^{3+} over Eu^{3+} was reported, which was more than any comparable figure obtained from other molecular diluents.

Jensen et al. [124] studied extraction of lanthanides in ionic liquid $[\text{C}_4\text{mim}][\text{nonafluoro-1-butanefluoroborate}]$ and extractant 2-thenoyltrifluoroacetone (Htta; Fig. 16) in the aqueous medium containing 1 M NaClO_4 . At lower concentration of the extractant, no coordination of lanthanides and extractant was observed however, at higher concentration of extractant, the cation complexes of lanthanides with Htta ($\text{La}:\text{Htta}$) species were observed in the ratio of 1:2 and 1:3 and were thus extracted.

Fu et al. [125] reported the extraction of Th(IV) using same extractant (Htta; Fig. 16) in aqueous medium by adding the ionic liquids $[\text{C}_n\text{mim}][\text{NTf}_2]$ ($n = 2, 4, 6, 8$). Ion chromatograph and slope analysis suggested a neutral complex extraction system. Stripping of the extracted ion was done by supercritical carbon dioxide (CO_2) by monitoring the temperature and pressure of carbon dioxide, polarity and

volume of modifiers and extraction time required for efficient stripping.

The extraction of uranyl ion was also investigated [126] by using six different solvent systems containing extractant 2-thenoyltrifluoroacetone (Htta) and the ionic liquid $[\text{C}_n\text{mim}][\text{X}]$ (where, $n = 4, 6$, or 8 and $\text{X} = \text{PF}_6^-$ or NTf_2^-). The D values for uranyl ion were 2.92 and 2.62 for $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{NTf}_2]$ respectively as compared to 0.23 which was obtained by using xylene. The extraction was studied by varying the solution acidity from lower to moderate pH. The distribution ratios increased with increasing pH leading to a plateau like profile as the pH rose high. These values for D were high as compared to other molecular diluents used. The thermodynamic studies rendered the process as endothermic.

Several sulphoxides with modified structures viz. allyl phenyl sulphoxide (APSO), Benzyl methyl sulphoxide (BMSO), di-hexyl sulphoxide (DHSO), and di-isobutyl sulphoxide (DISO) were used as extractants (Fig. 17) for the extraction of uranyl ions in ionic liquid, 1-Ethyl-2,3-dimethylimidazolium chloride and 1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [127]. These extractants in RTIL were highly efficient for the extraction of target metal as the steric crowding and extended resonance increases the formation of complexes between ligands and uranyl ions. Thermodynamic studies revealed the reaction to be spontaneous, endothermic, and kinetically slow which was due to the viscosity of the liquid. In a recent study [128] selective extraction of uranium using was performed from

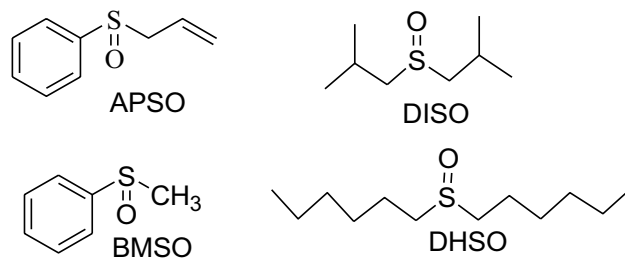
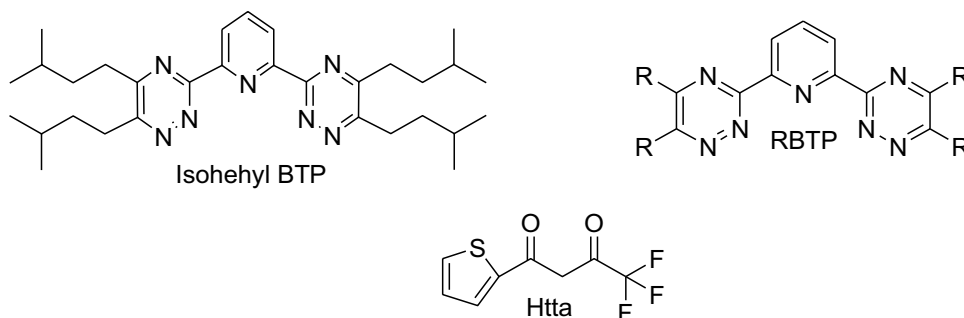


Fig. 17 Structures of Htta and BTP based ligands

Fig. 16 Structures of sulfoxide based ligands



alkaline medium containing 2 M ammonium carbonate. It was found that 15% addition of Aliquat 336 extraction was achieved up to 93% in 30 min.

X, CMPO mounted on Calix[4]arenes, pillar[5]arenes, crown ethers and tris-platforms in IL as organic phase have been investigated. Similarly amide based ligand e.g. mono-amides, malonamides, glycolamides, glycolamides organized on calix[4]arene and tripodal platforms have also been investigated. In general, on addition of IL to organic phase D_M is greatly increased. A maximum of 1040 folds increase on addition of 50% $[C_4mim][NTf_2]$ is reported, where TBP was used as ligand. Slow extraction kinetics is observed in all the cases due to increased viscosity of IL. Another thing being commonly observed is change in extraction mechanism from solvation to ion exchange. Extraction efficiency as a function acidity is investigated and it is observed that IL show maximum extraction at 0.1 M HNO_3 which decreases as acidity is increased. Among the various cations and anions studied for extraction best results are exhibited in $[C_nmim]^+$ cation and $[NTf_2]^-$ anion.

Task specific ionic liquids

In recent years focus has been shifted towards Functionalized Ionic Liquids (FILs) or Task Specific Ionic Liquids (TSILs). In TSILs an extracting moiety is part of IL. The extracting moiety can be incorporated either in cationic or anionic part. These FILs behave both as extracting agent as well as organic phase. Am(III) extraction was studied with Imidazolium-based 2-hydroxybenzylamine, (Fig. 18) with NTf_2 and PF_6 anions. This FIL showed good distribution ratio for Am(III) both in solution as well as in pure form [129]. Phosphoryl bearing quarternary ammonium cations having NTf_2 anions (Fig. 18) achieved two folds higher

distribution ratios for UO_2^{2+} compared to TBP in $[Me_3BuN][NTf_2]$ PUREX process conditions [130]. A FIL, tricaprilmethylammoniumthiosalicylate $[A336][TS]$ (Fig. 18) exhibited D value of more than 1000 for the extraction of U(VI) from natural water. A high SF was observed for U(VI) over Mg(II) and Ca(II) ions [131].

The extraction efficiency of [diethyl-2-(3-methylimidazolium)ethylphosphonate] $[NTf_2]$ ($[ImP][NTf_2]$) in $[C_nmim][NTf_2]$ ($n = 4, 8$) as a function of the HNO_3 was investigated for Am(III), Pu(IV) and U(VI). Lower distribution ratios for Am(III) and U(VI) were observed in $[ImP][NTf_2]/[C_nmim][NTf_2]$ at all nitric acid concentrations. However, a high SF for Pu(IV) was observed compared to other An(III) [132].

In another study a comparison was made between a malonamide based ionic liquid with imidazolium cation and NTf_2 anion (FIL-MA; Fig. 19), with that of the classical N,N' -dimethyl- N,N' -dibutylmalonamide (DMDBMA; Fig. 19). The FIL exhibited a 12 times higher extraction of UO_2^{2+} compared to DMDBMA [133].

In another study [134] an amide based ionic liquid N,N -dioctyl-2-(3-methylimidazolium)-acetamide bis(trifluoromethanesulfonyl)imide ($[DOAIM][NTf_2]$; Fig. 20) was used for the extraction of metals in nitric acid medium using $[C_nmim][NTf_2]$ at room temperature. The extraction as well as separation for Pu(IV) was significantly high at high nitric acid concentration. The extraction of Am(III) and U(IV) was found to be independent of nitric acid concentration. The distribution ratio for Am(III), U(IV) and Pu(IV) were 0.07, 0.015 and 52 respectively. The separation factor of Pu(IV) over Am(III) and U(IV) was 743 and 3466 respectively. This TSIL also showed separation of fission products when treated with high level of liquid nuclear waste.

A glycolamide based FIL (Gly-FIL; Fig. 20) was reported [135] for the extraction of the actinide ions and various

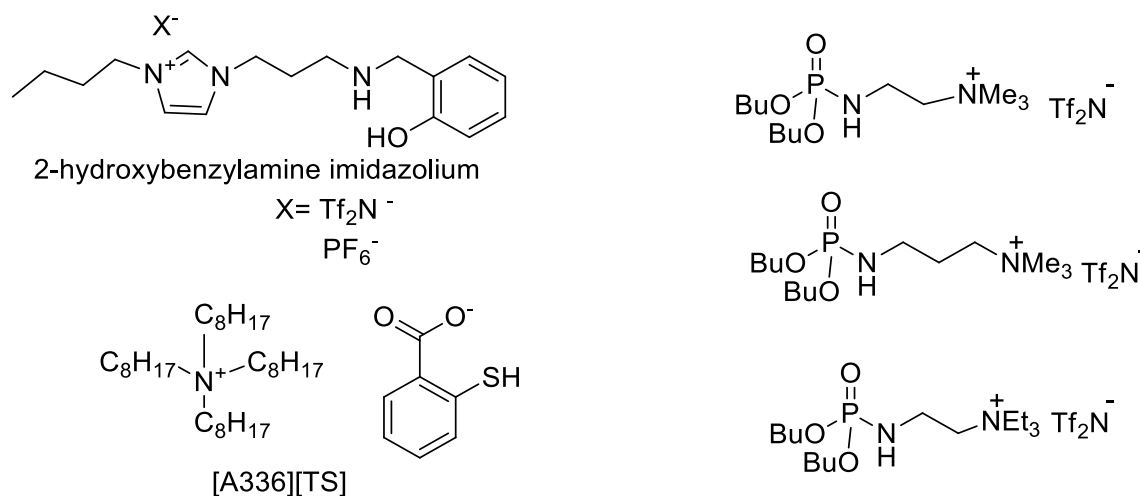


Fig. 18 Structures of phosphoramidate, thiosalicylate and hydroxybenzylamine derived ligands

Fig. 19 Structure of malonamide based ligands

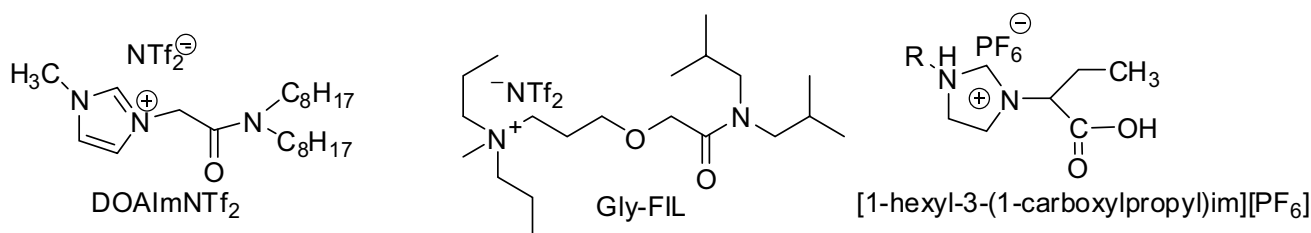
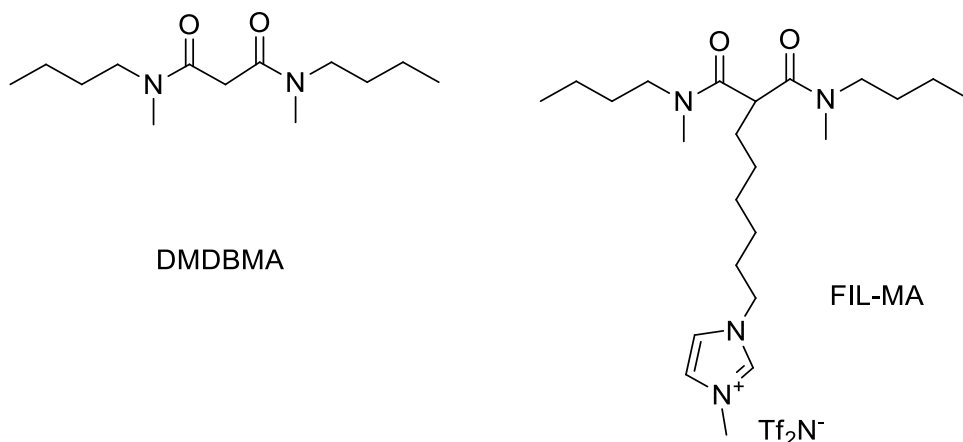


Fig. 20 Structure of monoamide and carboxyl based ligands

fission products such as Am(III), UO_2^{2+} , Pu(IV), Eu(III), Sr(II) and Cs(I) using the said FIL in $[\text{C}_4\text{mim}][\text{NTf}_2]$. The extraordinarily higher extraction of trivalent lanthanide and actinide ions at low acid feed was reported which decreased at higher acidity. The other metal ions such as mono-, bi-, tetra- and hexavalent ions were not significantly extracted. According to thermodynamics studies the reactions were highly endothermic due to dehydration of metal ions before the complex formation. More than 99 percent stripping was done using 2 M HNO_3 .

A hydrophobic ionic liquid [1-alkyl-3-(1-carboxylpropyl) im][PF_6] (where R = butyl, hexyl, octyl; Fig. 20) and its extraction properties were studied in nitric acid medium for the extraction of Y(III) [136]. The extraction was studied by keeping the factors of concentration, pH and temperature in control. It was concluded that this type of TSIL should be used after saponification as the extraction is dependent on acidity. The stripping of loaded organic phase was very easy and over 95% Y(III) was recovered.

Another TSIL containing *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amido structures [IL-TPTNA][NTf_2] (Fig. 21) was synthesized and its extraction behavior towards Eu(III) was reported [137]. The extraction equilibrium was attained in 1 h, and extractability of Eu(III) varied with the pH value. The TSIL showed greater efficiency towards heavier lanthanides, which can be used in the mutual separation of lanthanides in nitric acid solution.

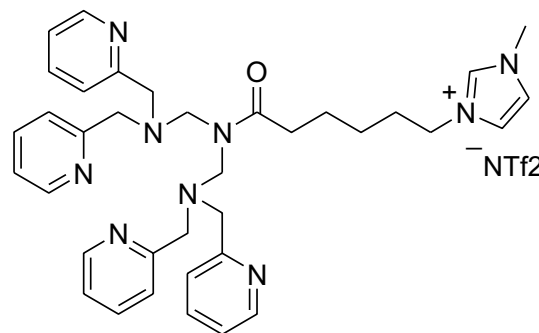


Fig. 21 Structure of [IL-TPTNA][NTf_2]

Extraction of uranyl ions from nitric acid media by two ionic liquids i.e. [Hbet][NTf_2] (Hbet: Betainium) and [TMPA][NTf_2] (TMPA: *N,N,N*-trimethyl-*N*-propylammonium) (Fig. 22) was also reported [138]. The results showed a 62% extraction of U(VI) from 0.01 M HNO_3 to ionic phase [Hbet][NTf_2] but U(IV) was not extracted into [TMPA][NTf_2] phase. This was explained by the complex formation of UO_2^{2+} with COO group of deprotonated betaine (bet).

Mori et al. [139] worked on decontamination of solid wastes from uranium and they used a thermomorphic ionic liquid [Hbet][NTf_2] (Fig. 22) for this purpose. The observations showed that uranium was extracted very efficiently i.e. $D > 1$ at lower acidities even without the addition of an

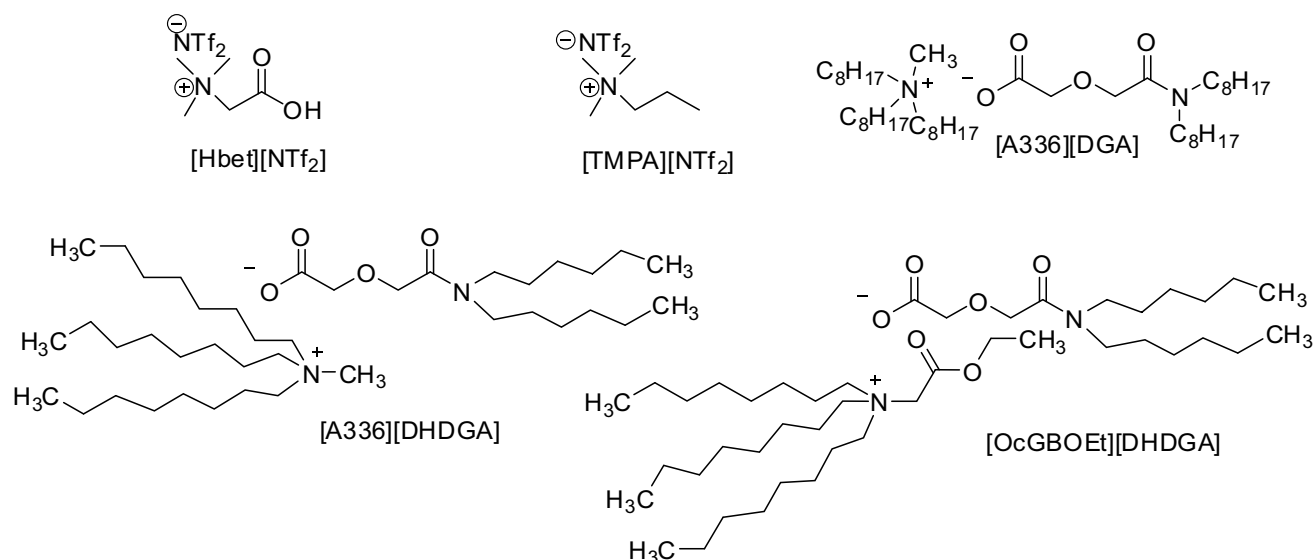


Fig. 22 Structures of Hbet and DGA based TSILs

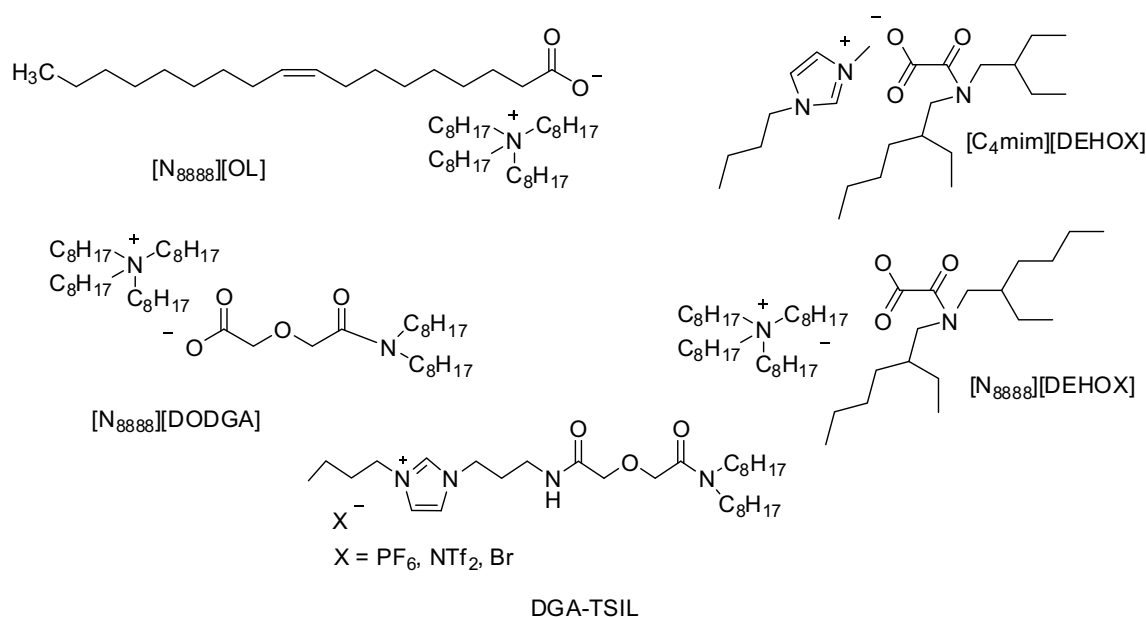
extractant suggesting that this ionic liquid also behaves as an extractant. The complex formation of U(IV) with ligand of the IL was the reason for good extraction. Recovery of U(IV) was also studied by using H_2O_2 . Extraction study of various REEs from nitric acid solution was carried out by using ammonium based TSILs, [140] such as [A336][DHDGA] (DHDGA: dihexyl diglycolamate; Fig. 22) and [OcGBOEt][DHDGA] (OcGBOEt: trioctyl(2-ethoxy-2-oxoethyl)ammonium; Fig. 22). [OcGBOEt][DHDGA] showed extraction efficiency due to the presence of three oxygen donor atoms. The extraction study was performed as a function of various parameters such as extraction time, FILs concentration in organic phase, REEs concentration in aqueous phase, pH of aqueous phase, and temperature. The results showed up to 98% and 87% extraction efficiency of [OcGBOEt][DHDGA] and [A336][DHDGA] respectively. Kinetic studies revealed fast extraction in [OcGBOEt][DHDGA] and 97% metal ions were extracted in 5 min.

Rout et al. [141] investigated extraction of lanthanides particularly Nd(III) from nitric acid media by using FIL trioctylmethylammonium dioctyldiglycolamate, [A336][DGA] (Fig. 22) in a non-fluorinated diluent i.e. trioctylmethylammonium nitrate, [A336][NO_3]. The distribution ratios obtained by extraction were compared to the precursor of this functionalized ionic liquid in same diluent i.e., HDGA in [A336][NO_3]. The results showed that the derived FIL [A336][DGA] gave better extraction results; D value of 28 at 5 M acidity as compared to around 8 when HDGA was used. This extraction was investigated as a function of some parameters such as concentration of the aqueous feed, salting-out agent, and the extractant, pH and temperature.

Thermodynamic parameters, stripping of Nd(III) and reusability of FIL were also studied.

Diglycolamide functionalized TSILs [142] (DGA-TSIL; Fig. 23) were used for the extraction of various actinides such as Pu^{4+} , Am^{3+} , UO_2^{2+} , Np^{4+} , PuO_2^{2+} and NpO_2^{2+} . It was found that extraction efficiency for trivalent ions was one order of magnitude higher than tetravalent ions which consequently was higher than hexavalent ions with the same order of magnitude. The D values were 34, 5.9, 3.5, 0.44, 0.38 and 0.32 for Am^{3+} , Pu^{4+} , Np^{4+} , UO_2^{2+} , NpO_2^{2+} and PuO_2^{2+} respectively. It was also reported that as the acidity of aqueous phase was increased, there was a decrease in the extraction for actinides which supported that an ion-exchange mechanism is responsible for this extraction. The reaction was rendered spontaneous due to negative ΔG values, which also resulted in high D values.

DGA-TSILs were also reported for the extraction of actinides viz. Pu(IV), Np(IV), Am(III), and UO_2^{2+} , lanthanides and fission product ions such as Eu(III), Sr(II), and Cs(I) from acid feed solutions [143]. The extraction efficiency of DGA-TSIL was compared with that of TODGA in *n*-dodecane and in ionic liquids. D value of 2.23×10^3 for Am(III) whereas 1.09×10^4 for Eu(III) was found, which was 11.9 and 42.4 for Am(III) and EU(III) respectively using TODGA-[C_4mim][NTf_2]. In TODGA-*n*-dodecane system D_{Am} and D_{Eu} values were 1.40 and 2.71 respectively. The $SF_{\text{Eu/Am}}$ for TSIL-DGA with PF_6^- and NTf_2^- counter anions values were 8.88 and 4.89 respectively which were double than that were obtained for TODGA in [C_4mim][PF_6], [C_4mim][NTf_2] and *n*-dodecane. Diluted solutions of DGA-TSILs in ionic liquids [C_4mim][PF_6] and [C_4mim][NTf_2] were used for the extraction, due to their lower



DGA-TSIL

Fig. 23 Structures of oxamate, oleate and diglycolamide based TSILs

viscosity as compared with their octyl analogues. The following distribution-ratio trend was obtained; Eu(III) > Am(III) >> Pu(IV) > Np(IV) >> UO₂²⁺ >> Sr²⁺ ≈ Cs⁺. Slope analysis was carried out to determine the nature of extracted species. The extracted species contained two DGA-TSILs molecules along with one nitrate anion.

The potential of DGA-based TSIL was further evaluated for the extraction of metal ions present in the simulated high level nuclear waste [144]. The trivalent lanthanide and actinide ions were selectively extracted along with various co-extracted metal ions such as Pd(II), La(III), Pr(III), Nd(III), Zr(IV), Sm(III), Ce(IV), and Y(III). Relatively higher extraction such as 99, 97, and 45% was obtained for Ce(IV), Zr(IV), and Pd(II) respectively. The higher extraction efficiency for Eu(III) has confirmed the similar mechanism shown by the other DGA based extractants. The distribution ratio values of tri- and tetravalent actinides ions were affected by the presence of various metal ions in SHLW and decreased significantly. In pure tracer at optimum acidity feed Eu(III) and Am(III) showed higher extraction efficiency as compared to those obtained in SHLW. D_{Eu} value was > 10,000 as pure tracer while around 1700 from SHLW whereas, D_{Am} was around 1000 as tracer and around 600 from SHLW. The increased concentration of DGA-TSIL molecules in complexes resulted in increased lipophilicity and thus showed high D values.

The complexation of uranyl ion with DGA-based TSIL having bromide anion was investigated [145] by cyclic voltammetry, solvent extraction and UV/Vis spectroscopic studies. The stoichiometry of the metal:ligand complex was determined by both the techniques and was found to be

1:1 with the formation constant of 1×10^3 . The extraction process was found to follow the conventional ion exchange mechanism often seen with RTIL based solvent systems.

Maria et al. [146] investigated the extraction and selective separation of REEs by using various ammonium and imidazolium based ILs in nitric acid feed solution. This study was carried out using four different extractants viz. [N₈₈₈][DEHOX] (DEHOX: di(2-ethylhexyl)oxamate, Fig. 23), [C₄mim][DEHOX], [N₈₈₈][OL] (OL: Oleate, Fig. 23) and [N₈₈₈][DODGA] (Fig. 23). These TSILs were diluted in toluene and results revealed the all the REEs were extracted up to 100% efficiency by [C₄mim][DEHOX] and [N₈₈₈][DODGA] under various experimental conditions within extraction time of 5 min.

Yun et al. [147] reported a novel Task-specific ionic liquid in which the alkyl chain of the imidazolium cation was bearing a grafted diglycolamide moiety (Fig. 24). These TSILs were used to complex trivalent lanthanide ions from aqueous phase. There was no transfer of lanthanide ions from aqueous phase to RTIL [C₆mim][NTf₂] phase in the presence of TSILs in aqueous phase showing that they are good candidates to retain lanthanides in aqueous phase. Complete stripping of some metals e.g. Lu(III), La(III) and Eu(III)

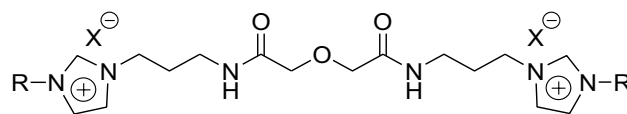
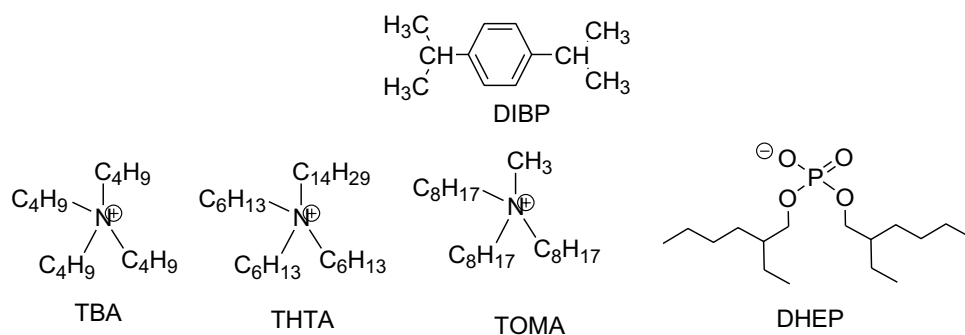


Fig. 24 Structure of Glycolamide grafted Imidazolium TSIL

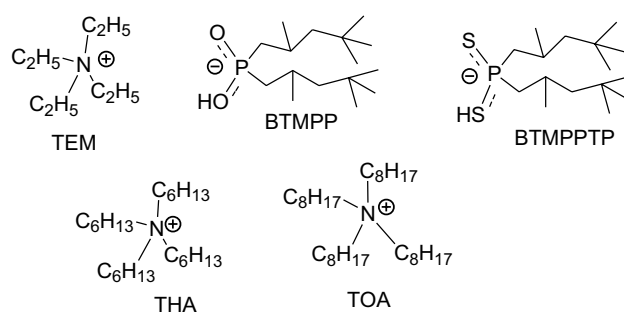
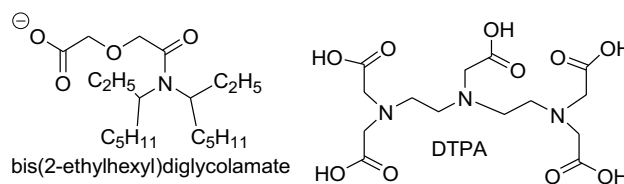
Fig. 25 Structures of DEHP derived TSILs

was observed using these TSILs, while TODGA in $[C_6\text{mim}][\text{NTf}_2]$ was used as organic phase.

Three di(2-ethylhexyl)phosphate (DEHP) based functionalized ILs were studied by Sun et al. [148] for the separation of rare earth metals. They prepared trioctylmethylammonium (TOMA), tetrabutylammonium (TBA), and triheyl(tetradecyl)ammonium (THTA) analogues of DEHP (Fig. 25). The solvent system that was used in this process consisted of diisopropylbenzene (DIPB; Fig. 25) along with di(2-ethylhexyl)phosphoric acid (HDEHP) and $[C_6\text{mim}][\text{NTf}_2]$. They concluded that DEHP-based ionic extractants are more soluble in $[C_6\text{mim}][\text{NTf}_2]$ than in DIPB. Also the distribution ratio for REEs in IL was 6 orders of magnitude higher than in DIPB. The synthesized ionic extractants also showed better $D_{\text{IL}}/D_{\text{DIPB}}$ ratio than HDEHP. The $D_{\text{IL}}/D_{\text{DIPB}}$ ratio for Lu^{3+} was 3.95×10^2 , 6.04×10^6 , and 2.16×10^3 , for $[\text{TBA}][\text{DEHP}]$, $[\text{TOMA}][\text{DEHP}]$, and $[\text{THTP}][\text{DEHP}]$ respectively, whereas it was 1.3 for Lu^{3+} in HDEHP.

An Aliquat-336 based ionic liquid [149] i.e., tri-*n*-octylmethylammonium bis(2-ethylhexyl)-phosphate ($[\text{A336}][\text{DEHP}]$; Fig. 25) was synthesized and its extraction properties for U(IV), Pu(IV) and Am(III) were evaluated. The medium was nitric acid and as the ionic liquid was miscible with *n*-dodecane, it was used in combination with *n*-dodecane and 1 M TBP (tri-*n*-butylphosphate) as well, which made a PUREX solvent. It was observed that D_{Pu} increased initially with an increase in acidity of the medium and the D value of 90 was observed at 4 M HNO_3 followed by decrease in extraction. The distribution ratio of Pu(IV) was found to increase from 20 to 120 by adding ionic liquid in TBP/*n*-dodecane system. On the other hand, D_{U} decreased from 35 to 20 on addition of IL. Am(III) could not be extracted significantly even with ionic liquid and a D value of 0.4 was observed.

Sun et al. [150] synthesized five new functionalized ionic liquids containing cationic part either tetraethylammonium (TEM), tetrahexylammonium (THA), or trioctylammonium (TOA) whereas anionic part was either bis(2,4,4-trimethylpentyl)phosphinite (BTMPP), di(2-ethylhexyl)phosphate (DEHP), or bis(2,4,4-trimethylpentyl)dithiophosphinite (BTMPDTP) (Fig. 26). The FILs

**Fig. 26** Structures of BTMPP and BTMPPTP based TSILs**Fig. 27** Structures of $[\text{A336}][\text{DGA}]$ and DTPA

were used as extractants in ionic liquid $[C_{10}\text{mim}][\text{NTf}_2]/$ bis(perfluoroethanesulfonyl)imide ($[\text{BETI}]$; Fig. 8) for the extraction of rare earth metals.

In another study conducted by Rout et al. [151] the extraction of Eu(III) was studied in ionic liquids tri-*n*-octylmethylammonium bis(2-ethylhexyl)diglycolamate ($[\text{A336}][\text{DGA}]$; Fig. 27) and tri-*n*-octylmethylammonium bis(2-ethylhexyl)phosphate $[\text{A336}][\text{DEHP}]$ and their precursors as well in different molecular diluents as a function of some parameters such as nature of diluent, pH and concentration of ionic liquid. The extraction of Eu(III) was dependent on the nature of diluent and as the carbon chain length increases the distribution coefficient decreases. Also the distribution of Eu(III) increased in the ionic liquids as the pH increased and it was significantly higher at $\text{pH} > 2$. The separation factor for Eu(III) and Am(III) remained constant at all pH values. Diethylenetriaminepentaacetic acid (DTPA; Fig. 27) was also used to separate Am(III) and Eu(III) and SF increased with the increase in concentration of DTPA but

after a certain concentration i.e. 10^{-4} M, it started decreasing. These new ionic liquids showed good separation of target metals in conventional molecular diluents.

In another study [152] extraction of rare earth metals from nitric acid medium by using bi-functional ionic liquid extractants (Bif-ILEs) such as trialkylmethylammonium[di(2-ethylhexyl)phosphate] ([A336][P204]) and [trialkylmethylammonium][di(2-ethylhexyl)orthophosphinate] ([A336][P507]) (Fig. 28) in *n*-heptane was investigated. The extraction efficiency was quite significant and was found to be 100% for La and above 80% for Eu. The studies depicted that these bi-functional ionic liquids are suitable to extract heavy metals in nitrate medium and light metals in chloride medium. The *SF* values in chloride media, using [A336][P507] as extractant were Sm/Nd (4.70), and Nd/Pr (9.52). Whereas in nitrate medium, by using extractant [A336][P204], the *SF* values were Yb/Tm (7.92), Tm/Er (3.36), and Lu/Yb (8.55).

Li et al. [153] synthesized a pyridine based TSIL viz. 1-dibutylphosphorylpropyl-3-pyridine bis(trifluoromethanesulfonyl)imide ([Phos-C₃-Pyr][NTf₂]) (Fig. 29) to extract uranyl ion from acidic medium. This was synthesized by introducing tri-butyl phosphates (TBP) functional structure in cationic part of the TSIL. The *D* value for U(VI) rose from 0.7 to 17 as the concentration of nitric acid was increased from 0.1 to 5 M. The results showed that this TSIL provides excellent results for the extraction of uranyl ions from acidic medium as the extraction rate and distribution ratios can be obtained more than 90% and 10 respectively.

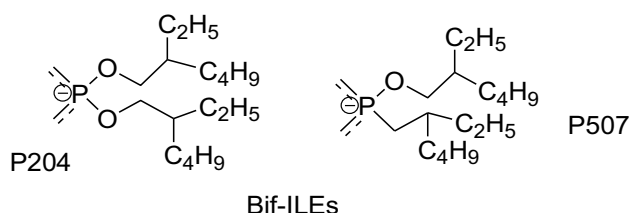
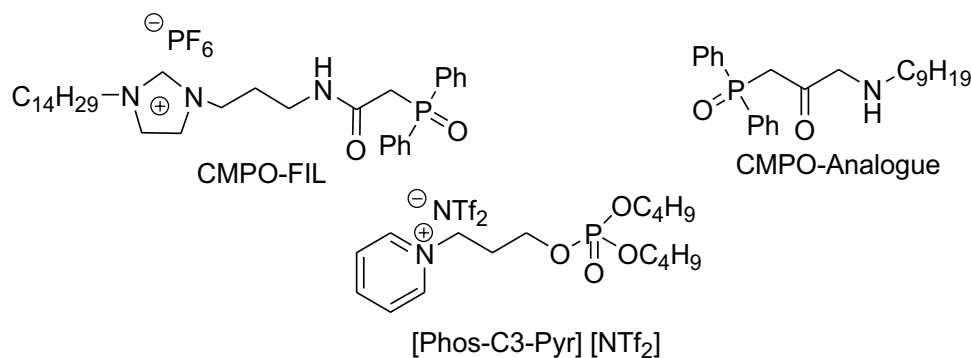


Fig. 28 Structures of Bif-ILEs

Fig. 29 Structures of phosphoryl and CMPO Ligands



Turanov et al. [154] investigated extraction of uranium, thorium and other lanthanides from nitric acid medium into organic molecular diluents with the help of FIL, 1-[3[[[(diphenylphosphinyl)acetyl]amino]propyl]-3-tetradecyl-1H-imidazol-3-ium hexafluoro-phosphate. This CMPO-FIL (Fig. 29) depicted better extractability for lanthanides than its non-functionalized analog, diphenylphosphorylacetic acid-*N*-nonylamide. This difference can be attributed to the partitioning of this FIL between the aqueous and organic phases. The distribution ratio for lanthanides when simple CMPO was used was 0.3 and rose to around 3 when it was functionalized to give CMPO-FIL and further rose to nearly 8–10 when ionic liquids such as [C₄mim][PF₆] or [C₄mim][NTf₂] were added.

In another study [155] a novel TSIL, diethyl-3-(3-butylimidazolium)propylphosphoramidate bis(trifluoromethanesulfonyl)imide ([BuImPA][NTf₂]) (Fig. 30) was synthesized and used to extract Am(III), U(IV), and Pu(IV) from nitric acid media into a RTIL, [C₄mim][NTf₂]. The extraction was carried out as a function of various parameters such as extractant conc., alkyl chain length of imidazolium group of RTIL, temperature and conc. of nitric acid. The results showed that the extraction of Pu(IV) was increased with increase in the acidity up to 5 M and then turned into a plateau. On the contrary the extraction of U(IV) showed a decrease and the extraction of Am(III) was negligible.

The solutions of CMPO based task specific ionic liquid with PF₆[−] and NTf₂[−] counter in room temperature ionic liquids RTILs such as [C_{*n*}mim][PF₆] and [C_{*n*}mim][NTf₂] were reported [156] for the extraction of actinides and lanthanides from 3 M HNO₃ solutions. The extraction kinetics for the CMPO-TSIL (Fig. 30) decreased with the increase in alkyl chain length and followed the order [C₄mim][NTf₂] > [C₆mim][NTf₂] > [C₈mim][NTf₂] which suggested that the metal ion extraction is based on cation exchange mechanism. Both CMPO task specific ionic liquid showed lower extraction for Am(III) and Eu(III), while CMPO-TSIL with NTf₂[−] ion showed significantly larger extraction of UO₂²⁺ and Pu⁴⁺ than CMPO in [C₄mim][NTf₂].

Fig. 30 Structures of CMPO and phosphoramidate based TSILs

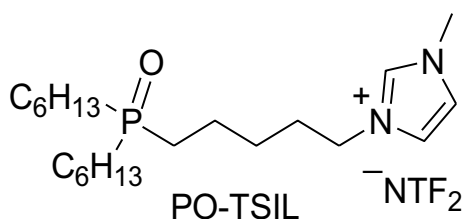
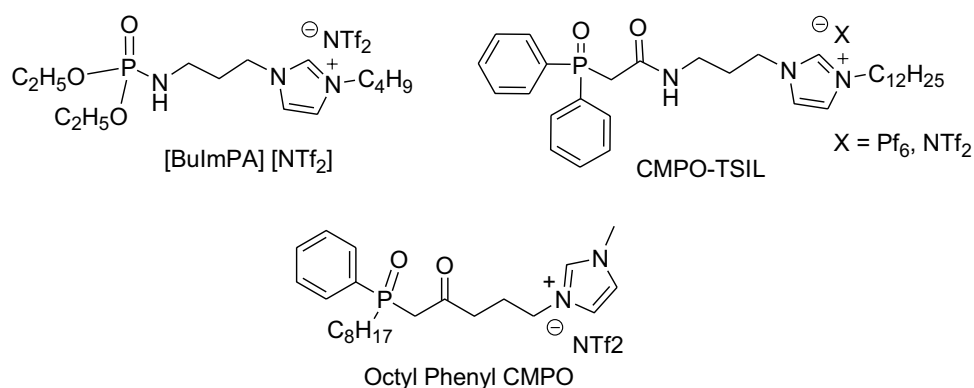


Fig. 31 Structure of PO-TSIL

More recently extraction of U(VI), Eu(III) and Am(III) was studied using octylphenyl-CMPO TSIL (Fig. 30) dissolved in the ionic liquid [C₄mim][NTf₂] [157]. A little amount of ligand (0.01 M) exhibited a *D* value of 209 for U(VI) at 1 M HNO₃. The *D* value decreases as the acid concentration (HNO₃ or HClO₄) increases and reaches to 18 at 7 M HNO₃. The nature of the acid has an influence on the separation factor between U(VI) and Eu(III). Metal ions are extracted via a cation exchange mechanism.

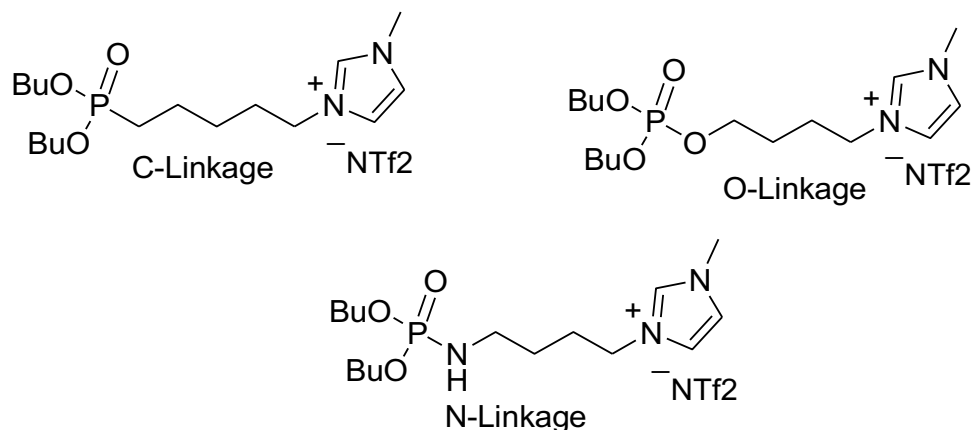
A trialkylphosphine oxide functionalized IL [158] (PO-TSIL; Fig. 31) with a NTf₂⁻ counter ion was evaluated for the extraction of actinide ions such as UO₂²⁺ and Pu⁴⁺ from acidic feed solutions using RTILs viz. [C_{*n*}mim][NTf₂]

(where, *n* = 4, 8) as the diluents. The extraction data were compared with those obtained with tri-*n*-octylphosphine oxide (TOPO) in the same set of RTILs. The extracted species following a cation-exchange mechanism were analyzed by the conventional slope analysis method.

In another study the influence of the linking group between the phosphoryl and bridging moieties in phosphoryl containing TSILs (Fig. 32) on the extraction of uranyl ions was investigated [159]. Theoretical studies were also conducted to determine complexation phenomenon. In this study phosphoryl group was linked to imidazolium cation through different linking groups i.e. carbon, oxygen and nitrogen. The amine group based TSIL exhibited highest extraction efficiency for uranyl ion compared to other phosphoryl-based TSILs. A *D* value of around 5000 was observed.

Biswas et al. reported trioctylmethylammonium hydrogenphthalate (TOMAHP; Fig. 33) as a TSIL [160]. TOMAHP TSIL was evaluated for extraction of lanthanides, actinides and transition metal ions such as U(VI), Th(IV), La(III), Nd(III), Y(III), Fe(III) from HNO₃ acidic aqueous solutions at different pH values. The carboxylic group present in TOMAHP acts as a functional group for the binding of metal ion. TOMAHP has shown better extraction of U(VI) than the

Fig. 32 Structures of phosphoryl based TSILs with different connecting atoms



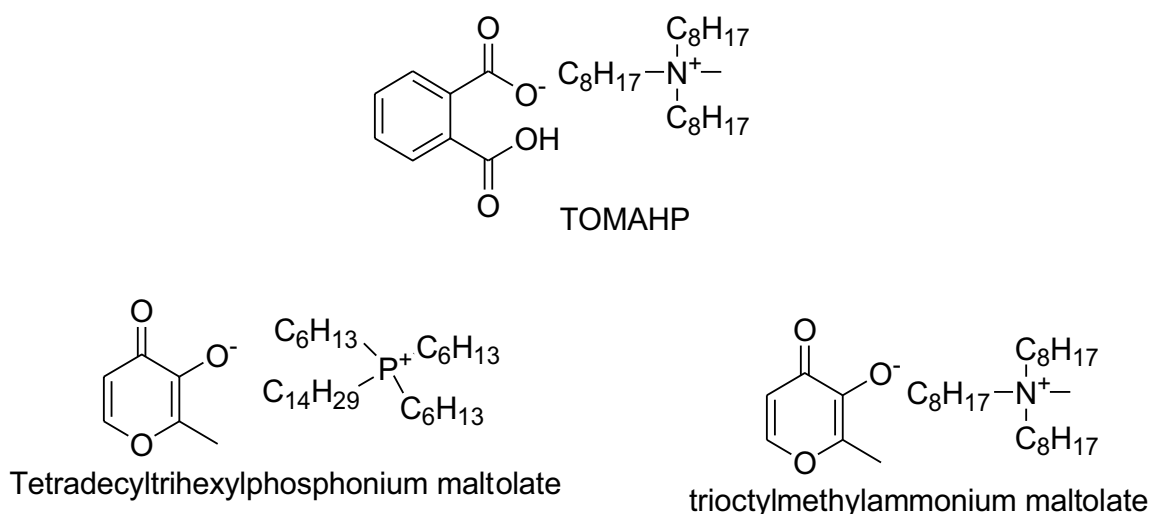


Fig. 33 Structures of phthalate and maltolate based TSILs

other metal ions in the following order: U(VI) > Th(IV) > Fe(III) > Y(III) >> Nd(III) > La(III). Selective extraction of U(VI), Th(IV) and Fe(III) was carried out very efficiently.

The extraction of various radionuclides viz. ²³⁸U and ²³⁴U, ²³⁴Th, ²²⁶Ra, ²¹⁰Pb and also its descendants ²¹⁰Bi and ²¹⁰Po was carried by platzer et al. [161] using maltolate based room temperature TSILs namely Tricaprylmethylammoniummaltolate and tetradecyltrihexyl-phosphonium-maltolate (Fig. 33). The TSILs exhibited high extraction efficiency towards these radionuclides due to their high affinity for various metal ions. Both of these ionic liquids completely extracted the uranium using various acidic feeds, and pH of solution has no effect the extraction of U(VI).

In summary, all classes of ligands used for extraction of Ln/An have been modified to TSILs. If we compare the extraction ability of various classes of TSILs glycolamide based TSILs exhibit highest distribution ration followed by maolonamides and then CMPOs. As it was described in previous section, on addition of RTILs to organic phase increases the distribution ratio for metal ions; modification to TSIL further enhances it. However, due to increased viscosity the extraction time increases in the same order. Another drawback is the low efficiency at high nitric acid concentration. Properly designed TSILs having low viscosity can be very effective as utilizing small amount of ligands metal ion can be extracted efficiently.

Solid phase extractants used in ionic liquids

There are a few examples where solid phase sorbents have been developed and used in combination with ionic liquid for extraction of metal ions. Gujar et al. introduced the extraction chromatographic resins [162] for the extraction

of actinides/lanthanides using TODGA as extractant in [C₄mim][NTf₂] ionic liquid. Three series of resins were prepared where in first series fractions of TODGA were kept 10–30% (w/w) in resins, and the fraction of IL (10% (w/w)) was constant. In the second series, the fraction for IL was varied (10–30% (w/w)) whereas the fraction for extractant was kept constant (10% (w/w)) and in the third series both the IL and TODGA had varying fractions (10–30% (w/w)). The loading of Eu(III) increased from 8.74 mg/g to 23.66 mg/g when the TODGA concentration was increased from 10 to 30% but there was no change in loading of the metal when the concentration of ionic liquid was increased. The distribution coefficients showed that trivalent *f*-elements showed selective sorption over hexavalent *f*-elements over a wide range of pH i.e. 0.01–6. This showed that concentration of ionic liquid is not important in case of solid phase extraction chromatographic resins.

In another study Gujar et al. used several diglycolamide ligands to extract Am(III) and Cm(III) from nitric acid medium to ionic liquid. The ligand (TEDGA) and the IL ([C₄mim][NTf₂]) were thoroughly mixed in methanol, and solid support (Chromosorb-W) was added to it. The ligand was impregnated on this solid support and the metal uptake was studied for this process [163]. The maximum capacity for metal uptake was estimated to be 20.05 ± 0.73 mg/g. Another finding of this study was that the *D* value increased as the carbon number of the alkyl substituent increased up to 4 then decreased as the carbon number increased further, thus deducing that tetrabutyl-DGA was most efficient in extraction of metals Am(III) and Cm(III). Separation factor *D*_{Cm}/*D*_{Am} was also > 1 by using these substituted diglycolamides in ionic liquid.

In another extraction chromatography done by Gujar et al. [164] the extractant ligands as well as the IL was

impregnated on the Chromosorb-W (inert solid support). The extractants used were tripodaldiglycolamide (T-DGA) and diglycolamide-functionalized calix[4]arene (C4DGA) which were dissolved in RTIL [C₄mim][NTf₂]. The sorption of the metals on the surface by using C4DGA and T-DGA was 2 and 3 times greater than TODGA, when 10% of each was impregnated on the surface. The K_d values were also > 10 times when 50% of each of these three extractants were used rendering C4DGA and T-DGA better extractants than TODGA. Also by the addition of IL the sorption increased by 5 times proving that presence of ionic liquids has enhancing effects on the extraction of the metals. The selectivity of resins for actinides was noticeable as distribution coefficients showed selective sorption of Am(III) on these resins as compared to Eu(III).

Solid phase extractants were prepared by immobilization of phosphonium ionic liquids on polyacrylonitrile (PAN) fibers through non covalent linkage. These diphenyldiisobutyl-CMPO (Ph₂iBu₂CMPO), containing extractants were investigated for the extraction of Pu(IV), U(VI), and Eu(III) and 99% of the metal was extracted [165]. Carbon nanotubes based CMPO-modified FILs were used as solid phase sorbents to give high *D* values of Eu(III), Am(III), Pu(IV), and U(VI) [166].

Recently Paramanik et al. [167] reported separation of U(VI) and Pu(IV) from nitric acid medium by polymeric material XAD-7 impregnated with a trialkylphosphineoxide functionalized TSIL (PO-TSIL; Fig. 31). An increase in sorption of both Pu(IV) and U(VI) was observed with increase in IL in resin. However, beyond 435 mg/g concentration no effect was observed. This impregnated resin exhibited high selectivity for U(VI) and Pu(IV) over other metals. Separation of uranium and thorium was performed in nitric acid medium using anion exchanged extractant [A336][Cl] through solid phase extraction [168]. The supporting material was Chromosorb-W having mesh size 60–80. The trimethyloctylammonium chloride was impregnated on Chromosorb-W to prepare chromatographic resin. The study focused on Th/U separation, and trace conc. of Th(IV) can be separated from Uranium by using resin column. The loading capacity for the sorption was found to be 29.12 per gram. The uptake mechanism was found to be anion exchange, as increase in sorption was observed with increasing conc. of acid.

Radiation stability of ionic liquids

For ILs to be efficient in nuclear fuel reprocessing, it is desired that the radiations generated by decaying nucleotides do not deteriorate them and affect their extraction. Ionic liquids undergo radiolysis on exposure to ionizing radiation, producing radiolytic fragments and excited species.

Extensive study of the radiolytic stability of these ILs and extractants is required to use them in most efficient way. Several studies have been carried out in this regard.

In a study of effect of gamma radiation on [C₄mim][PF₆] significant radiation damage was done to the [PF₆⁻] anion and *n*-butyl group went through chemical scission [169]. Pulse radiolysis of [C₄mim] salts under different conditions was also studied [170]. The results showed that it decays through radical–radical reactions, it gets reduced easily and form adducts. The radiolytic stability of [C₄mim][PF₆] and [C₄mim][NTf₂] was investigated under gamma radiation. Initial step of [C₄mim] radiolysis showed the loss of the Bu· and H· radicals from the butyl and from the 2 position on the imidazolium ring respectively. Recombinations of these primary products of radiolysis produced acidic and polymeric species [171]. Radiolytic degradation studies on [C₄mim⁺] cation containing [NTf₂⁻], [PF₆⁻] or [BF₄⁻] anions was also investigated at a radiation dose of 2.0 MGy. The results showed that the primary products of radiolytic degradation of anions and cations can form which can react to form more products showing involvement of complex pathways for irradiation doses. Despite these degradations, quantitative results showed that ionic liquids have radiochemical stability in the same range as the systems which are used in reprocessing of nuclear fuel [172]. The radiation stability of [C₄mim][BF₄] was compared with [C₄mim][PF₆] and less degradation was observed for the former IL [173]. Results showed that radiation cause small change in anion BF₄⁻ but it causes destruction of alkyl chain and dissociation of H atoms from imidazolium ring.

The radiation stability of phosphonium based ILs was investigated by Howett [174], where phosphonium-based ILs in water/ILs system was exposed to gamma radiation for several days. Very little change in terms of radiolytic degradation was observed even in the steady-state γ -radiation fields. In another study during irradiation of CMPO it was observed that the degradation products were different in different conditions using the same radiation source and that the extraction efficiency of CMPO was depending upon the nature of products formed after radiolytic degradation. The presence of nitric acid and oxygen resisted the degradation process [175].

A comparative radiolytic stability of thiazole, 1,2,4-triazol and 1-benzyl was investigated. These cations were irradiated with electron beam of 2.5 MeV. 1-benzyl and 1,2,4-triazol shows that benzyl radicals are eliminated from their adducts whereas no such radical is produced from thiazole due to its stabilization as dimer radical cation [176]. Shrokk et al. [177] demonstrated that 1-benzylpyridinium shows good resistance towards radiation due to delocalization of electrons in π -electron sandwich dimers which are found in the dimer radical cations. Fragmentation and loss of benzyl arms is greatly reduced by these delocalized electrons

thus presenting them as a very suitable option for the reprocessing of nuclear fuel. Ilawe et al. [178] computed the radiation and chemical stability of 42 different cations and anions. They stated that the stability of anion is dependent on electronegativity and ion size whereas the cation stability is related to branching and constituent alkyl chain. Shkrob et al. [179] studied the intermediates generated during the photoionization of ionic ligands consisting phosphonium, imidazolium, pyrrolidinium and ammonium cations having various anions. It was found that C-centered radicals were found in chains of ammonium, phosphonium and pyrrolidinium cations but not in the case of imidazolium. These alkyl radicals then compete with anions for electron transfer. The dissociation of anion is negligible.

In an extraction study of Am(III) using several C₄DGAs in [C₈mim]NTf₂ before and after irradiation a 49–72% decrease in extraction efficiency of Am(III) was observed on radiation exposure of 500 kGy, which was further decreased to 35–50% when radiation dose was increased to 1000 kGy [180].

Conclusions and outlook

Malonamides and Glycolamides based ligands are suitable for the co-extraction Ln(III) and An(III) exhibiting high distribution ratios however, they lack selectivity. Some thiophosphinic acids show selectivity for An(III) but only at low acidity of aqueous phase. Recently some nitrogen donor ligands have been developed showing selectivity for An(III).

High distribution ratios have been achieved using RTILs as extraction medium at low acidity compared with molecular diluents. A lot to be improved for RTILs like their efficiency at high acidity, cost effectiveness, equilibration time and selectivity for a certain metal. A large number of TSILs containing functionalities of some suitable molecular extractants e.g. glycolamides, malonamides and acid functionalities have also been developed successfully. TSILs due to much higher *D* values possess low discrimination between Ln(III) and An(III). The radiolytic stability of ILs is almost similar to that of molecular extractants, however properly designed cations and anions can improve radiolytic stability of ILs.

The challenges in processing of nuclear waste are quite clear however, properly designed extractants with desirable properties viz. optimum extraction ability at high acidity, selectivity for Ln(III) or An(III), in line with CHON principle, radiolytic stability and economic viability are still lacking. Thus further research in designing ILs having acceptable distribution ratio, selectivity for specific metal ion, low viscosity and high radiolytic and chemical stability is required.

Compliance with ethical standards

Conflict of interest The authors have no conflict of interest.

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