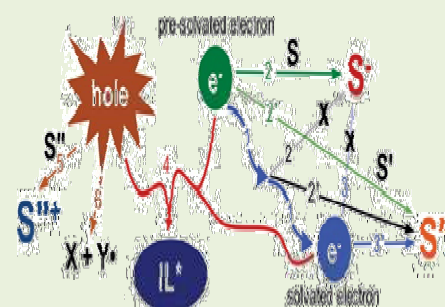
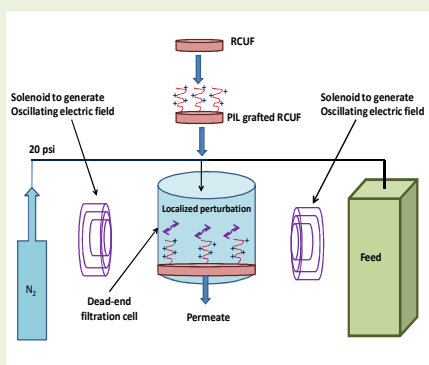
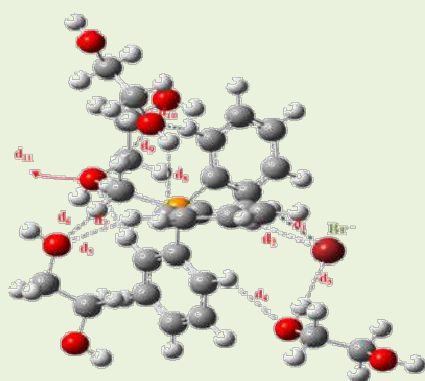




Ionic liquids and Deep Eutectic Solvents in Separation Science



Editors: Arijit Sengupta, Sumit Kumar, S Jeyakumar

Message Editor, ASSET



S. Jeyakumar

Greetings to all the members of ASSET.

This bulletin is conceptualized as a part of the BRNS one day theme meeting on “Ionic Liquids and Deep Eutectic Solvents in Separation Science”.

There is a tremendous attention towards the application of Room temperature ionic liquids (RTIL) in several areas with a view to practice Green and sustainable chemistry. Environmental concerns with many hazardous solvents can be reduced significantly with the use of RTILs. Ionic liquids (IL) are being investigated as possible substitute to molecular diluents in solvent extraction and other separation processes. In nuclear industry, there is a growing interest in using the RTILs for nuclear fuel reprocessing. It is well recognized that ionic liquids often display unique and usually unusual extraction behavior, when used as solvent medium.

Deep eutectic solvents (DES) were introduced as an alternative to ionic liquids (IL) to overcome the drawbacks of IL solvents. From their discovery deep eutectic solvents (DESS) have evolved into a wide range of fluids that are finding application in numerous fields such as, extraction, electrodeposition, etc. They can be hydrophobic or hydrophilic and even non-ionic. They have been found to be, in many cases, heterogeneous.

The necessity of advanced ionic liquids for nuclear fuel cycle applications was described in the first article by Prof. K.A. Venkatesan. The second article by Prof. Tamal Banerjee and Dr. Nikhil Kumar explained the dearomatisation and desulphurization using Deep Eutectic Solvents as extractants from petroleum fuels. Dr. Apurav Guleria and Dr. S. Adhikari described the radiochemical studies of RTIL and Deep Eutectic solvents and their applications in nano materials synthesis in an article. Dr. Arijit Sengupta reviewed briefly the role and applications of RTIL in separation science in the fourth article whereas Dr. Ruma Gupta justified the use of green solvents viz. ionic liquids and deep eutectic solvents in nuclear industry in the last chapter.

I sincerely thank all the authors who have kindly consented to our request to contribute their articles in the Special Bulletin of ASSET. My special thanks to Dr. Sumit kumar, Secretary and Dr. Arijit Sengupta for their kind support. I am sure that the articles are informative, interesting and beneficial to all the readers.

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Message
President, ASSET



Dr. P. K. Pujari

Chairman, Organizing Committee

Association of Separation Scientists and Technologists (ASSET) is organizing this theme meeting related to application of Ionic liquids and Deep Eutectic Solvents in Separation Science. As per its mandate, it regularly co-organizes symposium, theme meeting and releases thematic bulletin on topics related to the separation Science and Technology. Sensing the need of the hour, application of newer kind of solvents in separation science being followed in nuclear installations is being reviewed here. Experts from DAE and other research institutions are giving talk and I am hopeful that in this focused meeting, experts and researchers will have opportunity to discuss finer points regarding their application in work program of Dept. of Atomic Energy.

I wish great success of this theme meeting and look forward to concrete ideas coming out which is helpful to the Separation Science and Technology, in general, and the Separation work program related to Nuclear materials, in particular.

Necessity of Advanced Ionic Liquids for Nuclear Fuel Cycle Applications

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Introduction

Room temperature ionic liquids (RTILs) are receiving increased attention for possible applications in nuclear fuel cycle. RTILs are being investigated as possible substitute to molecular diluents in solvent extraction, and as an alternative to high temperature molten salts in non-aqueous reprocessing applications. It is well recognized that ionic liquids often display unique, and usually unusual extraction behavior, when used as solvent medium. These aspects make the subject of RTILs fascinating and challenging. This article provides some studies on room temperature ionic liquid research related to the extraction of actinides from nitric acid medium, and future directions to overcome the limitations associated with RTILs for maturing RTIL based technology.

Attractive Properties

The RTILs have many attractive properties such as insignificant vapour pressure, ability to dissolve a wide range of organic and inorganic compounds, wide electrochemical window and tunability of properties by suitable combination of cation and anion etc. Consequently, there has been a significant increase in the studies related to the use of RTILs in aqueous and non-aqueous reprocessing applications. In literature the RTILs are investigated as possible substitute to the molecular diluent in solvent extraction procedures and as an alternative to high temperature molten salt in non-aqueous reprocessing applications. However, some RTILs have also been employed as liquid ion exchangers in various solvent extraction procedures with conventional diluents. Some of the striking features of RTILs that make them promising for nuclear fuel cycle application are listed below.

- (1) The selectivity of target metal ion can be easily manipulated by the change of cation-anion combinations of RTIL diluent; rather than redesigning the structure of extractant,
- (2) Presence of ionic diluent in organic phase facilitates a new mode of recovery of metals by direct electrodeposition from the extracted phase,
- (3) Ionic liquids can be functionalized with organic moieties for task specific applications,

(4) RTILs can be designed to be completely incinerable, which would simplify the management of spent organic waste,

(5) Due to negligible vapour pressure of RTILs, the fire hazard is almost insignificant,

(6) In addition, unusual extraction of metal ions has been observed when traditional extractants are used in conjunction with RTIL diluents. Thus, RTILs provide excellent challenges and opportunities to researchers and also exhibit the potentials for technological applications.

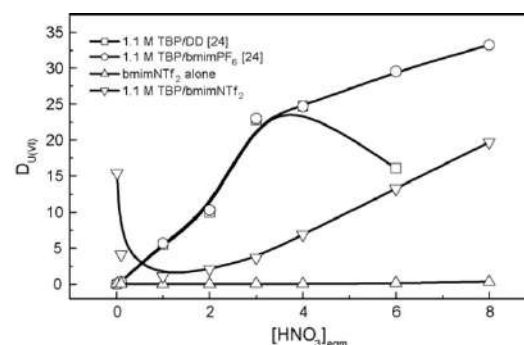


Fig. 1. Extraction behavior of $^{233}\text{U(VI)}$ in various ionic liquids systems at 298 K. Organic phase: C_4mimPF_6 (or $\text{C}_4\text{mimNTf}_2$) and 1.1 M TBP / *n*-DD (or C_4mimPF_6 or $\text{C}_4\text{mimNTf}_2$) and 1.1 M TBP/*n*-DD; Aq. Phase : 0.01 - 8 M HNO_3 , ^{233}U = tracer, $T = 298\text{ K}$

Actinide Extraction

The studies on the extraction of U(VI) from nitric acid medium in a solution of tri-*n*-butylphosphate (TBP) in C_4mimPF_6 or $\text{C}_4\text{mimNTf}_2$ has been reported in literature [1]. The extraction of uranium (VI) in 1.1 M TBP/ $\text{C}_4\text{mimNTf}_2$ (or C_4mimPF_6) is shown in figure 1. The distribution ratios are compared with those obtained using 1.1 M TBP/*n*-dodecane (DD). It is observed that the distribution ratio of U(VI) in 1.1M TBP/ C_4mimPF_6 gradually increases from 0.05 to 33.2 with increase in the concentration of nitric acid from 0.01 M to 8 M. At nitric acid concentrations lower than 4 M, the distribution ratios obtained for the extraction of U(VI) in 1.1 M TBP/ C_4mimPF_6 are comparable with the distribution values observed for the

extraction of U(VI) in 1.1 M TBP/DD. However, above 4 M, the distribution ratios of U(VI) in 1.1 M TBP/C₄mimPF₆ continue to increase, which is in contrast to the behaviour observed for 1.1 M TBP/DD. With 1.1 M TBP/C₄mimNTf₂, significant extraction of U(VI) is also observed at low nitric acid concentrations with a minimum distribution ratio at 1.0 M, followed by gradual increase in the D_{U(VI)} values.

The investigation on the mechanism of U(VI) extraction by TBP dissolved in ionic liquid revealed that the mode of uranyl ion partitioning was shown to change from ion-exchange (equation 4) to the traditional M-solvate complex (equation 5) with the increase of nitrate in aqueous phase and hydrophobicity of ionic liquid. This observation provide advantages as well as a number of challenges for maturing ionic liquid based robust technology.

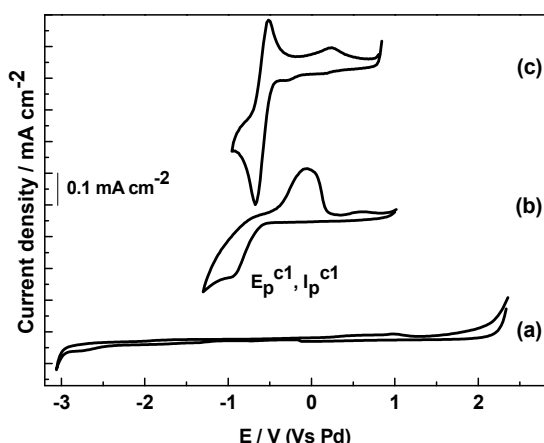
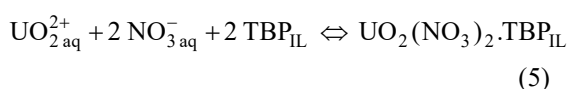
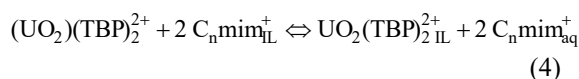


Fig.2. CV of (a) C₄mimNTf₂, (b) 80 mM UO₂(NO₃)₂ dissolved in C₄mimNTf₂ containing TBP (160 mM) and (c) 80 mM UO₂Cl₂ dissolved in C₄mimCl recorded at a glassy carbon working electrode at the scan rate of 100 mV.s⁻¹ at 373 K.

Extraction-Electrodeposition (EX-EL) approach

The conventional liquid-liquid extraction procedures involve the extraction of target metal ion from aqueous phase at a particular feed condition followed by stripping using aqueous reagents. However, the extracted metal ion can also be electrodeposited into metal/oxide form directly

from organic phase, provided the organic phase is a good conductor and has suitable electrochemical window. The advantage of this method is a large volume reduction of the waste and easy handling of reduced metal. To demonstrate this extraction – electrodeposition (EX-EL) approach for the recovery of uranium, the electrochemical behavior of U(VI) extracted into 1.1 M TBP/ionic liquid at glassy carbon working electrode by cyclic voltammetry. Uranyl ion in the ionic liquid phase was found to undergo a single step two-electron reduction process at the working electrode leading to the deposition of amorphous uranium oxide at the electrode (figure 2b). However, the Faradaic efficiency reported was low (~20%).

The voltammetric behaviour of UO₂(NO₃)₂ in a solution of C₄mimNTf₂ containing TBP was quite complicated owing to the coordination of TBP with uranyl nitrate in the form of [UO₂(NO₃)₂(TBP)₂] in C₄mimNTf₂ medium. The cathodic peak current density obtained for the overpotential reduction of UO₂²⁺ to UO₂ in the presence of TBP was quite low (figure 2b). To increase the current density and lower the overpotential of UO₂²⁺ reduction, C₄mimCl was added to the uranyl nitrate - TBP solution. The U : NO₃ : Cl : TBP mole ratio was varied from 1 : 2 : 1 : 2 to 1 : 2 : 6 : 2 in ionic liquid medium. Addition of C₄mimCl to ionic liquid medium minimized the overpotential and increased current density and diffusion coefficients for the reduction of UO₂²⁺ to UO₂.

To understand the electrochemistry of uranyl ion observed in the presence of neutral and anionic ligands, the speciation behaviour of uranyl ion in the presence of NO₃⁻, Cl⁻ and TBP was investigated by UV-Visible, ATR-FTIR and Raman spectroscopy[2]. The visible absorption spectrum of uranyl nitrate in the presence of TBP showed that the uranyl ion existed as UO₂(NO₃)₂(TBP)₂ in C₄mimNTf₂ medium in the absence of C₄mimCl. However, in the presence Cl⁻ ions the uranyl nitrate is transformed to various anionic complexes such as [UO₂Cl(NO₃)₂]⁻ or [UO₂Cl₃(NO₃)₂]²⁻ or [UO₂Cl₄]²⁻, depending upon the mole ratio of U : NO₃ : Cl. Since TBP was a neutral as well as a weak field ligand, it did not participate in complexation with these anionic uranyl species. The ATR-FTIR spectroscopic studies also indicated that the addition of Cl⁻ ions to UO₂(NO₃)₂(TBP)₂ gradually substituted the nitrate ions by Cl⁻ and displaced TBP from uranyl coordination sphere. When the mole ratio of U : NO₃ : Cl : TBP was 1 : 2 : 4 : 2 or above (i.e., Cl⁻ is more) majority of uranyl ion existed in the form of [UO₂Cl₄]²⁻ in ionic liquid medium. Raman spectroscopic studies showed that majority of uranyl species existed as [UO₂(NO₃)₂Cl]⁻ with residual [UO₂(NO₃)₂(TBP)₂] at 1 : 2 : 1 : 2 mole ratio of U : NO₃ : Cl : TBP, and at 1 : 2 : 6 : 2 mole

ratio the dominant uranium specie is $[\text{UO}_2\text{Cl}_4]^{2-}$. The study thus confirmed that the addition of Cl^- ion converted the bulky $[\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2]$ complex into smaller $[\text{UO}_2\text{Cl}_4]^{2-}$ complex. Since the reduction of such chlorocomplex resulted in the liberation of Cl_2 at the counter electrode, the reduction of UO_2^{2+} at the working electrode was favourable than the reduction of uranyl nitrate-TBP complex.

Need of Advanced RTILs for Extraction

The role of an “inert” diluent like *n*-dodecane in a solvent extraction procedure is to dissolve the extractant molecule and provide strong hydrophobicity to the organic phase such that the organic phase is immiscible with aqueous medium. In addition, the diluent also solvates the metal-ligand complex formed in organic phase after extraction. The conventional ionic liquids employed for solvent extraction applications are based on alkyl imidazolium cation, for instance, 1-butyl-3-methylimidazolium cation in conjunction with bis(trifluoromethyl-sulphonyl)imide anion results in a hydrophobic ionic liquid, $[\text{C}_4\text{mim}][\text{NTf}_2]$, which makes the ionic liquid immiscible with aqueous medium. Moreover, they dissolve a wide range of ligands suitable for solvent extraction applications. However, due to the characteristic ionic nature of ionic liquids, they often undergo cation and anion exchange reaction with target metal ions present in aqueous solutions, as discussed above. As a result, these ionic liquids show exceptional extraction of target metal ions, facilitated by a couple of modes, one involving cation exchange and the other, metal-ligand complex formation. In addition, the ionic liquids also stabilize the polar metal-ligand complex by solvation.

Even though the mass transfer of metal ions occurring through the dual mode enhances the extraction of metal ions to a remarkable extent, the ionic liquid is irreversibly lost from the organic phase. In addition, the presence of organic ions in aqueous phase pollutes the aqueous phase and therefore further treatment of aqueous phase becomes difficult. In view of this, it is necessary to choose appropriate cation-anion combinations of the ionic liquid that is devoid of undergoing any ion exchange, but retaining all the good properties of the ionic liquid for excellent solvent extraction application. Moreover, for the separation of target metals from radioactive feed solution, it is desirable to select the ionic liquid, which is made up of CHON-atoms so that the ionic liquid is completely incinerable and the waste disposal of the spent ionic liquid becomes easy. In connection with the CHON-based ionic liquids that are strongly hydrophobic, several authors [3,4] have

reported the synthesis of ionic liquids containing methyl-tri-*n*-octylammonium cation ($[\text{N}_{1888}]^+$) associated with a wide variety of anions for various applications. It should be noted that the $[\text{N}_{1888}]^+$ cation is an affordable and versatile source for combining with several anions by means of a simple substitution reaction for producing strongly hydrophobic ionic liquids. These ionic liquids have been exploited for various nuclear fuel cycle applications. The illustration is shown in figure 3.

For instance, it can be seen from figure 3 that the distribution ratios of U(VI) in 0.1 M dioctylhydroxyacetamide (DOHyA) in $[\text{N}_{1888}][\text{NO}_3]$ are higher than those observed in 0.1 M in DOHyA/*n*-DD at all nitric acid concentrations. This shows that the ionic liquid, $[\text{N}_{1888}][\text{NO}_3]$, facilitates the extraction of U(VI) in DOHyA/ $[\text{N}_{1888}][\text{NO}_3]$ phase. The extraction of U(VI) in organic phases followed in the order of DOHyA/*n*-DD << $[\text{N}_{1888}][\text{NO}_3]$

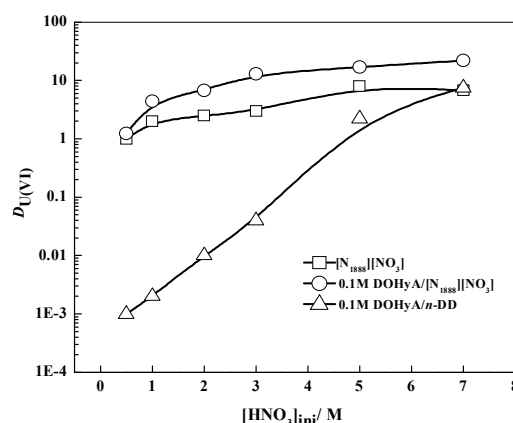


Fig.3. Variation in the distribution ratio of U(VI) in organic phase as a function of nitric acid concentration in aqueous phase. Organic phase: 0.1 M DOHyA/ $[\text{N}_{1888}][\text{NO}_3]$ (or *n*-DD) and $[\text{N}_{1888}][\text{NO}_3]$ phase alone; Aqueous phase: (0.5-7 M) nitric acid + 4×10^{-4} M U(VI); Equilibration time = 1 hour; Temperature = 298 K; Phase volume ratio = 1.

<DOHyA/ $[\text{N}_{1888}][\text{NO}_3]$, indicating that $[\text{N}_{1888}][\text{NO}_3]$ and DOHyA were involved in the extraction of U(VI) in the ionic liquid medium. From FTIR and Raman spectroscopic studies discussed elsewhere [4], the shift in the amidic carbonyl bands from 1650 cm^{-1} to 1620 cm^{-1} confirmed the participation of DOHyA in the extraction of uranium in DOHyA/ $[\text{N}_{1888}][\text{NO}_3]$ medium, similar to *n*-DD system. However, the growth of 1020 cm^{-1} shoulder at the expense of 1040 cm^{-1} intensity confirmed uranyl nitrate underwent nitrate ion association with $[\text{N}_{1888}][\text{NO}_3]$. Therefore, it appears that uranyl nitrate was extracted into DOHyA/ $[\text{N}_{1888}][\text{NO}_3]$ phase by two different modes, seems to be

independent of each other. They are U(VI) extraction through (a) the co-ordinate complex formation with DOHyA, and (b) through the association reaction of uranyl nitrate with nitrate ion of ionic liquid.

Future Directions

The advent of moisture stable room temperature ionic liquids has created vast opportunity for studying the extraction behavior of actinides and fission products in ionic liquid media and has produced wealth of data, worldwide, in the previous couple of decades. As the ionic liquids are composed entirely of ions, they exhibit significant solubility in aqueous medium, which, sometimes, synergistically facilitate or reduce the extraction of metal ions depending upon the nature of diluent and conditions employed for extraction. Regardless of this, the solubility of ionic liquid in aqueous phase is a concern for solvent extraction applications. Even though, the studies did show that the solubility could be minimized by the judicious selection of cation-anion of RTIL [90], it is not insignificant.

The viscosity and density of ionic liquid phase employed for extraction are generally higher than the traditional diluent, n-DD. These properties are important process parameters that dictate the hydrodynamics of mixing during solvent extraction. It is essential that the viscosity of organic phase is sufficiently low to permit, easy flow of solutions, low power agitators for phase dispersion and efficient phase separation. Since these values are significantly higher for the RTIL diluents, serious problems such as phase inversion, long time for disengagement etc. are encountered during solvent extraction. In view of this, it is suggested to identify the appropriate ionic liquid from the mammoth combinations (10^{18}) of cation and anions for meeting all the desirable properties of the diluent for reprocessing applications.

Several studies have reported unusual extraction of target metal ion from aqueous medium. Due to the ionic nature of the diluent, the separations are essentially governed by the ion exchange mechanism in almost all cases, even for the extraction of metal ions by neutral donors. Ion exchange results in the loss ionic liquid diluent from organic phase and contaminates the aqueous phase with unwanted cations/anions. Nevertheless, the studies also report that the ion exchange mode for extraction can be easily shifted to traditional metal-solvate extraction by the appropriate selection of cations and anions.

The electrical conductivity of ionic liquid provides a new mode of recovery of highly extracted metals by direct electrodeposition from the extracted phase (Ex-EI method). The wide electrochemical

window of RTIL helps to achieve the recovery of electropositive elements that cannot be usually electrodeposited from aqueous solutions. The recovery by electrodeposition has several advantages such as elimination of several complex processing steps for the manufacture of metal/oxide, minimizes the generation of secondary wastes, lowers the risk in handling radioactive raffinate, achievement of large volume reduction, easy handling of the deposit etc. However, the literature shows that only few elements such as palladium, silver, cesium, strontium, uranium oxide have been studied for the separation and recovery by Ex-EI method. Studies with other metal ions, knowledge of cathodic-anodic redox reactions, scaling-up studies etc. are needed for realizing a paradigm shift in the hydrometallurgical and reprocessing technology.

The ionic liquid studied usually contains elements such as halogen, sulphur, phosphorous etc. in the cationic or anionic part of the molecule. These elements tend to provide corrosive atmosphere during various processing applications especially concerned with the feeds from nuclear fuel cycle (nitric acid). Moreover, the ionic liquid containing these elements are likely to release corrosive gases upon thermal and radiolytic decomposition. Even though the studies on this subject are open to active research, it is suggested to design the ionic liquid composed only of CHON elements.

From the reprocessing applications point of view, only a few functionalized ionic liquids have been synthesized and studied for their applications. These FILs exhibited unusual extraction for actinides fission products and achieve high separation factor of target metal from the host of competitive metal ions. While these results show promise for task specific applications, the viscosity of FIL is quite high due to the functional group attachment. However, this could be minimized by preparing a new generation of ionic liquids that contain strongly coordinating anions, which is also finding quite good applications in the recent past.

Conclusions

In summary, the results reported so far on the separation of actinides and fission products using room temperature ionic liquid as a medium are encouraging. While, these emerging methods and new techniques using RTILs show great promise, at present, the physical and chemical properties of the ionic liquid needs to be tuned to suit the ionic liquid for robust applications in reprocessing and waste management. This could be realized only by investigating the physicochemical properties of room temperature ionic liquids at fundamental levels. It is therefore suggested to study the fundamental properties of ionic liquids that govern solubility in aqueous phase, hydrophobicity,

viscosity, electrochemical behavior etc. to design the RTIL/FILs having all the required properties for hydrometallurgical applications.

Acknowledgements

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Biodata



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Dearomatization and Desulphurization using Deep Eutectic Solvents as Extractants from Petroleum Fuels

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Green technology has become increasingly popular over the last few decades. Efforts have been made to provide safer, cleaner, more efficient, ecologically friendly, and economically viable neoteric solvents for the extraction. The notion of green engineering and sustainable solvents, in particular, has been adopted by an increasing number of academic publications. The study of ionic liquids (ILs) has spanned several scientific disciplines, including chemical synthesis, biochemistry and separation technologies, as well as electrochemistry and catalysis [1]. ILs are commonly referred to as "green" because of their low flammability and minimal vapour pressure, both of which contribute to environmental concerns. IL synthesis, on the other hand, includes a number of synthetic stages that frequently lead to the creation of waste and by-products. In addition, the toxicity and low biodegradability of the product have been noted. Because of this, the 'greenness' of ILs has been disregarded and misunderstood. In addition, the expensive expense of synthesizing them has limited their use in industry.

Introduction

Deep eutectic solvents (DESs) were found in 2003, a new class of environmentally friendly solvents [2]. To generate a mixture with a melting temperature significantly lower than that of its constituents [3, 4, 5, 6, 7, 8] hydrogen bond donors (HBD) and acceptors (HBAs) due to strong hydrogen bond interactions. There are some DESs that do not have a melting point, but rather a glass transition temperature. Due to their low transition temperature, these solvents are sometimes called LTTMs [6]. Because of their similar qualities (low vapour pressure, wide liquid range, thermal stability, and low flammability) and lack of some of the disadvantages of ILs, new DESs materials are emerging as possible substitutes. High purity can be achieved by simply mixing HBD and HBA in particular ratio. In addition, the solvent should be readily available and inexpensive, as well as environmentally friendly and biodegradable. Aside from corrosivity, toxicity, and flammability, there are many other issues to consider. Additionally, DESs are being touted as future green solvents in a wide range of industries. As an aside, it is worth noting that the "greenness" and sustainability of such solvents.

Liquid-liquid extraction technologies appeared to be one of the most promising alternatives to conventional hydrotreatment technique. This is due to the following benefits: There is no hydrogen consumption, no change in the structure of the molecules that have been extracted. There are many factors that contribute to the success of this procedure as an environmentally friendly alternative. Non-reactive physical extractant, high capacity and extraction efficiency, high solubility of aromatic molecules, high aromatic distribution ratio and minimal *n*-alkanes solubility are all important characteristics to look for in a solvent for this application. In addition, the solvent should be

readily available and inexpensive, as well as environmentally friendly and biodegradable. Aside from corrosivity, toxicity, and flammability, there are many other issues to consider.

The Chemistry of Deep Eutectic Solvents (DESs) formation

A concise understanding of chemistry of DES is necessary to gain an intuitive understanding of how it functions as an extractant. By definition, DES is a eutectic mixture composed of two or more components capable of forming strong hydrogen bonding that was mainly responsible for the significant drop in melting point from its constituents. They are also known as eutectic ionic liquid, low temperature molten salt, or ionic liquid analogue. Abbot et al. pioneered the investigation of DES from a combination of quaternary ammonium salts and zinc chloride [9]. The formation of DES is based on eutectic mixing of components with a high melting point, which results in a freezing point depression, which prevents it from solidifying from its original constituents such as HBAs and HBDs. Considering the well-known characteristic of DES, it can be considered a green solvent because all of its properties conform to green chemistry principles.

To understand the chemistry of DESs formation, Figure 1 depicts the complex DES cluster, which shows the molecular arrangement of HBA and HBD in the molar ratio of 1:4 to form the potential DES. It can also be observed that it forms a strong hydrogen bond mainly of O–H $\cdots$ Br[−] interaction with distances of 2.30 Å. Bromine (Br[−]) ion with negative charge also forms C–H $\cdots$ Br[−] type multiple bonds with the positively charged hydrogen atom attached to the phenyl ring of MTP cation with distance *d*₁ and *d*₂ of 2.67 and 2.95 Å, respectively. The ethylene glycol (HBD) part of DES also confirms the multiple strong non-covalent bonds of C–H $\cdots$ O type with the methyl or

phenyl groups of the HBA within the distance range of 2.42-2.69 Å (figure 4c). The strong hydrogen bonding interactions between the MTP cation and the bromide (Br^-) anion were found at a close distance of $d_3=2.30$ Å and $d_1=2.51$ Å. Experimentally, DES formation shows the drop in melting point due to the formation of such a strong hydrogen bond between HBA and HBD. In the DES cluster, the most significant distances of MTPB and EG were also highlighted for $\text{O}-\text{H}\cdots\text{Br}$, $\text{C}-\text{H}\cdots\text{Br}$, and $\text{C}-\text{H}\cdots\text{O}$ type non-covalent interactions in table 4. This strong interaction validates the integrity of the DES structure with reasonable interatomic distances between the MTPB and EG molecules in the specific molar ratio of 1:4. Therefore it reveals that drop in melting during synthesis due to strong non-covalent interaction.

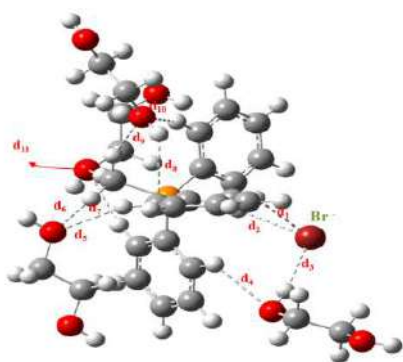


Figure 1. B3LYP-D3/6-311 + G** optimized geometry of DES cluster consisting of HBA and HBD in molar ratio of 1:4, along the significant structural distances associated with intermolecular interactions. The dark grey colour is applied for carbon atoms, red for oxygen atoms, yellow for sulphur atoms, orange for phosphorus atoms, and light grey for hydrogen atoms.

Application of different DESs

The usefulness of DESs in numerous applications linked to separation technologies in oil processing has been explored by scientists all over the world in the quest for more sustainable techniques to generating clean oil fuels. The aromatic hydrocarbons create azeotropes with aliphatic hydrocarbons, optimizing their composition is a difficult task in industry. Different aromatic compounds have been extracted successfully from aliphatic hydrocarbons using DESs [10, 11, 12, 13]. Selected investigations on dearomatization and desulfurization utilizing DESs are summarized in Table 1. Heptane/toluene and hexane/benzene mixtures have both been treated with phosphorus-based DESs [10, 12]. It was discovered that temperature has a significant impact on aromatic extraction. The extraction of the aromatic was aided by increasing the temperature. The DES was

not found in the hydrocarbon-rich stratum, which is unusual.

Sulfur-containing aromatics, such as thiophenes, have been removed from fuels using DESs, which follow a similar conceptual path to dearomatization [20]. Organosulfur-containing fuel burning is a substantial contributor to SO_x and H_2S emissions. Sulfur contents in fuels must be reduced to comply with EU and US Environmental Protection Agency (EPA) laws governing SO_x emissions. In the same way, the use of volatile organic solvents for desulfurization is a problem for environmental health. Green carboxylic acid based DESs have lately been used for deep extractive desulfurization of fuels. The removal of benzothiophene, dibenzothiophene, and thiophene from octane was quite effective. " Deep desulfurization can be achieved even after three extraction cycles, despite the efficiency being unaffected by the temperature of the extraction process (up to 98 percent efficiency). Using methyl tert-butyl ether as a back-extractant, the DES was successfully regenerated and the DES extraction property was completely restored. The DES structure hasn't changed in the regenerated DES, as shown by the NMR spectra, hence the recyclability is assured. The hydrogen bond interaction between DESs and the sulphur atom in thiophenes was also found to be a factor in the extraction.

Table 1: Selected applications of DESs for oil separation processes. The DES are presented as HBA: HBD in molar ratio, T is the temperature in K.

Aromatic compound	Mode diesel	Extraction Method	DESs	T (K)	Ref.
Dearomatization					
Benzene	Hexane	LLE	THABr:EG, THABr:Gly in 1:2	298	[13]
			THABr:EG, THABr:Gly in 1:2	308	
Benzene	Hexane	LLE	MTPPBr:EG in 1:4,1:6,1:8	300	[10]
			MTPPBr:EG in 1:4,1:6,1:8	308	
			MTPPBr:EG in 1:4,1:6,1:8	318	
Toluene	Heptane	LLE	TBPBr:EG, TB PBr:Sul in 1:2, 1:4,1:6,1:8	313	[12]

			TBPBr:EG,TB PBr:Sul in 1:2, 1:4,1:6,1:8	323	
			TBPBr:EG,TB PBr:Sul in 1:2, 1:4,1:6,1:8	333	
Benze ne	Hexa ne	LLE	ChCl:LA, ChCl:Gly in 1:2	298 308 318	[11]
Benz ene	Deca ne Dod ecan e Hex adec ane	LLE	MTPBr:EG (1:4)	298	[14]

Desulfurization

Benzo thioph ene, Diben zothio phene or Thiop hene	Octane	LLE	TBABr:FA in 1:1	293 – 323	[15]
Benzo thioph ene	Octane	LLE	ChCl:MA/Gly/ EG/Pr, TMACl:Gly/E G/PAA, TBACl:MA/Gl y/TEG/EG/PA A/CA/Pr/PEG in 1:2	298	[16]
Diben zothio phene and Thiop hene	Octane, Decane, Cycloh exane, isoocta ne and toluene in 30%, 30%, 30%, 10% respecti vely	LLE	TBPBr: stannous chloride dihydrate in 1:1	303 – 343	[17]

3- Methy lthiop hene, Benzo thioph ene or Diben zothio phene	Heptan e	LLE	Chlorinated paraffins- 52:AlCl3:Tolue ne/Benzene/ <i>p</i> - xylene/ <i>o</i> - xylene/Ethylbe nzene in 1:6:18	293	[18]
Thiop hene	Heptan e	LLE	TBABr:EG/TE G, MTPBr:EG in 1:4 and TBABr:Sul in 1:7	298	[19]
Benzo thioph ene	Decane	LLE	MTPBr:EG (1:4)	318	[20]

Single-stage liquid-liquid extraction from diesel model

The LLE data of experimental systems consisting of $\{n\text{-decane} + \text{benzene} + \text{DES}\}$, $\{n\text{-dodecane} + \text{benzene} + \text{DES}\}$, and $\{n\text{-hexadecane} + \text{benzene} + \text{DES}\}$ were measured at $T = 25^\circ\text{C}$ and Pressure $p = 0.1$ MPa. For the desulfurization $\{n\text{-decane} + \text{benzothiophene} + \text{DES}\}$ system LLE experiment was performed at 35°C and Pressure $p = 0.1$ MPa. The experimental data shown in table 2-5. The distribution ratio (D), selectivity (S), and extraction efficiency (EE) were considered for the purpose of estimating the performance of each model diesel fuel component explicitly with a particular DES. The experimental LLE data are plotted through a triangular phase diagram for each system in figure 2a-d. For LLE, the experimental tie line concentration of impurity in model diesel varies in the range of less than 20% by weight. It implies that only the feed % in impurity + *model diesel* was varied, but the overall moles of the feed were equal to the solvent for each tie line. The selectivity, distribution coefficient, and Extraction Efficiency for the corresponding tie-line are calculated from equations (1), (2) and (3), respectively.

$$D_i = \frac{x_i^{\text{Extract}}}{x_i^{\text{Raffinate}}}$$

(1)

$$S_{ij} = \frac{x_i^{\text{Extract}}}{x_i^{\text{Raffinate}}} \bigg/ \frac{x_j^{\text{Extract}}}{x_j^{\text{Raffinate}}}$$

(2)

$$\%EE = \left[\frac{x_{2,\text{initial}} - x_{2,R}}{x_{2,\text{initial}}} \right] \times 100$$

(3)

Here the symbols have their usual meaning while ‘*i*’ refers to aromatic and sulphur species impurity and ‘*j*’ refers to model diesel. ‘Extract’ and ‘Raffinate’ refer to the solvent-rich and aliphatic hydrocarbon-rich phases, respectively. In equation 3, $x_{2, \text{initial}}$ refers to the initial mole fraction of impurity in the feed, and $x_{2, \text{R}}$ is the final mole fraction of impurity in the *model diesel* rich phase after extraction.

The numerical values of experimentally obtained tie lines data of the equilibrium composition are given in Tables 2-4, as obtained by the quantitative analysis of both phases using the ^1H NMR. These Tables also contain the calculated values of D (Eq. 1) and S (Eq. 2) for the solvent to feed ratios of 1:1. Based on the calculated LLE composition data, it is found that the concentrations of *n*-decane, *n*-dodecane, and *n*-hexadecane in the extract phase for all three ternary systems are less. Furthermore, based on the obtained NMR results, there is no noticeable amount of DES in the raffinate phases of all three ternary systems. It gave an insignificant amount of *model diesel compounds* in the extract phases and the nonappearance of DES compound in the raffinate phases, which specify negligible cross-contamination between the extract and raffinate phases. This is highly favourable for the solvent recovery of the LLE process. It should be mentioned that the results obtained from ^1H NMR showed a distinctive peak for each impurity in both the DES rich phase and *n*-alkane rich phase and no new peaks were detected.

It can be established that the usage of DES for benzene and benzothiophene extraction is reasonable for model diesel fuel as it requires a smaller amount of solvent to feed ratio, which in turn gives higher values of selectivity and distribution coefficients. The main reason for a significant extraction was the higher solubility of specific impurity in DES as compared to aliphatic hydrocarbons, as shown in tables 2-4. Higher solubility behaviour can be explained by considering the π -electrons cloud around the benzene (due to the molecule's aromatic nature), due to which a strong electrostatic field is generated around the molecule. The presence of a strong π -electron cloud of aromatic molecules induces the interactions within the phenyl and hydroxyl group of DES and, as a result, provides higher extraction efficiency.

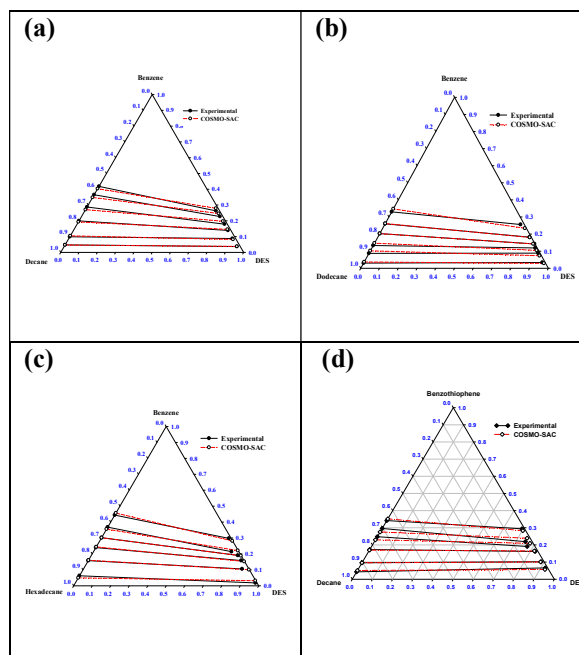


Figure 2. Experimental tie lines (●, Solid line) in mole fractions for the ternary systems (a) {*n*-decane + benzene + DES} (b) {*n*-dodecane + benzene + DES} (c) {*n*-hexadecane + benzene + DES} at $T = 25\text{ }^{\circ}\text{C}$ and atmospheric pressure and (d) {*n*-decane + benzothiophene + DES} at $35\text{ }^{\circ}\text{C}$ and atmospheric pressure.; Predicted equilibrium tie lines (○, dotted line) using COSMO-SAC model.

On the other hand, no such π -electron cloud is available around the aliphatic hydrocarbon's molecule; consequently, the aliphatic hydrocarbons-DES interactions are weaker than the benzene-DES interactions. It can be observed that increasing the initial concentration gradually decreases the extraction efficiency of impurity. For a single-stage extraction, the highest efficiencies were found for *n*-hexadecane followed by *n*-dodecane and *n*-decane for benzene separation. For all three systems, extraction efficiencies for the single-stage were found to be in the range of 60-72%. It also shows DES as an effective extractant that follows the order of *n*-hexadecane > *n*-dodecane > *n*-decane for benzene extraction from model diesel components.

The distribution coefficients and selectivities calculated at $T = 25\text{ }^{\circ}\text{C}$ and atmospheric pressure for the systems {*n*-decane + benzene + DES}, {*n*-dodecane + benzene + DES} and {*n*-hexadecane + benzene + DES} were compared to those systems using different DESs as extractants. It was observed that the selectivities of the reported systems follow the order of *n*-hexadecane > *n*-dodecane > *n*-decane, and distribution coefficients was also found highest for {*n*-hexadecane + benzene + DES} system. Overall, both the distribution coefficients and selectivity values are higher when compared to ammonium-based DES.

It is worthwhile to note that this higher with the ammonium-based DES when combined with the conventional solvent, namely sulfolane, or with the similar HBD, namely ethylene glycol.

Table 2. Experimental Liquid-liquid Equilibrium (LLE) tie-line data for the ternary system: DES + benzene+ *n*-decane at Temperature $T= 25^{\circ}\text{C}$ and Pressure $p=0.1\text{ MPa}^a$. The mole fractions of DES, benzene and decane are represented by x_1 , x_2 , and x_3 , respectively.

Extract phase			Raffinate phase			D	Selectivity (S)
x_{DES}	x_{ben}	x_{dec}	x_{DES}	x_{ben}	x_{dec}		
0.944	0.053	0.008	0.000	0.048	0.953	1.12	129.9
0.891	0.099	0.010	0.000	0.099	0.901	1.00	94.0
0.845	0.139	0.016	0.000	0.180	0.821	0.77	39.7
0.806	0.179	0.015	0.000	0.288	0.713	0.62	29.8
0.757	0.227	0.016	0.000	0.365	0.635	0.62	25.0
0.718	0.263	0.019	0.000	0.418	0.582	0.63	18.8

^a Standard uncertainties are $u(T) = 0.01^{\circ}\text{C}$, $u(x) = 0.001$, and $u(p) = 2\text{ kPa}$.

Table 3. Experimental Liquid-liquid Equilibrium (LLE) tie-line data for the ternary system: DES + benzene+ *n*-dodecane at Temperature $T= 25^{\circ}\text{C}$ and Pressure $p = 0.1\text{ MPa}^a$. The mole fractions of DES, benzene, and dodecane, are represented by x_1 , x_2 , and x_3 , respectively^a.

Extract phase			Raffinate phase			β	Selectivity (S)
x_{DES}	x_{ben}	$x_{hexadec}$	x_{DES}	x_{ben}	$x_{hexadec}$		
0.921	0.071	0.008	0.000	0.033	0.967	2.16	261.16
0.848	0.141	0.011	0.000	0.108	0.892	1.30	105.72
0.811	0.169	0.020	0.000	0.240	0.760	0.70	26.70
0.778	0.191	0.031	0.000	0.302	0.698	0.63	14.23
0.735	0.231	0.034	0.000	0.368	0.632	0.63	11.76
0.690	0.272	0.038	0.000	0.424	0.576	0.64	9.73

^a Standard uncertainties are $u(T) = 0.01^{\circ}\text{C}$, $u(x) = 0.001$, and $u(p) = 2\text{ kPa}$.

Table 4. Experimental Liquid-liquid Equilibrium (LLE) tie-line data for the ternary system: DES + benzene+ *n*-hexadecane at Temperature $T= 25^{\circ}\text{C}$ and Pressure $p = 0.1\text{ MPa}^a$. The mole fractions of DES, benzene, and hexadecane, are represented by x_1 , x_2 , and x_3 , respectively^a.

Extract phase			Raffinate phase			D	Selectivity (S)
x_{DES}	x_{ben}	x_{dodec}	x_{DES}	x_{ben}	x_{dodec}		
0.961	0.034	0.005	0.000	0.030	0.970	1.23	218.47
0.901	0.089	0.010	0.000	0.087	0.913	1.02	91.00
0.861	0.119	0.020	0.000	0.133	0.867	0.89	38.92
0.835	0.142	0.022	0.000	0.203	0.797	0.70	25.08
0.789	0.182	0.029	0.000	0.260	0.740	0.70	18.01
0.724	0.256	0.020	0.000	0.330	0.670	0.78	26.11

^aStandard uncertainties are $u(T) = 0.01^{\circ}\text{C}$, $u(x) = 0.001$, and $u(p) = 2\text{ kPa}$.

For figure 2d Distribution coefficient and selectivity values decrease for the given system as benzothiophene concentration in the feed increases as shown in table 5. Still, in lower concentrations of benzothiophene in the feed, the distribution coefficient and selectivity are significantly higher. These reported results suggest that DES is an excellent option for aromatic sulphur extraction on an industrial scale because of the amount of sulphur compounds required to be maintained at the ppm-level. Analysis of LLE results shows that the concentration of *n*-decane in the extract phase was as high as 3.9 % in the studied DES. This concentration was found at a higher concentration of feed tie line and became negligible at a lower concentration of the aromatic sulphur compound. Therefore, these results are favourable as actual model diesel fuel contains minimal benzothiophene in ppm-level. From the regeneration point of view of DES, it demonstrates that solvent regeneration at intermediate and lower benzothiophene levels can be accomplished with limited hydrocarbon loss. The corresponding DES concentration in the raffinate phase was found to be zero, reducing the recovery cost for solvent.

Therefore, it reveals that no transfer of DES in the hydrocarbon-rich phase as an impurity so reduces the solvent recovery costs. Table 5 gives the detail of extract and raffinate phase selectivity, distribution coefficients, and extraction efficiency with feed concentration. The reported DES of MTPB/EG (1:4) at 308.15 K and 1 bar was

superior to previously reported solvents in the literature for benzothiophene extraction in terms of extraction efficiency, distribution ratio, and selectivity.

Table 5. Liquid-liquid equilibrium tie-line data for the ternary system DES+ benzothiophene(BT)+n-decane(DC), at $T= 35^{\circ}\text{C}$ and 0.1 MPa pressure. The molar fractions of DES, benzothiophene, and n-decane are represented by x_1 , x_2 , and x_3 , respectively^a.

Extract phase			Raffinate phase			Distribution Coefficient (D_{BT})	Selectivity (S)	% EE
x_{DES}	x_{BT}	x_{DC}	x_{DES}	x_{BT}	x_{DC}			
0.922	0.006	0.002	0.000	0.004	0.957	1.53	122.41	78.36
0.884	0.010	0.004	0.000	0.009	0.904	1.06	68.61	69.26
0.824	0.016	0.004	0.000	0.017	0.827	0.94	55.32	63.52
0.770	0.019	0.003	0.000	0.024	0.752	0.77	19.31	53.41
0.747	0.021	0.003	0.000	0.029	0.704	0.74	15.32	47.62
0.693	0.029	0.003	0.000	0.034	0.658	0.86	12.57	43.72

^aStandard uncertainties are $u(T) = 0.01^{\circ}\text{C}$, $u(x) = 0.001$, and $u(p) = 2 \text{ kPa}$.

Conclusion and Future Perspective

The current critical Perspective provides the insights into deep eutectic solvents systems which are predominantly used to extract aromatic and sulphur compounds from model diesel compounds. Such solvent systems are also examined in relation to several sustainable extraction models for the selective extraction of a wide range of impurities such as benzene and sulphur-based compounds. DESs are a novel class of solvents that can be easily synthesized and they are less expensive compare to ionic liquids. The physical and chemical properties can be tuned according to the desired application that gives an opportunity to develop new suitable solvents. Additionally, it contributes significantly to their 'greenness' and sustainable characteristics. Fundamental studies and experimental data, including as characterization properties, phase behavior, and molecular interactions within the DES and explicit interaction with solute, are particularly desirable. However, promising outcomes were discovered for a variety of application fields. Similarly, to ILs, the thermal stability of DESs remains a problem due to the temperature sensitivity of the hydrogen bonding interactions. The regeneration/recyclability of DESs has been recorded in only a few applications, and additional research is required. Economic value, efficiency, cleanness, and renewability of DESs all make them extremely desirable for large-scale investment in the oil and gas processing industry. From a scientific curiosity to the future generation of solvents, DES are currently envisioned as the next generation of solvents, and while much study has to be done, this new class of solvents will undoubtedly make significant contributions to more sustainable industrial development.

Biodata



Dr. Tamal Banerjee is a professor, Indian Institute of Technology, Guwahati, India. His research interest is mainly on separations with Deep Eutectic Solvents and Ionic Liquids; Thermal fluids and supercapacitors. He has guided 12 Ph. D students so far, while another 7 students are persuing their Ph.D degree under his guidance. He is having 113 journal publications in reputed international journals (h index 27 and total citation 2500) and 3 book chapters. he is in the editorial board for Fluid Phase Equilibria since 2019. He is the receipient of Indo-US fellowship in 2011.

Room Temperature Ionic Liquids and Deep Eutectic Solvents: Radiation Chemical Studies and Applications in Nanomaterials Synthesis

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Introduction

Green and sustainable chemistry and engineering are becoming more important than ever as a result of resource constraints and environmental concerns. Replacing hazardous organic solvents, which are widely used in manufacturing industries, power plants, and research institutions, with novel non-conventional "green solvents" could be regarded as an important step in this direction. Examples of some of these solvents are room temperature ionic liquids (RTILs), deep eutectic solvents (DESs), cyrene, liquid polymers, and supercritical carbon dioxide (scCO₂) [1, 2]. However, this article will be focused on RTILs and DESs, their radiation chemical studies, and applications in the synthesis of nanomaterials with complex features.

RTILs: A brief introduction

In general, RTILs are defined as molten salts comprising of cations and anions, and have melting points below 100°C. The first RTIL (ethylammonium nitrate) was reported by Paul Walden in 1914 [3-6]. However, over a century, the field of RTILs has passed through various stages of development. Broadly, the advancement in the area of RTILs (till now) can be categorized into 3 generations, as illustrated in Figure 1. Nonetheless, the RTILs belonging to the 3rd generation are hydrolytically more stable, biodegradable, and offer lower toxicities. Apparently, several RTILs belonging to this generation are being explored/used as active pharmaceutical ingredients (API) or precursors [3-6].

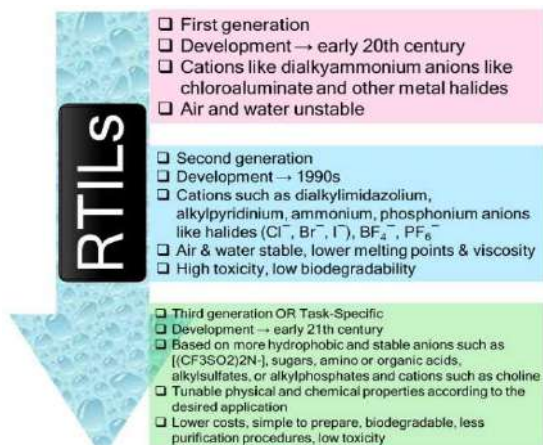


Fig.1. A schematic representation of the development of RTILs over various generations.

Undoubtedly, a surge in the interest of the scientific community on the R and D of RTILs, especially in the last two decades, could be attributed to their unique physicochemical properties such as high polarity, negligible vapor pressure, high ionic conductivity, wide electrochemical window, and thermal stability [3, 4, 6]. Moreover, these fluids are generally referred to as "designer" solvents considering their characteristics such as hydrophobicity, miscibility, polarity, and other physicochemical properties that can be easily tuned by altering the cation-anion combination. As per an estimate, there may be >10¹⁴ combinations of anion and cation possible [4-6]. Nevertheless, some of the most common cations and anions of RTILs that have been mainly studied so far are shown in Figure 2.

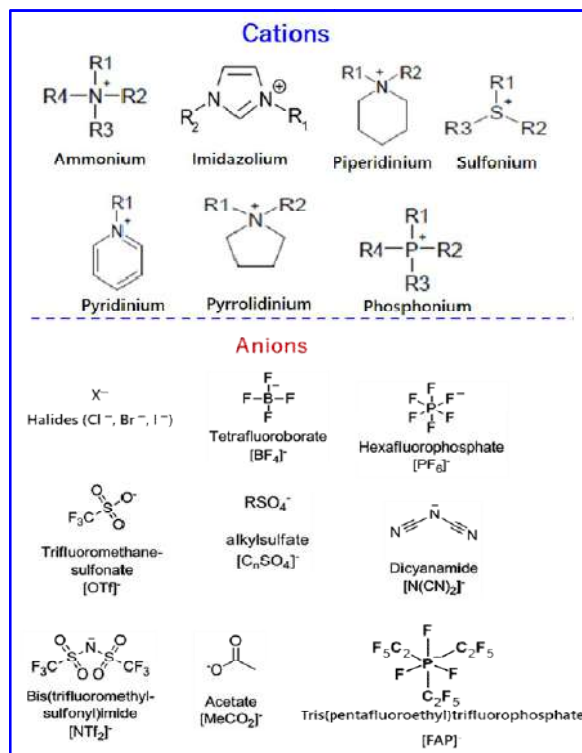


Fig.2. Some examples of common cations and anions of RTILs.

The complex 3-D microheterogeneous structure of RTILs, which encompasses multiple co-existing bonding interactions along with polar and non-polar regions, is one of the main structural characteristics that distinguishes them from conventional solvents. These interactions range from weak, nonspecific, and isotropic forces (e.g., van der Waals) to strong (Coulombic), specific, and anisotropic forces (e.g., hydrogen bonding, dipole-dipole, magnetic dipole, electron-pair donor/acceptor interactions) [4, 6, 8]. Figure 3 illustrates a diagrammatic representation of the different bonding interactions that can coexist in imidazolium-based RTILs.

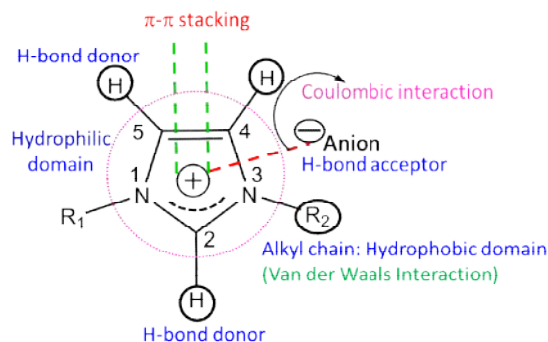


Fig.3. Diagrammatic representation of the various bonding interactions co-existing in an imidazolium-based RTILs.

The unique physicochemical features of RTILs have grabbed the attention of researchers working in fields as diverse as energy, healthcare, catalysis, and environment (Figure 4) [5, 7, 9-12].

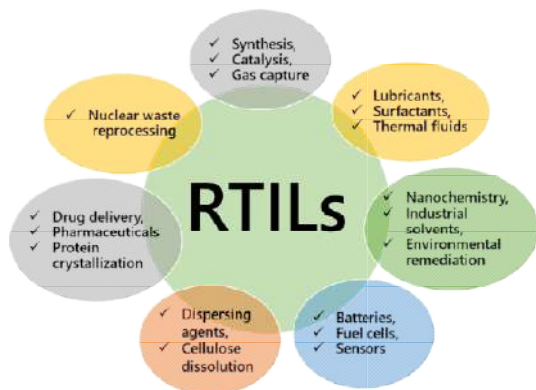
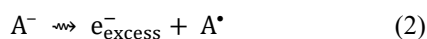
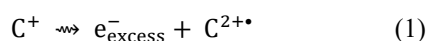


Fig.4. Applications of RTILs.

Radiation chemical studies of RTILs

An interesting facet about RTILs (especially, aromatic cation-based), which aroused much interest was their high radiation stability. This particular observation led to numerous exploratory works on the potential applicability of RTILs in areas involving radiation-filled environments, such as nuclear fuel cycle and space [13-18]. Essentially, the back end of the nuclear fuel cycle includes activities such as storage, reprocessing, and disposal of spent nuclear fuel obtained from thereactor. The most well-known reprocessing technique called PUREX

(plutoniumuranium reduction extraction) process is based on dodecane as a diluent and 30 % TBP (Tributyl phosphate) as extractant. However, substantial damage to the extractant leading to contamination and poor extraction efficiency of the PUREX process is well-reported [17, 18]. With the advent of 3rd generation RTILs, various studies have been carried out which indicate these solvents as superior alternatives to TBP or n-dodecane. Additionally, RTILs exhibit desirable physicochemical properties that can help in improving the safety and efficacy of extraction and fuel (spent nuclear fuel) reprocessing procedures, including tunability by design, negligible vapor pressure, high combustion resistance, a broad electrochemical window, thermal stability, and the ability to dissolve a wide variety of materials. However, the use of RTILs as a substitute for conventional organic solvents in the extraction and reprocessing processes increases the complexity of the system chemistry [13-15, 17-20]. Considering the high levels of radiation exposure during the various stages of spent nuclear fuel reprocessing, RTILs must exhibit radiation stability. Undoubtedly, this is one of the most important requirements, along with detailed information on their radiolytic products and degradation routes. Furthermore, uncovering radiation-induced chemical processes pertaining to excitation and ionization events in RTILs is critical. Of course, a great deal of work related to the radiation chemical studies on RTILs has already been reported over the last two decades [13-32]. A general scenario of the early events in the radiation chemistry of RTILs is illustrated in Figure 5. The energy channeling pathways followed by the interaction of ionizing radiations with RTIL could be broadly categorized into excitation and ionization. It has been observed [13] that in an ionization event, cation (denoted as “C⁺”) yields a dication radical (Eqn. 1) and ionization of an anion (denoted as “A⁻”) yields a neutral (or zwitterion) radical (Eqn. 2).



In RTILs, both the ionization events represented by equations (1) and (2) occur in relative proportion to the respective electron counts of the cation and anion. The excited states of the parent ions may promptly fragment, yielding radicals and other reactive intermediates, whereas the majority ionize to yield short-lived electrons and holes, which are rapidly trapped by the parent ions and ion vacancies in the RTILs. The liquid ions/molecules that have lost electrons are referred to as “holes” [13, 20].

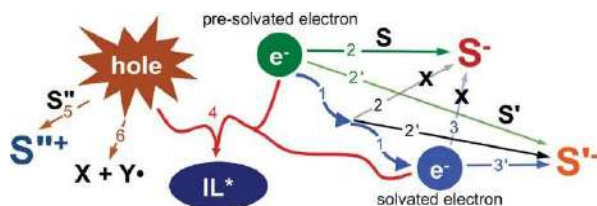


Fig.5. Scheme showing the major reactions following radiolytic ionization of an RTIL (labelled "IL"). S and S' represent different types of electron scavengers. The numbering on the arrows correspond to the following processes: (1) electron solvation; (2 and 2') presolvated electron scavenging by S and S' , respectively; (3 and 3') solvated electron scavenging by S and S' ; (4) electron-hole recombination to produce a ground or excited state of the ionic liquid anion or cation (IL or IL^*); (5) hole scavenging by hole scavenger S'' ; (6) hole fragmentation. X and Y designate any type of charged or uncharged fragments. Reprinted (adapted) with permission from [20]. Copyright {2010} American Chemical Society."

Recombination of holes and electrons can result in the formation of excited or ground states of the original parent molecules. In particular cases, the presence of scavengers (S) in RTILs results in a competition between the capture of surplus electrons and the solvation process. Holes can oxidise or fragment solutes, generating a variety of radical species. Nevertheless, subsequent reactions followed by excitation and ionization events are different for aromatic and aliphatic cation containing RTILs, as can be observed from Figure 6 [21].

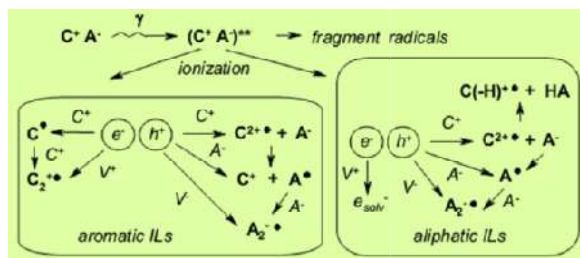


Fig.6. Schematic representation of the occurrence of possible events on radiation (γ) interaction with RTILs. The ensuing reactions depend on whether the cations (C^+) are aromatic or fully saturated, and the structure of the anions (A^-). V^+ and V^- represent cation and anion vacancies. Reprinted (adapted) with permission from [21]. Copyright {2010} American Chemical Society.

In aromatic cation based RTILs, the electrons are trapped by the cations and/or anion vacancies and the final product in both cases is primarily a dimeric radical cation, ($C_2^{\bullet+}$). Whereas, hole is trapped by either RTIL parent ion or the anion vacancy and the final product in both cases could be either $A^\bullet$ or ($A_2^{\bullet+}$). Interestingly, in aliphatic cation-based RTILs, electrons are predominantly trapped by cation vacancies yielding solvated electrons, which are fully

analogous to F-centres in ionic crystals. The holes are trapped by the RTIL parent ions and also by anion vacancies yielding $A^\bullet$ or ($A_2^{\bullet+}$). The holes trapped by the cations either transfer electrons from nearby anions, producing the same anion-derived radicals, or deprotonate, yielding C-centered radical cations [20, 21].

The aforementioned observations/findings represent a general picture of the radiolytic events during the interaction of ionizing radiations with RTILs. Nonetheless, these investigations not only unraveled intriguing differences in the radiolytic behaviour of RTILs compared to conventional solvents but also provide critical information that could be used to design radiolytically robust separation systems for spent nuclear fuel. Some of the other important findings of such studies are mentioned below in brief:

1. Higher radiation resistance (in general) have been reported in the case of aromatic cations (imidazolium, pyridinium) than non-aromatic cations (pyrrolidinium, ammonium, and piperidinium), which has been attributed to the aromatic ring facilitating higher dissipation/diffusion of energy [13, 15-18, 21, 22].

2. Unsubstituted imidazolium cations appear to be at a distinct disadvantage (on radiation interaction) due to the vulnerability of the C(2) position [15, 21, 23-25]. Various studies have shown aliphatic side chains (of the cation) as one of the centres of radiation damage [15, 21, 23-25].

3. In aliphatic cations-based RTILs (such as phosphonium, ammonium, and pyrrolidinium cations), H atom abstraction reactions by the products of anion radiolysis at the penultimate and terminal carbon positions of the alkyl chains result in high yields of carbon-centered radicals at those locations [15, 20, 21].

4. Alkyl group length influences radiolytic stability of RTILs, which could be seen from the variation of UV-vis absorption peak after irradiation [15, 20-22].

5. High extraction efficiencies have been reported in the case of fuel-cycle actinide complexing agents (such as tetraoctyldiglycolamide (TODGA), and tributylphosphate) using RTILs as diluents [13-15, 17, 18].

6. Compared to conventional solvents, the solvated electron reaction rate constant was found to be slower in RTILs (e.g., quaternary ammonium [Tf_2N] based RTILs) by as much as two orders of magnitude [15, 20, 21, 25]. Besides, partially solvated ("pre-solvated" or "dry") electrons may persist on time scales of tens of nanoseconds in RTILs and exhibit more mobility than solvated electrons [21].

7. Aromatic cations containing RTILs exhibit rapid electron attachment to the ring, resulting in radicals with an absorption peak at 300-400 nm. This is in contrast to ammonium RTILs, which have a near-infrared absorption band due to solvated electrons [15, 20, 21].

8. The G-values for radiolytic hydrogen gas production from RTILs are lower than those for alkanes. This has been attributed to the fact that the significant fraction of the total radiation stopping power of the RTIL resides in the anion, and the majority of commonly used anions do not contain hydrogen atoms [15, 20, 21, 25-28].

9. Radiation exposure leading to the appearance of colour (or darkening), especially in the case of imidazolium RTILs have been attributed to the formation of oligomers as radiolytic products containing “double bonds” [28-31].

10. Large yields of C-centered radicals were observed in the aliphatic chains of phosphonium, ammonium, and pyrrolidinium cations, but not the imidazolium cation [15, 17, 21, 31, 32].

Undoubtedly, the results/observations of numerous studies indicate high radiation stability of RTILs (especially, aromatic cation-based). However, the majority of these investigations are based on imidazolium RTILs that contain halogens and fluoroanions (such as NTf_2^- , PF_6^- and BF_4^-), which are prone to hydrolysis, decomposition as well as reductive reactions [17, 21].

The two most desirable characteristics of any solvent to be used in the nuclear fuel cycle are high hydrophobicity and wide electrochemical window. FAP (tris(perfluoroalkyl)trifluorophosphate) based imidazolium RTILs, which have excellent hydrolytic stability, low viscosity, wide electrochemical window, and high thermal stability, could be suitable candidates in this scenario. Furthermore, the impact of various functional groups (such as the -OH group) on the radiation behaviour of imidazolium RTILs is rarely documented. With these goals in mind, we investigated the radiation stability of FAP RTILs as well as the effect of a -OH group substituted at the alkyl chain of the imidazolium cation. 1-ethyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate, ([EMIM][FAP]) and 1-(2-Hydroxyethyl)-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate, ([EOHMIM][FAP]) were chosen as the representative members of this new class of RTILs (molecular structure shown in Figure 7) [29, 30].

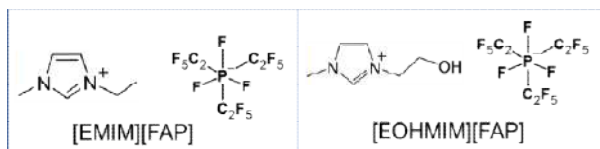


Fig.7. Structures of FAP-based imidazolium RTILs.

The selected FAP RTILs were irradiated by high energy electron-beam (7 MeV) sourced from a linear accelerator (LINAC). The absorbed dose was varied from 50-400 kGy. On irradiation, the colorless and transparent RTILs became yellow to orange to red with the increase in radiation dose, as can be seen from the picture shown in Figure 8.



Fig.8. Pictures of pre-and post-irradiated [EMIM][FAP] RTIL. A similar color appearance was observed in the case of [EOHMIM][FAP]. Reproduced from Ref. [29] with permission from the Royal Society of Chemistry.

To ascertain the species (cationic or anionic) responsible for the color evolution of post-irradiated FAP RTILs, two more RTILs with similar cation-anion combinations were selected and irradiated to the same dose. These were 1-ethyl-3-methylimidazolium ethyl sulphate, [EMIM][EtSO₄], and trihexyl(tetradecyl) phosphonium FAP, [PH(3)T][FAP]. Interestingly, only [EMIM][EtSO₄] exhibited a similar color change as [EMIM][FAP], however, [PH(3)T][FAP] remained colorless. This observation indicated that the color darkening on irradiation of FAP RTILs occurs due to the radiolytic degradation of the imidazolium cation. The ESI-MS studies confirmed the formation of oligomeric double-bond containing radiolytic products derived from the imidazolium cation. Meanwhile, it has been well-reported that the oligomeric products of imidazole derivatives are chromophoric having a high molar extinction coefficient (ϵ) of the orders of $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and exhibit similar optical absorption spectral features as in the present case of irradiated RTILs [34, 35].

The radiation stability and the effect of the -OH group were further investigated by measuring the physical properties of pre-and post-irradiated FAP RTILs [28, 29]. As can be seen from Table 1, there are negligible variations in the physical properties of [EMIM][FAP] even at a high absorbed dose of up to 400 kGy. However, considerable changes in the conductivity and thermal stability of [EOHMIM][FAP] were observed at higher absorbed doses. These variations in the case of post-irradiated [EOHMIM][FAP] signifies the influence of the -OH group, as the bonding interactions between the ionic species are appreciably different compared to [EMIM][FAP].

Table 1: Physical properties of pre-and post-irradiated FAP RTILs measured at various absorbed dose levels. Reproduced from Ref. [29] with permission from the Royal Society of Chemistry.

FAP IL	Dose (kGy)	Refractive Index	Density, (g/cc)	Viscosity, cP	Conductivity, mS.cm ⁻¹	Electrochemical window (V)	Decomposition Temp., T _d (K)
[EMIM][FAP]	0	1.36886	1.7065	57	3.20	5.5	361.2
	100	1.36892	-	52	3.50	5.6	-
	300	1.36919	1.7067	-	-	-	-
	400	1.36925	-	50	3.21	5.5	360.15
[EOHMIM][FAP]	0	1.37775	1.7618	177	1.0	4.7	301
	100	1.37821	-	174	1.02	5.1	-
	300	1.37847	1.7627	-	-	-	-
	400	1.37841	-	179	0.636	4.8	283

The considerable changes in the physical properties of [EOHMIM][FAP] on irradiation indicate their low radiation resistance as compared to [EMIM][FAP]. Apart from this, the H_2 gas yield ($G(H_2)$) was found to be more in case of post-irradiated [EOHMIM][FAP] (i.e., $(8.5 \pm 0.4) \times 10^{-9}$ mol/J) than what was observed for [EMIM][FAP] ($7.6 \pm 0.2 \times 10^{-9}$ mol/J) on irradiation.

Pulse radiolysis studies carried out to delineate the mechanism for the radiation-induced changes in [EMIM][FAP] and [EOHMIM][FAP] showed changes in OD values (Figure 9) and a marked difference in the transient decay behaviors (Figure 10) in the presence of O_2 indicating the formation of a new species (Figure 10B).

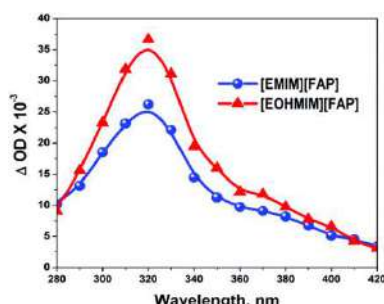


Fig.9. Transient absorption spectra (at 3 μ s after the e-pulse) of neat [EMIM][FAP] and [EOHMIM][FAP]. Reproduced from Ref. [29] with permission from the Royal Society of Chemistry.

The formation of an alkyl radical at the cation's ethoxy side-chain is highly probable, and the subsequent addition of O_2 results in the formation of a peroxy radical, which exhibits strong absorption in the 320-370 nm range. In a radiation-filled environment, the two RTILs behave differently, which is reflected in the number and yield of products.

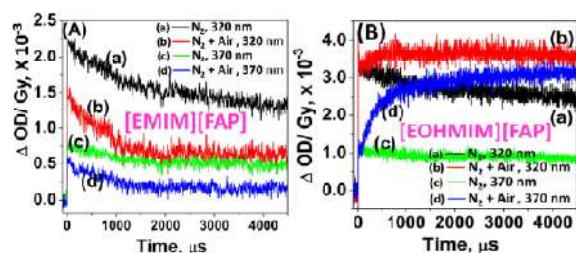


Fig.10. Transient decay in the absence and presence of oxygen for [EMIM][FAP] (A) and [EOHMIM][FAP] (B). Reproduced from Ref. [29] with permission from the Royal Society of Chemistry.

Nonetheless, experimental observations suggest the critical role of the FAP anion in strengthening the radiation resistance of the FAP-based imidazolium RTILs. Essentially, the radiation resistance of various anions (with the same cation) could be quantitatively explained based on their fractional stopping powers (i.e., electron counts of anions relative to the total (cation + anion) electron count). Assuming the same

cation (i.e., EMIM), the fractional stopping powers of some anions studied most extensively in radiation stability studies (of RTILs) were calculated to be 0.78, 0.69, 0.54, 0.53, 0.40 for FAP^- , Tf_2N^- , TfO^- , PF_6^- and BF_4^- , respectively [28]. Thus, it is anticipated that FAP-based imidazolium RTILs would exhibit better radiation stability than the aforementioned anions.

Although the physicochemical properties of FAP-based imidazolium RTILs were found to vary insignificantly even at high absorbed doses, the photophysical investigations categorically point out significant changes in the orientations and molecular rearrangements of the ions on irradiation. The observations/findings of this particular study are provided in reference [30]. Briefly, subsequent quenching and enhancement of fluorescence at lower and higher excitation wavelengths respectively were observed in the case of post-irradiated [EMIM][FAP]. This behavior has been attributed to the irradiation-induced breakdown of different pre-existing associated structures of ions and subsequent formation of various radiolytic products including oligomers. The fluorescence lifetime behavior of post-irradiated FAP RTILs also confirmed it. Besides, Raman spectral studies indicated very interesting changes in the molecular structure of [EMIM][FAP] on irradiation.

Nonetheless, such studies may aid in gaining a comprehensive understanding of the radiation-induced degradation of RTILs and their mechanistic pathways.

DES: Brief introduction and radiation chemical studies

The word “eutectic” originates from the ancient Greek *eutēktos*, which means easily melted [33]. And, a eutectic point signifies a temperature at which a mixture of two solids becomes fully molten at the lowest melting temperature, relative to that of either compound (Figure 11).

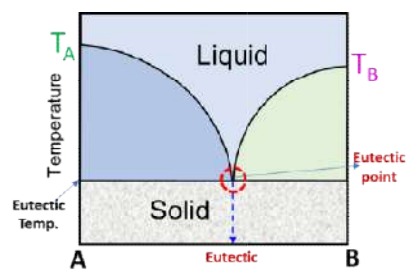


Fig.11. General solid-liquid phase diagram of a binary mixture. T_A and T_B represent the melting temperatures of compounds A and B, respectively.

Defining a deep eutectic solvent (DES) is still a controversial subject and there are various reported definitions. In general, DES can be defined as the solutions of Lewis (or Brønsted) acids and bases, which form a eutectic mixture [33-36]. The concept of DES was first described by Abbot et al. [37] in 2001. These

solvents are considered as a new class of RTIL-analogues since they share many characteristics of the latter, such as low vapor pressure, high polarity, and tunable chemical properties. Moreover, because of the limitations of RTILs, such as toxicity, poor biodegradability, and high cost, DESs have emerged as a viable alternative. Other advantages of DESs are facile synthesis, no post-synthesis purification, and inexpensive constituents [33-36]. In the majority of the cases, a DES is obtained by mixing a quaternary ammonium or phosphonium salt with a hydrogen-bond donor (HBD). Some common hydrogen-bond acceptors (HBAs) and HBDs used for preparation of DESs are shown in Figure 12.

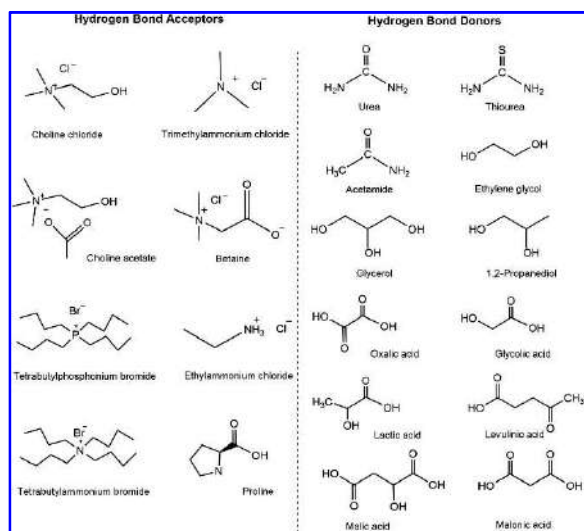


Fig.12. Common HBAs and HBDs used for the preparation of DESs.

The commonly used DESs along with their freezing points and constituent HBAs and HBDs are provided in Table 2.

Table 2: Freezing point temperatures (T_f) of a selection of DESs [34-36].

HBA	HBA mp/°C	HBD	HBD mp/°C	HBA:HBD	DES T_f /°C
choline chloride	303	urea	134	1:2	12
choline chloride	303	thiourea	175	1:2	69
choline chloride	303	1-methyl urea	93	1:2	29
choline chloride	303	1,3-dimethyl urea	102	1:2	70
choline chloride	303	1,1-dimethyl urea	180	1:2	149
choline chloride	303	acetamide	80	1:2	51
choline chloride	303	benzamide	129	1:2	92
choline chloride	303	ethylene glycol	-12.9	1:2	
choline chloride	303	glycerol	17.8		
choline chloride	303	adipic acid	153	1:1	85
choline chloride	303	benzoic acid	122	1:1	95
choline chloride	303	citric acid	149	1:1	69
choline chloride	303	malonic acid	134	1:1	10
choline chloride	303	oxalic acid	190	1:1	34
choline chloride	303	phenylacetic acid	77	1:1	25
choline chloride	303	phenylpropionic acid	48	1:1	20
choline chloride	303	succinic acid	185	1:1	71
choline chloride	303	tricarballic acid	159	1:1	90
choline chloride	303	MgCl ₂ ·6H ₂ O	116	1:1	16
Methyltriphenyl phosphonium bromide	231	glycerol	17.8		-4.03
Methyltriphenyl phosphonium bromide	231	ethylene glycol	-12.9		-49.34

Compared to RTILs, the research into DESs is comparatively in its infancy. Nonetheless, the studies on DESs and their potential applications in a variety

of fields, including energy, healthcare, and the environment, have accelerated significantly over the last two decades [33-36].

As RTIL analogues, DESs are also being considered for use in radiation-filled environments such as the nuclear fuel cycle and space. Of late, a representative family of DES (ChAcDigA made of a combination of choline acetate and diglycolic acid) was tested for processing nuclear waste, to selectively recover minor actinides (MA) from highly active raffinate solutions [38]. The radiolytic stability of the DES was also tested by irradiating it to absorbed doses in the range 25–100 kGy. The mass spectrometric studies of the irradiated solutions were found to be unaltered with respect to fresh ones. Apparently, it highlights the radiation resistance aspect of the DES used. Besides, some other preliminary studies have demonstrated the use of DESs in the speciation and redox chemistry of lanthanides and actinides, which has implications for nuclear fuel reprocessing [38-40].

Nonetheless, successful use of DESs in radiation-filled environments will require a fundamental understanding of their radiation chemistry, which involves characterizing the primary steps of DES radiolysis, solvation dynamics, charge transport, stability, and lifetimes of reactive intermediates, redox reactions, and so on. More so, these radiation chemical studies of DESs will aid in the development of a database that could be beneficial for their applications in energy production, the chemical industry, environment, healthcare, etc.

In one of the very first radiation chemical investigations, the formation of solvated electrons has been reported in a DES, i.e., reline, composed of choline chloride as a hydrogen bond acceptor and urea, as hydrogen bond donor, at a molar ratio of 1:2. [41]. The transient absorption spectra obtained from deaerated reline after electron pulse radiolysis are shown in Figure 13.

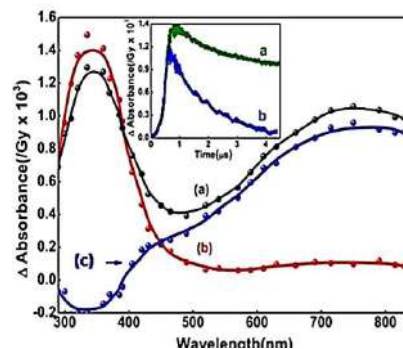


Fig.13. Transient absorption spectra obtained at 700 ns in argon-purged (a) neat reline, (b) reline containing 150 mM sodium nitrate, and (c) subtracted spectra. The inset shows the kinetic traces obtained in argon-purged neat reline at (a) 340 nm and (b) 760 nm. Reprinted (adapted) with permission from [41]. Copyright {2018} American Chemical Society.

A broad peak at 760 nm could be assigned to the solvated electron, which is based on its faster decay, and nearly complete disappearance in the presence of appropriate concentrations of NO_3^- ions (Figure 13b). Scavenging by N_2O and formation of a pyrene anion were other evidences in favour of this attribution. Further, an absorption peak centered at 350 nm was unaffected by the presence of nitrate anion (Figure 13b), and it was most likely caused by the contribution of the hole itself and hole-generated species. The hole-eliminated transient absorption spectrum of the solvated electron is thus solely represented by curve c of Figure 13. The solvated electron in a choline cation (and NTf_2^- anion) containing RTIL shows a peak in the wavelength range of 630–650 nm, close to that in alcohols and RTILs containing alcohol-substituted ammonium cations [13, 20, 21]. Nevertheless, the solvated electron absorption exhibited a red-shift to 760 nm in reline as compared to that in choline- NTf_2^- . This has been attributed to the fact that, while reline contains a choline cation, the presence of urea, a hydrogen bond donor, creates an overall different environment for solvation in addition to the chloride anion. Besides, the solvated electron has been observed in two other DESs, ethaline, and glyceline, which are composed of choline chloride as a hydrogen bond acceptor and ethylene glycol, and glycerol (Gly) as hydrogen bond donors, respectively, at a molar ratio of 1:2. Table 3 provides comparative data of the absorption maxima, decay rate constants, and yield of e_{sol}^- in reline, ethaline, and glyceline (at 500 ns).

Table 3: Comparative Study of the absorption maxima, decay rate constant, and yield of e_{sol}^- in reline, ethaline, and glyceline (at 500 ns). *Reprinted (adapted) with permission from [41]. Copyright {2018} American Chemical Society.*

DESs	$\lambda_{\text{max}}(e_{\text{sol}}^-)$ (nm)	$k(e_{\text{sol}}^-)$ (s^{-1})	τ (avg. lifetime) (ns)	$G(e_{\text{sol}}^-)$ ($\mu\text{mol J}^{-1}$)
reline	760	$(7.00 \pm 0.05) \times 10^5$	1400 ± 10	0.093
ethaline	650	$(1.22 \pm 0.01) \times 10^6$	800 ± 5	0.163
glyceline	610	$(9.60 \pm 0.03) \times 10^5$	1000 ± 3	0.160

The variations in the transient absorption spectra and the associated kinetics of solvated electrons in these DESs have been explained based on polarity, hydrogen-bonding effect, and the moieties responsible for creating the environment for solvation. Apart from that, an intriguing but important finding is that presolvated electron capture by a DNA base, which is important in cancer radiotherapy, could be easily monitored in these liquids over a much longer time scale than in aqueous solutions.

To summarize, such fundamental radiation chemical investigations are valuable in understanding the diverse applications of these futuristic solvents.

Applications of RTILs and DESs in Nanoscience

The development of economically viable and value-added sustainable processes for manufacturing nanomaterials is becoming an important task. In this perspective, there has been an increasing interest in the use of green solvents such as RTILs and DESs for the synthesis of nanomaterials [42–45].

Essentially, RTILs and DESs are structured solvents and possess heterogeneity at the microscopic level. The unique physicochemical properties of these solvents offer unique advantages compared to traditional organic and aqueous solvents such as high polarity, negligible vapor pressure, high chemical and thermal stability, and high ionic conductivity. Additionally, recycling and the flexibility to tailor the properties are other advantageous aspects of these solvents over the conventional ones [4, 6, 8, 33–36].

In the literature, multifarious ways have been reported in which RTILs can interact, shape, and stabilize nano- and microparticles. Further, RTILs may play multiple roles in the nanostructure preparation processes, such as a solvent, a reducing agent, a stabilizer, and a structuring agent (or a soft template). Various studies indicate different kinds of nanoparticle stabilization provided by RTILs, such as electrostatic, steric, viscous, solvation, and by intermediates or by-products [42, 44–46]. Apart from this, the low surface tension of the RTILs results in a high nucleation rate, which facilitates the generation of very small particles with weak Ostwald ripening.

Various nanomaterials of metals, semiconductors, metal oxides, ceramics, carbon-based, etc. have been synthesized in RTILs by using different methodologies [42, 44–46]. Our group has also demonstrated the use of RTILs as a host matrix for the synthesis of a variety of nanomaterials, especially belonging to the chalcogen family and II–VI, IV–VI groups [47–55]. Both wet-chemical and radiation-driven methodologies have been employed therein. Some of these studies have been briefly summarized as follows.

CdSe islands embedded in Se nanofibers were obtained by using electron beam irradiation while using RTIL as a host matrix [47]. Herein, RTIL (1-Ethyl-3-methyl imidazolium ethyl sulfate, [EMIM][EtSO₄]) simultaneously played the role of a solvent, stabilizer and a shape guiding template. On irradiation, imidazolium-derived radical species are formed (along with other radiolytic species/products), which are reducing in nature. These radicals reduce the precursors dissolved in the RTIL. A 3-D fibrous networking structure formed in electron-beam assisted approach could be attributed to the high dose rate, while 1-D anisotropic structure comprising of nanosheets and needles were obtained in case of $\square$ -irradiation method. Most probably, the $\square$ - $\square$ stacked structure of the RTIL is playing a shape directing template. The schematic representation of the formation mechanism is provided in Figure 14 [47].

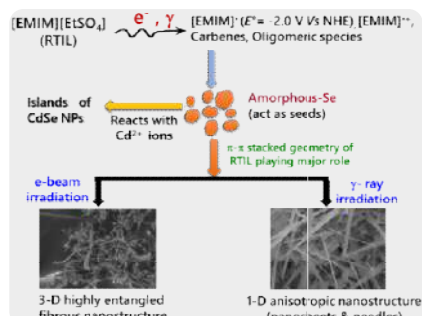


Fig.14. Scheme showing the proposed mechanism for the nanomorphology i.e., Islands of CdSe nanoparticles within Se nanofibers. Reproduced from Ref. [47] with permission from the Royal Society of Chemistry.

In another work, a highly porous nanomorphology of SnSe was obtained in *neat* imidazolium-based RTIL by electron-beam assisted technique [48]. The nanomorphology of the SnSe could be tuned from mesoporous (in electron beam irradiation) to corn-flake-shaped structure (in γ -ray irradiation) by varying the dose rate.

The structural and the fluidic aspects of the RTILs in controlling the morphology of the nanomaterials were explored by synthesizing CdSe nanoparticles at ambient conditions (Figure 15) [49].

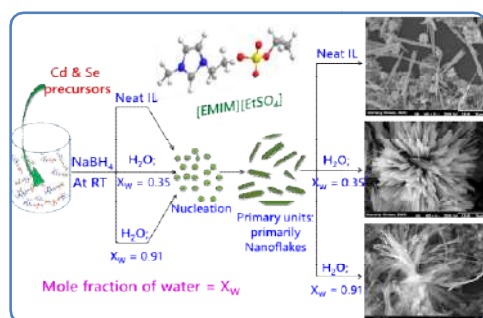


Fig.15. Schematic representation showing the probable intermediate stages with different nano/micromorphologies of CdSe synthesized in RTIL ([EMIM][EtSO₄]), at various time intervals and mole fractions of water. Reproduced from Ref. [49] with permission from the Royal Society of Chemistry.

The co-existence of anisotropic 2D and 3D nano/microstructures was observed in the case of neat RTIL. It was accredited to the fluidic aspects of the RTIL in conjunction with its *hydrogen bond-co- π - π stacking* mechanism, which enabled it to perform a function of a diffusion controller and an anisotropic growth director, respectively. It was proved by adding a calculative amount of water into the RTIL. The well-oriented 3D flower-like morphology was formed predominantly when a small amount of water (mole fraction, $X_w = 0.35$) was added to RTIL. Further addition of water ($X_w = 0.91$) resulted in irregular alignment and random fusion, which eventually gave distorted flower-like structures [49]. RTILs as a host matrix were found to be an excellent candidate for the synthesis as well as prolonged

stabilization of α -Se nanoparticles, which otherwise are highly susceptible for phase transformation (low glass-transition temperature $\sim 35^\circ\text{C}$). Both conventional wet-chemical [50-52] and radiation-assisted methods [53-55] were used for their preparation.

In the wet-chemical approach [51], stirring of the reaction mixture comprising of only RTIL, i.e., 1-Ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]), and sodium selenite (Na_2SeO_3) resulted in the formation of α -Se nanoparticles (Figure 16). Apparently, the RTIL itself played the role of a solvent, a stabilizer, and a reducing agent. Interestingly, the phase as well the morphology of the α -Se nanoparticles could be tuned by simply increasing the reaction temperature from 35 to 70 and 120°C . Besides, the prolonged stabilization of α -Se nanoparticles, the reuse of RTIL for the synthesis of the next batch of nanoparticles, addanew dimension to this work. The α -Se nanoparticles exhibited antioxidant behaviour and selectively killed cancer cells, demonstrating their potential for societal relevance.

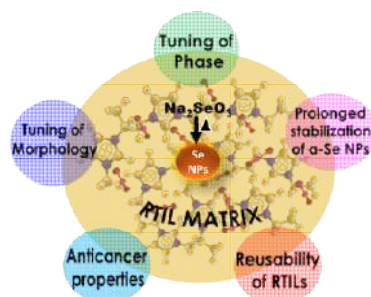


Fig.16. Graphics representation of the synthesis of α -Se nanoparticles in RTIL, tuning of their phase, morphology and anticancer applications. Reproduced from Ref. [51] with permission from the Royal Society of Chemistry.

A radiation-assisted rapid approach was reported for the synthesis of α -Se nanoparticles in the RTIL [55]. The effects of cation-anion combination and $-\text{OH}$ functionalization of RTILs on the size and phase stability of α -Se nanoparticles were investigated (Figure 17). It was observed that the density (or packing order) of RTILs influences the size of nanoparticles, whereas their stability (against size variations) can be primarily related to the viscosity (of RTILs). Besides, in the case of $-\text{OH}$ group-containing RTIL, an overall improvement in control over the size of the nanoparticles, polydispersity, and stabilization efficiency was observed.

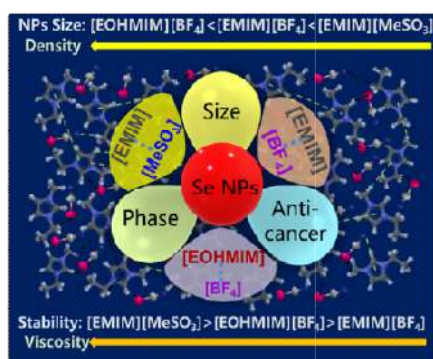


Fig.17. Graphics representation of the synthesis of □-Se nanoparticles in RTIL, tuning of their phase, morphology, and anticancer applications. Reprinted (adapted) with permission from {55}. Copyright {2021} American Chemical Society.

In comparison to RTILs, the research into the application of DESs in nanoparticle synthesis is still in its early stages. DESs are distinct from RTILs as they may not be necessarily ionic, while RTILs are purely comprised of ions [42, 43]. Further, in RTILs, the default structure is of amphiphilically separated domains (presence of a defined d-spacing) that are exploitable in synthesis. However, due to the extensive hydrogen bonding, DESs are generally not sufficiently amphiphilic in character. Nonetheless, the excitement surrounding DES stems primarily from the fact that they provide RTIL-type performance in applications but with an additional molecular component (the HBD), which makes them inexpensive and simple to produce.

In the last decade, DESs have been explored for the synthesis of different kinds of nanomaterials [42, 43, 56]. One of the very first works on the combination of nanotechnology and DES was reported as late as 2008 for the synthesis of gold nanoparticles. Since then, the nanomaterials of other noble metals (such as platinum, palladium, and silver), carbon-based, metal oxides (TiO_2 , CeO_2 , Mn_3O_4), spinel ferrites, and alloyed nanoclusters (PtCu) have been synthesized in DESs [42, 43, 56].

Of late, our group has recently reported the synthesis of non-toxic and photoluminescent tin oxide (SnO_2) nanoparticles in DESs by radiation and solvothermal methods (Figure 18) [57].

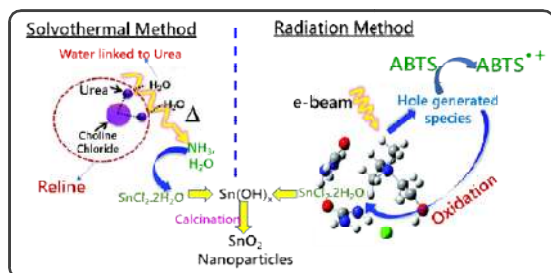


Fig.18. Graphics representation of the synthesis of SnO_2 particles by solvothermal and radiation-assisted methods. Reproduced from Ref. [57] with permission from the Royal Society of Chemistry.

An electron beam radiation-assisted approach showed better results in tuning the size and morphology compared to the solvothermal process. The nanoparticles exhibited marginal cytotoxicity even up to a concentration of 100 μM , which rendered them safe for cell imaging studies. Additionally, the antioxidant studies revealed the excellent potential of these nanoparticles to inhibit oxidative damage by reactive radical species.

Overall, DESs provide significant opportunities and new perspectives for creating advanced nanostructures in an anhydrous or low-water environment.

Conclusions

There exists an intertwining connection between population, energy, and the environment. Any sort of imbalance may have a devastating influence on the ecosystem. The judicious use of available resources is one of the key steps to avoid such a situation. Besides, scientists have a big responsibility to maintain and satisfy the above equation. It is pertinent to explore and promote technologies employing green and sustainable protocols. In this pretext, the advent of novel green solvents such as RTILs and DESs may provide a better alternative to the organic solvents being used at mass scales in industries and other commercial sectors.

This article provides a brief introduction of these novel solvents along with an overview of their radiation chemical studies and applications in the controlled synthesis of nanomaterials.

The findings/observations of the radiation chemical studies conducted over the last two decades clearly suggest the high radiation stability of RTILs. However, there are still a lot of challenges and unanswered questions in realizing their actual use. One of the foremost is the cost-effective development of “task-specific” RTILs with desirable features. Furthermore, RTILs in spent nuclear fuel reprocessing require an understanding of their reactivity with diverse chemical species (posing as scavengers, poisons, impurities, or contaminants) present in the system. Apart from this, RTILs are also being explored for their applications in the energy and healthcare sectors, which could be highly affected by the redox chemistry involved therein. Therefore, radiation chemical investigations of RTILs are critical for their practical uses.

While DESs are considered analogues to RTILs, their composition, and physicochemical properties are not identical. Radiation chemical studies of DESs are still in their early stages and require additional attention before they can be considered for use in radiation-filled environments.

RTILs have already proved their utility for nanosynthesis. A variety of nanomaterials have been synthesized in these solvents. Likewise, DESs have aroused a lot of interest in nanoscience. Moreover, both these solvents have some obvious advantages in

nanomaterial synthesis. For instance, (a) both the fluids possess the ability to dissolve both inorganic and organic precursors, (b) low interfacial tension of these solvents can increase the nucleation rate, (c) their properties can be tuned easily, (d) efficient stabilization of particles and so on. However, thermal instability and high viscosity are currently major limitations of DESs that must be addressed before they can be effectively utilized in nanosynthesis.

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Biodata



Dr. ApuravGuleria joined Bhabha Atomic Research Centre, Mumbai, India, as a scientific officer in 2009 after completing a one-year orientation course from 52nd batch of BARC Training School. His current research area includes a fundamental level understanding of the radiation-induced chemical processes in microheterogeneous media such as RTILs and microemulsions, and exploring the use of high energy ionizing radiations in the fabrication of nanomaterials with unique features for various applications related to sensing, biomedical, and forensics. To date, he has published about 42 research papers in peer-reviewed national & international journals. He was twice awarded the Dr. Hari Mohan Memorial Award in Radiation Chemistry for best poster presentation, as well as the Department of Atomic Energy's "Young Scientist Award-2016." In the year 2021, he was elected as a Young Associate of the Maharashtra Academy of Sciences for his significant contributions to the field of Chemical Sciences.



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Application of ionic liquids in Separation Science

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Introduction

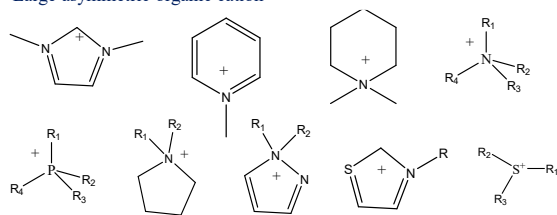
On the growing awareness of the environmental impact associated with the use of volatile organic compounds, room temperature IL(IL) has gained an worldwide acceptance as a potential 'green' alternatives to the volatile organic compounds due to the advantageous properties like

- Low vapour pressure
- Wide liquid range
- High chemical and radiation stability
- Wide electrochemical window
- High flash point
- High degree of solubility in for a wide range of organic, inorganic and polymeric materials

The most fascinating properties of IL is the high degree of tunability [1-3]. A small modification either in cationic or anionic moieties can induce a significant change in the physico-chemical properties of the IL and hence, they are called as 'designer solvents'. If the structure and activity relation is established for certain property of ionic liquids; they can be tuned accordingly.

Cation

Large asymmetric organic cation



Anion

Inorganic or organic anions



Water immiscible → Water soluble

Fig.1. Structures of some common ionic liquids

IL is composed of large organic cations with organic or inorganic anions (Fig.1). Due to the charge delocalization, the lattice energy of the system becomes too low to exist as solid crystal and hence remains in the liquid state. Ionic liquids have been extensively used in organic synthesis, sensor applications, electrochemistry, separation science and membrane technology [4-6]. Sometimes IL

evidenced some unique chemistry, which otherwise not observable conventionally. In functionalized ionic liquids, the selectivity and efficiency were induced to the IL itself by covalently linked the functional groups to the IL moieties (Fig.2). These functionality can be introduced either in cationic or anionic part of ionic liquid. Diglycolamide functionalized (DGA) IL, carbamoyl methylphenyl phosphine oxides (CMPO) functionalized ILs showed high efficiency as well as selectivity towards trivalent actinides (Am^{3+} , Cm^{3+} etc) over other oxidation states [7-8]. The phosphine oxide, monoamide functionalized IL showed high affinity towards actinides [9-10]. Beta diketonate functionalized IL has also been employed for task specific applications [11].

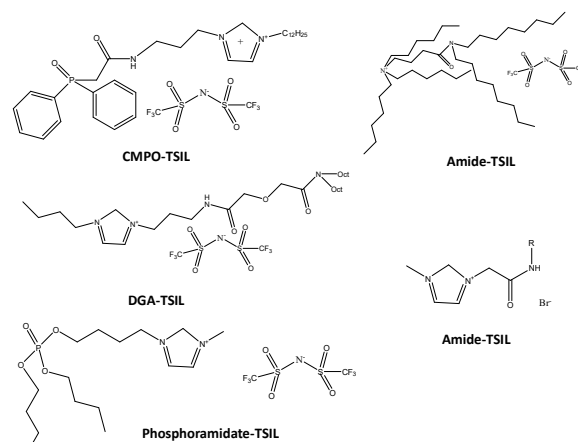


Fig.2. Structures for functionalized ionic liquids for task specific applications

In nuclear establishment the potential use of ionic liquids are found for aqueous as well as non-aqueous reprocessing [12-13]. As a diluent, IL in combination with conventional or novel ligands have extensively been used for actinide separation. In most of the cases, the use of IL was found to enhance the distribution ratio for actinides (Table 1). Not only efficiency, the selectivity was also found to improve [14]. However, several cases have also been reported in literature, where application of IL did not improve the extraction efficiency of actinides [15]. For most of the cases, the trend in actinide extraction remained the same (Table 2), as seen for conventional diluents [16]. The actinide contraction also influenced the complexation and the subsequent mass transfer. Some comparative evaluation of the extraction

characteristics of using ILvis-a-vis conventional molecular diluent are discussed subsequently.

Table 1: The improvement in D values in ILvis-a-vis molecular diluents

Ligand	Ligand conc. (M)	Feed acidity (M)	Diluent	D _A _m	Ref
TODGA	0.01	1 M HNO ₃	C ₄ mimPF ₆ n-dodecane	102 0.2	[1]
TDGA	0.001	0.5 M HNO ₃	C ₄ mimNTf ₂ dodecane-isodecanol	91 0.0 5	[16]
C4GDA	0.005	0.5 M HNO ₃	C ₄ mimNTf ₂ dodecane-isodecanol	748 8	[14]
C8DGA	0.005	0.5 M HNO ₃	C ₄ mimNTf ₂ dodecane-isodecanol	0 68	[12]
DGA pillar[5]arene	0.002	0.5 M HNO ₃	C ₈ mimNTf ₂ octanol	728 1.5	[17]
CMPO pillar[5]arene	0.001	1 M HNO ₃	C ₈ mimNTf ₂ octanol	173 5	[18]
Pyrazine functionalized Calix[4]arene	0.001	3 M HNO ₃	C ₄ mimNTf ₂ Nitrobenzene	850 13	[19]

Extraction mechanism and speciation

For a combination of neutral ligand and molecular diluent, the extraction was reported to proceed via 'solvation' mechanism, involving neutral complex; while the extraction mechanism can be tuned by application of ionic liquid. Most of the literature reported the use of alkyl methyl imidazolium based ILs. It was observed that, on replacing the chain length of alkyl group at C₃ position of methylimidazolium IL, the extraction characteristics changes. For lower homologue of alkyl group, the extraction predominantly proceeds via 'ion exchange' mechanism, while for higher homologue the extraction proceeds via 'solvation' mechanism. The distribution ratio for actinides was found to follow the

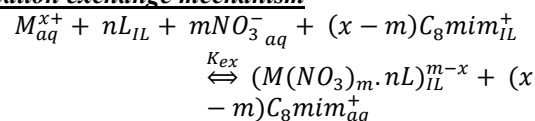
Elements	Ligand	C ₄ mimNTf ₂	C ₆ mimNTf ₂	C ₈ mimNTf ₂
Am(III)		91	33	3.1
Pu (IV)		30	17	1.4
U(VI)		0.24	0.23	0.06
Cs(I)	0.001	0.12	0.04	0.02
Sr(II)	M	0.27	0.12	0.02
Eu(III)	TDGA	218	64	12.7

trend C₄mim⁺ > C₆mim⁺ > C₈mim⁺ [16]. This trend can be attributed to the solubility of the cations in aqueous phase during extractive mass transfer via 'cation exchange' mechanism. It was also reported in the literature that, the methylimidazolium based IL with shorter alkyl substituent followed 'cation exchange' mechanism, while that with longer chain length followed 'solvation' mechanism.

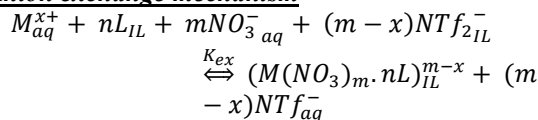
Table 2. Effect of structural modification of IL on D values for actinides/lanthanides and long-lived fission products

The plot of D values as a function of aqueous phase acidity is an indication of the mechanism of extraction. For conventional 'solvation' mechanism, the D values were found to increase with increase in aqueous feed acidity due to law of mass action, followed by a plateau, attributed to the competition of H⁺ ions. In case of 'cation exchange' mechanism, the D values were found to decrease with increase in aqueous phase acidity (as seen in case of most of the IL based systems). On the other hand, the example of anion exchange mechanism is very rare. At higher aqueous feed acidity (beyond 6 M HNO₃), UO₂²⁺ ion was found to be extracted via anion exchange mechanism in IL using 1.1 M TBP [15]. The Sr²⁺ extraction by DCH18C6 in 1-ethyl-2-methylpyridinium bis(trifluoromethyl sulfonyl imide) also followed 'anion exchange' mechanism [20]. During the extraction of uranyl ion by diamide (5-bromo-N1, N3-diisopropylisophthalamide) in bicyclooctanium ionic liquid, the extracted species was [UO₂(NO₃)₃L₂]⁻, predominantly following 'anion exchange' mechanism. In piperidinium and pyridinium-based IL, the species were UO₂(NO₃)₂L and UO₂(NO₃)₂L₂, respectively, following 'solvation' mechanism. In imidazolium-based IL, the species was [UO₂(NO₃)L]⁺, following 'cation exchange' mechanism [21] (Fig.3).

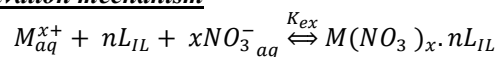
Cation exchange mechanism



Anion exchange mechanism



Solvation mechanism



The equilibrium constants for the extractive mass transfer can be expressed as follows

$$K_{ex} = \frac{[(M(NO_3)_m \cdot nL)_{IL}^{m-x}][C_8mim_{aq}^+]^{x-m}}{[M_{aq}^{x+}][L_{IL}]^n[NO_3^-]_{aq}^m[C_8mim_{aq}^+]^{x-m}}$$

$$K_{ex} = \frac{D_M[C_8mim_{aq}^+]^{x-m}}{[L_{IL}]^n[NO_3^-]_{aq}^m[C_8mim_{aq}^+]^{x-m}}$$

$$K_{ex} = \frac{D_M [NTf_2^-]_{aq}^{m-x}}{[L_{IL}]^n [NO_3^-]_{aq}^m [NTf_2^-]_{IL}^{m-x}}$$

$$K_{ex} = \frac{D_M}{[L_{IL}]^n [NO_3^-]_{aq}^m}$$

$$\log D_M = \log K_{ex} + n \log [L_{IL}] + m \log [NO_3^-]_{aq}$$

A plot of log D vs Log ligand concentration should follow a straight line (at a constant NO_3^- concentration) with a slope 'n', which is the number ligand molecules associated with each metal ion. Similarly, at a particular ligand concentration, the variation in LogD values as a function of $\log[NO_3^-]$ should follow a straight line, whose slope value indicates the number of NO_3^- , associated with each metal ions. This can reveal the speciation involved in extractive mass transfer. The 'cation exchange' involved the transfer of IL cations to the aqueous phase to maintain the electrical neutrality during mass transfer of metal-ligand complex. Similarly, in case of 'anion exchange' mechanism, the anionic part of IL got exchanged. Therefore, the water-soluble salt comprising either of the IL constituted ions can be utilized in perturbing the extraction equilibrium. Addition of water-soluble salt with similar cation would drive the equilibrium towards backward direction in case of cation exchange mechanism, resulting reduction in D values; while for 'solvation' mechanism or 'anion exchange' mechanism, it remained insensitive. Similar effect can also be seen for dissolution of water-soluble salt with same anion on 'anion exchange' mechanism.

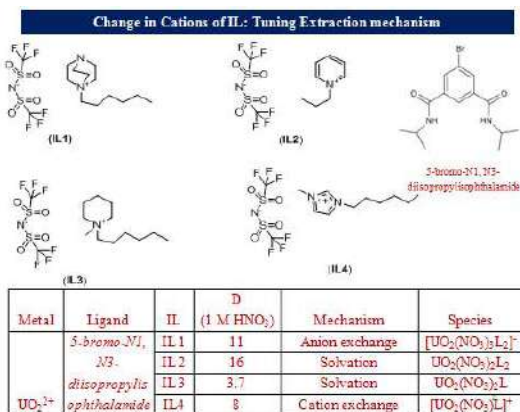


Fig. 3. Tuning the extraction mechanism by changing the cationic part of ILs [21]

The speciation in IL was found to be different compared to that in conventional molecular diluents. In some cases, the lower metal-ligand stoichiometry was reported in ionic liquid. The local environment around trivalent f-block element was investigated using Eu complex (as Am³⁺ surrogate) both in IL and molecular diluents. Photoluminescence was used to probe the same (Fig.4).

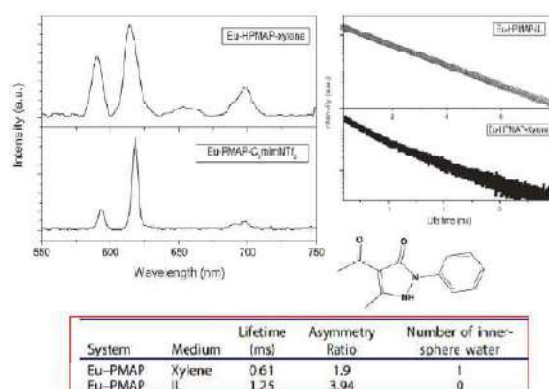


Fig.4. The emission profile and decay profile of Eu³⁺ DGA complexes in IL and molecular diluent [19]

The asymmetry around the metal ion was found to be more in IL compared to that in molecular diluents. The number of water molecules present in inner-sphere complex of Eu³⁺ was reported to be less in IL based system. The other radiative and non-radiative photophysical properties (Judd-Ofelt parameters, radiative transition probability, non-radiative transition probability, magnetic dipole moment, electrical dipole moment etc.) were quantitatively estimated and were reported to differ in IL based system than in conventional solvents. The cyclic voltamogram and the diffusion coefficients for the metal-ligand complex in IL and in conventional solvent were also reported to differ significantly, evidencing the difference in the speciation.

Stripping

Back extraction/stripping was found to be one of the most challenging aspects in using IL as media for actinide/lanthanide separation. In IL the metal ion forms very strong complex with the ligand molecules. Moreover, at lower aqueous pH mol. ty also the D values for metal ion was found dil y high unlike in conventional solvent. In view of that, either aqueous phase complexing agents were required for stripping of metal ions, or electrochemical stripping can be used to serve the purpose. In case of trivalent actinides a mixture of EDTA and guanidine carbonate was found to be successful in stripping the actinides from loaded IL phase. For tetra and hexa valent actinides aqueous solution of oxalic acid and sodium carbonate were found to serve the purpose.

Radiolytic Stability

Radiation induced performance deterioration is one of the major challenges faced by the separation scientists while encountering the processing of radiotoxic actinides, as there are continuous emission of high energy radiation and particles like alpha, beta etc. The ideal solvent system should be highly radio-resistant. ILbased systems showed high radiological

stability due to the formation of stable aromatic radicals on absorbing high energy radiation. Electron paramagnetic resonance investigation has been utilized for understanding the high radiological stability of IL based solvent systems. In C₃ alkyl methylimidazolium based ionic liquids, the formation of methylimidazolium radical ion has been evidenced [22] (Fig.5).

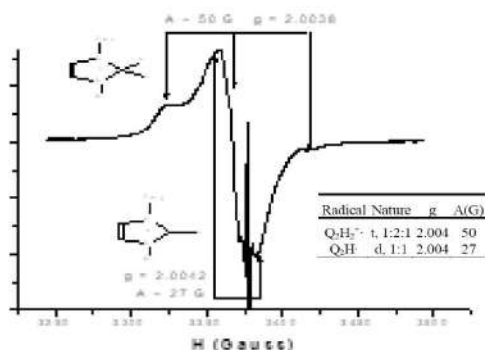


Fig. 5. The EPR spectra for methylimidazolium radical and radical cations generated during gamma irradiation [22]

Though the IL was reported to absorb a huge quanta of radiation energy forming radical cations, there was also some evidence of formation of radicals from the ligand architectures (Fig.6) [20].

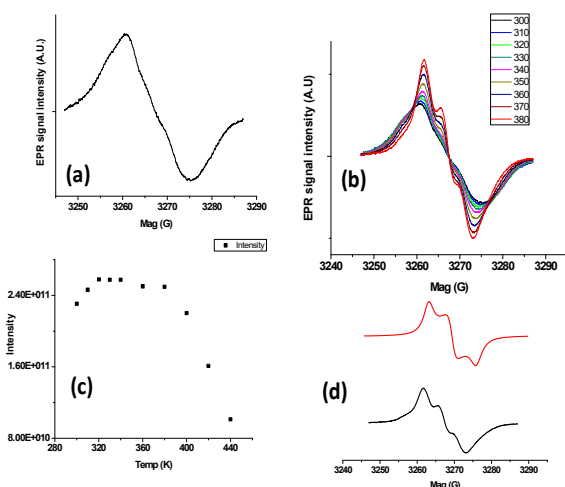


Fig.6. (a)EPR spectra of DHCC at 300 K after gamma irradiation; (b) Temperature dependence of the EPR spectra (c) Integrated intensity of EPR spectra as a function of temperature; (d) Experimental (black) and simulated (red) EPR spectra ($g_x=2.00105$, $g_y=2.00475$, $g_z=2.00835$, linewidth=2.0, 1.7, 1.7 G (Lorentzian)) [20]

Kinetics and thermodynamics

The extraction kinetics and thermodynamics are two very important aspects, which must be looked into. In ionic liquid, the overall mass transfer rate was found to be slower compared to that of molecular diluent

based systems due to the high viscosity coefficient of ionic liquid. An attempt was also made to establish a correlation between structural modification in ionic liquids to the kinetics of extraction. As the length of alkyl group in C₃ position of methylimidazolium based IL increased, the kinetics became slower. If the anions changed from PF₆⁻ to NTf₂⁻, the kinetics became faster [23]. All these were the artifact of the viscosity effect of ionic liquid (Fig.7).

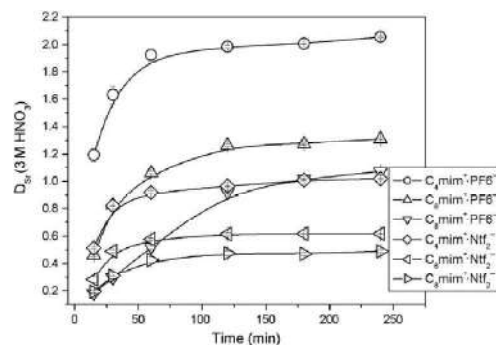


Fig. 7. The variation D_{Sr} as a function of time of equilibration for the ligand ditertiarybutyldicyclohexano 18crown 6 ether in IL with different structural modification [23]

The Gibb's-Helmoltz equation analysis can be exploited for understanding the variation in enthalpy change during extraction. The exothermicity/endothermicity can be calculated from the slope of the plot of log of extraction constants vs the reciprocal of the absolute temperature. At a particular temperature, change in Gibb's energy can be calculated from the extraction constant and hence this would give the indication of spontaneity of the extraction. The change in entropy can be evaluated from known Gibb's free energy and enthalpy change. The calculated thermodynamic constants in IL based systems were found to differ largely than that reported for conventional solvents (Table 3). The change in Gibb's energy was more negative in IL based systems indicating the formation of stronger complex.

Table 3. The comparative evaluation of thermodynamic parameters obtained during extraction of UO_2^{2+} and Th^{4+} using amide ligands in ILvis-a-vis dodecane [24]

Syst em	Metal ion	Dodecane			IL		
		ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
L I	UO_2^{2+}	-5.3	46	2	-7.5	1.1	28.7
		-4.1	41	1	-5.8	0.9	22.5
L I	Th^{4+}	-6.8	60	7	-9.2	1.6	36.0
		-6.0	55	2	-7.3	1.4	24.7

Items	3M HNO ₃	6M HNO ₃
Vol of Org. required for 1 sample	10 mL	20 mL
Vol of Org. required for 100 samples	1000 mL	2000 mL
Time of analysis of 1 sample	0.5 h	1 h
Time of analysis of 100 samples	50 h	100 h

units: ΔG (kJ/mol); ΔH (kJ/mol); ΔS (J/K/mol)

Non-aqueous reprocessing

A new approach has been reported in the literature employing IL in non-aqueous reprocessing. Considering the criticality issue of aqueous reprocessing; high temperature operation and drastic chemical conditions in molten salt reprocessing, IL was exploited as an alternative medium for direct dissolution of spent fuel and subsequent selective electrochemical stripping of the metal ions of the interest. The high degree of solubilizing the materials, good thermal and radiation stability, wide electric potential windows have been exploited to serve the purpose.

In Chemical Quality Control (CQC) of nuclear materials

The IL based separation has also been employed in CQC of nuclear fuel and associated materials. During the trace metal assay of U and Th based nuclear fuel by ICP-OES, the matrix separation is a prerequisite to avoid the spectral interference of emission rich matrix. The ideal solvent should be such that, it would preferentially separate the emission rich matrix elements (U, Th, Pu, Am etc) without any loss of metallic constituents (B, Be, Cd, Cu, Al, Dy, Eu, Fe, K, Na, Mn, Mo, Ni, Sn, V, W, Zn etc) even at trace level (**Fig.8**). The application of IL led to faster analysis (lesser analysis time than conventional solvents) and generation of lesser volume of organic waste, without any compromise on the analytical performance (**Table 4**). The reliability of the data has been evaluated by statistical t test, while the reliability of the precision has been evaluated by the F-test.

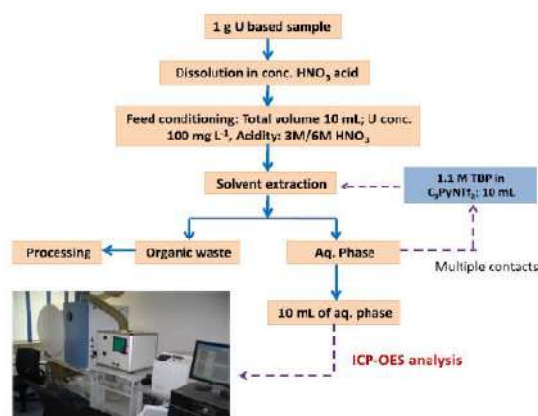


Fig.8. The steps used for CQC of U based nuclear materials by ICP-OES: application of IL for preferential removal of U [25]

Table 4. Application of IL to reduce analysis time and volume of organic waste [25]

Poly(ionic liquids) or supported ionic liquids in Membrane Science

The polymerization of either of the ionic parts of the monomers of IL can lead to the formation of poly(ionic liquids) (PILs). These substances have the advantageous properties of polymers as well as the ionic liquids. These polymers have been extensively used for the removal of dyes and other micro-pollutants from different aqueous industrial waste streams. The supported IL membranes and poly(ionic liquid) grafted/augmented membranes have been utilized for achieving the separation between the aliphatic/aromatic homologues: hexane/benzene; heptane/toluene etc, not achievable by conventional sieving mechanism [26-27]. The interaction between the pi electron clouds of the aromatic moieties, present in the IL and the elements of interest is the driving force. The fractionation of benzene, naphthalene and anthracene was also achieved. The electron withdrawing/ releasing effect, inductive effect and resonance effect have been used for the fractionation nitrobenzene, toluene, phenol etc. This membrane has also been used for fractionation of regio-isomers, sugar and dye molecules. The grafting of PIL brush was found to improve the antifouling characteristics of the membrane. Due to the presence of repeated cationic and anionic charge on the PIL brushes, the membrane exerted electrostatic repulsive interaction to avoid scaling of inorganic salts and adhesive interaction with the micro-pollutants having surface charge.

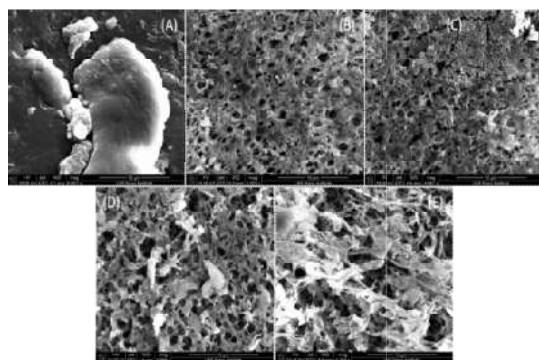


Fig. 9. The SEM images for (A) PVDF membrane; (B) zwitterion modified membrane; (C) IL modified membrane; (D) potassium permanganate modified membrane; (E) sodium hydroxide modified membrane challenged with PW[28].

This antifouling characteristics were evidenced from the SEM images of the fouled membrane during processing of actual produced water and was found to be better than hydrophilic modification (using hexaethyleneglycol dimethacrylate, ethylene diamine etc) of hydrophobic membranes (polyvinylidene fluoride, polypropylene, polytetrafluoroethylene etc) during membrane distillation (Fig.9).

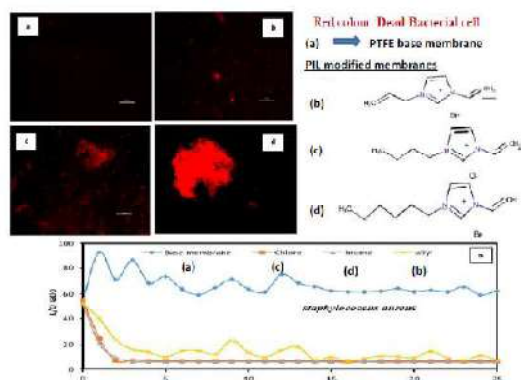


Fig. 10. The antibacterial characteristics of (a) PTFE base membranes; and PIL grafted membranes for gram positive bacteria [26].

The IL based membrane exerted antibacterial activity for gram positive as well as gram negative bacteria. There was a significant reduction in the live/dead bacterial cell ratio in presence of IL based membrane and also reduction in numbers of colonies formed by bacteria on incubation (Fig.10).

Electric-Responsive membrane

Concentration polarization is one of the major fouling issues faced by the membrane technologists. The membrane with PIL grafted polymer brush can create local perturbation in presence of external oscillating electrical field. Depending on the frequency of the oscillating electrical field, the local perturbation can be externally tuned. At very high frequency, this can lead to heating. The remotely

controlled local perturbations near the interface break the concentration polarization, while, the local heating led to enhancement in the permeability (Fig.11).

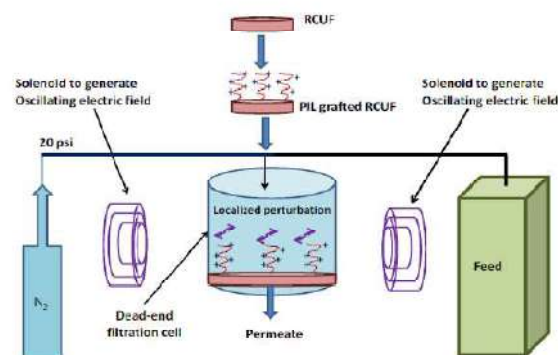


Fig. 11. Electric responsive membrane under oscillating electric field generating local perturbation to break concentration polarization[29]

Conclusions

IL based separation brings new era of tuning properties by minute structural modifications. It widens the applicability in the field of modern technology, energy application and even in fuel cell applications. There is a thirst on exploring novel ionic liquids to evidence interesting chemistry. Commercial scale production of IL must be started to reduce the overall cost. To improve mass transfer kinetics, IL with low viscosity must be identified. The research must go on in establishing new structure-activity relationship in ionic liquids. Research has also begun in finding the alternatives of conventional IL in the form of Deep Eutectic Solvents to resolve the shortcomings in ionic liquids.

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Biodata



Dr. Arijit Sengupta joined Radiochemistry Division, BARC after completing 51st batch of OCES Training School, BARC. He has extensively worked on application of multi-functional materials for actinides sequestration. He has worked on responsive membranes and surface modification of membranes for novel separation. He is actively involved in chemical quality control of nuclear fuel and associated materials and recovery and purification of valuable actinides from analytical assorted waste solutions. He is having 208 Journal publications (citation ~3750), 2 Book Chapters, 1 BARC report and 1 BARC News Letter to his credit.

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Green Solvents in Nuclear Industry: from Ionic liquids to Deep Eutectic Solvents

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Nuclear energy provides about 11% of the world's electricity from about 450 power reactors[1]. It is one of the world's largest sources of low-carbon power which is free from greenhouse gases or other environmental contaminants and hence this has been profoundly considered as a solution for mitigating climate changes[2]. However, the central bottleneck is the disposal of radioactive waste which is one of the major drawbacks for promoting the widespread acceptance of nuclear energy[3-4]. Existing methods for the purification and recovery of actinides are based on a very well-known PUREX (Plutonium Uranium EXtraction) process[5]. Another method is the pyrochemical reprocessing method in which the actinides are separated from the high temperature molten salt media electrochemically[6-7]. There are, however, many disadvantages associated with the above traditional methods viz. a lot of aqueous radioactive waste generation, requirement of high temperature and strongly corroding nature of molten salt media[8-9]. Hence, the suitability of these methods has thus been critically questioned for the purification and recovery of nuclear fuel materials. Thus, it warrants the development of alternative approaches that could lend a hand to solve several concerns with current methodology including non-proliferation issues, criticality, safety, apparatus corrosion, and stiffness of the process.

The most promising outlook is associated with new solvents. The problem could be radically solved by replacing the customary molecular volatile solvents/extractants and diluents by new solvents of a different nature that would be devoid, at least partially, of the drawbacks of existing solvents. Such solvents appeared and, in the last decades, they have been actively investigated. These new generation solvents include ionic liquids (ILs) and low-melting combined solvents called deep eutectic solvents (DES). ILs were first discovered by P.I. Walden in 1914 and long remained relatively unnoticed exotic species. However, at the turn of the 21st century, hydrolytically stable ILs appeared, some of which were found to be hydrophobic. In this connection, there was a surge of studies of extraction of lanthanides and actinides employing ILs. This was promoted by the fact that even an early publication

reported record-high distribution ratios of strontium extracted with crown ether from an aqueous solution into ILs (1,3-dialkylimidazolium with fluorine-containing anions)[10]. Numerous new / task specific ILs suitable for extraction and separation of lanthanides and actinides were synthesized and studied [11]; obvious advances were made in the synthesis and investigation of ionic liquids. However, the prices and the range of available solvents have become critical issues for the widespread use of ILs. Their scope was significantly extended when it was found that not only hydrophobic, but also hydrophilic ILs are applicable for direct dissolution and subsequent separation of species containing f orbitals. One more trend that appeared during studying ILs and formed as a separate rapidly growing area is the use of eutectic solvents [12]. It was found that liquids can be obtained using solid salts mixed with appropriate partner compounds. Remarkably, these solvents are prepared using rather simple chemical means. For example, the classical Abbot liquid, reline, is a mixture of an organic salt (choline chloride) with urea. Both initial compounds melt at a temperature markedly higher than 100 °C; it is important that both components of the mixture are very cheap and readily available. The annual output of choline chloride is hundreds of thousand tons and that of urea is tens of million tons. Currently, DESs are actively used, in particular, for extraction, especially for extraction from solid matrices. The solubility, coordination and speciation of f-block elements in DESs have been recently explored and very limited data are available [13-21]. There is a need for extensive research to understand the behavior of the complexes involving f-block elements in DESs and their electrochemical behavior so as to have a simplest approach of recovering actinide species without generating waste.

Ionic Liquids: Overview, Prospects and Applications

Ionic liquids are salts with melting points of <100 °C. Certainly, the temperature threshold is conventional and intentionally generous: one can consider that this threshold separates 'ionic liquids' and 'salt melts'. There is a subclass of ILs that is liquid at room temperature called room temperature

ionic liquids (RTILs). Exactly these ILs are of most interest for practical purposes and can be used as extraction/separation solvents. Most ILs contain a large organic cation, usually with a positively charged heteroatom, coupled with one of the wide range of organic and inorganic anions. [22] Usually these are anions with delocalized or shielded charge.

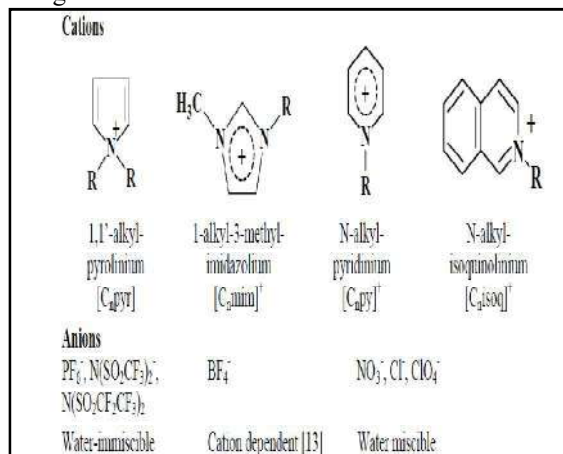


Figure 1: Some common cations and anions present in ionic liquids

The common cationic components of RTILs are pyridinium, imidazolium, phosphonium, and tetraalkylammonium ions while some of the common anions are hexa-fluoro phosphate (PF₆⁻), bis(trifluoromethylsulfonyl)imide (NTf₂⁻), tetrafluoroborate (BF₄⁻), and triflate (OTf⁻). The structural formulae of frequently encountered cations and anions are given in Figure 1. The physical properties of the RTILs are known to be dependent on their constituent cationic and anionic parts. Hence, it is possible to prepare ionic liquids with the required viscosity, density, dielectric constant and interfacial tension (important factors for the extraction of metal ions) by suitably tuning the constituent ions. Subsequent studies involving ionic liquids have suggested their applications in diverse areas such as catalysis, synthesis, and separations [23].

RTILs have attracted considerable attention as possible replacements for conventional molecular organic solvents in biphasic liquid-liquid extraction systems for the separation of metal ions. The potential advantages of using a water-immiscible IL in such separations include exceedingly low volatilities and low flammability, the efficient extraction of metal ions that are difficult to extract with molecular organic

solvents [24-26], and the possibility of easily coupling liquid-liquid extraction and electrorefining [27]. RTILs offer large electrochemical window and superior conductivity for their potent use in electrochemical investigations over conventional solvents. Dialkyl substituted imidazolium cation based ionic liquids are usually air and moisture stable and have been used extensively in the electrochemical studies [28]. For application in nuclear fuel cycle, the radiolytic stability is a very crucial factor. RTILs, containing imidazolium and pyridinium cation, are fairly stable to radiolytic degradation due to the presence of aromatic rings. For imidazolium cation based ionic liquids, physical properties such as density, surface tension, refractive index, etc. are not considerably affected upon irradiation, but the viscosity is reported to be slightly higher due to the polymerization of the imidazolium cation [29]. We generated adequate data for the basic understanding of the electrochemical behaviour of actinides in ILs.

CMPO is considered as an efficient extractant for actinides extraction from spent nuclear fuel and have been extensively studied [30-32]. The behaviour of the extracted species in ionic liquids, its transport properties in ILs, structures of the extracted complexes, photophysical characteristics and the corresponding kinetic properties were studied extensively. Despite of the differences in oxidation and reduction chemistry of the actinides, electrochemical techniques have poorly been applied for nuclear fuel reprocessing. There is a need to develop selective extractants for safe recovery and recycling of actinides from the spent nuclear fuel. The electrochemical, theoretical and luminescence studies of NpO₂⁺/NpO₂²⁺ with carbamoyl methyl phosphine oxide (CMPO) ligand in ionic liquid [C_nmim] [NTf₂] have been studied by our group [33]. To understand the role of ionic liquid in these studies, the redox behavior, complexation, and photophysical characteristics NpO₂⁺ complexes were carried out. The electrochemical behavior of NpO₂⁺ extracted by CMPO in 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₆mim] [NTf₂] (IL) was studied at glassy carbon (GC) electrode. The redox reaction of NpO₂⁺ to NpO₂²⁺ and vice versa in [C₆mim] [NTf₂] is quasi-reversible (Figure 2) and controlled by diffusion as well as charge transfer kinetics. The transport properties and kinetics of NpO₂⁺ are deduced from electrochemical calculations.

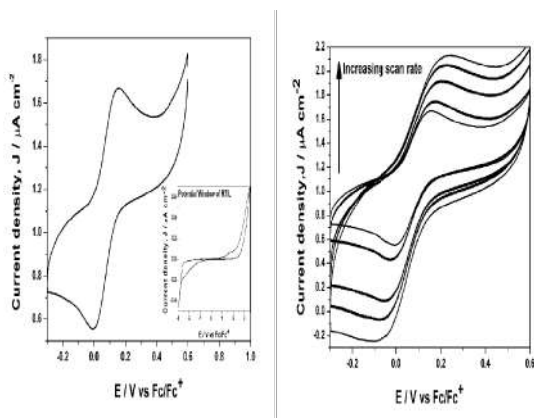


Figure 2: Cyclic voltammogram of NpO_2^+ in $\text{C}_6\text{mimNTf}_2$ ILs and recorded at different scan rates. Inset shows the potential window of $\text{C}_6\text{mimNTf}_2$.

We have studied the electrochemical studies and extraction of Pu, U and Np employing two new bifunctional ligand system (N, N- dialkyl carbamoyl methyl) (2-pyridyl-N-Oxide)sulfide $\text{C}_5\text{H}_4\text{NOSCH}_2\text{CONR}_2$, (where R = octyl) (NOSCO) and N, N-dioctyl - α -hydroxy acetamide (DoHyA)[34]. Cyclic voltammetry studies of these actinide ions in aqueous as well as in ($[\text{C}_4\text{mim}][\text{NTf}_2] + \text{NOSCO}$) and ($[\text{C}_8\text{mim}][\text{NTf}_2] + \text{DoHyA}$) media respectively have been carried out. Shifts of

cathodic and anodic peak potentials of Pu(IV) in cyclic voltammograms were observed towards negative potentials in the extended electrochemical window for ionic liquid medium compared to aqueous medium (Figure 3). The diffusion coefficient and heterogeneous charge transfer coefficient were calculated for both aqueous and ionic liquid media.

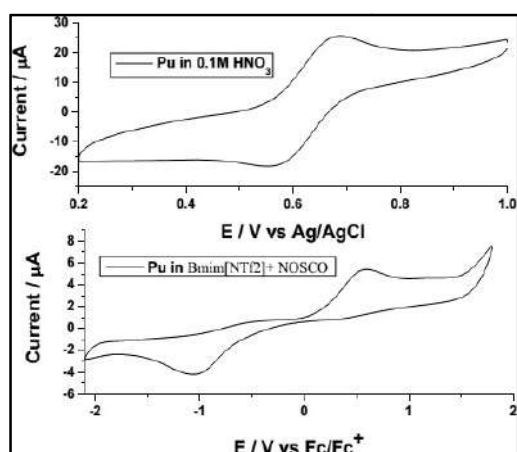


Figure 3: Comparison of cyclic voltammograms of Pu(IV) obtained in ionic liquid and aqueous solution

Furthermore, task specific ionic liquids (TSILs) can also be employed for extensive studies of lanthanides and actinides. Herein, functional groups are covalently attached to either the cationic or anionic part of the ionic liquid so as to enhance the extractability of lanthanide and actinide complexes. In spite of the usage of ionic liquids for the separation of f-block elements, the primary issue of poor solubility of lanthanides and actinides in ILs is still unsolved. Hence, there is a need for extensive research to understand the behaviour of the complexes involving the f-block elements in TSILs and their electrochemical behaviour so as to find the simplest approach of recovering actinide species without generating waste. The most important actinide oxides in the nuclear industry are UO_2 and PuO_2 . We have envisaged an approach for direct dissolution of PuO_2 in protonated betaine bis (trifluoromethylsulfonyl) imide $[\text{Hbet}][\text{NTf}_2]$ and electrodeposited plutonium from the solution of TSIL and PuO_2 [35]. The carboxyl functional group attached to the TSIL played a key role in facilitating the dissolution of plutonium ions by making strong bonding. In addition, the electrochemical and thermodynamic properties of plutonium in $[\text{Hbet}][\text{NTf}_2]$ at glassy carbon electrode are also investigated. The diffusion coefficient and heterogeneous charge transfer coefficient of plutonium at the electrode – electrolyte inter phase are determined at various temperatures. Furthermore, the fundamental nature of the interaction between the betaine based TSIL and plutonium ions was theoretically studied (figure 4).

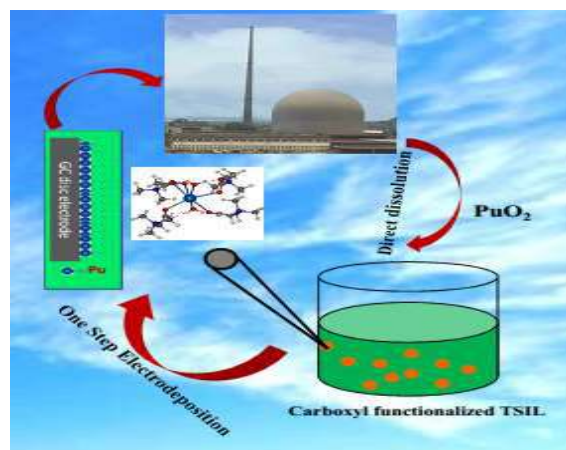


Figure 4: Schematic for the recovery of plutonium from ionic liquid.

The above-mentioned results are highly promising in countering the doubts on the possible applications of ionic liquids for nuclear fuel cycle applications. Ionic liquids offer improved extraction, higher loading (without the formation of

the third phase), lower radiolytic damage and a large electrochemical window. Though RTIL based solvent systems appear to be superior on many counts, their application to the nuclear fuel cycle needs a lot more studies to be carried out which can establish their recycling options and sustainability. Apart from chemical and radiolytic stabilities, the effects of loading and radiation exposure on the hydrodynamic parameters also need to be evaluated. Also, reusability of the ionic liquids after extraction and stripping needs to be assessed after subjecting to the conditions prevalent in actual radioactive waste processing plants.

Deep Eutectic Solvents: Overview, Prospects and Applications

Deep Eutectic Solvents are neoteric solvents and appears to be intermediate between ionic liquid and water [36-38]. They have been envisaged as the promising green solvents in a variety of applications such as analytical chemistry, electrochemistry, metal oxide dissolution, catalysis, carbon dioxide absorption, separation science, oil recovery, polymerization, nanostructure synthesis, and other synthetic chemistry. In general, DESs are formed by eutectic mixture of a salt/hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD). The lowering of melting point than either of the individual components in thus formed eutectic system has been attributed to self-association by the hydrogen-bonding interactions between salt/HBA and HBD. DESs resemble with ionic liquid not only in terms of electrostatic interactions (mostly organic salts) but also due to similarity in their physicochemical properties such as low vapor pressure, high thermal stability, high viscosity and chemical inertness. However, DESs differ from ionic liquid due to involvement of extensive hydrogen bonding in their structural components. Unlike traditional molecular solvents having homogeneous hydrogen bonding, DESs involve self-association of two or more components originating from the maximization of hydrogen bonding network of interactions and delicate balance of different forces to stabilize the eutectic system. They could be made either hydrophilic or hydrophobic depending upon the choice of the HBA and HBD and may or may not involve ionic components. Due to the heterogeneous hydrogen bonding, the solute-solvent interactions in DES differ significantly from that observed either in ionic liquids or conventional molecular solvent. The most explored ones are DESs based on quaternary ammonium salt and HBDs such as amine, amide, alcohol, and carboxylic acid. The first example in this series has been made by Abbott et al. using (2-hydroxyethyl) trimethylammonium chloride, commonly known as choline chloride (ChCl) and urea as HBD in 1:2

molar mixture, which is commonly known as Reline[39].

DES's are considered as one of the highly potential alternatives to existing ILs because they are cheap and easy to synthesize. The other advantages are their very low volatility and they can be tailor made to exhibit wider liquid range stability, water-compatibility, non-flammability, non-toxicity, biocompatibility or biodegradability. Moreover, their properties can be tuned by judicious choice of nature and ratio of the hydrogen bonding pairs. Nevertheless despite of these many advantages they are not much explored for the application in nuclear fuel cycle [13-20]. To understand basic solvation and complexation mechanism of uranium in these neoteric solvents detailed investigation was carried out. Considering the enriching actinide chemistry and involvement of complex 5f orbital; its speciation in relatively unexplored cheap and green DESs will open up new possibility in nuclear industry specifically from reprocessing perspective. We have carried out the mechanistic aspects of solvation, speciation and redox chemistry of uranyl ion in Reline. We have synthesized Reline in our laboratory using mechanochemical synthesis and characterized it extensively using Fourier transformed Infrared (FTIR) spectroscopy. A microscopic insight to the solvation and speciation of UO_2^{2+} ion in DES and on associated changes in physical composition of the DES was investigated extensively using electrochemical and X-ray absorption spectroscopy (XAS) techniques along with the molecular dynamic (MD) simulations¹³. Moreover, MD simulations were also carried out to investigate the extent of H-bonding in reline on uranyl ion interactions in presence and absence of water (Figure 5). The most stable oxidation states of uranium are U(VI) (UO_2^{2+}) and U(IV) (U^{4+}), but UO_2^{2+} ion is the most stable species in the aqueous solution under ambient condition.

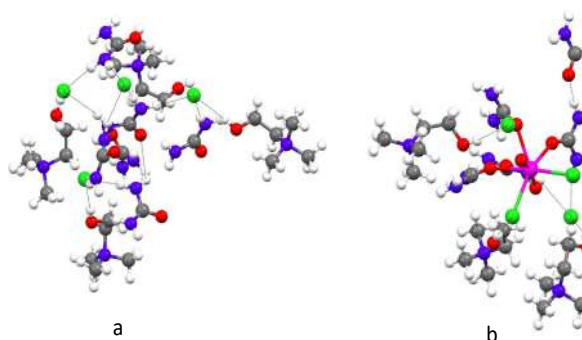


Figure 5. Structure of reline-uranyl system. (a) pure reline (b) $\text{UO}_2\cdot 2\text{Cl}\cdot 2$ urea. Here, U: pink; O: Red; Cl: green; N: Blue; H: white; C: cyan.

The hydrogen bonded structure of Reline stabilizes the most unstable pentavalent uranium (UO_2^+) (Figure 6). This could be attributed to the strong complexation of chloride ion and urea with uranyl ion. MD was also carried out to evaluate the number of H-bonds which was found to recede in reline in presence of uranyl ion; both in absence and presence of water suggesting high stability of UO_2^+ in DESs. However, hydrogen bond breaking at elevated temperature promoted

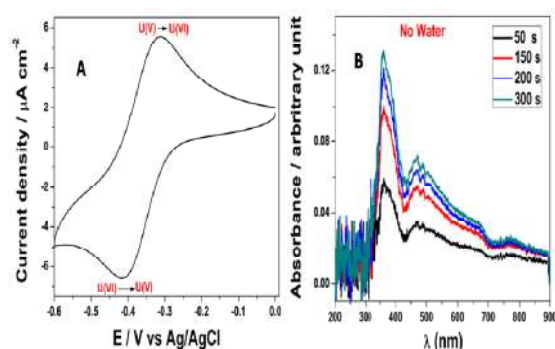


Figure 6. (A) Cyclic voltammogram of Reline in presence of 10 mM UO_2^{2+} (B) In-situ spectroelectrochemical measurements recorded at different time interval in presence of 0.4M UO_2^{2+} ions.

UO_2^+ disproportionation to U^{4+} and UO_2^{2+} ions. The presence of water in reline was found to influence the redox chemistry of uranium ions. Binnemans et. al. reported the dissolution of metal oxides in p-Toluenesulfonic Acid-based DESs [40]. They proposed enhanced metal oxide solubility with increase in acidity of the hydrogen bond donor (HBD) and hence considered p-toluenesulfonic acid monohydrate (PTSA) as HBD. Considering the importance associated with reprocessing of spent nuclear fuel as well as fuel fabrication; dissolution of uranium oxides is an important research which will not only fetch substantial attention from basic understanding of actinide chemistry in DESs but also provide a cost effective alternative to ILs for the same. These prompted us to take this challenging research problem of investigating the dissolution behavior of different uranium oxides in PTSA based DES and also investigate its electrochemical behavior for understanding the redox chemistry of U-DESs complex [15]. Additionally to identify the speciation of uranium in these complexes; luminescence spectroscopy was also carried (figure 7).

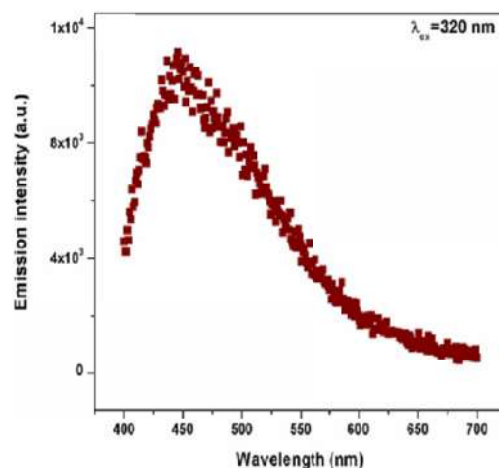


Figure 7. Emission spectrum of U(VI) in PTSA:ChCl(1:2) DES

The metal concentration dissolved was determined by EDXRF and it was found that PTSA: ChCl (1:2) was found to be better in terms of solubility for uranium oxides as compared to PTSA: ChCl (1:1) and Malonic acid: ChCl(1:1). The formation of DES consisting of Hydrogen bonding network is confirmed using attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy. It could also be found that uranium oxide dissolution doesn't distort the H-bonding network of DESs. Based on CV results it was proposed that U(VI)/U(V) reduction is controlled not only by diffusion of U(VI) ion in PTSA:ChCl (1:2), but also by the kinetics of the charge transfer reaction occurring at the electrode-electrolyte interphase.

For the very first time, we explored to synthesize uranium type (IV) deep eutectic solvent employing uranyl nitrate hexahydrate and Urea via mechanochemical synthesis which is indeed the first report on actinide deep eutectic solvent (AnDES)[14]. The optimum mole fraction for formation of DES was found to be 0.2:0.8 for UNH: Urea respectively which was further confirmed using thermodynamic phase diagram. The formation of DES was confirmed using Fourier Transform Infrared spectroscopy. Various physical properties were also evaluated for this type (IV) DES such as melting point, moisture contents, viscosity, and density. Thermal studies suggested that this DES was stable from -5.2 to 300°C and there is a strong interaction parameter obtained which was attributed to hydrogen bonding and the complexation of urea with uranyl nitrate hexahydrate. Uranium ion was found to exist in U(VI) oxidation state in the form of uranyl ion in DES. Electrochemical investigation suggested the stabilization of most unstable U(V) state by virtue

of the formation of hydrogen bonded complex uranium and urea in the DES. Further scanning the potential to more negative direction leads to further reduction of U(V) ion to UO_2 . The optimized electrochemical parameters were further used for the electrosynthesis of UO_2 nanoparticles and thus offer a very green and cost-effective synthesis of UO_2 nanoparticles.

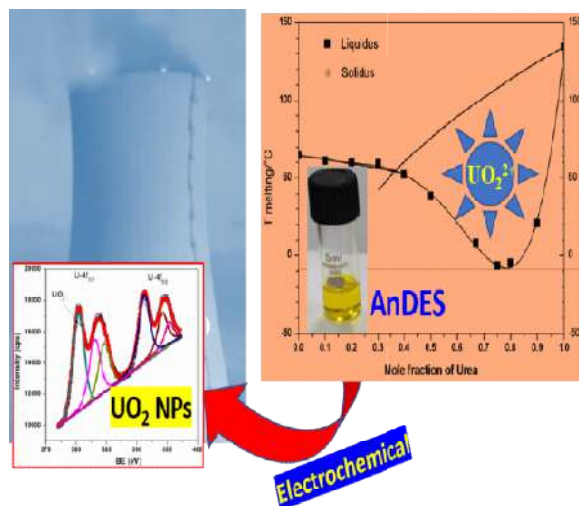


Figure 8. Schematic representing actinide type(IV) DES and subsequent formation of UO_2 nanoparticles from it

To resolve the issue of aggregation induced quenching (AIQ), poor adhesion/dispersion on film and fiber, limited dispersability/solubility and non biocompatibility issue; phosphor powder particles are casted into solution form. There are several solvent media utilized for the same such as water, ionic liquid (ILs), etc. But it was found that lanthanide luminescence and lifetime reduced substantially in aqueous medium and ionic liquid. Deep eutectic solvent (DES) has been found to be an alternate and more efficient solvent for lanthanide luminescence. With similar intention we have synthesized europium type (IV) DES (EuDES) via mechanochemical synthesis employing europium nitrate and urea. Cyclic voltammetry (CV) confirms that europium ion exists as +3 oxidation state in EuDES. Fourier transformed infrared spectroscopy (FTIR) studies confirms that in DES, the Eu^{3+} ion is surrounded by bidentate nitrate ions and urea is coordinated to europium centre by C=O group. There is no water molecule in primary coordination sphere of Eu^{3+} ion. Stabilization of EuDES inherently will resolve the issue of concentration quenching as bulk concentration of europium ion can be used. Interestingly with rigid H-bonding and strong chemical interaction offered by DES; Eu^{3+} CTB is quenched whereas very high intensity of Eu^{3+} intra f-f transition appears which

was reversal from usual trend. Moreover asymmetry ratio was found to be more than 3 with predominantly high intensity of electric dipole transition suggesting very asymmetric environment around Eu^{3+} in DES[16,18]. But the distribution of europium was found to be very homogenous with luminescence lifetime of ~ 3.7 ms and point group symmetry $\sim \text{C}_{6v}$. Judd-Ofelt analysis suggested very low non-radiative channels present in DES resulting in extremely high quantum yield $\sim 90\%$ which was also assisted by absence of any water molecule as suggested by FTIR as well. Branching ratio value suggested very high color purity for red emission. Europium luminescence in DES has offered a new design strategy in tackling the issue of powder aggregation and lowering the non-radiative channels for advanced optoelectronic and solid state lighting applications.

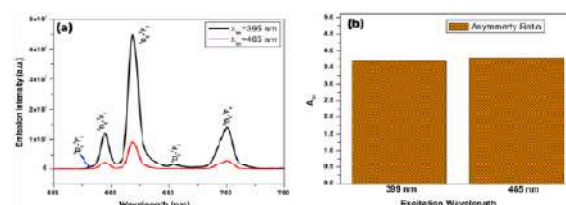


Figure 9. Emission spectra ($\lambda_{\text{ex}}=395$ and 465 nm) and (b) Asymmetry ratio of EuDES

We have synthesized alkyltriphenylphosphonium bromide and DA (as a hydrogen bond donor) based DES with varying alkyl chain (viz. C7, C9 and C12) and for the very first time discovered extraordinary photoluminescence (PL) properties in pristine DES⁴¹. Unlike in commercialized phosphors where light emission is driven by dopant or activators doped into inorganic host matrix, our DES consists of no metal activators or dopant ions or any form of fluorophores, but could emit intense blue light under the excitation of 365 nm near-ultraviolet (NUV) radiation. This potential of the DES as a liquid scintillator was further demonstrated with radioactive sources emitting alpha and gamma radiations[41].

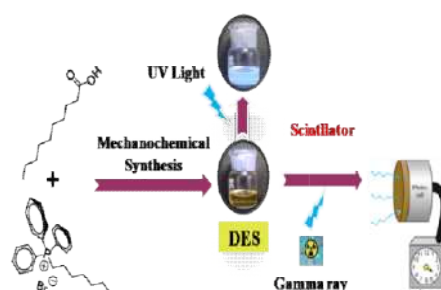


Figure 10. Schematic showing synthesis and application of novel hydrophobic DES.

The three DESs synthesized was further explored for uranium redox chemistry[42] and selective separation of plutonium from a dissolver solution and analytical waste solution[43] and promising results were obtained. Since the actinide species are very crucial important systems in nuclear reactors in view of their potential applications in nuclear industries and at the same time, they are environmental hazardous materials, we strongly believe that the work highlighted in the present article will make profound and insightful impact in the energy and environmental sectors.

Summary

Several basic concepts of processing of spent nuclear fuel and the problems associated with it have been explained in this article. The speciation, coordination and complexation behavior of different actinides in ionic liquids and deep eutectic solvents have been explained. More detailed knowledge is needed in the field of solvation chemistry of actinides and lanthanides in ILs and DESs as well as in the field of electrochemistry of these elements in the same environment. However, the present lack of this knowledge doesn't mean that ILs and DESs should not be taken into account when thinking about the areas of spent nuclear fuel reprocessing and radioactive waste management because the added value of using these systems seems to be very promising. The nuclear industry has relatively low carbon footprint per unit of energy, therefore, it can play a very important role in combating climate change. Concerns about the effect on the environment or human health by waste produced throughout whole fuel cycles are perfectly justified and it is necessary to study all possibilities that have potential ability to make all the processes safer and that lessen the effect on the environment. Processes based on ILs and DESs have the potential but only further research will make it possible to reach an industrial scale.

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Biodata



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