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Ionic liquids: Green solvents of sustainable chemistry

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Abstract
Sustainable chemistry is determined for the reduction or replacement of chemicals which causes irreparable damage to ecosystem and raises environment, health and safety concerns. Conventional organic solvents are main culprit in increasing the non-greenness of chemical processes by emitting out volatile organic carbons into the atmosphere. Novel and green solvents such as ionic liquids (ILs) are proved as stepping stone for the design of more eco-viable chemical processes. ILs are ‘liquid’ ‘salts’ which consists of large hydrophobic cationic part and smaller inorganic anionic part. They have a unique array of physic-chemical properties which make them suitable in numerous applications in which conventional organic solvents are not sufficiently effective or not applicable. Main factor which contribute in green nature of ILs is their non-volatile nature which is due to electrostatic forces of attraction between cationic and anionic part. This force is strong enough to negate their vapor pressure by holding the cations and anions in ILs and weak enough to make them to exist in liquid state. ILs have been successfully used as substitutes of conventional solvents & catalysts in organic synthesis, extraction of variety of chemicals and metal ions, dissolution of lignocellulosic material, nanoparticle synthesis etc. In this present review article, various aspects of ILs including their application in various fields are addressed.

Keywords: Ionic liquids, green solvents, sustainable chemistry, green chemistry

Introduction
Green chemistry is striving to enhance sustainability and alternative methods for reducing the environmentally hazardous substances, to optimize chemical processes and to minimize waste production. It is in continuous search of solvents that are less toxic, eco-friendly and have larger efficiency as compared to conventional organic solvents. Solvents and catalysts used in chemical processes emit out volatile organic compounds (VOCs) that raises concerns regarding environment, health and safety. In chemical and pharmaceutical industries, kind of solvents used play an instrumental role in deciding the environmental credentials (i.e. low volatility and eco-toxicity) and competitiveness of the process in market. By providing non-exclusiveness of financial performance and environmental compatibility, green solvents can be efficient tool in replacement of conventional hazardous solvents by eco-viable green solvents in chemical processes. Consumption of green solvents has increased through 2014 and it was due to record high feedstock pricing of conventional solvents. Market forecast shows that green solvents growth to markedly outpace the conventional solvents market [1, 2]. Moreover, the fundamental 12 principles of green chemistry postulated by Paul Anastas & John Warner, envisaged the use and production of less hazardous chemicals, design of safer solvents and chemicals, reduction in derivatization and inherently safer chemistry for accidental prevention [3]. Immense research has been conducted on green solvents such as ionic liquids, ethyl lactate, supercritical water and supercritical carbon dioxide. Present review article emphasize the role of ionic liquids in various fields of chemistry and their greenness from different points of view.

What are ionic liquids?
An ionic liquid (IL) consist of large nitrogen containing organic cation and smaller inorganic anion. Generally ionic compounds are solid at room temperature due to strong electrostatic force of attraction between cation and anion in crystal lattice, but ionic liquids are liquid at room temperature due to presence of asymmetry in the compound which reduces the lattice energy of crystalline structure and hence melting point of the salt.

Although these are liquid at room temperature, yet their vapor pressure is very low or negligible in comparison to conventional organic solvents [4]. It can be explained on the basis of electrostatic force of attraction between ions in ionic liquids which hold the ions strongly and reduces their escaping tendency. Common cations and anions used in ILs are shown in fig. 1.

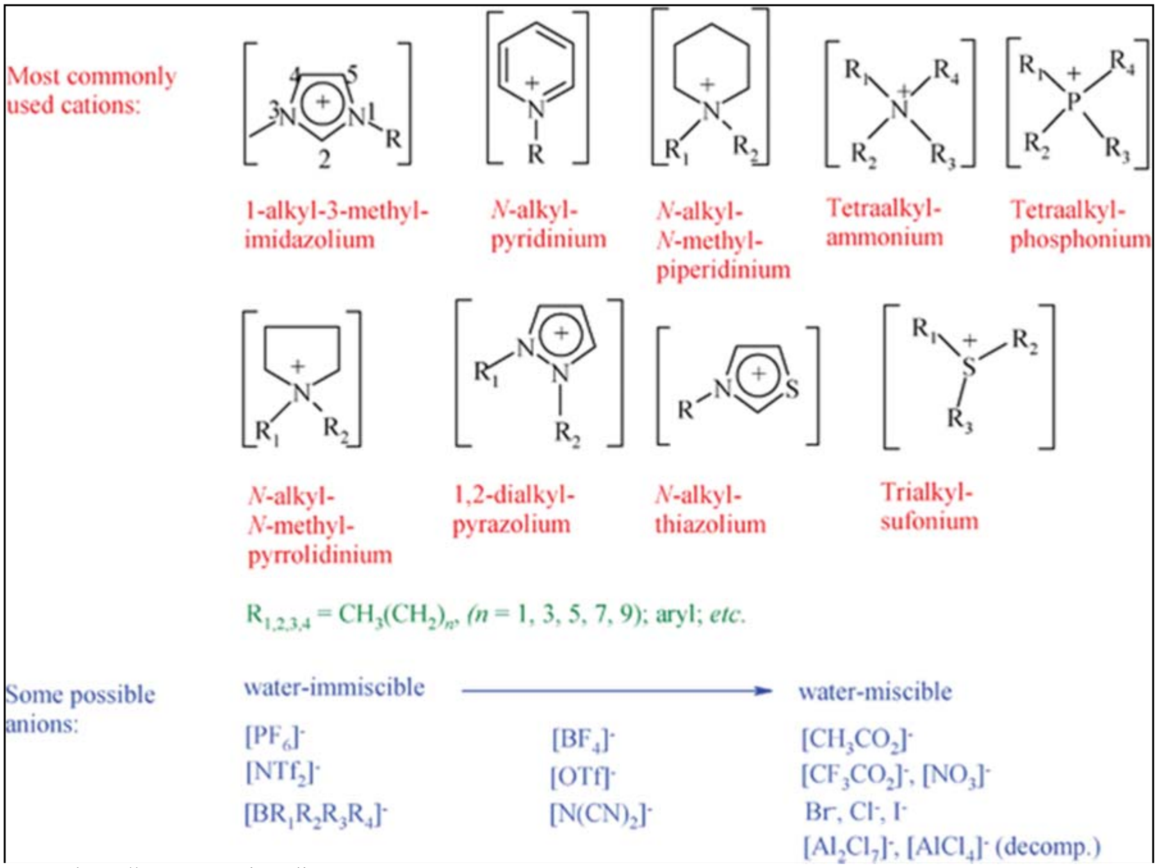

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Fig 1: common cations and anions in ILs

Properties of ionic liquids that make it "green"

- Desirable ILs can be designed by suitable combination of cations and anions.[5]
- Multicomponent ILs can be formed by mixing of liquid salts with inorganic salts.
- Certain properties such as miscibility, hydrophobicity, viscosity, density etc. can be adjusted or fine tuned to suit a particular application.
- The ions in ILs are held together by coloumbic forces and thus exerts near-zero vapor pressure above the liquid surface [6]. So ILs do not emit out potentially hazardous VOCs during their transportation, handling and use.
- ILs are non-oxidising so non-flammable and non-explosive.
- The velocity of the reaction increases in ILs due to its ionic character.
- ILs can be stored without decomposition for a long time.
- ILs are suitable for stereoselectivity control [7].
- ILs do not form coordinate bond with metal complexes.
- ILs are stable over a wide range of temperature.
- Common anions present in ILs are- nitrate, phosphate, tetrafluoroborate, tetrafluoromethane sulphonate, hydrogen sulphate, benzoate, acetate, formate & halides and commonly used cations in ILs are imidazolium, pyrrolidinium, ammonium, phosphonium & pyridinium cations.[8]
- Large organic cationic part and smaller inorganic anionic part makes them capable for dissolving both organic and inorganic material.

Application of ILs

ILs in organic synthesis

Green chemistry emphasizes the need of clean technologies which utilizes less toxic reagents/catalysts. The replacement of conventional volatile organic solvents by solvents of new era such as ILs can be proved as stepping stone in making the organic synthesis sustainable and eco-viable. The easily adjustable properties of ILs just by altering the cationic and anionic part make it task specific solvent. Most advantageous property if ILs that contribute in greenness of synthesis reactions in them is their negligible vapor pressure. ILs can act as reaction media as well as catalyst in many organic reactions such as Aldol condensation, Knoevenagel reaction, Doebner condensation, Michael reaction, Biginelli & Hantzsch reaction etc. Not just rate but it also determines the stereoselectivity of the reactions [7].

Stille reaction involves the formation of carbon-carbon bond between an electrophillic reagent and organotin compound in the presence of Pd catalyst. The IL [bmim]BF_4 was used for Stille reaction between iodocyclohexanone and vinyltributyl tin and product of this reaction was extracted with ether. IL and catalyst can be reused again and again due to stability of IL/catalyst phase towards air and moisture [9].

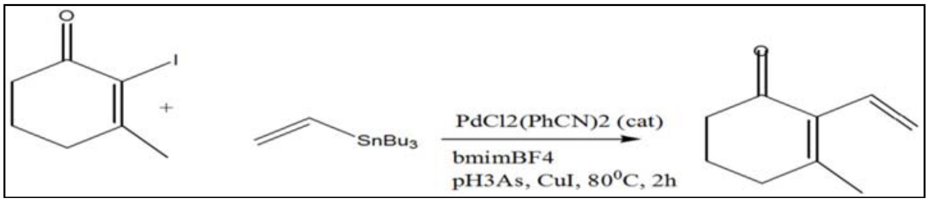

Fig 2: Stille reaction in ionic liquids

Many other reactions such as modified Mannich reaction employed green solvent [bmim] [NTf_2] as shown in Fig.3.[10]

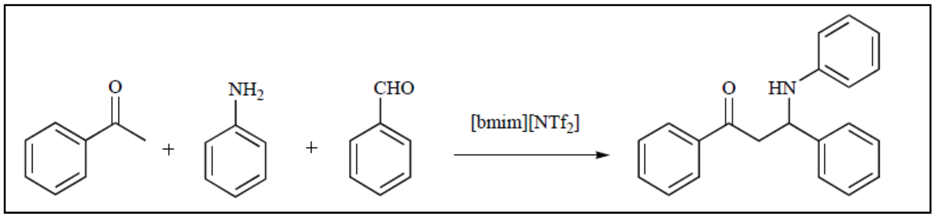

Fig 3: Modified Mannich Reaction in [bmim][NTf_2]

ILs can act as solvents as well as catalysts in many chemical reactions due to their fine tunable properties such as solvating power, viscosity, density etc by suitable combination of cation and anion. For fluorination of heterocyclic compounds [bmim]BF_4 is used [11]. In certain ring opening reactions, ILs can be used as reaction media for synthesis of certain biologically active molecules in high yield even at low temperature [12]. Moreover, reduction of certain aldehydes to alcohols can be achieved even at room temperature in the presence of ILs such as [bmim]BF_4, [emim]BF_4 & [emim]PF_6 [13]. In Suzuki-Miyaura coupling reactions, biaryls are obtained from aryl halides and aryl boronic acids in the presence of Pd catalyst and a base. The advantage of using ILs in this reaction is that catalyst can be retained which is difficult in the absence of ILs [14]. Hydrogenation reactions which involve the addition of hydrogen across carbon-carbon double bond requires transition metals or their compounds as a catalyst. This conventional method of hydrogenation has the disadvantage that recovery of catalyst and product separation is difficult but when hydrogenation reactions are carried out in ILs, catalyst remained in the IL phase and product in the alcoholic phase. So the catalyst and product can be separated by simple physical method such as decantation, paving the way for reuse of the catalyst [15]. Reformatsky reactions are carried out for the formation of β-hydroxyesters from condensation of an aldehyde or ketone with an α-haloester in presence of Zn dust. Solvents employed in this reaction are dichloromethane and ethereal compounds as lewis bases which emit out volatile organic compounds. These solvents have been successfully replaced by ILs, which have negligible vapor pressure, in Reformatsky reaction as shown in figure. 4 [7].

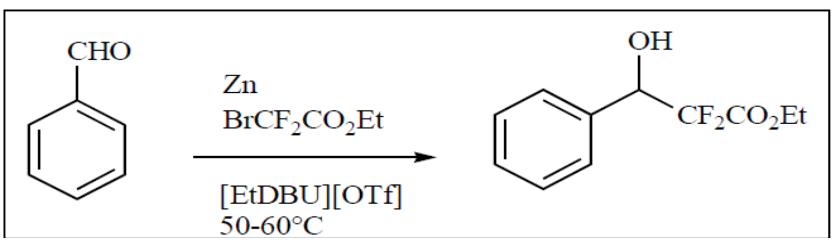

Fig 4: Modified Reformatsky Reaction in IL

In nanoparticle synthesis:-

Due to undetectable vapor pressure, ILs have been used as eco-friendly solvent in comparison to traditional organic solvents that emit out VOCs in atmosphere. ILs can be used for nanoparticle synthesis and their properties can be moulded to serve as both protecting agent & reducing agent [16, 17]. Ionic nature of these organic salts permit better salvation and protection of metal ions as compared to conventional solvents [16]. Nanoparticle formed in ILs have greater resistance against agglomeration due to formation of protective layer around them in ILs [18]. Better reducing capabilities of alcohol ionic liquids (AILs) make them better solvent in the formation of gold nanoparticles (AuNPs) [16]. It has been reported that in (HEMMor) (BF_4) size of nanoparticle is dependent on the size of alkyl chain of cation. Larger the alkyl chains, smaller is the size of nanoparticles formed [16]. Many ILs also behaves as green catalysts in the formation of nanoparticles. For e.g. in multiphase reactions, 1-n-butyl-3-methylimidazolium (imidazole ILs) acted as efficient green catalyst [18].

Extraction of lignocellulosic materials

Through proper design of ILs, reactions can be optimized in terms of yield and selectivity. ILs offer significant potential for extraction of cellulose by dissolving it in considerable amount. In particular ILs having 1-butyl-3-methylimidazolium cations ([$C_4mim]^+$) & chloride anion were able to dissolve upto 25 wt% with pulsed microwave heating. This was comparatively higher than the dissolution of cellulose in binary solvent system (DMAC/Licl). This binary solvent system is also eco-friendly solvent system and is extensively studied in the literature for non-derivitizing extraction of cellulose from biomass [19, 20]. Solvents that can disrupt & penetrate the intramolecular hydrogen bonding present in supramolecular cellulose structures, are able to solubilize the cellulose. Chloride anions present in these solvents interact with the cellulose hydroxyl groups so the solubilizing power of these solvents is directly related to the activity of chloride ions present [21]. Thus, ILs are more preferable than binary solvent systems such as DMAC/Licl:-

- In case of ILs, the effective concentration of chloride ions is not confined by the solubility of these salts.
- Activity & mobility of chloride ions in ILs can be significantly controlled by fine-tuning the ionic constituents in ILs [21].

New ILs systems for dissolution of cellulose are under progress. Great success in this direction has been achieved by employing systems having MIM (Methyl imidazolium) and MPy (methyl pyridinium) as cations [21]. Furthermore, small anions such as chlorides & hydrogen bond acceptors have been shown to be most efficient for cellulosic dissolution. Major hurdle in achieving ILs as green solvents for extraction of lignocellulosic material is the high sensitivity of solubility towards water impurities. Moreover, some toxicological properties & environmental impacts associated with some ILs delimit its scope as green solvents.

ILs are also referred as Task Specific Ionic Liquids (TSILs). This term indicates that functional groups attached to cation/anion or both of ILs impart it the ability to act as solvent as well as reagent and/or catalyst in chemical reaction [22, 23]. For example:

- CO_2 can be separated from the gas stream by employing ILs having appended amines.
- Extraction of aromatics in aqueous biphasic system can be done by using ILs with large aromatic head groups [22].
- In the synthesis of ethoxybenzene, ILs with attached –OH groups has been used as phase transfer catalysts [22, 23].
- ILs containing sulphonic acid groups were used as solvent and/or catalyst for esterification and other acid catalyzed reactions [23].
- ILs having such groups that can form complexes with metal ions can be used for extraction of metal ions from aqueous solutions [24].

ILs can be used as acid, base or organocatalysts in organic reactions.

ILs as acid catalysts

Reusable TSILs as most promising catalytic systems are rapidly replacing the harmful mineral acids in many synthetic reactions. For e.g. Bronsted acid IL, N-methyl-2-pyrrolidinium methyl sulphonate has successfully replaced the conventional catalyst i.e. halogenated mineral acids in esterification of carboxylic acid and alcohols [25]. For condensation of indoles with benzaldehyde under microwave conditions, 1-benzyl-3-methylimidazolium hydrogensulphate ([bnmim][HSO_4] has been successfully used as a catalyst [26]. The products of this reaction are medicinally very important as they are used for tumour chemotherapy [27]. Lewis acidic ILs such as [bmim]Cl.$AlCl_3$ are used for Friedal-Craft acylation [28]. Bronsted acidic 1-methyl-3-propanesulphonic imidazolium hydrogensulphate ([mimps][HSO_4] was used for synthesis of xanthene which is extensively used in laser technology and for biological & pharmaceutical use.[29] Sulphonyl containing ILs has been used as a recyclable catalyst for synthesis of 3-vinyl indoles from indoles & ketones [30]. In the above reaction catalytic activity was well augmented due to simultaneous presence of sulphonyl and sulphonic acid groups in the same IL. Bronsted acidic triflate IL [MIMBS][OTf] in a biphasic reaction medium was employed for effective and selective alkylation of phenol and anisole.[31] This method is advantageous over the conventional one as it negates the need for neutralisation of excess acid formed as a by-product. Greater selectivities in the above method are due to less oxophillicities of ILs in comparison to mineral acids.

ILs as base catalysts

For some base-catalyzed processes ILs possess convenient recycling and higher catalytic efficiency than the mixture of inorganic base & IL. Basic IL ([bmim]OH) was used as a catalyst and reaction medium in Michael addition of N-heterocycles α,β- unsaturated compounds at room temperature [32]. In Pd catalyzed Heck reaction, ethanol functionalized TSIL performed multifunctional role of base, ligand & reaction medium with added advantage of recyclability of the system [33]. Methanol can be activated for transesterification with ethylene carbonate by employing $BrTBDPEG_{150}TBDBr$. It would activate methanol due to presence of secondary and tertiary nitrogens in it. Therefore, the use of basic IL $BrTBDPEG_{150}TBDBr$ as a catalyst in above reaction allows the integration of cycloaddition as well as transesterification as a single process [34]. Biodiesel can be produced from soyabean oil in the presence of basic IL catalyst i.e. choline hydroxide [35]. Substituted ureas has been successfully prepared in presence of basic IL ([bmim]OH) as an efficient catalyst [36]. Main advantages of this method are-

- Solvent-free reaction conditions
- No need of dehydrating agent to remove water formed as a by-product
- Recyclability of catalyst
- Operation simplicity

As Organocatalysts

ILs as organocatalysts are successfully used in Diels-Alder cycloaddition due to their ability to interact by H-bonding. In Diels-alder reaction of various dienes and dienophiles, ILs having cation derived from H-bond rich D-glucopyranoside derivative & low coordinating bistriflimide as anion were successfully used as organocatalysts [37].

ILs in removal of metal ions

Conventional techniques for extraction of metal ions from a solution employed such extractants which can increase the concentration of metal ions in hydrophobic extracting phase. These extractants provided hydrophobic environment to the metal ions and enabled their transfer to the extracting phase [38]. But TSIL (Task Specific Ionic Liquids) contains appended groups that can form integral part of extracting solvents i.e. ILs. In other words TSILs can act simultaneously as extracting solvent and extractant. Strontium nitrate is fission product of radioactive nuclides and there is no available technique for its removal from radioactive waste. Crown ethers in the presence of certain ILs having PF_6 anion or Tf_2N^- anion play significant role in removal of strontium nitrate [39]. Cadmium and mercury were removed from contaminated water by utilizing the concept of TSILs. Imidazolium cation used for this purpose had different appended functional groups that can act as ligand for binding to the Hg and Cd. These synthesized TSILs cations were used with PF_6 anion and its mixture with another IL [bmim]BF_4. TSILs can act as extractant as well as hydrophobic solvent at the same time [40]. Metal ion binding ligands forms the integral part of imidazolium cation in TSILs so the probability for IL loss to the aqueous phase is reduced. Radioative lanthanides and actinides can be extracted efficiently by the use of suitable ILs so it helps in handling of nuclear material [41]. Extraction of Na^+ and Cs^+ was successfully carried out by using $[C_nmim][PF_6]$ (n=4,6,8) [42]. Rare earth metals were efficiently extracted out from aqueous solutions with the help of ILs. The extracting ability of ILs can be varied by using different functional groups as complexing agents on the side chains of its cationic part. Extraction of metal ions by ILs can be optimized by keeping in mind that:

- Crown ethers can act as extractants of metal ions in ionic liquids. As salvation of crown ether complexes in ILs is thermodynamically more favourable as compared to that of in organic solvents. So nature of extractants can be modified to achieve optimal selectivity for a specific application [43].
- Hydrophobicity of ILs can be varied by changing the structure of ILs so the partition coefficients of metal ions can be improved [44].
- Extraction of metal ions by ILs and extractants can be varied by change in pH of the system [45].

Table 1: Examples of IL extractions of metal ions [46].

	Substances	IL	Extractant/ligand/metal chelator
Alkali metals	Li+, Na+, K+, Rb+, Cs+	[C*n*MIM][PF6] *(n* = 4–9*)*	DC18C6
	Na+, Cs+	[C*n*MIM][PF6] (*n* = 4, 6, 8)	18C6, DC18C6, Dtb18C6
	Cs+	[C*n*MIM][Tf2N] (*n* = 2, 3, 4, 6, 8)	BOBCalixC6
	Na+, K+, Cs+	[C*n*MIM][Tf2N] (*n* = 2, 4, 6, 8)	DC18C6, *N*-alkyl aza-18-crown-6 ethers
Alkaline earth metals	Mg2+, Ca2+, Sr2+, Ba2+	[C*n*MIM][PF6] *(n* = 4–9*)*	DC18C6
	Sr2+	[C*n*MIM][PF6] (*n* = 4, 6, 8)	18C6, DC18C6, Dtb18C6
	Sr2+	[R1R2MeIM][PF6], [R1R2MeIM][Tf2N]	DC18C6

Note: C*n*MIM = 1-alkyl-3-methylimidazolium; DC18C6 = dicyclohexano-18-crown-6; 18C6 = 18-crown-6; Dtb18C6 = 4,4_-(5_)-di-(*tert*-butylcyclohexano)-18-crown-6; BOBCalixC6 = calix [4] arene-bis(*tert*-octylbenzo-crown-6); Tf2N = bis[(trifluoromethyl)sulfonyl] amide; R1R2MeIM = 1-R1-2-R2-3-methylimidazolium (R1 =Bu, Et, or Pr; R2 = H, or Me).

ILs in biological systems

Due to stability of enzymes in ILs, they can be used for synthesis of pharmaceutically important chemicals and in extraction of amino acids [46]. Carbohydrates are renewable and easily available sources of energy for chemical industries. Insolubility of carbohydrates in organic solvents prevent their transformation into suitable chemicals hence limits their application in various chemical fields. This limitation has been overcome due to their appreciable solubility in ILs [47]. For e.g. acetylation of glucose in presence of lipase enzyme was carried out in IL with more regioselectivity and increased rate of reaction [48]. Carbohydrates such as sucrose which is insoluble in commonly used organic solvents and in weakly coordinating ILs such as $[bmim]BF_4$ can be made to undergo esterification with dodecanoic acid in another IL [bmim][dca] in which it shows high solubility [47].

Water immiscible ILs such as $[bmim]PF_6$, $[bmim][Tf_2N]$ do not damage cells of *E. coli* and *S. cerevisiae*. So they can act as substrate reservoirs and in situ product extracting agents for biphasic whole cell biocatalytic processes. Toxic organic solvents have been used as substrate reservoir in above systems but are used less frequently due to their non-biocompatibility [49].

Extraction of organic/bio/biofuel molecules

Many organic molecules which contain charge on them have significant solubility in ILs and this property make the ILs as ‘green’ solvents for recovery of many biomolecules. Table.(2) shows the extraction of many biomolecules/fuels by suitable combination of ILs and extractants [41].

Table 2: Extraction of biomolecules with the help of ILs

	Substances	IL	Extractant
Phenolic compounds	phthalic acid, aniline, 4-hydroxybenzoic acid, benzoic acid, *p*-toluic acid, benzene, chlorobenzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, 4,4_-dichlorobiphenyl	[BMIM][PF6]	None
	Phenol, tyrosol, *p*-hydroxybenzoic acid	[C*n*MIM][BF4] (*n* = 1, 3, 6, 8, 10) [C*n*MIM][PF6] (*n* = 6, 10)	None
Amino acids	Tryptophan, glycine, alanine, leucine, lysine, arginine	[BMIM][PF6]	DC18C6
Carbohydrate	Xylose, fructose, glucose, sucrose	[C*n*MIM][X] (*n* = 4, 6, 8, 10; X = Cl^-, $PF6^-$, $BF4^-$)	None
	Glucose, sucrose, lactose, cyclodextrin	[BMIM][dca] (carbohydrate solubility is approximately 200 g/l	None
	Cellulose	[C*n*MIM]X (*n* = 4, 6, 8)	None
Organic acids	Lactic acid, acetic acid, glycolic acid, propionic acid, pyruvic acid, butyric acid	[C*n*MIM][PF6] (*n* = 4, 6, 8)	TBP (in some cases)

Note: BMIM (or C4MIM) = 1-butyl-3-methylimidazolium; Beti = bis (perfluoroethylsulfonyl) imide; dca = dicyanamide.

Limitations of ILs

- ILs are generally synthesized from materials which use fossil fuels as their resource. Greenness of ILs can be enhanced by their synthesis from renewable raw materials. For example, ILs synthesized from sugars possessing hydroxyl groups which make them highly coordinating solvents. So these ILs can be used in metal catalyzed reactions.
- ILs can be termed as ‘novel chemicals’ and may require sufficient research regarding their impact on

environment, health and safety prior to their widespread use [50].

- There has been reported some structural similarities among ILs, growth regulators and herbicides. These structural similarities raise significant environment, health and safety [50, 51].
- Certain polymers which are synthesized in the presence of ILs possess significant amount of ILs residue in them. These polymers are used for food packaging and personal care products so they have caused significant danger regarding health and safety.
- Water soluble ILs may enter the aquatic environment by accidental spills or effluents. The most commonly used ILs [bmim][PF_6] and [bmim][BF_4] are known to decompose in the presence of water and as a result hydrofluoric acid and phosphoric acid are formed.[52] Therefore, both toxicity and eco-toxicity information which provide metabolism and degradabilty of ILs are also required to label them as green solvents or investigate their environmental impact.
- Some ILs show high persistence in environment.

Conclusions
From the discussion of applications of ILs as a solvent or catalyst or both, it seems that these are effective and preferable in replacement of conventional solvents and catalyst without altering the efficiency of the reactions. ILs are very effective tool in meeting the requirements of clean technologies practiced under the umbrella of green chemistry. So ILs holds very promising position in the heart of sustainable chemistry. But it is very important that significant amount of research must be carried out in establishing their environment, health and safety impacts.

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