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An Introduction to Room Temperature Ionic Liquids (RTILs)

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ABSTRACT

RTILs or ILs (Ionic Liquids) are an important tool to achieve the targets of green chemistry. They have opened new vistas for practical green chemistry. Their role as a replacement of organic solvents has been discussed in this review. Also, many of their unique properties and applications have been studied. ILs are being seen as designer solvents as their properties can be varied by altering the anion or the cation. As the ILs have desirable properties like negligible vapour pressure high thermal stability etc., they are considered more environment friendly than organic solvents. ILs have found applications in several fields like solvent extraction, chromatography, capillary electrophoresis, voltammetry, etc.

Keywords : Green chemistry, Ionic liquids, novel solvents, analytical applications

I. INTRODUCTION

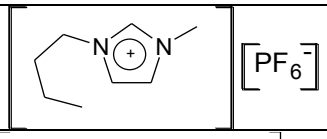
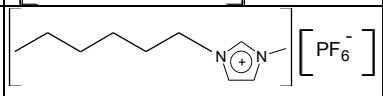
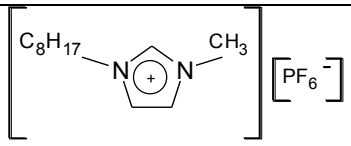
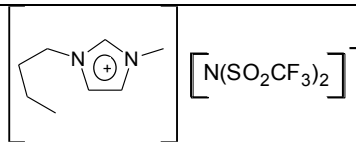
Ionic Liquids (ILs) are widely being seen as clean substitutes for organic solvents. These are called green solvents for being environment friendly and are liquid at room temperature or slightly above it, so they are also referred to as Room Temperature Ionic Liquids (RTILs). RTILs resemble ionic melts of metallic salts as every entity in them is an ion [1], but they should not be mistaken for molten salts. Actually, RTILs are salts with low melting points (<100 oC) and represent a new class of non-molecular ionic solvents [1] which have been successful in replacing organic solvents in many fields like for solubilising complex polar molecules like cyclodextrins, glycopeptides, cellulose [1,2,3], solvent extraction [4-8] etc.

In a typical RTIL, N containing substituted organic cations like, imidazole, pyrrole, pyridine, etc. are attached with inorganic anions like Cl-, PF6 -,BF-4, etc. Due to this unique composition they can have both hydrophobic and hydrophilic properties. 1-butyl-3-methyl imidazolium chloride (BMIM-Cl), 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIM-PF6) and 1-octyl-3-methylimidazolium hexafluorophosphate [C8MIM] [PF6] are some of the common ILs.

These are easy to prepare from relatively inexpensive materials [4,9] and hence are very accessible. Some of the physical and chemical properties responsible for their unique behavior are as follows:

1) IL's are thermally more stable than organic solvents and have a liquid range of 300 oC [1]. Their decomposition temperatures are around 400oC [10].
2) Being non-toxic, non-flammable and non-volatile, they are considered
3) more safe and environment friendly than organic solvents.
4) ILs suppress conventional solvation and solvolysis phenomenon and can dissolve many inorganic molecules to a very high concentration [11]. These can be custom synthesized to be water miscible or immiscible [12].
5) The low melting nature of ILs can be engineered by combining cationic and anionic species to produce salts with low lattice energies [13,14].
6) These are also called designer solvents as many desirable properties can be incorporated by changing the anion or cation [15].
7) Functionalised IL's were obtained by incorporating thiourea, thioether and urea into derivatized imidazolium cations [4]. These ILs were how higher distribution ratios and these can act as extractant as well as the hydrophobic phase. RTILs may also increase the lifetime of species like [RuCl6]3- which are unstable in conventional molecular solvents [11].

Table1: Physical Properties of Ionic Liquids

Ionic Liquid	Structure	Mol. Wt.	M. pt. ^{o}C	T_g ^{o}C(dried)	Density g/ml	Viscosity at 25 ^{o}C, cP dried	Surface Tension (dyn/cm	Solubility in Water (g/100ml)
$[C_4MIM][PF_6]$		**284**[c]	**10**[a]	**-80**[a]	**.37**[c]	**393**[c]	**48.8**[c]	**1.88**[c]
$[C_6MIM][PF_6]$		**312**[c]	**-61**[a]	**-78**[a]	**1.3**[c]	**560**[c]	**43.4**[c]	**0.75**[c]
$[C_8MIM][PF_6]$		**340**[c]	-	**-82**[a]	**1.2**[c]	**710** [c]	**36.5**[c]	**0.20**[c]
$[C_4MIM][NTf_2]$		--	**-25**[a]	**-104**[a]	**1.43**$_a$	**52**[a]	**37.5**[a]	--

Tg; Glass Transition Temperature, [a] Reference [10], [b] Reference [12], [c] Reference [13]

II. Synthesis of some Ionic Liquids

Preparation of [C4mim][Cl]

Wei et al [4] prepared 1-butyl-3-methylimidazolium chloride [C4mim][Cl] by adding equal amounts i.e. 0.3 mole each of 1-chlorobutane and 1-methyl-imidazolium refluxed for 24 h at 800C till formation of a golden viscous liquid.The liquid portion [C4MIM][Cl] was potassium hexaflorophosphate at 4oC in 30 min and stirred at room temperature for 30 minutes. The purity of final product was characterized with 1H NMR. The yield was about 60%.

Preparation of 1-butyl-3-methylimidazolium chloride (BMIMCl)
Khadilkar and Rebeiro [9] mixed 1-methylimidazole and 1-BuCl in a microwave reactor and irradiated in MW oven at 300 W power, programmed to 1500C for 2min, and irradiation was continued at this temperature for 22 min. A white solid on refrigeration was formed. The yield was 91%. Products were characterized by 1H and 13C NMR spectroscopy.

Sonochemical Synthesis of Imidazolium based Ionic liquids
A green process; sonochemistry [16] was used for the synthesis of imidazolium based ILs with the help of ultrasound assisted process.

III. Applications of Ionic Liquids

The applications of ILs in chemical procedures and analytical chemistry will be briefly discussed here.
The most widely studied application of ILs is in solvent extraction, where these are used as a substitute for organic solvents. Several researchers have discussed the use of ILs as alternative solvents [4-8]. ILs were found to be recyclable as well as with high extraction efficiency.
The wide applications of ILs in the field of chromatography are also noteworthy. The ILs are

making inroads into different fields of chromatography. ILs have been used as modifier in Miscellar electrokinetic chromatography [18], Liquid chromatography [19,20], column chromatography [21], Gas liquid chromatography [12] and gas chromatography [22]. ILs have been found useful in other techniques like voltammetry [23], capillary electrophoresis [24-29].

ILs have been successfully used in various catalytic systems for reaction rate enhancement [30,31]. The simultaneous use of ILs and ultrasonic irradiation (US) has been employed as an alternative to traditionally used catalysts in Kabachnik-Fields reaction [30].The yield greatly improved to 93-96% and reaction time was also reduced.

Armstrong et al [32] examined the use of ILs as matrices for UV-MALDI due to high solubilizing power, negligible vapour pressure and broad liquid temperature range of ILs.

Many ionic matrices were tested using peptides, proteins and poly (ethylene glycol)[PEG-2000] and the ILs showed excellent solubilising properties and vacuum stability as compared to commonly used liquid and solid matrices. Some ILs produced homogeneous solutions of greater vacuum stablilty, higher ion peak intensity and equivalent or lower detection limits than currently used solid matrice.

IV. CONCLUSION

The environment friendly properties of ILs make them perfect alternatives for VOCs (Volatile Organic Compounds). These were found to be better solvents for extraction of Pb2+ than chloroform. Due to negligible vapour pressure, RTILs were found to be useful in LPM Extraction [13]. In chromatography, their unique properties like selectivity and dual nature could be used to separate complex mixture of molecules with different polarities. RTILs can be engineered to suit the needs of chromatography by altering the cation structure or replacing the anions. More research needs to be carried out on the unique properties and applications of ILs for a clean and green chemistry.

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