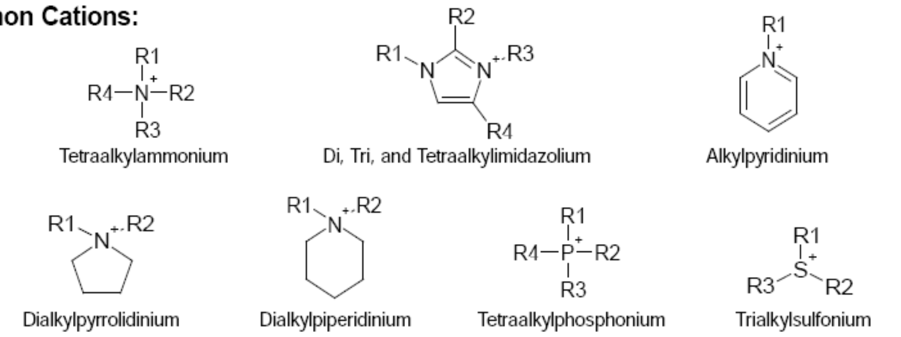
CHEMCOS THE CHEMICAL SOCIETY, IIT DELHI July 2008 Issue II

SCIENTIFIC VERSES

ROOM TEMPERATURE IONIC LIQUIDS: NEW AGE ELECTROLYTES

Ushati Das,
Solid State & Structural Chemistry Unit, Indian Institute of Science, Bangalore. (ushati@gmail.com)

Common Cations:



Common Anions:

BF_4^-, $B(CN)_4^-$, $CH_3BF_3^-$, $CH_2CHBF_3^-$, $CF_3BF_3^-$, $C_2F_5BF_3^-$, n-$C_3F_7BF_3^-$, n-$C_4F_9BF_3^-$, PF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$, $N(SO_2CF_3)_2^-$, $N(COCF_3)(SO_2CF_3)^-$, $N(SO_2F)_2^-$, $N(CN)_2^-$, $C(CN)_3^-$, SCN^-, $SeCN^-$, $CuCl_2^-$, $AlCl_4^-$, $F(HF)_{2.3}^-$ etc.

The next big thing in modern day electrolytic devices, critics agree, would be the extensive use of room temperature ionic liquids (RTILs) or fast ion conductors as potent electrolytes replacing the age old lead acetate and aqueous electrolyte based batteries. Ionic liquid, as the name implies, is a liquid that contains a majority of ions rather than molecular species in dynamic equilibrium. Simply put, even molten NaCl is an ionic liquid (above 800 °C). Thus, salts which have a low melting point and are liquids at room temperature form a new class of liquids and are referred to as RTILs. The opus today lies in synthesizing and optimizing the conducting properties of these room temperature ionic liquids. Physicochemical properties of RTILs are similar to those of high temperature ionic liquids, but the practical aspects of their maintenance or handling are different enough to merit a distinction [1].

Room temperature ionic liquids date back to 1914 when Walden identified and characterized the electrical conductivity of ethylammonium nitrate [2]. It was followed by the synthesis of a large number of electrolytes based on the tetraalkylammonium and imidazolium cations, primarily because of the low vapor pressure that these afforded. Since there are no intermediate solvent molecules, the vaporization energy is much more than the lattice energy; thereby guaranteeing almost zero vapour pressure at ambient temperature.

Over the last five decades, smart RTILs have been synthesized which have tunable conductivity, viscosity and melting points. Way back in 1978, Gordon and Subba Rao [3] reported the rapid fall in melting points of tetraalkylammonium salts to sub-100 °C range as one increased the number of carbons around nitrogen to >20. In 1998, MacFarlane's group [4] found that increasing the asymmetry of the substituents around the tetrahedral ammonium cation induced a marked decrease in the viscosity; hence increase in conductivity of these electrolytes. Ionic liquids based on tetraalkylammonium cation and chloroaluminate anions have been extensively studied by Osteyoung's group [5], followed by systematic research on chloroaluminates as ionic liquidus solvents in 1980's. A major drawback of RTILs based on aluminium halides is their moisture sensitivity and, though to a somewhat lesser extent, their acidity/basicity; although the latter can sometimes be used to an advantage. In 1992, Wilkes and Zawarotko [6] reported the preparation of ionic liquids with alternative, 'neutral', weakly coordinating anions such as hexafluoro-phosphate ($[PF_6]^-$) and tetrafluoro-borate ($[BF_4]^-$), allowing a much wider range of applications for ionic liquids. Also, binary and ternary eutectic mixtures of these RTILs have been used to further decrease the melting point and hence increase the liquidus working range [4]. It was not until recently that a class of new, air- and moisture stable, neutral ionic liquids was available that the field attracted significant interest from the wider scientific community.

A plethora of distinct physical and chemical properties make RTILs an interesting hotbed of intellectual pursuit, not only in terms of electrolytic devices; but also as potent applications in the fields of biocatalysis (as solvents, [7]), food science [8] and low temperature lubrication [9]. RTILs have a strong tendency to supercool; as a result, the same compound is often described in literature as a solid or liquid at room temperature. ***The difference between melting point and temperature of solidification in one case was found to be as high as 200 °C!*** [10] The room temperature conductivities of RTILs lie within a broad range of 0.1-14 mS/cm. Although this is much lower than that characteristic of conventional aqueous (500-700 mS/cm) and non-aqueous (50-70 mS/cm) electrolytes, it is comparable to lithium electrolytes (10 mS/cm). Nevertheless, it scores over lithium batteries in terms of safety due to their non-volatility. Also, this effectively eliminates a major pathway for leakage and pollution, thus keeping environmentalists happy as a lobby for green chemistry! Due to their broad electrochemical window of about 4-5 V, conductivity upto 14 mS/cm coupled with a double-layer specific capacity of around 10 μF/cm^2, RTILs are excellent electrolytes for double layer capacitors. The specific capacity of electrodes based on high surface carbon and ionic liquids can be as high as 180 μF/kg [1]. RTILs are being widely used as electrochemical mechanical actuator devices, dye sensitized photoelectrochemical cells, electrochemical supercapacitors and as lithium ion battery electrolytes [11].

Recently, there has been a number of interesting phenomena concerning ionic liquids that have come up in literature. Prof. Borra's group [9] in Quebec has coated silver on ionic liquids as a means of preparing a giant lunar telescope, of 20-100 m aperture located on the Moon, that would be able to observe objects 100 to 1,000 times fainter than the proposed next generation of space telescopes. Peter Licence and colleagues at the University of Nottingham, UK were using mass spectrometry to study ionic liquids when they noticed that the particle beam from the spectrometer created a pattern of charge on the surface of a frozen ionic liquid. The beam knocks electrons from the material, leaving a charge deficit that the frozen liquid cannot dissipate. When the liquid melts, the charge spreads out and the pattern disappears. This interesting observation can be modulated into a data storage system technology! [12]

RTILs have great potential for electrochemical applications in science and technology. Skeptics may hold the opinion that RTILs are "messy, intractable" solvents, i.e., hard to make and hard to purify, and to some extent this is true. But, there is no longer any doubt about the attractiveness of RTILs as solvents for electrochemistry because some have excellent physicochemical properties for this purpose, including ample intrinsic conductivities, wide electrochemical windows, and negligible vapor pressures [11]. Among the various classes of known solvents, only RTILs have this combination of desirable characteristics ***and hence is the future of designer solvents.***

References:

1. M.Galinski *et.al. Electochimica Acta*, *51*, **2006**, 5567-80.
2. P. Walden, *Bull.Acad.Imper.Sci*, **1914**, 1800.
3. Gordon, J. E.; Subba Rao, G. N. *J. Am. Chem. Soc.,* **1978**, *100*, 7445.
4. MacFarlane *et.al. J. Phys. Chem. B* **1998**, *102*, 8858-8864
5. Osteryoung *et.al. J. Am. Chem. Soc*., **1979**, *101*, 323.
6. J. S. Wilkes, M. J. Zaworotko *Chemical Communications*, **1992**, 965-967.
7. Adam J. Walker and Neil C. Bruce *Chemical Communications,* **2004**, 2570.
8. Zhao *et.al. J. Am. Chem. Soc.*, **2004**, *126*, 15876.
9. Borra *et.al***.** *Nature*, **2007**, *447*, 7147, 979-981.
10. Ngo *et. al.Thermochim. Acta,* **2000**, *27*, 357/358.
11. Tsuda and Hussey *The Electrochemical Society Interface* • Spring **2007**
12. Licence *et. al. Angew. Chem. Int. Ed.* **2007**, *46*, 22, 4163.

 Copyright © 2008 All Rights Reserved