

IONIC LIQUIDS



IONIC
LIQUIDS

Let's
Conclude

[BMIM][
PF6]

Application

Green
chemistry

what is
IONIC
LIQUID

History

Why

References

Research
Interest

Sujoy Saha

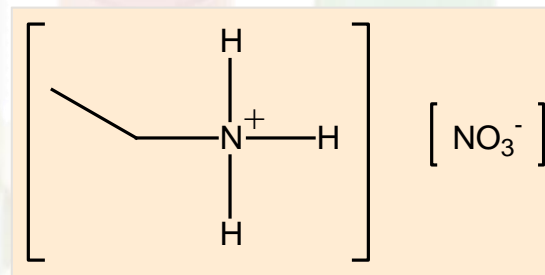
Jerrin George

Ionic Liquids

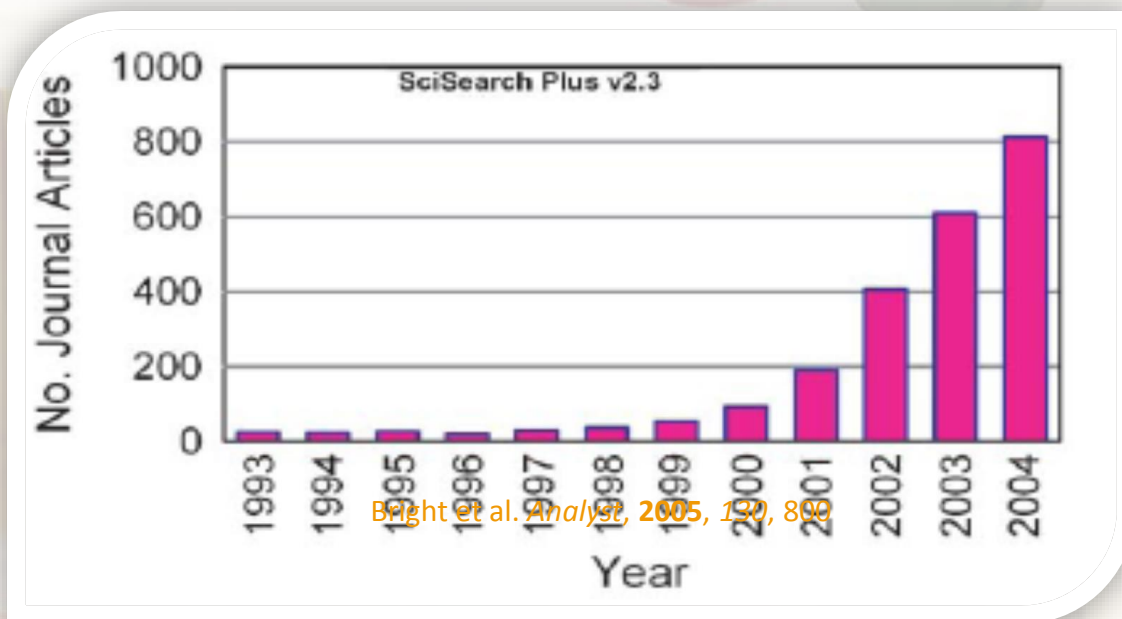
Green Chemistry

- Era of ionic liquids -began in the eighteenth hundreds- Gabriel & Weiner reported an ionic liquid.

- First ionic liquid: ethyl ammonium nitrate (1914, Paul Walden)



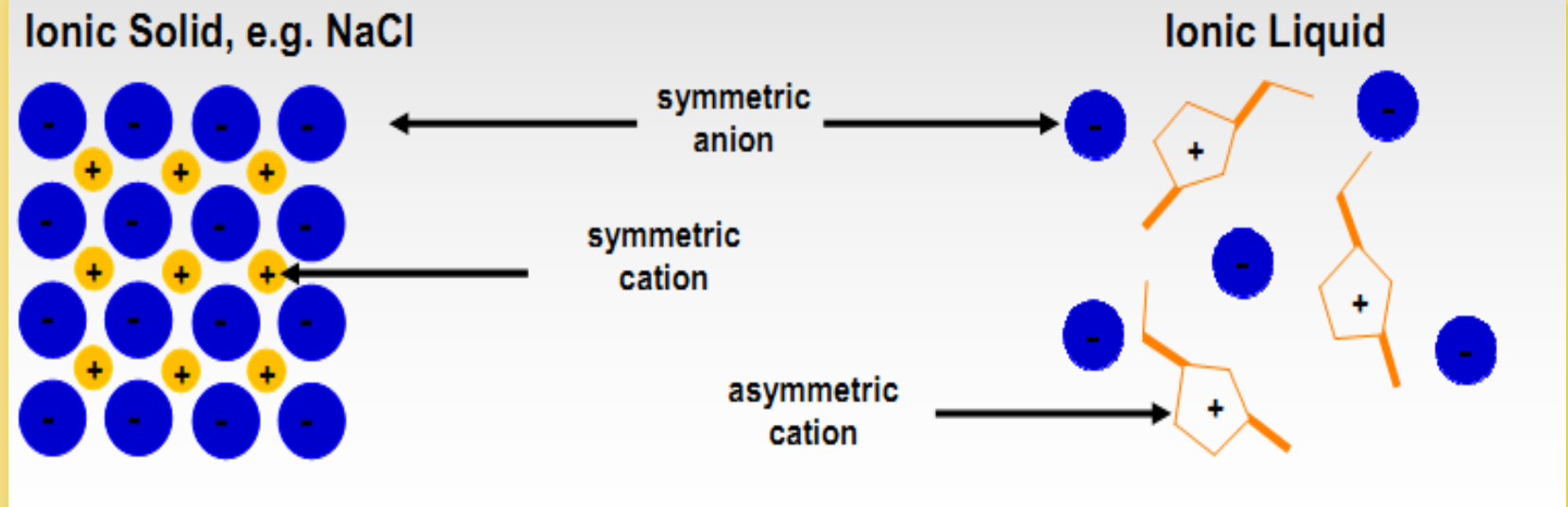
- Recent progress



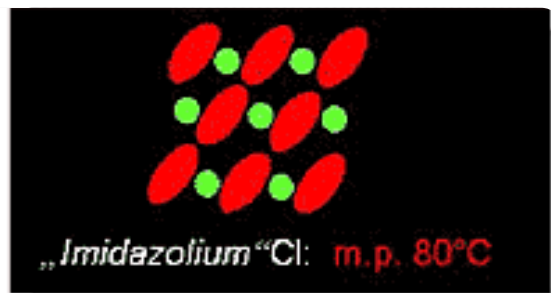
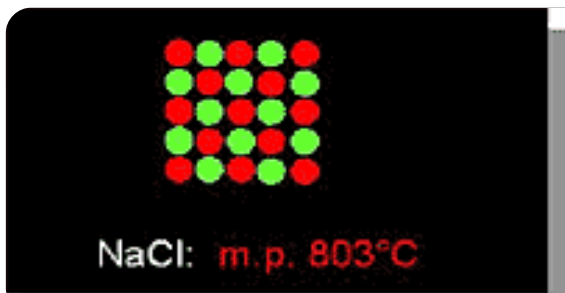
Bright et al. *Analyst*, 2005, 130, 800

The 'Ionic State'

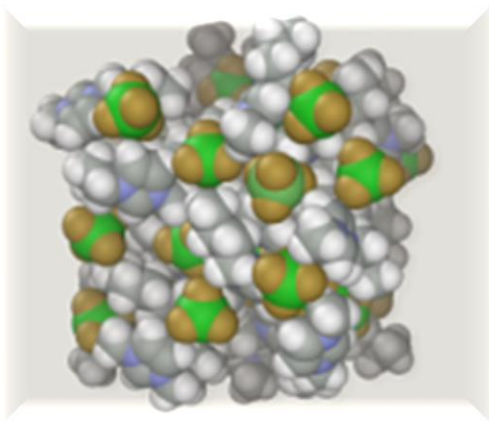
- Class of materials-consisting entirely of ions and being liquid below 100°C.



Why are ionic liquids “liquids”?



- Traditional salts like sodium chloride pack efficiently to form a crystal lattice



- Ionic Liquids-cations are asymmetrically substituted with different **Bulky groups**- to **weaken** this ionic interactions
- prevents packing of the cations/anions into a crystal lattice

A simulated model of an Ionic Liquid

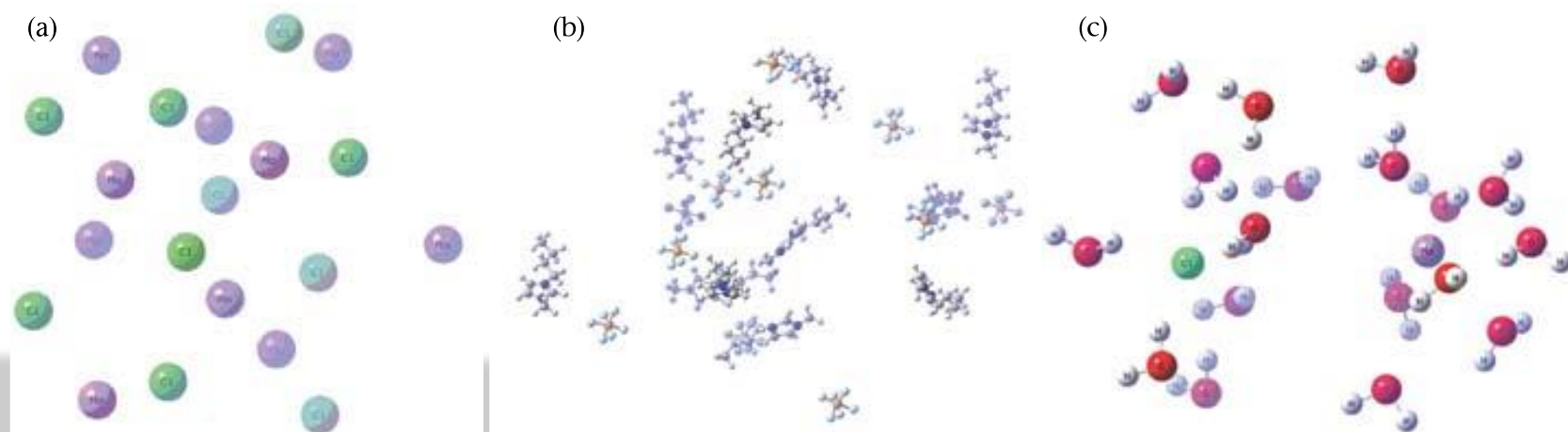


Fig. 1. Representation of (a) liquid NaCl, (b) molten BMIM PF₆, and (c) aqueous NaCl.



Examples of common Ionic Liquids:

- Ethyl-3-methylimidazolium (EMIM) Chloride,
- EMIM dicyanamide,
- 1-butyl-3,5-dimethylpyridinium bromide,
- 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]

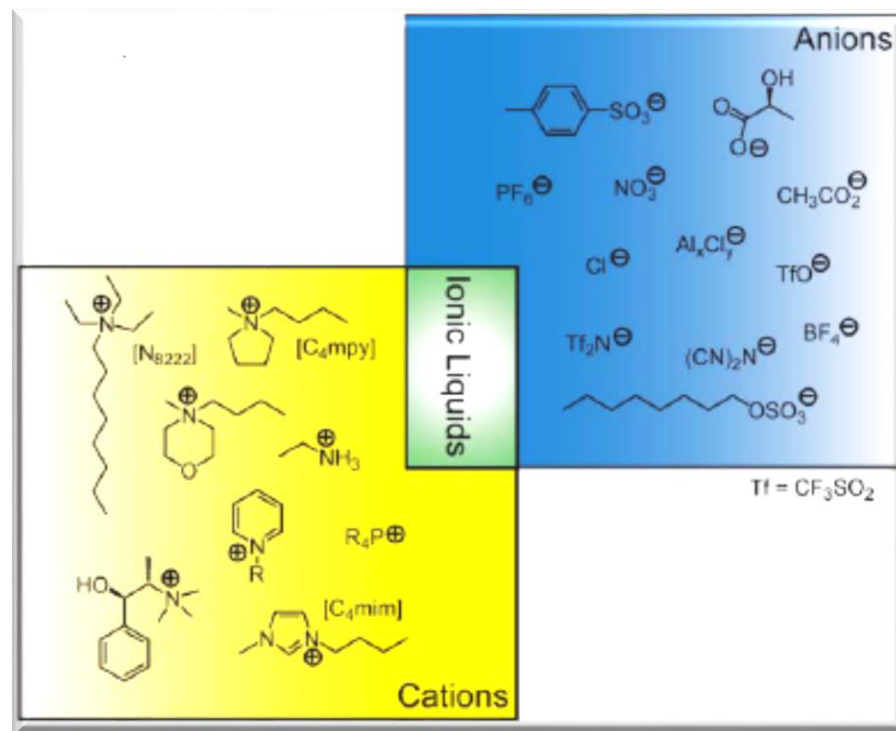
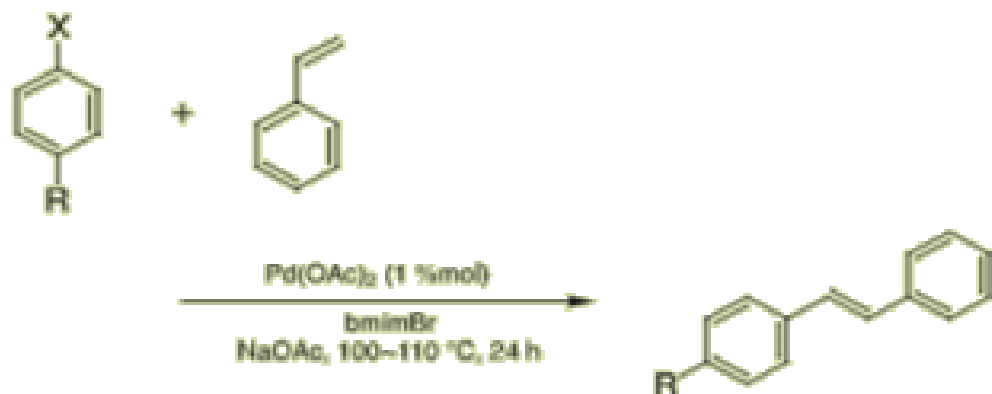


Fig: Some common cations in Ionic Liquids

- * [PF₆]⁻ for moisture stable, water immiscible IL
- * [BF₄]⁻ for moisture stable, but water miscible IL
- * [AlCl₄]⁻ (or other Lewis acids) decomposes in water

Room Temperature Ionic Liquids (RTILs)

- Exist as room temperature liquids.
- Excellent solvents for many reactions: Diels-Alder reactions, Friedel-Crafts, Heck reaction...



- The low vapor pressures in most instances contrast the environmental problems of volatile organic solvents
- **Green chemistry.**

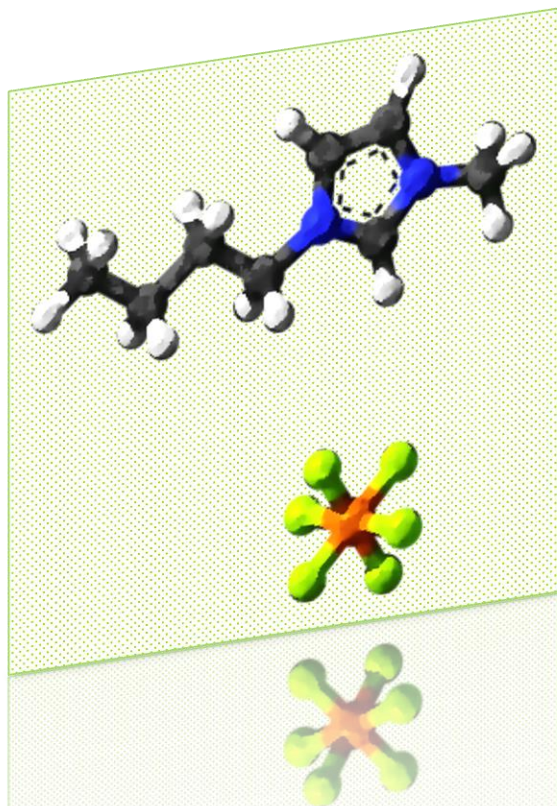
Why Ionic Liquids ?

- Electrically conductive
- Thermal stability
- Extremely low vapour pressure
- Non flammable
- And application in **Green Chemistry**.

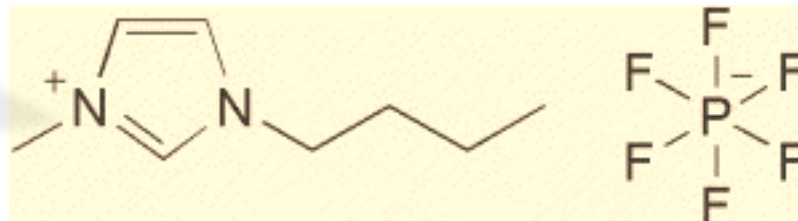


[BMIM][PF₆]

1-Butyl-3-methylimidazolium hexafluorophosphate



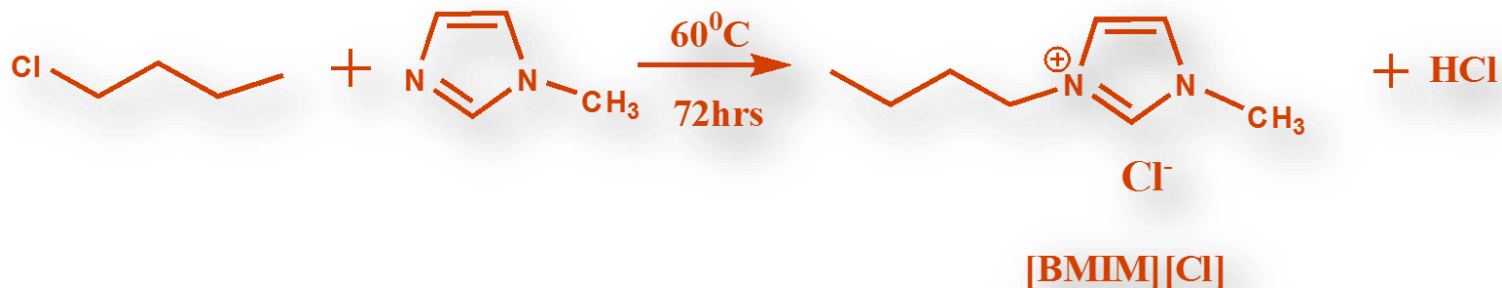
- A viscous, colourless, hydrophobic and non-water soluble ionic liquid.
- Molecular mass: 284.18 g mol⁻¹
- Density: 1.38 g/mL
- Melting Point: 10°C



Synthesis

- Two Steps:

(1) Quaternization step



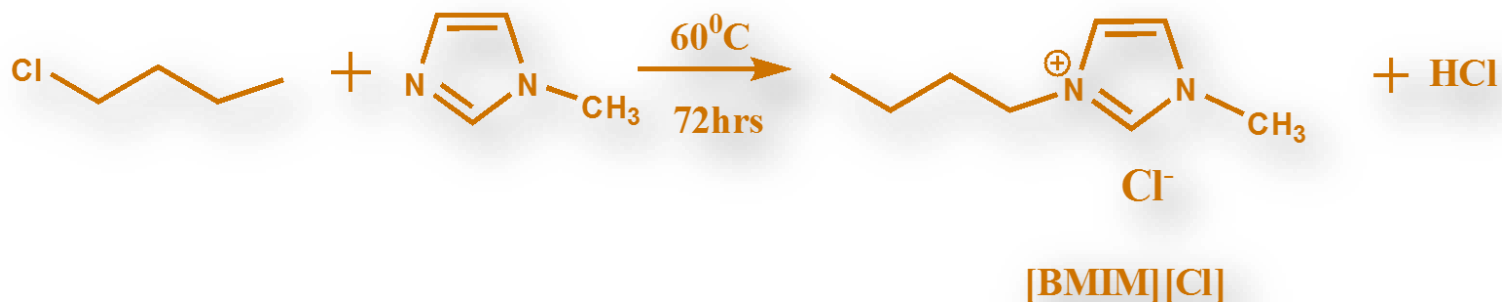
White solid salt -washed several times with dry warm ethyl acetate until -free from unreacted 1-methylimidazolium.

Organic Syntheses, Coll. Vol. 10, p.184 (2004); Vol. 79, p.236 (2002).

Synthesis

- Two Steps:

- (1) Quaternization step

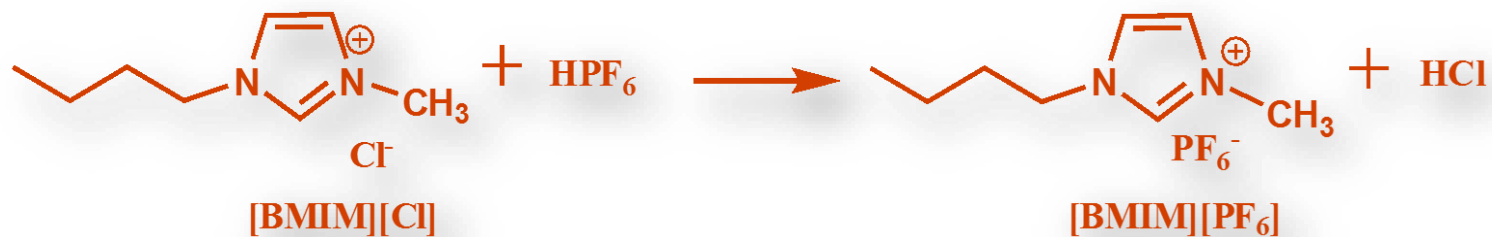


White solid salt -washed several times with dry warm ethyl acetate until -free from unreacted 1-methylimidazolium.

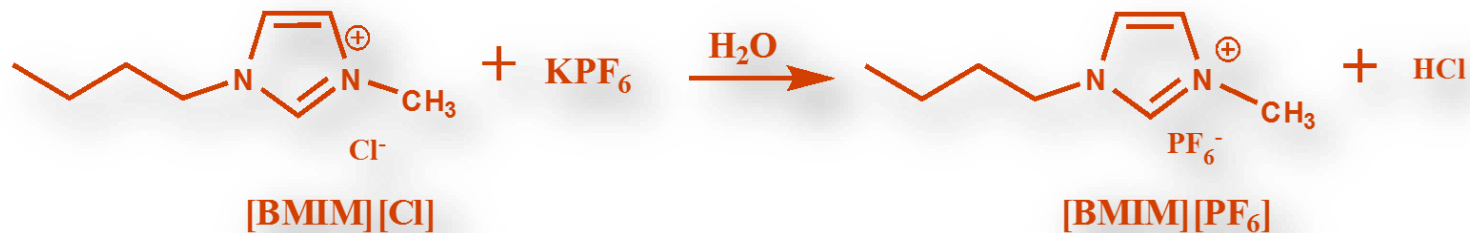
Organic Syntheses, Coll. Vol. 10, p.184 (2004); Vol. 79, p.236 (2002).

- Metathesis reaction

Using HPF_6 :



Using KPF_6 :



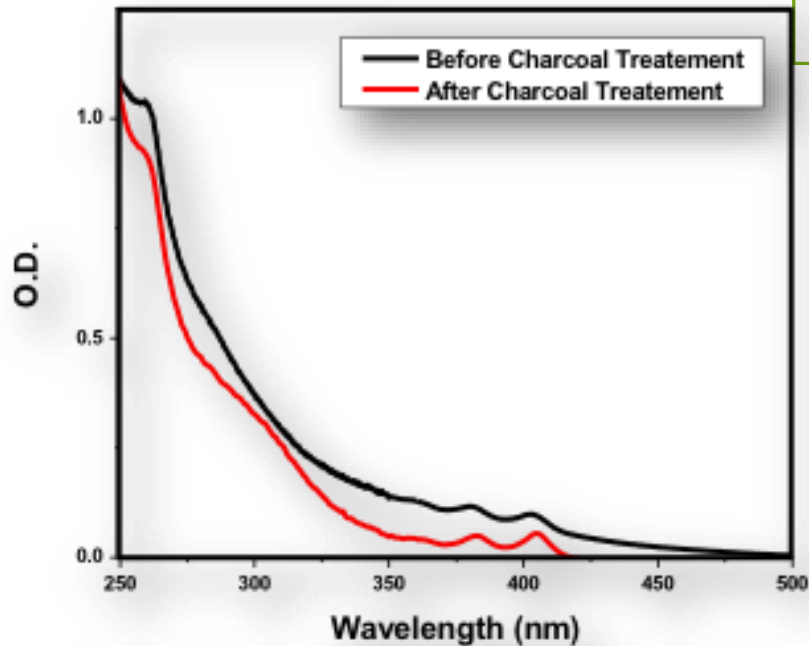


Figure 1: Absorption spectrum of [BMIM][PF₆] before and after charcoal treatment.

Two additional peaks were also observed at 404 nm and 383 nm.

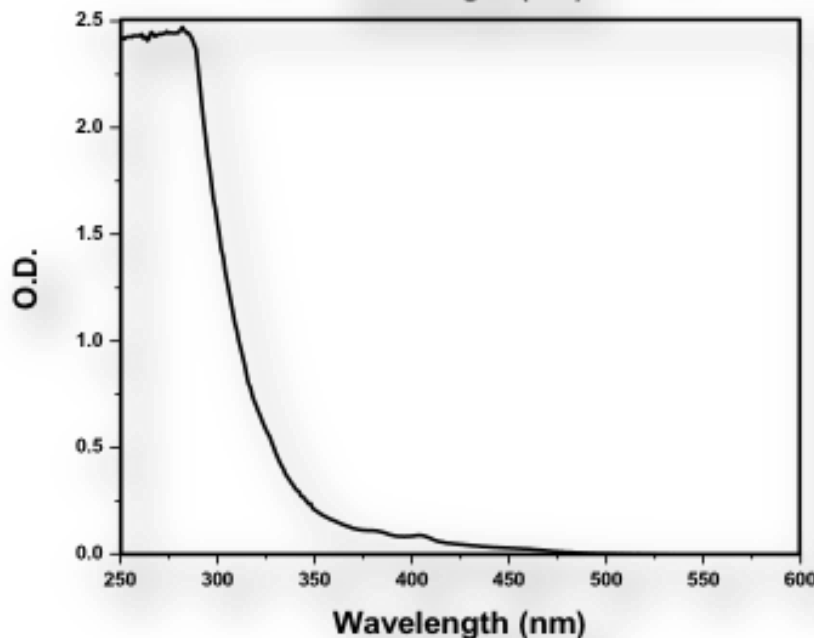


Figure 2 : Absorption spectrum of [BMIM][PF₆] after passing through specially designed celite column. 383nm and 404nm peak persisted.

Metathesis Reaction using KPF_6

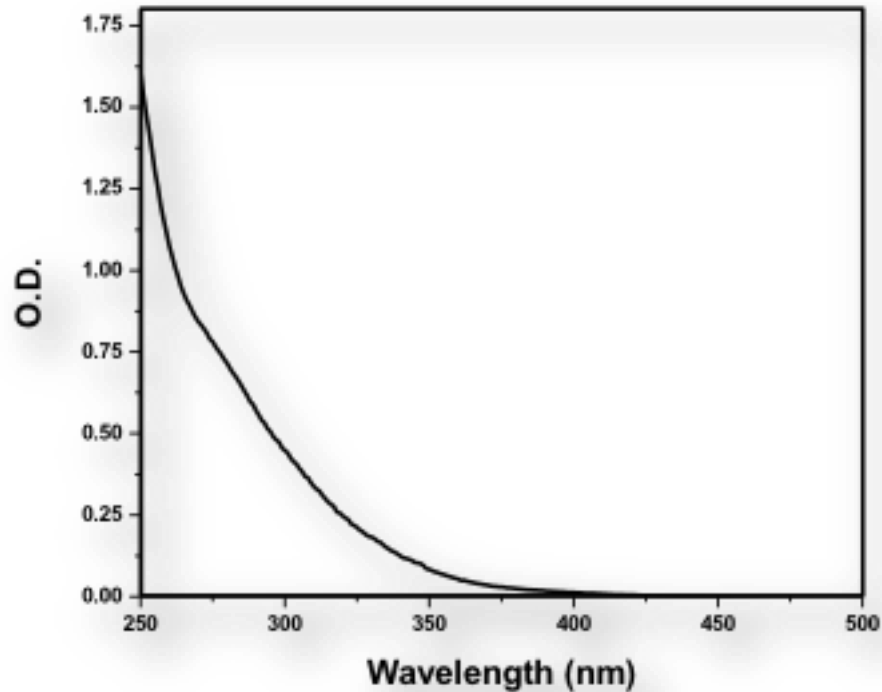


Figure 3: Absorption Spectrum of $[\text{BMIM}][\text{PF}_6]$ prepared by using KPF_6

The impurities that came along the preparation of ionic liquid with HPF_6 might be result of products obtained by this corrosive nature of HPF_6 on glass.

Ionic liquids for liquid-in-glass thermometers

- Tris(2-hydroxyethyl) methylammonium methylsulphate ([TEMA][MeSO₄]).

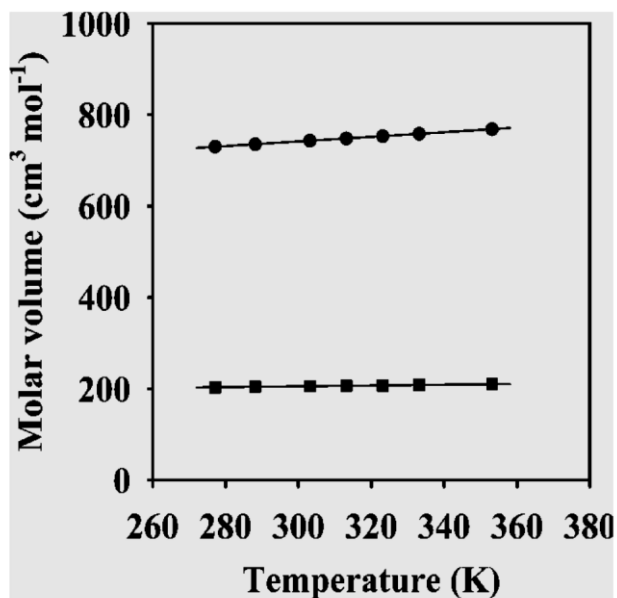
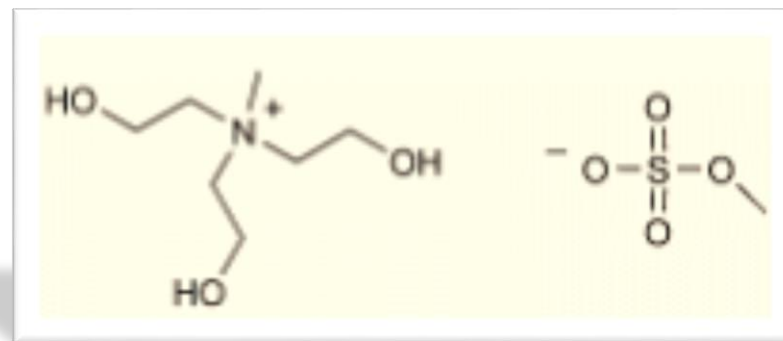


Fig. 2 Molar volume V as a function of temperature T for [TEMA][MeSO₄] (squares) and [P₆₆₆₁₄][NTf₂] (circles). The solid lines represent the linear regressions.

- Range: -50 °C to 140 °C
- Glass transition temperature $T_g = -81$ °C
- Stable up to 200 °C



$$\alpha = \frac{1}{V_T} \left(\frac{\partial V_T}{\partial T} \right)_p$$

$$\Delta h = \frac{4V \Delta \alpha}{\pi D^2} \Delta T$$

α - Volume expansibility of a pure fluid.

V_T -Total Volume.

T- Absolute Temperature.

h- Height of liquid column.

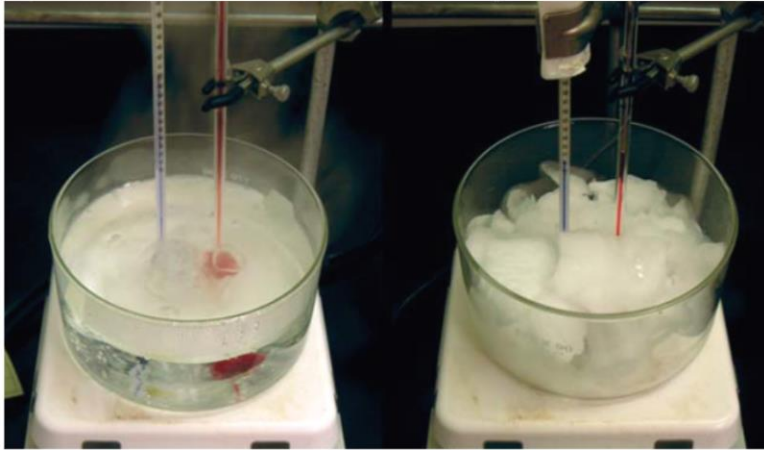
D-Diameter of Tube

- Coloration of Liquid was done to distinguish the liquid

Parameter	Result
Acute oral toxicity	Not harmful
Skin irritation	Non-irritant
Eye irritation	Non-irritant
Sensitization	Non-sensitizing
Mutagenicity	Non-mutagenic
Biological degradability	Readily biodegradable
Toxicity to <i>daphniae</i>	Not acutely harmful
Toxicity to fish	Not acutely harmful



For a Greener Chemistry



Experimental setup for the calibration of the standard thermometer with the red-dyed [TEMA][MeSO₄], in baths of boiling water and melting ice for determining the marks at 100 °C and 0 °C respectively, while compared with the readings of a commercial LIG thermometer (with blue filling fluid).

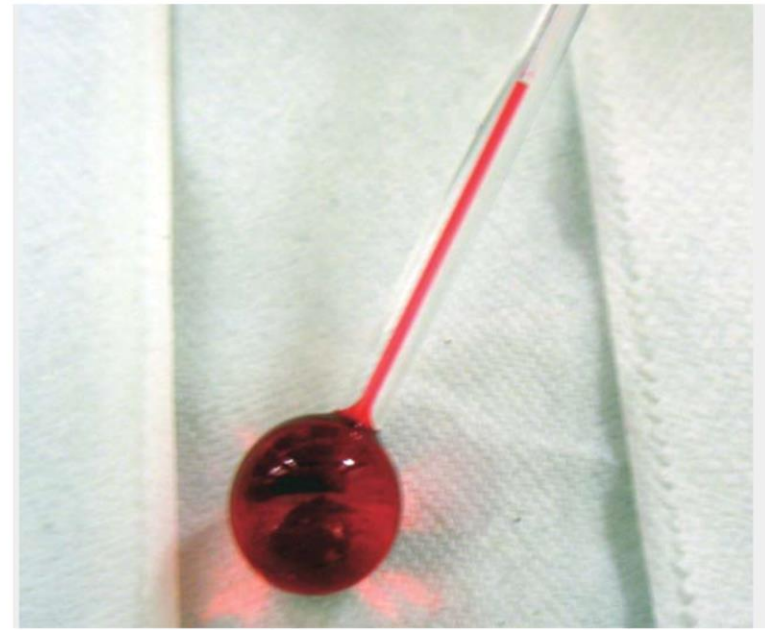


Fig: Colored [TEMA][MeSO₄] filling the reservoir and part of the bore of the glass holder of the standard thermometer prototype.

Green chemistry

'Utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.'

Green Chemistry – Theory and Practice, P. T. Anastas & J. C. Warner, Oxford, 1998

- Ionic liquid-act as solvent in reactions -prevents the waste of solvent.
- Ionic liquid –Reused.
- The miscibility gap of most ionic liquids with alkylated aromatics allows product isolation by simple decantation.

Application

- Ionic liquids –used in microreactors to synthesize & purify extremely reactive organometallic compounds (using the Green Chemistry principles.)
- Ionic liquids -used for efficient heat storage and transfer in solar thermal energy systems.
- Ionic Liquids -dispersing agents in paints to enhance appearance and drying properties
- 1-butyl-3-methylimidazolium hexafluorophosphate-used-non aqueous electrolyte medium -recovery of uranium in spent fuel rods.
- Some ionic liquids -advantage of both homogeneous and heterogeneous catalysts.

Conclusion

- Ionic liquids ,as the new materials of wide use in various of fields.
- “Greener” alternative
- The **FUTURE**

Conclusion

- Ionic liquids ,as the new materials of multifunction , widely used in various of fields.
- Environmentally-friendly reaction process have vigorously been studied from the standpoint of green chemistry and based on the properties of easy separation , low toxicity , selective miscibility , ILS play an important role in organic synthesis as the green alternative solvent.
- With the development of multifunctional ILs , we can expect ILs would apply in more fields .

References

1. Martyn J. Earle, Charles M. Gordon, Natalia V. Plechkova, Kenneth R. Seddon, Thomas Welton, *Anal. Chem.* 2007, 79, 758-764
2. Aniruddha Paul, Ph.D Thesis, University Of Hyderabad, Hyderabad, India, 2008.
3. Peter Nockemann, Koen Binnemans, Kris Driesen, *Chemical Physics Letters*, 2005, 415, 131-136.
4. Hector Rodriuez, Margaret Williams, John S. Wilkies, Robin D. Rogers, *Green. Chem.* 2008, 10, 501-507.
5. Aniruddha Paul, Prasun Kumar Mandal, Anunay Samanta, *Chemical Physics Letters*, 2005, 404, 375-379.
6. Jairton Dupont, Crestina S. Consorti, Paulo A. Z. Suarez, and Roberto F. de Souza, *Organic Syntheses*, 2004,10, 184; 2002 ,79, 236 .