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Ionic Liquids-Designer Solvents for Green Chemistry

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Abstract* - *Ionic liquids, as green solvents have been studied widely now a days due to their appealing properties such as negligible vapour pressure, large liquid range, high thermal stability, high ionic conductivity, large electrochemical window, and ability to solvate compounds of widely varying polarity. Utilizing ionic liquids is one of the goals of green chemistry because they create a cleaner and more sustainable chemistry and are receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes. Ionic liquids have been investigated for a wide range of synthetic applications, they have fascinated considerable interest for used as non-volatile solvent based electrolytes in the field of organic synthesis, catalysis, electrochemistry, solar cells, fuel cells, etc., as they possess many benefits than volatile organic solvents.

Index Terms*— *Green chemistry, applications, classification, ionic liquids, properties.

I. INTRODUCTION

The Need for Green Solvents

Transferring waste into useful products is one way to improve “greenness.” Another move toward “source prevention is the final goal in the field of green chemistry. If we want to avoid the toxic effects of a substance, don’t generate it in the first place” (Wilkinson, 1997). -The utilization of solvents in the chemical industry and in the chemical-related industries is very common. Beyond “chemical industries,” solvent use has become an essential part of life in the twenty-first century. In 1991, the manufacturing of the 25 most commonly used solvents was more than 26 million tons per year. Five of the top 10 chemicals disposed of were solvents like methanol, toluene, xylene, methyl ethyl ketone, and dichloromethane. The total amount of these chemicals released or disposed of was over 687 million pounds, which accounts for 27% of the total quantity of TRI-listed chemicals released and disposed of in that year (Sullivan, 1997). Because solvents are essential in such high volumes that, hazards associated with them and safety issues associated with their use have always been a concern in the development and selection of solvents. Some of the initial and most noticeable hazards, that if solvents -were found to possess would cause them to be selected against, include properties such as high flammability or explosivity. With the greater understanding of the health and environmental effects that could be caused by other hazardous properties that solvents may possess or by their use in such large volumes, alternative solvents are being carefully scrutinized for all hazardous properties, and new solvent systems are being developed to be more environmentally benign.

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Many solvents used in large volumes for many decades have been found to create serious toxic or otherwise hazardous properties. Halogenated solvents such as carbon tetrachloride, perchloroethylene, and chloroform, for example, have been implicated as probable and/or suspect carcinogens, while other classes of solvents have demonstrated neurotoxicological effects. The search for an unconventional solvent is an important step in making an analysis and separation process “greener” and environmentally friendlier. It appears that alternative solvents like ionic liquids (ILs) and supercritical fluids have one extra aspect which makes them even more attractive for researchers—tunability. The ability to fine-tune the properties of the solvent medium will allow this to be chosen to replace specific solvents in a variety of different processes or generate new methods for processing (analyzing) samples. Ionic liquids supposed as novel chemical agents and widely regarded as a greener substitute to many commonly used solvents because they are designable, recyclable and non-volatile.

II. WHAT ARE IONIC LIQUIDS?

The terms room-temperature ionic liquid (RTIL), nonaqueous ionic liquid, molten salt, liquid organic salt, and fused salt have all been used to explain salts in the liquid phase (Welton T.1999). Ionic liquids are composed exclusively of anions and cations. They are molecular solvents composed of neutral species such as benzene, methanol, chloroform, water etc. Usual molten salts show a high melting point (i.e., 801 ◦C for sodium chloride and 614 ◦C for lithium chloride), which greatly confine their use as solvents in most applications. RTILs, however, continue to be liquids at or below room temperature. The adopted upper temperature limit for the classification "ionic liquid" is 100 °C (though some solidify to glasses on cooling) and higher melting ion systems are normally referred to as molten salts(Visser et.al 2002)

A. Why are they Chemically Interesting?

These are liquids with broad temperate range and slight vapour pressure. For example1-butyl-3-methylimidazolium hexafluorophosphate shows steadiness in air upto 300^{o}C. Ionic liquids exhibit excellent solvent properties and can often aid and influence chemical reactions without being altered in the process (Welton, 1999). An ionic liquid is a salt in which the ions are weakly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature (room temperature ionic liquids, RTIL's). At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice (Wasserscheid ,2000). Due to the large amount of possible combinations of cation and anion, they are vulnerable to numerous permutations that allow the various physical and chemical properties to be adjusted almost at will

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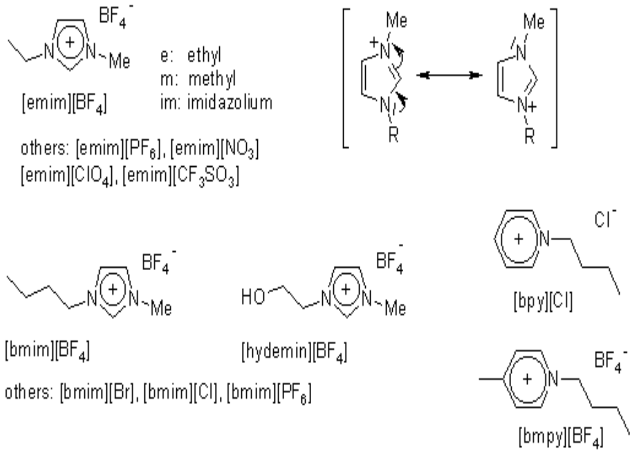
(Anon, 2001).

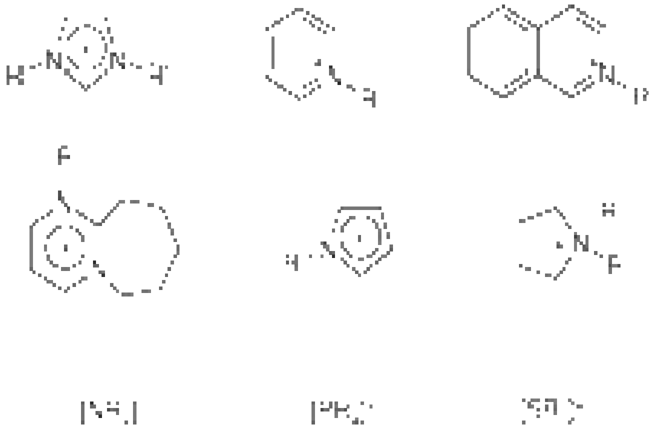
B. Classification of Ionic Liquids:

A simple ionic liquid consists of one cation and one anion. The anions are generally small and the cations bulky with alkyl chains. Some usually used anions for simple ionic liquid systems are Cl, Br, BF4, CF3SO3 (OTf), N(SO2CF3)2 (NTf2) etc. There are a few dissimilar commonly used cations for ionic liquids, the commonly studied ones are the 1-alkyl-3-methyl-imidazolium cations. Other cations are phosphorus or nitrogen containing organic ions with attached alkyl chains of varied length.

1-Alkyl-3-methyl-imidazolium cation

The name of an ionic liquid first states the cation followed by the anion. For the most commonly studied systems (imidazolium based cations) the cations are named according to the alkyl chains lengths followed by imidazolium. A 1-butyl-3-methyl-imidazolium cation are sometimes abbreviated as C4C1Im, BMIm, BMIM, bmim or ByMeIm. The anions are genererlly named in accordance to general principles, eg. Ac meaning Acetate. More than 600 ionic liquid systems can, in principle, be generated from around 10 simple anions such as (BF4)− and (PF6)− and the 1-alkyl-3-methylimidazolium cation substituted with various alkyl groups in the 2-, 4-, or 5-position, or N-alkylpridinium substituted in the 3- or 4-position. When heteropolyanions and tetralkylammonium and tetraalkylphosphonium cations are added to the list, a grand total of more than a quarter of a million ionic liquid systems is possible. With this enormous variety, it is usually feasible to tailor the solvents to specific chemical reactions. Ionic liquids have a range of physical chemical properties that can be tuned with an accuracy that is hard to see for a given reaction.





C. Physicochemical Properties of ILS

Study and synthesis of ionic liquids is still very latest, and they reveal a wide range of properties. The ionic liquids (also called as Room temperature ionic liquids) stay liquid in a temperature range that is broader than that of other liquids. Most of 1-alkyl-3-methyl-imidazolium ionic liquids have a glass transition temperature between -10oC and -60oC and are chemically stable in the temperature rang of 250oC-400oC depending on the alkyl chain length and the selection of anion. Ionic liquids normally form glasses when below their melting point and also demonstrate a strong tendency for supercooling (Bonhote et.al 1996). The high temperature acceptance and insignificant vapor pressure makes ionic liquids ideal for reactions at high temperature. The melting point of ionic liquids reduces with rise in alkyl chain length and increases with increase in the degree of symmetry. The heat capacity of some commonly used imidazolium based iionic lidquids were reported in 2003 (Holbrey et.al 2003). Negligible vapor pressure of the majority of the ionic liquids is due to the tough Columbic forces between the anions and cations of the liquid. Ionic liquids are more viscous then organic solvents sometimes by several times. The extensive variation of the physicochemical properties of ionic liquids and the simplicity with which the design of the ionic liquid can be changed gave ionic liquids the name “designer solvents” in the latter part of the 1990s.

Usually ionic liquids are polar solvents due to presence of cation and anion but it can dissolve both polar and nonpolar solutes due to its polarity i.e. salvation capability. In ionic liquids salvation takes place due to ion-ion interactions, van der Waal’s forces, dipole interaction as well as pi-pi interactions. The solubility of ionic liquids in water is of great consideration. The extent of solubility in water depends mostly on the degree of coordination feasible with the ions. Basic ions (NO3)$^-$ can strongly coordinate with water, while acidic ions are non-coordinating and neutral ions (BF4)- and (NTf2)- are weakly coordinated with water. The length of alkyl chains on the cation also affects the miscibility of water in an ionic liquid. A larger chains result in a more hydrophobic ionic liquid (Wasscheid, 2000).

D. Preparation of Ionic Liquids

Ionic liquids can be made by three methods namely quatermerization, metathesis of halide, and direct combination of halide salt with metal halide.

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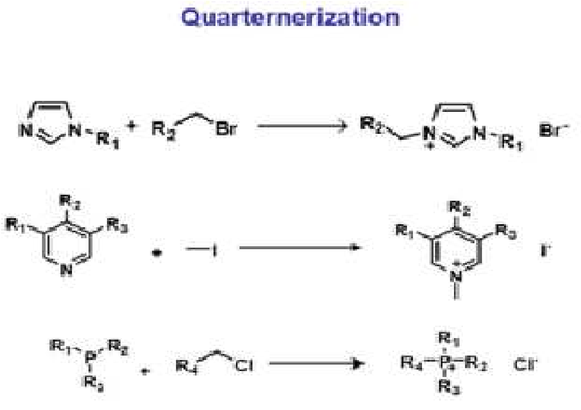


Quaternization Reaction:

Most quaternization reactions involving an annular nitrogen atom and alkylating agent proceed by means of SN^2 reaction in which inversion of configuration of an achiral reagent takes place. The majority of such reactions give products reflecting kinetic control. Products usually are formed irreversibly. Alkyl halides are extensively used as alkylating agents in a quaternization reactions. In this reaction the amine and the preferred alkyl halide are mixed and the reaction mixture is heated in an inert N or Argon atmosphere (Bonhote et.a. 1995 and Chauvin 1995).The quaternization can also be carried out under microwave situation (Namboodiri et.al.2002)

Comparison of Organic Solvents with Ionic Liquids*

Property	Organic Solvnets	Ionic Liquid
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multi function
Catalyticability	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius-Clapreyron Equation	Negligible vapour pressure under normal conditions
Chirality	Rare	Common and Tuneable
Flammability	Usually flammable	Usually nonflammable
Polarity	Conventional polarity	Questionable
Tuneability	Limited range of solvent available	Virtually unlimited range i.e. designer solvents
Cost	Normally cheap	2-100 times costly than organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity, cP	0.2-100	22-40,000
Desnsity, g/cm3	0.6-1.7	0.8-3.3
Refractive index	1.3-1.6	1.5-2.2

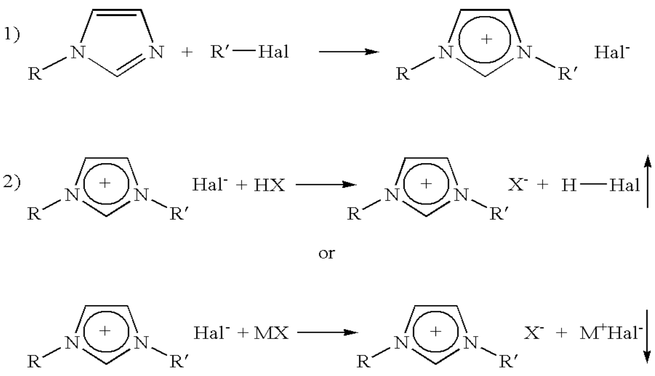
*Plechkova, 2008

Metathesis of Halide:

A great many ionic liquids are made by a metathesis reaction from a halike or similar salt of the desired cation. The meththesis reaction can be divided into two categories on the basis of water solubilituy of the target ionic liquid : metathesis via metal salts and Methathesis via Ag salt (Wikes et.al 1990).

R+X + M+A- → R+A- + M+X+

Scheme 1



E. *Applications of Ionic Liquids:*

ILs find a great variety of industrial applications. A few industrial applications are given below:

Chemical Processes : Ionic liquids are found to be promising solvents in many of the organic reaction such as Diels-Alder, Bails-Hillman, Heck Reaction, esterification, isomerization reactions and many coupling reaction(Kumar A., 2005 and Fischer T., 1999)

Electrochemical Devices : Excellent reviews are published indicating the applications of ionic liquids to electrochemical devices such as super capacitors, lithium ion batteries, polymer-electrolyte fuel cells and dye-sensitized solar cells. In an electrochemical apparatus, an ionic liquid acts as electrolyte (Lu W. et.al. 2002 and Silvester D., 2006).

Extraction Technology : Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, processing of perfumes and other industries. The application of ionic liquids to separate toxic metal ions and organic molecules has been investigated. Presently, ionic liquids have been used as extraction solvents for the extraction of metal ions by crown ethers. Hence, ionic liquids have got much more attention in extraction processes (Ahou D.et.al.2003 and Dai S. 1997).

Pharmaceuticals: Recognizing that approximately 50% of commercial pharmaceuticals are organic salts, ionic liquid forms of a number of pharmaceuticals have been investigated. Combining a pharmaceutically active cation with a pharmaceutically active anion leads to a Dual Active ionic liquid in which the actions of two drugs are combined (Stoimenovski J et.al 2010 and Frank P et.al 2013).

Gas Handling: ILs have several properties that make them useful in gas storage and handling applications, including low vapor pressure, steadiness at high temperatures, and solvation for a wide variety of compounds and gases. They also have weakly coordinating anions and cations which are able to stabilize polar transition states. Many ionic liquids can be reused with minimal loss of activity.

Solar Thermal Energy: ILs have potential as a heat transfer and storage medium in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers center the sun's energy onto a receiver which can generate temperatures of around 600 °C (1,112°F). This heat can then produce electricity in a steam or other cycle

Waste Recycling: ILs can help the recycling of synthetic goods, plastics and metals. They suggest the specificity required to separate similar compounds from each other, such as separating polymers in plastic waste streams. This has been achieved using lower temperature extraction processes than current approaches[50] and could help avoid incinerating plastics or dumping them in landfill.

Batteries: Researchers have recognized ILs that can substitute water as the electrolyte in metal-air batteries. ILs have great potential because they evaporate at much lower rates than water, increasing battery life by drying slower. Further, ILs have an electrochemical window of up to six volts [51](versus 1.23 for water) supporting more energy-dense metals. Energy densities from 900-1600 watt-hours per kilogram appear possible.

III. CONCLUSION

Ionic liquids believed as novel chemical agents and widely regarded as a greener alternative to many frequently used solvents because they are designable, recyclable and nonvolatile. Based on it, ionic liquids have been studied for a wide range of synthetic applications, they have attracted considerable interest for used as non-volatile solvent based electrolytes in the areas of organic synthesis, catalysis, electrochemistry, solar cells, fuel cells, etc., as they possess many benefits than volatile organic solvents. Several studies indicate the successful synthesis of ionic liquids using simple chemical reactions for large extent processes.

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Dr. Sadhana Vishwakarma, is born in Nagpur on 14thAugust 1967. She completed her under graduation from Shri Shivaji Education Society, Nagpur, India, in 1988 and stood third in order of merit and received Gold medal in Zoology. She completed her post graduation in organic chemistry in 1990 from Science College, Nagpur, India and stood first in order of merit and received gold medal in Organic chemistry. In 1991 she has completed her degree in Education from Nagpur university, India and diploma in pharmacy in 2005 from Karnataka Board, Karnataka, India. She has completed her MSCIT certificate course in 2005. She acquire Ph.D. from Nagpur University in 1996 and topic of the thesis was " Recovery of value added chemicals from fermentation broth". She has 2 years research experience as junior project fellow under DBT sponsored project " Production of 2,3-butanediol from water hyacinth and 3years experience as senior project fellow under the DBT sponsored project" Production of Hydrogen and chemicals from waste" in National Environmental Engineering Research Institute (NEERI), Nagpur, India. She worked as Head of the Department of Medical Laboratory Technology in Gramin Polytechnique, Vishnupuri, Nanded, India successfully for 9 years. Then she worked as Assistant Professor of chemistry in All Saints' college, Bhopal, India for 1 year and now she is working as Professor of Engineering Chemistry in Technocrats Institute of Technology Bhopal, India till date. She worked as a coordinator of Jalswarajaya Project titled " 100 % Analysis of government drinking water sources of Latur and Washim districts".Dr. Sadhana Vishwakarma various international publications and National publications. She is author of book Energy Environment Ecology & Society.