A Brief Review of Ionic Liquids: Synthesis and Applications

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Received Date: April 02, 2021; Accepted Date: April 07, 2021; Published Date: April 10, 2021


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Abstract
The natural contamination and pollution caused by the chemical industries has expanded in large number for a few decades. The desire of generating environmentally friendly materials and less hazardous substances has been increased among the researchers and scientists. This is being fulfilled through the principles of Green chemistry. Ionic liquids (ILs) have emerged as an environmentally friendly alternative to various organic solvents and catalysts with high activity and selectivity. In this review, the history of ionic liquids, its properties, synthesis and applications in various fields have been discussed. The list of commercially available ionic liquids also has been added in this review. The present review is aimed for giving general overview of ionic liquids and processes involved in preparation and development of ionic liquids and also their applications.

Keywords: green chemistry, ionic liquids, organic solvents

Introduction

The Green Chemistry has been a burgeoning topic over last few decades. This has been the driving force for the growth in research on the development of compounds with enhanced health and environmental features [1-3]. In this regard, the industrial and scientific evolution has boosted the production of Ionic Liquids (ILs).

The specific definition of what is an ionic liquid may vary from one person to another, the prevailing definition would be that they are molten analogs of the inorganic salts containing melting point below 100°C, in which asymmetrical ions are held by directional forces.

The interests in ILs emerged because of their many advantageous characteristics, such as low melting point, negligible vapor pressure, high thermal stability, inflammability, wide electro chemical window, recyclability and so on. Since the introduction of ILs in 1914, they are extensively employed in various fields such as organic, inorganic, physical and biological chemistry; however, recently they have been explored as a promising solvent in the extraction and separation of biomolecules, organic compounds, cell organelles and transition and inner-transition metal ions [4-7].

History

There are several beginnings to the history of ionic liquids in which they were discovered independently. It is most commonly dated back to 1914 and the work of Walden on the use of alkylammonium nitrates.

Paul Walden was in search of molten salts which were liquid at temperatures, so that he could use his equipment without any special adaptations. He discovered that [EtNH3][NO3] has a melting point of 12 °C. This was the first example of a protic ionic liquid (PIL), which were later to become an important sub-class of ionic liquids after being rediscovered by Hiroyuki Ohno (Hirao et al. 2000);

The next burst of interest occurred with the discovery of chloroaluminates which were formed by combining the quaternary heterocyclic cations with aluminum chloride. These promised a great deal of potential for use in various different fields, but all failed due to extreme sensitivity to moisture.

Early in 1980s, John Wilkes and group introduced 1, 3-dialkylimidazolium cations into ionic liquids to form the 1-alkyl-3-methylimidazolium chloride aluminum chloride ionic liquids ([CnC1im]Cl-AlCl3, where n = 1-4), with [C2C1im]+ being preferred because it gave ionic liquids with the best transport properties (Wilkes et al. 1982).

A major step forward was made by Wilkes in the early 1990’s, with the report of moisture stable ionic liquids created by replacing the aluminum chloride with other anions, such as tetrafluoroborate or hexafluorophosphate [8].

Since then ionic liquids has seen rapid growth. Starting with imidazolium cations, the cationic components have been varied including ammonium, phosphonium, thiazolium, pyridinium and triazolium species.

Structure

Some of the common cations of ionic liquids:

Keywords: green chemistry, ionic liquids, organic solvents
There are various properties of ionic liquids such as density, viscosity, hydrophobicity, solvation of ionic liquid system. These properties can be influenced by choosing the anion or alkyl chains of the cation [13-17].

**Density**

The density of the ionic liquids is generally higher than the density of water. But the ionic liquids may also contain traces of water for the purpose of dilution, however such traces do not have much impact and possess relatively very small effect.

**Viscosity**

Viscosity plays a major role in many conditions and it is also one of the most important physical property. The ionic liquids have a broad range of viscosity from 0.035-0.500 Nsm. When compared with the molecular solvents, the ionic liquids are generally viscous. Due to the presence of water in ionic liquids, its viscosity may get effected as similar to the density, they get diluted and become less viscous.

**Hydrophobicity**

The selection of proper cations and anions will result in the formation of hydrophilic or hydrophobic ionic liquids. The increase in the length of alkyl chain in the cations leads to the development of hydrophobicity in an ionic liquid. The anions such as [PF6]– and (CF3SO2)2N– are responsible for making ionic liquids immiscible in water. Whereas, the nitrates, acetates and trifluoroacetate are responsible for making ionic liquids miscible with water.

**Melting Point**

The melting point of the ionic liquids is very less. Most of the ionic liquids are in molten form at the room temperature. Some of the ionic liquids have very low boiling point such that at even below –80 °C they will be
in liquid state. The melting point of the ionic liquids decreases with the increase in the amount of water molecules available in the ionic liquids. By increasing the substituent chain length, the melting point can be increased.

**Vapor Pressure**
The vapor pressure of the ionic liquids at room temperature is negligible.

**Polarity**
The ionic liquids are best suitable for catalytic reactions because number of ionic liquids have high polarity and are non-coordinating. These ionic liquid systems can be designed in such a way that we can obtain desired range of properties, which particularly can be utilized in any required application.

**Thermal Conductivity**
Thermal conductivity is a crucial parameter for the heat transfer applications. The result of the water contamination on the thermal conductivity is remarkable. For ionic liquids the temperature dependence is very weak and it befits into a straight line with adjustable parameters.

**Heat Capacity**
The temperature dependence of the ionic liquids is relatively weak. Valkenburg et al. reported the heat capacities of several ionic liquids, and the temperature range of -50 to -300°C is recorded and is also available in the literature.

**Heat of Fusion**
The hydrophilic ionic liquids have substantial effect on the heat of fusion due to the availability of the water. The water has heat of fusion *times higher than that of the ionic liquids.

**Sensible Heat Storage Density**
The heat storage is easily calculated from the density, heat capacity and temperature range chosen. The heat storing capacity of the ionic liquids plays very important role in applications in solar energy production.

**Solvation Properties**
By changing the constituent ions, the solvating properties of the ionic liquids can be changed. With the help of ethers, hydrocarbons and various organic solvents, the ionic liquids can be made miscible or immiscible. This converts them into a very beneficial solvent when combined with the characteristic of negligible vapor pressure.

1. **List of commercially available ionic liquids:**

<table>
<thead>
<tr>
<th>S.No</th>
<th>NAME</th>
<th>CAS-NO.</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>655249-87-9</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>2</td>
<td>1-Ethyl-3-methylimidazolium methanesulfonate</td>
<td>145022-45-3</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>3</td>
<td>1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>382150-50-7</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>4</td>
<td>1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>79917-90-1</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>5</td>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate</td>
<td>174501-64-5</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>6</td>
<td>1-Ethyl-3-methylimidazolium acetate</td>
<td>143314-17-4</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>7</td>
<td>1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide</td>
<td>223436-99-5</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>8</td>
<td>5-(Trifluoromethyl) dibenzo thiophenium trifluoromethanesulfonate</td>
<td>129946-88-9</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
</tbody>
</table>
Table 1: List of commercially available ionic liquids.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ionic Liquid</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Tributylmethylammonium methyl sulfate</td>
<td>13106-24-6</td>
</tr>
<tr>
<td>10</td>
<td>1-Butyl-1-methylpyrrolidinium iodide</td>
<td>56511-17-2</td>
</tr>
<tr>
<td>11</td>
<td>Tributylmethylammonium bis(trifluoromethylsulfonyl)imide</td>
<td>405514-94-5</td>
</tr>
<tr>
<td>12</td>
<td>4-(Triphenylphosphonio)butane-1-sulfonate</td>
<td>164982-05-2</td>
</tr>
<tr>
<td>13</td>
<td>(6-Bromo-1-oxohexyl)ferrocene</td>
<td>57640-76-3</td>
</tr>
<tr>
<td>14</td>
<td>Methyl-trioctylammonium bis(trifluoromethylsulfonyl)imide</td>
<td>375395-33-8</td>
</tr>
<tr>
<td>15</td>
<td>1-Ethyl-3-methylimidazolium tetrachloroaluminate</td>
<td>80432-05-9</td>
</tr>
</tbody>
</table>

2. Synthesis of Ionic Liquids

Ionic liquids can be mainly classified into two main categories, simple salts (these are made up of single cation and single anion) and ionic liquids (these are salts in which equilibrium is involved) [20].

There are two major steps involved in the synthesis of ionic liquids.

- **Formation of the Desired Cation**: Our desired cation can be achieved by the protonation of amine by an acid or through quaternization reactions of amine with a haloalkane and heating the mixture.
- **Exchange of Anion**: By treating the halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis, the exchange of anion is carried out.

![Figure 3: Synthesis of ionic liquids.](image)
3. Applications of Ionic Liquids:

There are various applications of ionic liquids in various sectors and departments, they are used in multiple ways such as described below: [28]

1. Ionic Liquids as Catalysts:
The ionic liquid may act as acidic or basic or organocatalyst based upon the functional group attached to the cation or anion, a) As Acid Catalysts: the ionic liquids acidic nature is used for many organic transformations like Beckmann rearrangement, synthesis of chalcones, oxidation reactions, Pechmann reaction, Koch carboxylation, asymmetric Aldol condensation, Aza-Michael reaction, Prin’s reaction, synthesis of furfural, biodiesel, Hantzsch reaction, and Mannich reaction.

Esterification of alcohols by carboxylic acids is carried out in a halogen-free Bronsted acidic ionic liquid, N-methyl-2-pyrrolidinium methyl sulphonate under mild conditions and without additional solvent.

![Figure 4: example as acid catalyst.](image)

b) As Base Catalyst: The interest in the basic functionalized ionic liquids increased due to their high catalytic efficiency than mixture of inorganic base and ionic liquids for base catalyzed processes and also due to convenient recycling.

These basic ionic liquids have been utilized to catalyze many reactions such as condensation reaction of aldehydes and ketones with hydroxylamine, aza-Michael addition reaction, Michael addition of active methylene compounds, synthesis of quinolines, pyrroles.

Xu et al. developed a green protocol for the Michael addition of N-heterocycles to α,unsaturated compounds at room temperature by using a basic ionic liquid [bmim]OH as a catalyst and reaction medium.

![Figure 5: example as base catalyst.](image)

c) As Organocatalysts: Ionic liquids have great potential as catalyst which can be used in many reactions and these act as organocatalysts. One of the best example of ionic liquids as organocatalysts is through hydrogen bonding interactions.

The reaction on which ionic liquids are mostly applied are Diels-Alder cycloadditions and their derivatives.

Luo and coworkers used a functionalized chiral ionic liquid as an efficient reusable organocatalyst for asymmetric Michael addition of ketones/aldehydes with nitroalkenes.

![Figure 6: example as organocatalyst.](image)
2. Ionic liquids as Soluble supports:
Ionic liquids have practically nonvolatile nature and have tunable solubility. Due to these characteristics of the ionic liquids, they are being used as soluble supports for catalyst/reagent immobilization. This has been successfully employed in various organic reactions such as 1,3-cycloadditions, synthesis of thiazolidinones, Knoevengeal reaction, Suzuki coupling, oligosaccharide synthesis, and Grieco’s multicomponent synthesis of tetrahydroquinolines.

Xie et al. developed a novel and efficient route for the synthesis of 1,4-benzodiazepine-2,5-dione using ionic liquids as soluble supports.

3. Separation of solutes from ionic liquids by distillation/stripping:
As the ionic liquids have negligible vapour pressure, the ionic liquids can be recovered using distillation from the compounds having low boiling points. Before the adaption of ionic liquids as solvents for the production of nitroaromatics, Dal and Lancaster studied two different ionic liquids, [bmpy][OTf] and [bmpy][N(Tf)2], and developed a regime by which the solvent may be recovered and reused.

The recycling of the IL was achieved by dissolving the post-reaction mixture into dichloromethane and adding water. It was then possible to extract any unreacted nitric acid, plus the acetic acid (HOAc) generated by the reaction with water. After removing the dichloromethane, the organics were removed from the IL by steam distillation.

The samples of the ionic liquids are withdrawn after each run, and analyzed before being reused and it revealed that there was no difference between the recovered and the original Ionic liquid [Dal & Lancaster, 2005].
4. Ionic liquids as Lubricants:

Ionic liquids get readily adsorbed onto metal surfaces, which typically have some form of charging and form layers. The surface adsorption and long alkyl chains typically present in the cation are thought to result in the formation of relatively thick, low friction layers that lead to a reduction in friction and wear, particularly in the boundary lubrication wear. Ionic liquid lubricants have been shown to outperform commercially available lubricants, such as fully formulated engine oils.

5. Ionic liquids as heat storages:


Feasibility of ionic liquids as liquid thermal storage media and heat transfer fluids in a solar thermal power plant was investigated. Many ionic liquids such as [C 4min][PF 6], [C 8min][PF 6], [C 4min][bistrifluoromethane sulfonimide], [C 4min][BF 4], [C 8min][BF 4], and [C 4min][bistrifluoromethane sulfonimide] were synthesized and characterized using thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), nuclear magnetic resonance (NMR), viscometry, and some other methods. Properties such as decomposition temperature, melting point, viscosity, density, heat capacity, and thermal expansion coefficient were measured. The calculated storage density for [C 8min][PF 6] is 378 MJ/m 3 when the inlet and outlet field temperatures are 210°C and 390°C. For a single ionic liquid, [C 4min][BF 4], the liquid temperature range is from -75°C to 459°C. It is found that ionic liquids have advantages of high density, wide liquid temperature range, low viscosity, high chemical stability, non-volatility, high heat capacity, and high storage density. Based on our experimental results, it is concluded that ionic liquids could be excellent liquid thermal storage media and heat transfer fluids in solar thermal power plant.

6. Ionic liquids in Protein Crystallization:

Cryst. Growth Des. 2009, 9, 8, 3463-3469
Publication Date: May 4, 2009.
https://doi.org/10.1021/cg900410b

Crystals grown using ionic liquids as precipitating agents or as additives provided X-ray diffraction resolution similar to or better than that obtained without ionic liquids. The ionic liquids improved the crystallization behavior and provided improved diffraction resulting in the determination of the structure. Ionic liquids should be considered as useful additives for the crystallization of other proteins [38].

Conclusion

Over the past few years, ionic liquids have been kept on utilization altogether as a medium and catalyst for numerous reactions. The potential of ionic liquids is huge but still there are reports that appears in few cases where ionic liquids responds with the reactants and thus they cannot be considered as idle solvents. There is still development and research going on in these aspects of ionic liquids.

We have discussed about the origin of ionic liquids, their properties and processes involve in synthesis. The applications in various fields like catalysis, in providing soluble supports, separation of solutes, in protein crystallization and also as lubricants and heat storages have been explained. There is still requirement of more infinitesimal understanding and research to be carried out of ionic liquids.

Acknowledgement

All the authors are grateful to Asst. Prof. Dr. K. Naresh, and all the faculty of Department of Pharmaceutical Chemistry, G. Pulla Reddy College of Pharmacy for providing the necessary facilities to carry out this study.

Conflict of Interest

All the authors declare that they have no conflict of Interest.

Reference


