

IONIC LIQUIDS AS POTENTIAL REACTION MEDIA FOR GREEN CHEMICAL REACTIONS: A SHORT REVIEW

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ABSTRACT

Currently chemists are focusing on reducing the environmental hazards, which can be accomplished by using less toxic substances in chemical reactions carried out on laboratory scale as well as on industrial scale. The center of attention is the compounds which can act as environmentally-friendly alternatives to the volatile organic solvents and catalysts. The intention of this review is to analyze the role of ionic liquids (ILs) also known as "task specific ionic liquids" in chemical reactions as ILs are considered to work as designer solvents which can be modulated to suit the reaction conditions.

Keywords: Ionic liquids, alternative solvents, volatile organic solvents.

1. INTRODUCTION

With rising environmental issues, it is imperative to reduce the use of volatile organic compounds (VOCs). Consequently, green chemistry [1,2,3] plays the role. The principles of green chemistry are broad categories of underlying fundamental approaches or guidelines needed to achieve environmental friendly reactions. The principles of green chemistry speak about the reduction or removal of dangerous or harmful substances from the synthesis, production and application of chemical products and thus the use of substances dangerous to human health and the environment are reduced or eliminated [4]. When designing a green chemistry process, it is impossible to meet the requirements of all twelve principles of the process at the same time, but it attempts to apply as many principles as possible during certain stages of synthesis. One foremost step towards this is to make use of solvent less reaction medium or development of cleaner, efficient solvents and recently water which is readily available, non-inflammable, non-toxic has been abundantly used as environmentally friendly green solvent. However, inability to dissolve organic solutes limits the use of aqueous media as reaction solvent. Therefore, it seems reasonable to seek alternative reaction media.

2. IONIC LIQUIDS

The class of solvents which has received considerable attention as alternate for volatile organic solvents is room-temperature ILs. These are organic salts that are liquid below 100°C. The ILs are considered favorable medium for chemical reactions because of their exceptional solvating potential [5] and thermal stability [6]. They are nonflammable, non-volatile and after melting are stable as liquids over wide range of temperature, hence are classified as green solvents. Ionic liquids have several tremendous characteristic features that render it preferable over the traditional type of solvents [7]. Fig. 1.



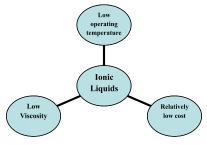


Figure 1: Properties of Ionic Liquids

2.1. HISTORY AND CHEMICAL STRUCTURE OF IONIC LIQUIDS

The first type of ionic liquids to be synthesized was the protic ionic liquids, involving proton transfer during synthesis. The first ionic liquid, to be synthesized was ethyl ammonium nitrate $[C_2H_5NH_3][NO_3]$. [8]. Another category of ionic liquids are the aprotic ionic liquids in which the cations are usually derived from the alkylation or alkyl–cation-transfer reaction of organic compounds with alkyl halides. The discovery of water-stable ionic liquids containing hexafluorophosphate, nitrate, sulfate, and acetate anions by Wilkes and Zaworotko [9] revolutionized the use of IL's in chemical reactions. The large variety of cations, anions and their combinations has lead to development of numerous potential ionic liquids [9].

The ionic liquid cation generally consists of an organic structure with positive charge. The most common cations in ionic liquids are nitrogen or phosphorous containing organic ions. Physical and chemical properties of ionic liquids are influenced by the cation present in them. The ionic liquid anion generally consists of weakly basic organic or inorganic compounds which are negatively charged. The most common anions in ionic liquids are acetate, nitrate, borate or sulphate ions. (Table 1, Fig. 1.)

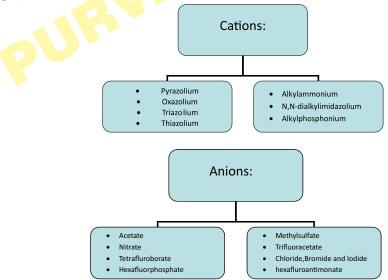
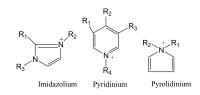


Table 1: Cations and Anions of Ionic Liquids

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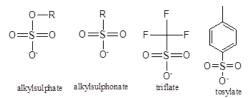


Fig. 2. Structure of some common cations and anions used in ionic liquid synthesis.

ILs have been further divided into many types, e.g., chiral ILs [10], high energetic ILs [11], taskspecific ILs [12], supported ILs [13], polymeric ILs [14], acid ILs [15], basic ILs [16] and organometallic ILs [17].

2.2. PROPERTIES OF IONIC LIQUIDS

Ionic liquids are commonly known as "designer solvents" [18], as their physical and chemical properties can be adjusted by the variation of the length and branching of the alkyl groups incorporated into the cation and then these IL's can be used for specific synthetic problems. Ionic liquids have several tremendous characteristic features that render it preferable over the traditional type of solvents [19,20].

Solvating ability

When an ionic liquid is used as a reaction solvent, the solute is solvated by ions only, where the reaction proceeds under quite different conditions as compared to using water or ordinary organic solvents which are neutral molecule.

Melting point

In order to behave as room temperature ionic liquids to replace the organic solvents ILs must have low melting point. The magnitude of the melting point is related to the structure i.e. cation and anion present in the ionic liquid. They have large liquid ranges too.

Density

Density of Ionic liquids is determined by the size of the cation and anion present in ionic liquid. Density tends to decrease with an increase in bulkiness of the organic ions present in the ionic liquid.

Thermal, chemical and electrochemical stability

A thermally stable solvent allows a reaction to proceed at all working temperatures. Ionic liquids are found to be much stable at or above 400°C when compared to organic solvents.

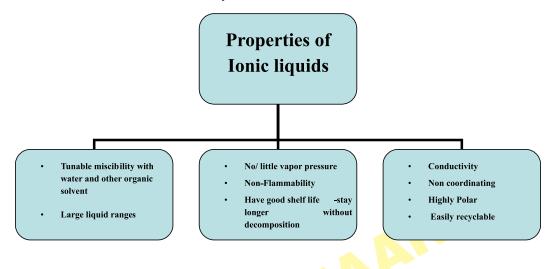
Viscosity

Ionic liquids are neither highly viscous nor have low viscosity which make them easy to handle and act as convenient solvent for the starting material for synthesis.



Volatility

Ionic liquids are mostly non-volatile hence the reaction procedures can be repeated again and again which makes the use of IL economically viable too.





2.3. ADVANTAGES OF IONIC LIQUID

Ionic liquids (ILs) have very good properties as a reaction medium for chemical reactions; generally, they are non-volatile, non-flammable and have low toxicity and good solubility for many organic and inorganic materials.

Ionic liquids find very vast and versatile application as compared to organic solvents (Figure.4). Some of these applications are illustrated and discussed as below [21, 22].

1. Ionic liquids can be used for metal extraction for both radioactive and rare earth metals.

2. Ionic Liquids can be used as solvents in chemical and pharmaceutical industry. IL's have proved to be advantageous in many chemical reactions e.g. coupling reaction [23], Aldol condensation [24], Diels-Alder reaction [25] and Reduction reactions [26].

3. Ionic liquids can be used for purification of environment by carbon dioxide capture, a culprit of global warming.

4. Ionic liquids also find application in solar cells and fuel cells in the electronic industry.

5. Ionic liquids are used as stable catalysts in many chemical reactions.

6. In recent times, ionic liquids are used in the development of bioplastic-based coating materials, suggesting their wider use in the future



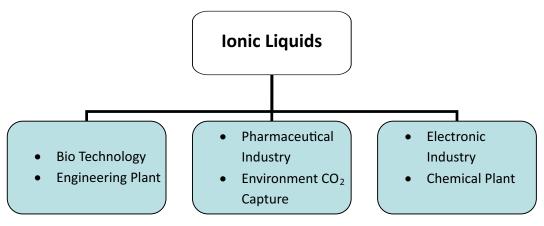


Figure 4: Applications of Ionic Liquids

2.4. CONCLUSION

This review is focused on the applications of green chemistry in view of use of the ionic liquids. In this regard, the historical back ground of ionic liquids, the different properties of ionic liquids; different advantages over conventional volatile organic solvents were reviewed. Further, applications of ionic liquids are found in environmental chemistry, engineering, biotechnology and electronic industries. Ionic liquids have all potential to replace conventional solvent in both laboratories and industry. The review was aimed to explore the field of the environmentally friendly ionic liquids which hold enormous possibilities still to be explored.

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