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GREEN CHEMISTRY: IONIC LIQUIDS IN INDUSTRIAL APPLICATIONS

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Abstract: *Chemical reactions are generally performed in the presence of volatile, flammable, and toxic organic solvents, whether on a small scale in the laboratory or on a large scale in the industry. Every year, approximately 20 million tons of volatile organic chemicals are discharged into the atmosphere. Consequently, the change in global climate, air pollution, and health issues have come into the forefront. Thus, alternative, andgreen solvents are becoming more popular within years. Fluorinated solvents, water, and supercritical liquids are utilized as alternatives to volatile organic solvents. The interest of ionic liquids as green solvents is due to their several advantages such as low vapour pressure, low flammability, a wide liquid range, excellent thermal stability, adjustable polarity, and miscibility with other organic and inorganic chemicals. Ionic liquids are an ideal "environmentally friendly solvents" alternative to organic solvents used today for synthesis, homogeneous catalysis, and chemical processes. They have developed as reinforcing family of chemicals for the applications of electrochemistry, organic synthesis, catalysis, gas separation, protein preservation, as well as other applications due to their outstanding characteristics and vast combinations of the cations and anions. Consequently, this review focuses on the use of ionic liquids, especially in biotechnology and leather manufacturing.*

Keywords: *biotechnology, green solvent, green chemistry, ionic liquid, leather, organic solvents*

INTRODUCTION

Chemical reactions are generally carried out in the presence of volatile, flammable, and poisonous organic solvents and every year, nearly 20 million tons of volatile organic chemicals are discharged into the atmosphere. Due to the environmental and health issues, new processes of synthesis that do not use solvents or employ ecologically benign alternative solvents are becoming more popular. Fluorinated solvents, water, and supercritical liquids are utilized as alternatives to volatile organic solvents, but ionic liquids, which are a new class of solvents made entirely of ions, have received a lot of attention as green solvents in recent years. [1-3]

Ionic liquids are salts that contain an organic cation and an organic or inorganic anion and have a melting point less than 100°C. Ionic liquids, which are liquid at room temperature, have a melting point less than 25°C at atmospheric pressure and they are referred to as "room temperature ionic liquids. Low vapour pressure, low flammability, a wide liquid range, excellent thermal stability, adjustable polarity, and miscibility with other organic and inorganic chemicals are the advantages of ionic liquids. Today, they are ideal "environmentally friendly solvents" alternative to organic solvents for synthesis, homogeneous catalysis, and most of the chemical processes due to the mentioned advantages. [4-6] In general, they represent fewer hazards or environmental risks compared to conventional solvents when they used in 'closed' processes. [2,7]

Bulky organic cations such as imidazolium, pyridinium, piperidinium, ammonium, phosphonium, and sulfonium, as well as comparatively tiny anions like tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, methanesulfonate, trifluoromethanesulfonate, and nitrate, are used in ionic liquids. [6] However, imidazolium has reported weakly biodegradable and has low biocompatibility among the enormous number of ionic liquids despite the great qualities. [8]
The influence of ionic liquids on biomacromolecules can be explained by the cosmotropicity and chaotropicity of the ions. [9] Based on their capacity to interact with water, ions are classed as cosmotropic or chaotropic. The ions are chosen based on the Hofmeister series' descriptions of cosmotropic and chaotropic activity. Proteins are supposed to be stabilized by chaotropic cations and cosmotropic anion, while they are believed to be destabilized by cosmotropic cations and chaotropic anion. [10,11] A cosmotropic anion is said to interact with water more strongly than it interacts with itself, which stabilizes the protein structure by promoting irreversible H-binding. The interaction of anions with proteins in aqueous media is explained by inference from the behaviour of Hofmeister series ionic liquids on protein stability. Therefore, ion selection is crucial in the stabilization and destabilization of proteins. [12-14]

DEVELOPMENT OF IONIC LIQUIDS

During the last 30 years, ionic liquids have been reported in several industries because of their beneficial features such as negligible vapor pressure, non-flammability, non-explosiveness, electrochemical and thermal stability, easy recovery, and high conductivity characteristics. [12,15-17]
For nearly a century, substances that meet the definition of ionic liquid have been known. However, the contemporary era of ionic liquids can be regarded to have begun in the second half of the twentieth century with several research projects targeted the use of ionic liquids in electrochemical applications and generating molten salts at the lowest temperatures conceivable. [4,18,19]
Paul Walden (1914) created the first known ionic liquid, ethylammonium nitrate $[C_2H_5NH_3]^+[NO_3]^-$, by neutralizing ethylamine and concentrated nitric acid. It has a melting point of 12-14°C. This study, which drew little attention at the time, is now regarded as a pioneering work in the field of ionic liquids. [17,20,21] Since that time, the synthesis of ionic liquids containing various cations and anions has accelerated, and the number of scholarly articles and patent studies has exploded. More than 2000 publications in 2006 on the synthesis of novel ionic liquids and the investigation of the physicochemical properties of ionic liquids as well as their usage as a solvent or in various domains were published. [4, 20,22,23]
Aryl-/alkyl imidazolium ionic liquids were developed for the first time by Ahrens et al., (2009) that electronic effects can alter depending on not only the sigma system but also the pi system. [24]
Thus, this change reflected the ionic liquid properties and next generation ionic liquids is the name that given to these ionic liquids. [25-26]

PROPERTIES OF IONIC LIQUIDS

To generalize the common qualities for all ionic liquids is challenging due to the enormous number of members of this family of chemicals. [4] The complicated correlation between Coulomb- and Van- der-Waals-interactions, solutes, and surfaces, as well as possible hydrogen bonds between ions in ionic liquids, lead to multifarious features. Ionic liquids have a comparatively high viscosity and density when compared to molecular solvents. Additionally, they have great solubility and miscibility. Ionic liquids also fit well into the Hofmeister series, often known as the lyotropic series, in which the solubility of a variety of salts, proteins, and their secondary and tertiary structure is defined by their stabilizing effects on solution. [17,27,28]
When the chemical properties in general are summarized; [2,23,29-33]

1. Melting point

Ionic liquids have different melting points depending on the nature of the cation and anion.

2. Density

Ionic liquids have a density of 1.0 to 1.6 g/mL, which is higher than the water. The density of the ionic liquid drops as the length of the alkyl chain in the cation grows.

3. Viscosity

Ionic liquids have viscosities that are 1-3 times greater than water and molecular organic solvents. It ranges from 10 mPa.s to 500 mPa.s at ambient temperature.

4. Thermal stability

Ionic liquids have been employed in a variety of high-temperature applications, including analytical applications such as mass spectrometry as a matrix and gas chromatography as a stationary phase. The correct and safe use of ionic liquids at high temperatures necessitates the determination of thermal breakdown temperatures. The structure of the anions has a direct impact on the thermal stability of ionic liquids.

5. Conductivity

Ionic liquid conductivity is a critical characteristic for electrochemical applications. Because ionic liquids are made up entirely of ions, they have a high conductivity. However, many ionic liquids have lower conductivity than expected. Ionic liquids have a higher conductivity than the molecular organic solvents but have lower conductivity than the concentrated aqueous solutions of ionic liquids. The quantity of free charge carrier ions and their mobility determine the conductivity of solutions. The ion mobility and conductivity decrease as the size of the ions increases.

6. Electrochemical window

The electrochemical window (EW) is the range of electrochemical potential in which the electrolyte is not oxidized and reduced at the electrode. The EW value reflects the electrolyte's electrochemical stability. In the usage of ionic liquids in semiconductors and metal electroplating, the EW value is a critical parameter and usually quite large.

7. Miscibility with water and organic solvents

The nature of the anion determines the miscibility of ionic liquids with water. Ionic liquid miscibility with organic solvents is determined by the polarity of the ionic liquid.

8. Refractive index

The dielectric response of the electric field induced by electromagnetic waves and it is referred as the index of refraction. Ionic liquids have different refractive indexes based on the nature of the cation and anion. As a result, it is a polarizability indicator for cations and anions.

9. Steam pressure

Ionic liquids are regarded compounds with low or insignificant vapor pressure even at high temperatures due to their ions. Ionic liquids, unlike organic solvents, do not easily evaporate due to their features. The other advantage of low vapor pressures is the easy separation of volatile products from ionic liquids by distillation.

Controlling the outcome of a process by creating the best solvent for the desired output has a lot of promise for both fundamental and applied research. The structures of ionic liquids, unlike those of traditional molecular solvents, can be easily changed. As a result, using 'action-specific' ionic liquids in a range of processes can give extra benefits. [7,8,34-35]

IONIC LIQUID APPLICATIONS

Ionic liquids are utilized as solvents or catalysts in synthesis, catalysis, nano-chemistry, multiphase reactions, and leaching processes, as well as electrolytes in lithium-ion batteries, dye-sensitized solar cells, fuel cells, and metal plating, due to their unique features. [36-40] They are also used aslubricants and plasticizers in the field of engineering. [41] In analytical chemistry, they are used as a stationary phase for HPLC, as a column material in gas chromatography, and as a matrix in mass spectrometry, and in biology, they are employed in biomass processing, drug release, personal care products, and embalming operations. [15,12,21,36,42]

Ionic liquids are reinforcing family of chemicals and can be utilized in electrochemistry, organic synthesis, catalysis, gas separation, protein preservation, and other applications due to its outstanding characteristics and vast combinations of cations and anions. [8,20,34,43-46] They are an excellent stabilizing medium for cytochrome C, lysozyme, and nucleic acids, allowing them to be stored for longer periods of time without losing function. [13,36,,47] Choline ester ionic liquids are widely used in protein-based medicinal formulations and cellular therapies. [48,49]

The use of ionic liquids in dissolution, regeneration, and modification of biopolymers is gaining popularity as a viable alternative to conventional, ecologically unfriendly organic solvents. [50] Ionic liquids, as a next-generation solvent for natural polymers, offer a new platform for the effective usage and conversion of high-value biopolymer derivative products. However, there are a few issues to be resolved. [5,17] Toxicology, biodegradability, and the influence on human health are unknown; second, the dissolution mechanisms of starch, β-CD, lignin, and protein, as well as the reaction mechanisms of biopolymers in ionic liquids, are not well understood. [12,13,51] Finally, the biopolymer / ionic liquid solution's physicochemical properties, the relationship between the properties and structure of the biopolymer, and the physicochemical properties of biopolymer derivatives should all be thoroughly investigated. [7,17,52-54]

Ionic liquids have the potential to reduce the environmental effect of chemical industrial processes by a significant amount. [1,2,7,23,33,55] Ionic liquids have been used to dissolve and regenerate natural polymers such as cellulose fibers, silk fibroin fibers, wool keratin fibers, chitosan, starch, and collagen fibers. Only a few imidazolium ionic liquids, such as [BMIM]Cl, [EMIM]Cl, and [AMIM]Cl, have been employed in ionic liquids for collagen fiber disintegration and regeneration. [6,8,36,56]

CONCLUSIONS AND RECOMMENDATIONS

Ionic liquids have replaced volatile organic solvents as environmentally friendly alternatives. Ionic liquids, made up of cationic and anionic components, can be created to have a variety of properties. The term "tailor-made" has been used to describe the chemical reaction potential of the ecologically friendly ionic liquids. They're called "action-specific ionic liquids" since they're particularly formulated solvents that can be tailored to certain reaction circumstances. Ionic liquids are currently used in domains as diverse as catalysis, electrochemistry, spectroscopy, and materials research, despite their origins as solvents.

Ionic liquids have been successfully used in a variety of catalytic applications, demonstrating significant catalytic activity and reducing the detrimental effects of typical organic solvents or other catalysts during catalytic reactions. It has been revealed that, ionic liquids have the ability to affect the proteins at various hierarchical levels depending on the nature and type of cation and anion. This ability makes ionic liquids popular at the leather and biotechnology fields as an alternative green solvent. Regeneration and dilution of keratin and collagen fibers has been the most popular subject for ionic liquids since 2005. Because it has been found that ionic liquids could refract hydrogen and ionic bonds of collagen and α-helix structure of keratin. Studies on ionic liquid syntheses are acceptable for the intended features and applications of ionic liquids should be continued.

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