A Review of Ionic Liquids as A Versatile Designer-Greener Solvent

Sulochana Sharma[1*], Kailash sharma[2] and Praveen Kumar Sharma[3]

[1]*Department of Chemistry, S.B.R.M. Govt. College, Nagaur, Rajasthan, India*

[2]*Department of Chemistry, Kartik College, Nagaur, Rajasthan, India*

[3]*Department of Chemistry, Lovely professional University, Phagwara, Punjab, India*

Abstract

The research into the properties of biodynamic heterosystems has proven to be the most appealing and useful for the development of possible medications with exceptional qualities and that work successfully in the treatment of a wide range of diseases, including pandemics. The synthesis of promising therapeutic materials is quite difficult and requires sufficient time for clinical studies, testing, licenses from relevant authorities, production, and distribution. As a result, researchers typically concentrated on novel approaches' including a high yield of already approved chemical substances. This review article focuses on the synthesis of medicinally important heterocycles and on sustainable practices green synthesis approaches that incorporate multicomponent processes (MCR), ionic liquids.

Keywords: Green chemistry, Heterocycles, High yield, Ionic Liquids, Multicomponent reactions (MCRs)

Address of correspondence
Dr. Sulochana Sharma,
Department of Chemistry,
S.B.R.M. Govt. College,
Nagaur, India-341001
E-mail: sharmaknath@yahoo.co.in

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Introduction

In recent years, increased environmental awareness has focused chemical research on the need for greener and more environmentally friendly alternatives in the chemical sector [1]. The term "sustainable chemistry" refers to chemical research aimed at optimizing chemical processes and products in terms of material and energy consumption, toxicity, intrinsic safety, atmospheric degradability, and furthermore. Green chemistry can play a major role in producing greener and more efficient synthetic processes in this area. The chemistry community has banded together to create new chemical approaches that are less harmful to individuals and the environment. The green chemistry activity, which is founded on 12 principles created to reduce pollution, is one of these techniques [2].

Green chemistry is not a subfield of chemistry, but rather a technique of thinking about and doing things more efficiently and effectively. Despite all of the environmental legislation and increased awareness of environmental issues, old thinking continues to stymie the implementation of green chemistry concepts as normal practices in the establishment of new industries. One of the key principles of green chemistry is the reduction of unsafe solvents in chemical synthesis, which avoids the use of costly toxic solvents and the formation of waste [3]. Green chemistry is not just a subfield of chemistry, but it is also a way of thinking about and doing things that is superior and more effective. Considering all of the environmental legislation and increased awareness of environmental concerns, old thinking continues to stymie the implementation of green chemistry concepts as normal practice in the establishment of innovative industries. In order to eliminate the use of costly harmful solvents and the production of waste products, one of the key tenets of green chemistry is the suppression of dangerous chemicals from chemical synthesis. Following is a list of the 12 green chemistry principles.

1. Prevention
   It is preferable to prevent waste rather than treat trash after it has occurred.
2. Atom Economy
   Synthetic procedures should be devised to incorporate as many materials as possible into the final result.
3. Less Hazardous Chemical Syntheses
   Wherever possible, synthetic processes should be developed to employ and manufacture compounds that are safe for human beings and the environment.
4. Designing Safer Chemicals
   Chemicals and other substances should be developed to perform their intended purposes while being as hazardous as possible.

5. Safer Solvents and Auxiliaries
   Auxiliary compounds (e.g., separating intermediaries, chemical solvents, etc.) need to be avoided whenever possible and used sparingly.
6. Design for Energy Efficiency
   Chemical processes' energy consumption should be recognized for their environmental and economic consequences and minimized. If possible, synthetic procedures should be carried out at room temperature and pressure.
7. Use of Renewable Feed stocks
   When technically and economically feasible, an unprocessed commodity or source should be regenerative rather than diminishing.
8. Reduce Derivatives
   Unnecessary degradation (application of blocking groups, protection/deprotection, interim adjustment of chemical/physical activities) should be minimised or avoided if feasible, as such actions necessitate the use of additional substances and can generate waste.
9. Catalysis
   Stoichiometric chemicals are inferior to catalytic chemicals, which should be as targeted as feasible.
10. Design for Degradation
    Chemicals and their derivatives should be made to degrade into harmless substances at the completion of their useful life and not linger in the natural world.
11. Real-time analysis for Pollution Prevention
    To enable instantaneously, ongoing control and observation before the creation of hazardous chemicals, techniques for analysis must be developed further.
12. Inherently Safer Chemistry for Accident Prevention

Materials and the form of a substance implemented in the chemical process should be specified to reduce the possibility of chemical catastrophes such as accidental releases, explosions, and fires.

The fifth green chemistry principle covers the use of auxiliary chemicals to reduce or remove solvent leakage in chemical manufacturing. Considering solvents are frequently required in chemical processes, alternate solvents for chemical transformations have been created. The most suitable solvent should be extremely low in volatility, both chemically and physically stable, able to be recycled, reused, and relatively simple to handle. In view of the growing environment concerns, the ionic liquids possess sparked increased attention in the organic synthesis field and as potential replacements for standard organic solvents in chemical processes due to the distinctive characteristics.

Physical properties

1. Ionic liquid having essentially no vapour pressure hence are non-volatile and as a result, they could be used as prospective alternatives for volatile organic compounds (VOCs) in chemical manufacturing.
2. They have a favourable thermal stability and are unlikely to disintegrate across an extensive range of temperatures, allowing them to be used for extreme temperatures processes.
3. They are effective solvents for a broad spectrum of organic as well as inorganic organometallic compounds, and unique combinations of reagents.

4. They provide an excellent medium for the solubilization of gases such as CO, H_2, CO_2 and O_2 and numerous reactions will be carried out utilising ionic liquids and supercritical CO_2.
5. Ionic liquid solubility is determined by the type of the positive particles and corresponding anions.
6. They usually are unable to supervise with metal complexes, enzymes, or other organic substrates.
7. The majority of ionic liquids can be kept in storage for an extended period of time without degrading.
8. Hydrophilicity/lipophilicity and polarity can be modified by suitable choice of anion/cation and it is possible to create ionic liquids that fully satisfy all the conditions for the chemical response under study by combining a variety of cations and anions. The room temperature ionic liquids are therefore named as designer solvents [4-5]. Important properties can be summarized in fig.1

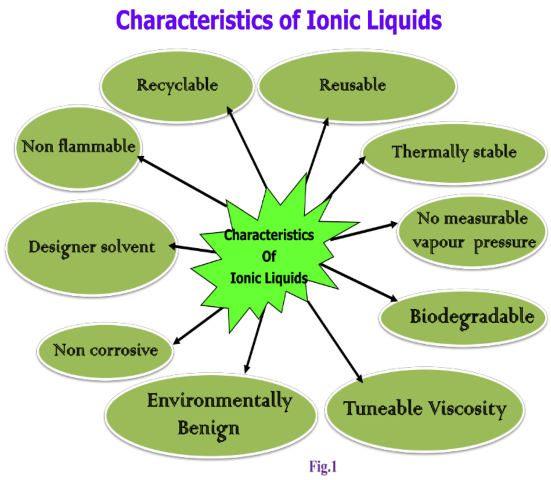

Fig 1: Characteristics of Ionic Liquids

Preparation

ILs has surprisingly a long history. The first (RTIL) room temperature ionic liquid, $[EtNH_3]$ $[NO_3]$ ethyl ammonium nitrate (melting point 12 °C) was reported in 1914 [6]. Hurley and Wier [7] created AlCl3-based ionic liquids in 1951 at Rice Institute in Texas as a bath medium for electroplating aluminium followed by preparation of room-temperature ionic liquid chloroaluminate in the 1970s, by Oster young [8]. Hussey and Seddon [9] succeed in the 1980s, to use alkyl pyridinium tetrahalido aluminates, $[Rp_y][AlCl_3X]$, ionic liquids in transition metal complex studies as solvents. The first organic reaction, a Friedel-Crafts alkylation, was performed using an acidic tetrachloro aluminate ionic liquid.10 and since then, a variety of organic processes have exploited ionic liquids as reaction solvents.

A room temperature ionic liquid (RTIL) is described as a material that contains exclusively ionic species and has a melting point of below 25 °C. There are numerous anion and cation combinations that can be used to synthesize IL. Numerous kinds of ILs allow for the modification of the IL's chemical and physical characteristics. RTILs mainly include organic cations such as 1,3-dialkylimidazolium,11,12 trialkyl sulphonium, tetra alkyl phosphonium, tetra alkyl ammonium-alkyl pyridinium and N,N-dialkyl pyrrolidiniumetc.(Fig. 2).

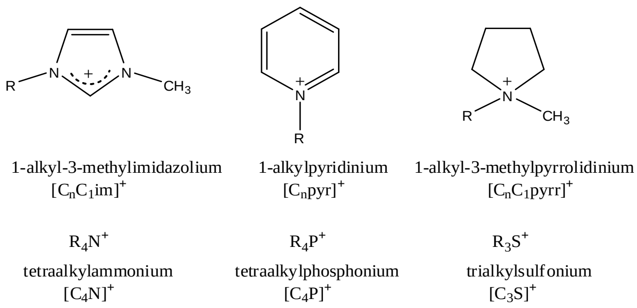

Fig. 2

Different species have subsequently been propagated by anion exchange reactions. Ionic liquid [bmim]PF6 was obtained via ion exchange reaction between potassium salt of hexafluorophosphate and the most applicable [bmim]X (X=Br− or Cl−) intermediate ionic liquid, was formed by the alkylation's of N-methylimidazole with 1-chlorobutane or 1-bromobutane (Fig. 3).

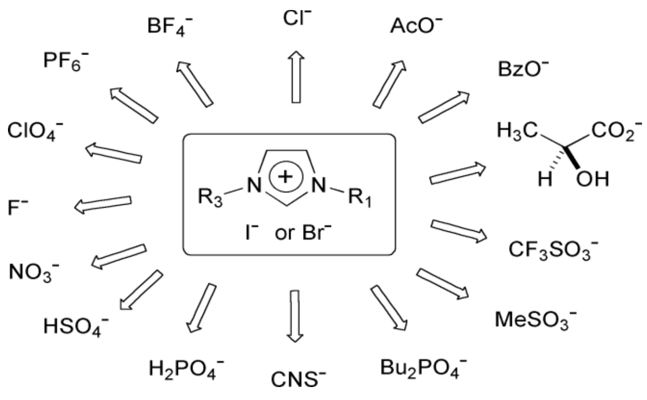

Fig. 3 Halide exchange in imidazolium ionic liquids.

Alkyl sulfonic acid group (-SO3H) Bronsted acidic ionic liquids were prepared and successfully applied in 200213. These ionic liquids are created in two processes.

(i) Production of the requisite zwitterions in excellent yields by the reaction of the neutral nucleophiles N-butyl imidazole or triphenylphosphine with 1, 4-butane- or 1, 3-propane sultone, respectively.

(ii) In the second step, the zwitterions' latent acidity was identified and they were instantly transformed into ionic liquids. Furthermore, the findings of the experiments showed that these standard Bronsted acidic ionic liquids were able to be regenerated and recycled numerous times without significantly diminishing the catalytic activity. (Fig. 4).
Ionic liquids with functional groups covalently attached to their cation or anion, particularly to the two N atoms in the imidazole ring, have recently become possible because to advancements in the domain of ionic liquids exploration. (14) The IL makes a potent Bronsted acid while an alkyl sulfonic acid unit is covalently attached to the IL cation [15].

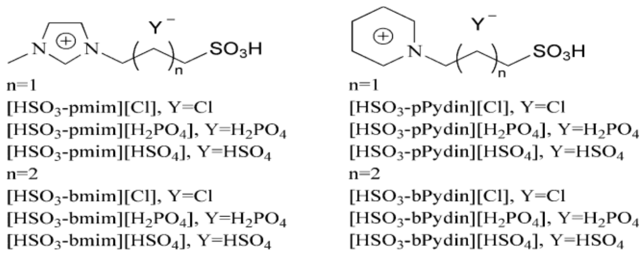

Fig. 4. ILs with one alkyl sulfonic acid component that are Bronsted acidic

Although they are fluxible, non-volatile, noncorrosive, and indistinguishable with a variety of organic solvents, these SO3H-functionalized ionic liquids have shown considerable promise as a replacement for typical homogenous and heterogeneous acidic catalysts [17] and could serve as both catalysts and dual solvents. Acidic Bronsted ionic liquids, which comprise an alkane sulfonic acid unit coupled to a pyridinium cation, imidazole, triphenylphosphine, or quaternary amine, have recently been identified as promising novel reaction media with broad application in chemical processes. Acidic Many common acid-catalysed chemical reactions have used Bronsted ionic liquids containing acid counter anions $[H_2PO_4]$ and $[HSO_4]$.

Application of Ionic liquids:

Ionic liquids have a wide range of applications due to their specific chemical and physical features, including reaction and synthesis conditions. ILs can be used as solvents for organic synthesis and catalysis, in electrochemistry, in separation technologies, as liquid crystals, as precursors for the synthesis of nano-sized components and materials for tissue conservation, and in the fabrication of polymer-gel catalytic membranes, among numerous other applications.

Table 1 Major applications of ionic liquids (ILs)

ELECTROCHEMISTRY -Electrolyte in batteries -Metal plating -Solar panels -Fuel cells	PHYSICAL CHEMISTRY -Refractive index -Thermodynamics	ENGINEERING -Coating -Lubricants -Dispersing agents -Plasticizers
SOLVENTS AND CATALYSTS -Organic Synthesis -Surface Catalysis -Microwave (chemistry	ANALYTICS -Matrices for mass spectrometry	BIOLOGICAL USES -Drug delivery -Embalming -Biocides

-Multiphase reactions and extractions	-Gas chromatography columns -Stationary phases for HPLC	

In a variety of reactions, ionic liquids have been effectively used as ecologically friendly solvents or catalysts.[21-22] such as the asymmetric hydrogenation, Beckmann rearrangement, Balz–Shiemann reaction, Benzoin condensation, Biginelli reaction, carbonylation, catalytic oxidations, Claisen rearrangement, Diels–Alder reactions, esterification, Fischer indole synthesis, Fischer esterification, Friedel–Crafts reactions, Grignard reactions, Heck reaction, hydroformylation, hydrogenation of olefins, Knoevenagel reaction, Michael reaction, Mannich reaction, oxidation reactions, Pechmann condensations, Robinson annulations, Tsuji–Trost reaction, Wacker oxidation, Witting reaction etc.

ILs have also been successfully exploited in the synthesis of heterocycles [23-26] such as synthesis of quinolines, quinazolinones, benzothiazoles, benzimidazoles, pyrimidines, Indoles, isoxazolidines, aziridines, pyrroles, oxazoles, pyridines, pyranes, styryl quinolines [26] and other heterocycles.

Conclusion:

The combination of multicomponent reactions (MCRs) with RTILs allows for the creation of novel approaches for the effective production of structurally varied heterocycles. MCRs in ionic liquids provide several benefits over traditional techniques, including higher yields, reduced reaction times, milder reactions that are less harmful to the environment, secure performance, quick set-up, and effective recovery and recycling of the IL. Thus, integrating MCRs and RTILs brings up an intriguing eco-friendly alternative to traditional techniques for synthesis of heterocyclic molecules. As a result, one of the most significant issues in modern organic synthesis is the establishment of efficient and ecologically conscious synthesis methods.

Ionic liquids are gaining popularity daily in educational and industrial research, and they appear to be effective substitutes for volatile organic solvents. However, given to the inadequate chemical, physical, and toxicological information available on the ILs, there is debate regarding how environmentally friendly they are. Nevertheless, many potential industrial uses are severely limited by the ILs' current costs. However, there is hope that the advantages and disadvantages statistics of the ILs will bring economic feasibility to their more widespread use in the near future.

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