

Ionic Liquids: An Ever-evolving Discipline

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Abstract: Ionic liquids have evolved over the time as a greener alternative to the conventional volatile organic solvents. This mini review article aims to provide a brief introduction to these ionic liquids and their various classifications. This article also provides a brief idea on the unique physicochemical properties of the ionic liquids (ILs), which include conductivity, viscosity, electrochemical and thermal stability, acidity, density, surface tension, surfactant properties and solvatochromic parameters. The versatile applications of the ionic liquids by the virtue of their unique physicochemical properties are also discussed concisely. The concluding part of the chapter highlights the various challenges associated with the use of ionic liquids and their potential applications in the future.

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1. Introduction

The concept of green chemistry has become quintessential for encouraging sustainable development in laboratories and industries. Over the years, the growing concerns regarding the crucial environmental threats such as atmospheric emissions, contamination of water effluents etc. posed by the volatile organic compounds (VOCs), particularly chlorinated hydrocarbons have retorted in finding greener alternatives for them. From this perspective, the recent decades have seen emerging number of research publications for replacement of the VOCs as reaction media with environmentally benign solvents like ionic liquids in organic reactions (Shen et al. 2008; Das et al. 2020; Saikia et al. 2019). Ionic liquids are a broad

class of organic salts containing an organic cation and an anion which can either be organic or inorganic; and are liquids below 100°C. The ionic liquids (ILs) which are liquid at room temperature are called room-temperature ionic liquids (RTILs). The low volatility of the ionic liquids coupled with their other unique properties like high polarity, high conductivity, electrochemical and thermal stability, and ability to dissolve a wide range of solutes have helped them to cement their position as the greener alternative. Though primarily used as solvents, they are now finding applications in various fields like catalysis (Das et al. 2020; Saikia et al. 2019; Rebeiro et al. 2001; Gu et al. 2008), pharmaceuticals (Ma rrucho et al. 2014), separation and extraction processes (Tian et al., 2019), analytical chemistry (Ho et al. 2014), biomass conversion (Xu et al. 2016), surfactants (Smirnova & Safanova, 2010), nanotechnology (Gardella et al. 2015), polymer science (Lu et al. 2009), sensors (Silvester, 2014), energy conversion devices (Van Valkenburg et. al. 2005) etc.

The most common organic cations found in the ionic liquids are imidazolium, ammonium, pyridinium and phosphonium cations, which are combined with inorganic (BF_4^- , NO_3^- , PF_6^- , OH^- , Cl^- , etc.) or organic (OTf^- , OAc^- , CF_3OO^- , Tf_2N^- , etc.) anions (**Figure 1**). The ability to mix and match the cationic and anionic constituents of ILs and to vary and functionalize their side chains allows amazing tunability of their physicochemical properties, including ionic conductivity, viscosity, thermal stability, water sensitivity, electrochemical stability, solubility of diverse solutes in them, and miscibility/immiscibility with a wide range of solvents. The variations of ion-pair combinations with their physical properties have earned them the accolade of ‘designer solvents’ and is widely utilized to develop ionic liquids for specific uses, called ‘task-specific ionic liquids’ (TSILs) (Das et al. 2020; Zhao & Lu, 2019).

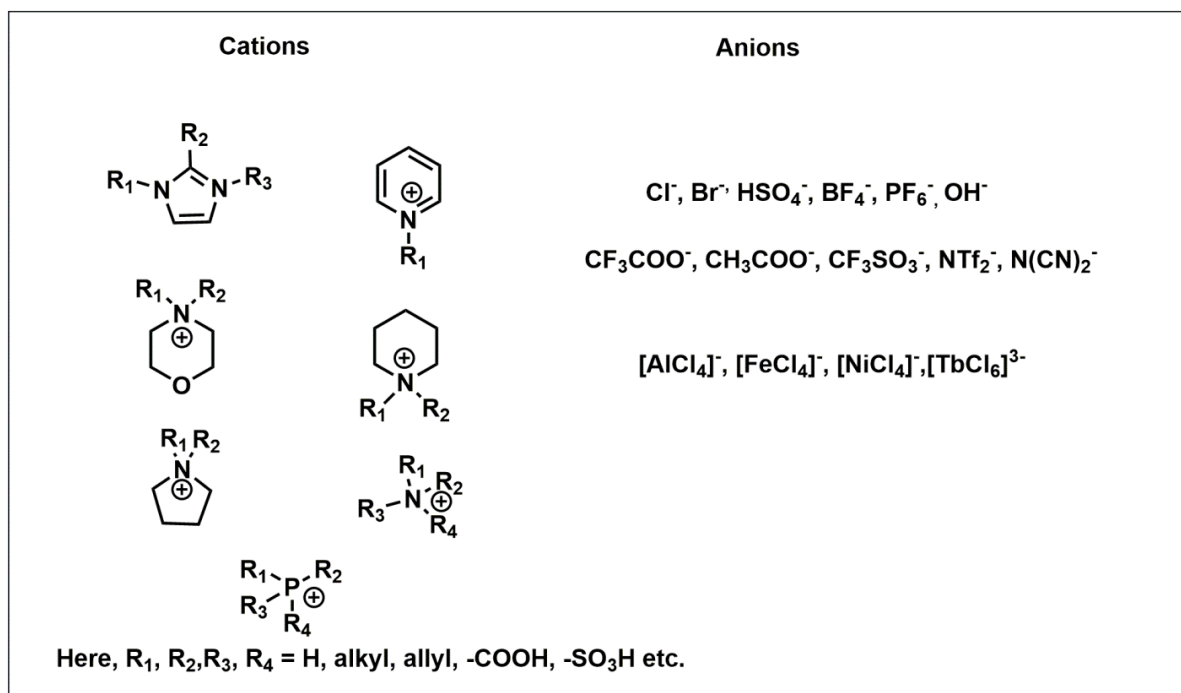
The origin of the story of ionic liquids can be traced back to 1914, when Paul Walden while searching for molten salts that were liquid at temperatures at which he could use his equipment without special adaptations, discovered ethylammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ (Walden, 1914). It was the first ionic liquid to be reported and had a melting point of 12°C. Walden’s interest in these molten salts was the relationship between their molecular size and their conductivity. Unfortunately, the potential of this breakthrough went unnoticed for a long time.

Nearly four decades later, another group led by Hurley and Weir, independently recognised the potential benefits of lowering the melting points of molten salts with which they were working (Hurley & Weir, 1951). They were mixing 1-alkylpyridinium halides with ‘true inorganic salts’, such as metal halides to make solutions from which the metals could be electroplated. During this study, they discovered that 2:1 molar ratio mixture of 1-ethylpyridinium bromide-aluminium chloride ($[\text{C}_2\text{py}]\text{Br}-\text{AlCl}_3$) was liquid at room temperature and they attributed its physical state to the

formation of bromochloroaluminate species in the melt. This discovery paved the way for the emergence of the field of halometallate ionic liquids.

Figure 1

Structures of Some Commonly Used Cations and Anions in ILs.



Around 1980s, John Wilkes' group introduced the imidazolium cations into ionic liquids for the first time in the form of 1-alkyl-3-methylimidazolium chloride aluminium chloride ($[\text{C}_n\text{C}_{1im}]\text{Cl}-\text{AlCl}_3$, where $n = 1-4$) (Wilkes et al. 1982). These cations enriched the ionic liquids with better transport properties and they went on to become by far the most popular cations for designing ionic liquids (Das et al. 2020; Saikia et al. 2019). Their introduction started an almost decade long debate over the role of hydrogen bonding in the structures of these ionic liquids.

The competing ideas were that interionic interactions in these ionic liquids were either via hydrogen bonding (Tait & Osteryoung, 1984) or that they had a stacked structure with anions positioned above and below the plane of the imidazolium ring (Fannin et al. 1984; Dieter et al. 1988). This debate was finally resolved by recognising that the imidazolium ring protons can indeed act as hydrogen bond donors, but only in the presence of sufficiently strong hydrogen bond acceptors (Lungwitz & Spange, 2012; Hunt 2017), and that stacked structures were also present (Elaiwi et al. 1995), particularly for ionic liquids with large anions that are poor hydrogen bond acceptors. In 1992, Wilkes and Zawarotko obtained ionic liquids with 'neutral' weakly coordinating anions such as hexafluorophosphate (PF_6^-) and

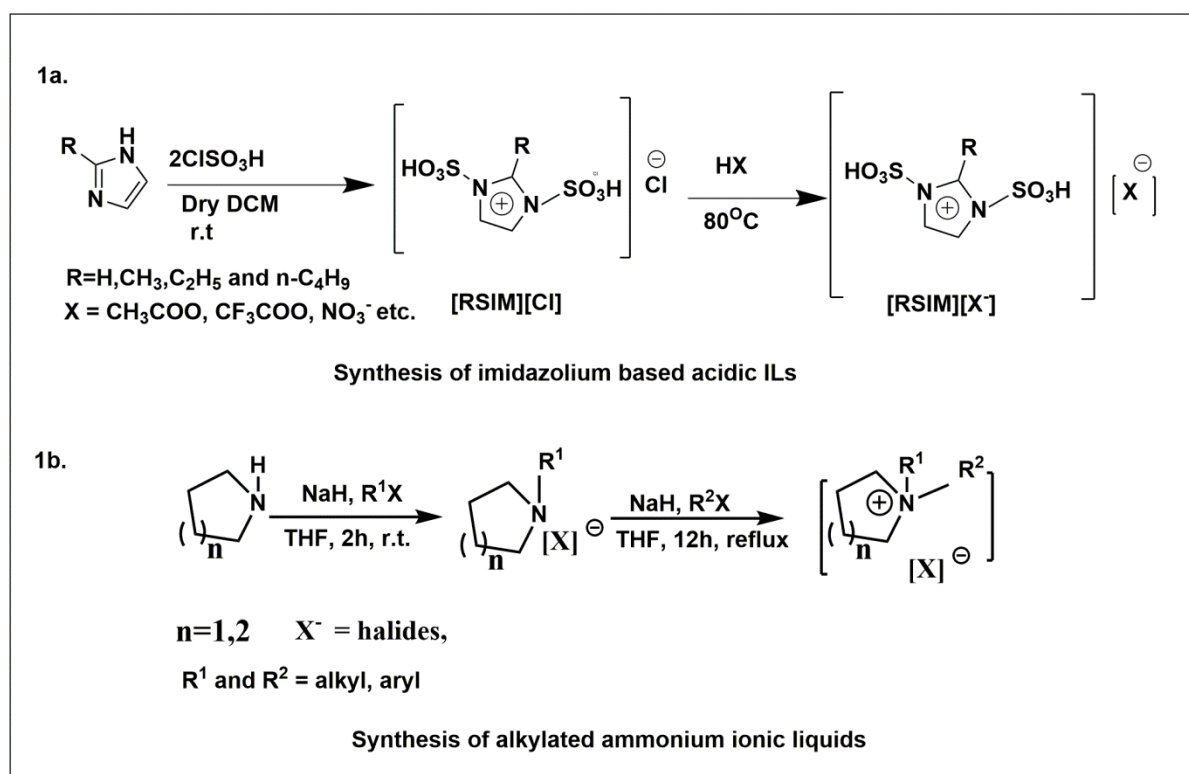
tetrafluoroborate (BF_4^-), allowing a much wider range of applications (Wilkes & Zawarotko, 1992). Since then, the field of designing novel ionic liquids has been constantly evolving.

2. CLASSIFICATION OF IONIC LIQUIDS AND DEVELOPMENT OF IONIC LIQUID-BASED MATERIALS

Ionic liquids can be classified as acidic, basic, or neutral based on the nature of its constituent ions (**Figure 2**). Most of the ILs are neutral or weakly basic in nature in presence of discrete anions like BF_4^- , SCN^- , p-toluene sulfonate, NTf_2^- , etc., with lower viscosities due to weak electrostatic interactions between the cation and the anion. If acidic or basic functional groups are bound to the constituent ions, then they behave as task-specific acidic or basic ILs and can work as functionalized dual solvent-catalytic systems in organic reactions. Basic IL-forming anions include lactate, formate, carboxylate, dicyanamide, hydroxide, etc. A few 'amphoteric' ILs are also known, whose anions bear the capacity to both accept and donate protons (for example: bisulfate, dialkyl phosphate, etc.) depending on the type of substrates present (Olivier-Bourbigou et al. 2010). Synthetic routes of some commonly available ILs are shown in **Scheme 1**.

Scheme 1

Synthetic routes of some common ILs



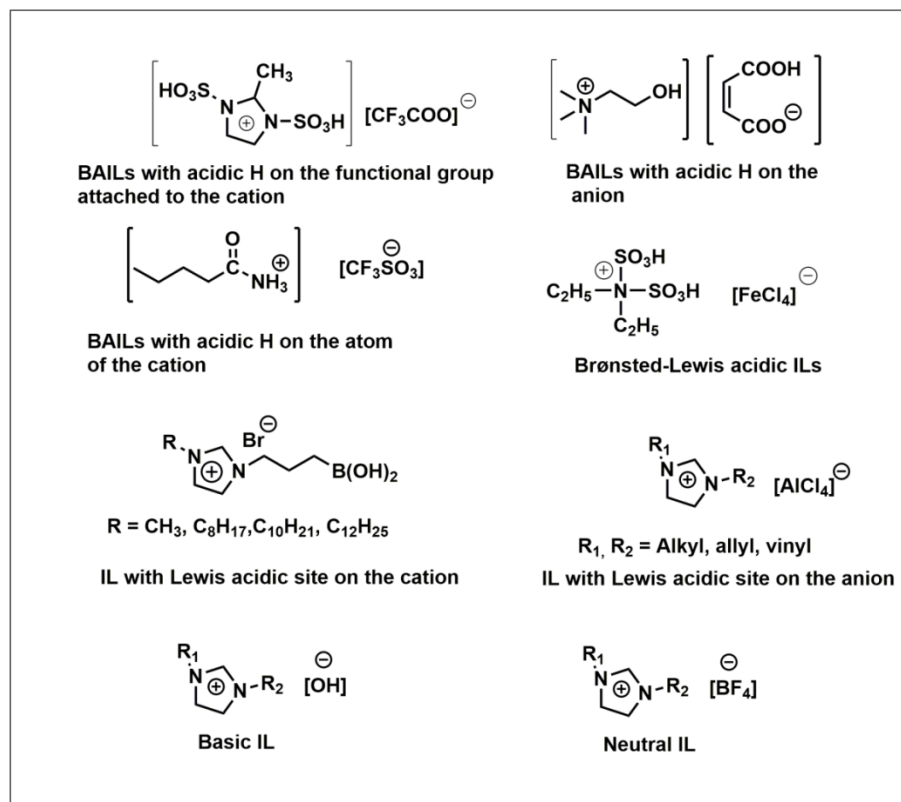
The acidity of the ILs can be Brønsted, Lewis or both Brønsted-Lewis in nature depending on the type of acidic sites present (**Figure 2**) (Das et al. 2020). The Brønsted acidic ionic liquids (BAILs) can be further sub-divided into three types based on the position of the acidic proton. These are: (i) BAILs with the acidic H on an O or N atom in the cation, (ii) BAILs with the acidic H on the anion, (iii) BAILs with the acidic H present on the functional group ($-\text{SO}_3\text{H}$ or $-\text{CO}_2\text{H}$)

attached to the cation. Lewis acidic ionic liquids (LAILs) have their acidity arise from their electron accepting ability and this ability is often present in their anions which are mainly halometallate ions. However, few LAILs with electron accepting ability in the cation are also known. The Brønsted-Lewis acidic ILs, also known as dual-functionalized acidic ILs, contain both the Brønsted and Lewis acidic functions. In general, the Brønsted function in such ILs resides on the cationic part while the anionic part is Lewis acidic (Das et al. 2010).

In the recent years, we have seen the development of many ionic liquid-based materials where ionic liquid is supported on different frameworks like zeolites (Saikia et al. 2019), graphene/graphite nanoparticles (Gardella et al. 2015), clay (Noskov et al. 2010), silica (Askalany et al. 2019), polymers (Kim & Chi, 2004), MOF (Luo et al. 2018) etc. Such supports modify the properties of the ionic liquids. The resultant materials usually have higher thermal and electrochemical stability, water resistivity, semiconductor properties, enhanced acidity, and larger surface area for heterogeneous catalysis, to name a few. These new materials can be used as electro-sensors, catalysts, electronics, and photonics.

Figure 2

Different Categories of ILs.



PHYSICOCHEMICAL PROPERTIES OF IONIC LIQUIDS

Ionic liquids are well known for their fascinating properties and additionally, they provide us the privilege of tuning their physicochemical properties by manipulating the combination of their constituent ions. The ionic conductivity or simply conductivity of ILs is a vital property to consider since it is related to their uses as solvents, electrolytes and binders in various electrochemical devices and reactions. The conductivities of ILs have values as high as 20 mScm^{-1} (Fernandes et al. 2011). It is affected by several factors like temperature, concentration, viscosity, density, type of ions, ion size and mobility, ionic charge delocalization, aggregation of ions, presence of solvents, etc (Olivier-Bourbigou et al. 2010; Yuan et al. 2018; Pinkert et al. 2011; Wu et al. 2010). The conductivity and viscosity of the ILs have an inverse relationship (Wu et al. 2010). For example, replacing the ammonium cation with the imidazolium cation allows us to obtain RTILs with lower viscosities and higher conductivities (Olivier-Bourbigou et al. 2011, Yuan et al. 2018). Increasing the chain length of alkyl substituents in ILs is known to decrease their conductivities and conversely increase their viscosities (Das et al. 2019).

ILs are well known for their electrochemical stability. In fact, the electrochemical windows of some typical ILs are found in the range of 4.5-5V, which is comparable to (or slightly larger than) that of the conventional organic solvents, but larger than that of aqueous electrolytes (Olivier-Bourbigou et al. 2011). Like the other physicochemical properties, the electrochemical stability of the ILs are also affected by the nature of their constituent ions, and this is indicated by the higher electrochemical window of the alkyl-substituted imidazolium ILs compared to their unsubstituted counterparts (Das et al. 2019). The electrochemical stability of the ILs is measured using analytical techniques like cyclic voltammetry or linear-sweep voltammetry. The presence of alkyl substituents on the imidazolium cation increases the reductive stability of ILs. Quaternary ammonium ILs are generally more stable toward redox reactions than imidazolium ILs, however ammonium ILs are more viscous than imidazolium ILs, which limits their electrochemical uses (De Vos et al. 2014).

The polarity of ILs is found to be similar to that of many polar solvents (Yalchin et al. 2020; Padro and Reta, 2016). It is usually evaluated by determining the various solvatochromic parameters like H-bond donor (α)/acceptor ability (β) ability, dipolarity values (π^*) etc. of the ionic liquid using UV-Visible spectroscopy. Betaine dyes are often used as probe molecules for this purpose. As a general trend, more basic anions in ILs lead to lower polarity. Further, increasing the alkyl chain length on the cation and/or the anion led to a decrease in the polarity of the ILs (Yalchin et al. 2020).

ILs are complex and non-isotropic fluids and their fluid properties can be understood by determining their surface tension values. The surface tension of ILs depends on the relative orientation of the cations and anions at the surface

and hence is highly sensitive to the structure of the constituent ions (Das et al. 2020). Surface tension also varies with temperature. The three methods which are generally employed for the measurement of surface tension of ILs are the Du Nouy ring (DNR) method, the pendant drop (PD) method and the capillary rise (CR) method. The surface tension values of many room temperature ionic liquids are known to be higher than those of many common organic solvents. As a general trend it is often observed that surface tension of ILs decrease with increasing alkyl chain on the cation or anion (Greaves et al. 2006).

Most room temperature ILs have density values higher than that of water. The density of ILs is governed by several factors including temperature and ion packing, which again depend on their sizes and shapes as well as the cation-anion interactions. Usually density of the ILs decrease with increasing temperature (Das et al. 2020). At room temperature, the density of ILs is a function of the alkyl chain length and decreases with the increasing chain length of alkyl group of alkylammonium, alkyl imidazolium cations or carboxylate anions. This is due to the fact that increasing alkyl chain increases the free space between the two IL molecules and hence reduces the compactness of the ILs and hence, their densities (Das et al. 2019).

ILs also express high thermal stabilities which make them eligible to be used in heat conversion devices, batteries and in high temperature reactions (Das et al. 2019; Hajipour et al. 2019; Mayrand-Provencher et al. 2009;). Ionic liquids supported on solid supports like zeolites or clay tend to thermally stable up to very high temperatures like 400-600°C. The acidity or basicity of ILs can be measured using UV-Visible, NMR and FT-IR spectroscopy and is also a function of their constituent ions. Brønsted acidity of the ILs are usually evaluated by determining the Hammett acidity function (H°) (Equation 1) for using UV-Vis spectroscopy. Many BAILs have Hammett acidity function (H°) values in the range of 0.5-1.5, indicating their highly acidic nature (smaller the H° values, greater the acidity) (Das et al. 2019). The Hammett equation is given below,

$$H^{\circ} = pK(I)_{aq} + \log\left[\frac{[I]}{[IH^+]}\right] \quad \text{(Equation-1)}$$

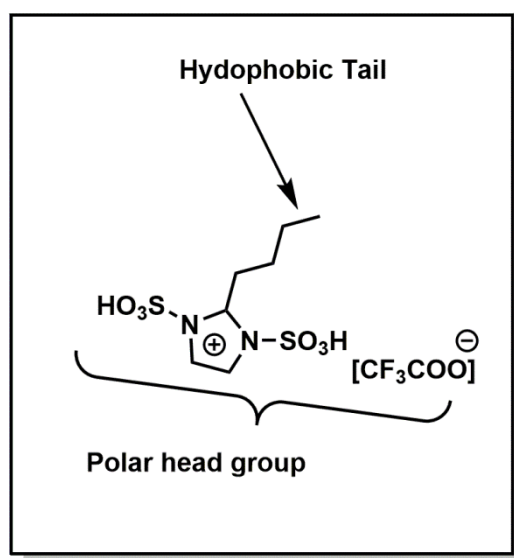
Where $pK(I)_{aq}$ is the pK_a value of the basic indicator in aqueous solution. The typical procedure involves mixing of equal concentration of the indicator (5 mgL^{-1} , $pK_a = 0.99$) and IL (5 mmol L^{-1}) in ethanol solution. The absorbance of the basic indicator [I] in the IL solutions decreased with the increasing acidity of the ILs. The protonated form $[HI]^+$ of the indicator never appeared because of its lower molar absorptivity (Das et al. 2019).

Lewis acidity of the ILs can be measured using FT-IR spectroscopy with pyridine as a probe molecule or by using ^{31}P NMR and triethylphosphine oxide (TEPO) as a probe molecule (Duan et al. 2006; Estager et al. 2010).

ILs are amphiphilic substances containing pronounced hydrophilic and lipophilic molecular fragments, which determine their surface activity and the ability to self-organize in the individual state and in solutions (Das et al. 2019; Canongia Lopes et al. 2006). The existence of longer alkyl chains on the ions also promotes the surfactant-like aggregation tendencies of ILs. The aggregation tendencies of the ILs reduce their ionicity. Extensive studies (both experimental and theoretical) have been conducted on the self-organizing tendencies of ILs (Canongia Lopes et al. 2006; Wang et al. 2005). These studies confirmed the formation of two types of domain: the first one consists of positively charged cations and negatively charged anions arranging in three-dimensional polar networks supported by strong electrostatic interactions, whereas the second one comprises hydrophobic alkyl groups aggregating to form non-polar domains where short-range van der Waals interactions are predominant (**Figure 3**) and are thus, known to display characteristics similar to that of the classical surfactants (Smirnova & Safanova, 2010).

Figure 3

Hydrophilic Head Group and Hydrophobic Tail in an Ionic Liquid.



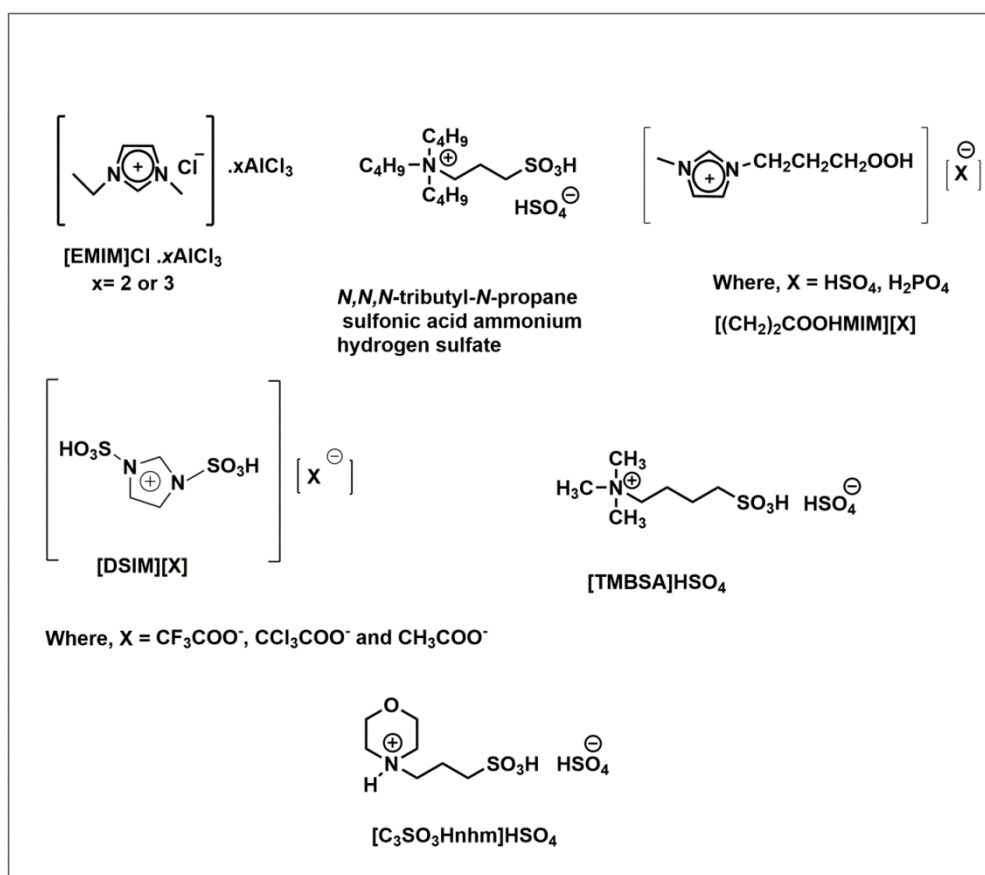
3. APPLICATIONS OF IONIC LIQUIDS AND IONIC LIQUID BASED MATERIALS

Originally, ionic liquids were intended to be used as a greener alternative to the volatile organic solvents in the organic reactions. Later, the increasing number of publications on ionic liquids discovered that they could be employed as a dual solvent-catalyst system in organic reactions. The development of task-specific ionic liquids (TSILs) with a specific acidic or basic group tethered to it further contributed to the use of ILs as catalysts. Their acidity/basicity, combined with their polarity and recyclability, are responsible for their successful application in the field of catalysis, by employing environmentally benign methods and replacing the traditional non-recyclable Brønsted/Lewis acid/basic

catalysts. Many organic reactions have been successfully done involving ionic liquids as solvent or solvent-catalyst systems. Examples of such reactions are aldol condensation, cross-aldol condensation, Knoevenagel condensation, Michael addition, Henry reaction, Friedel-Crafts alkylation/acylation, preparation of N-heterocycles and O-heterocycles, Mannich reaction, Pechmann reaction, Biginelli reaction, Fries rearrangement, Fischer indole synthesis, Oxidation reactions and many more (Shen et al. 2008; Das et al. 2020; Saikia et al. 2019; Zhao et al. 2012; Sindhu et al. 2015; Fang et al. 2007; Zheng et al. 2006, Kunes et al, 2000, Davoodnia et al. 2010; Yeung et al. 2002; Boruah & Borah 2019; Kashyap et al. 2021; Harjani et al. 2001; Xu et al. 2007; Potdar et al. 2001; Dutta et al. 2001; Qian et al. 2011). **Figure 4** shows the structures of some ionic liquids used as catalysts in these organic reactions.

Figure 4

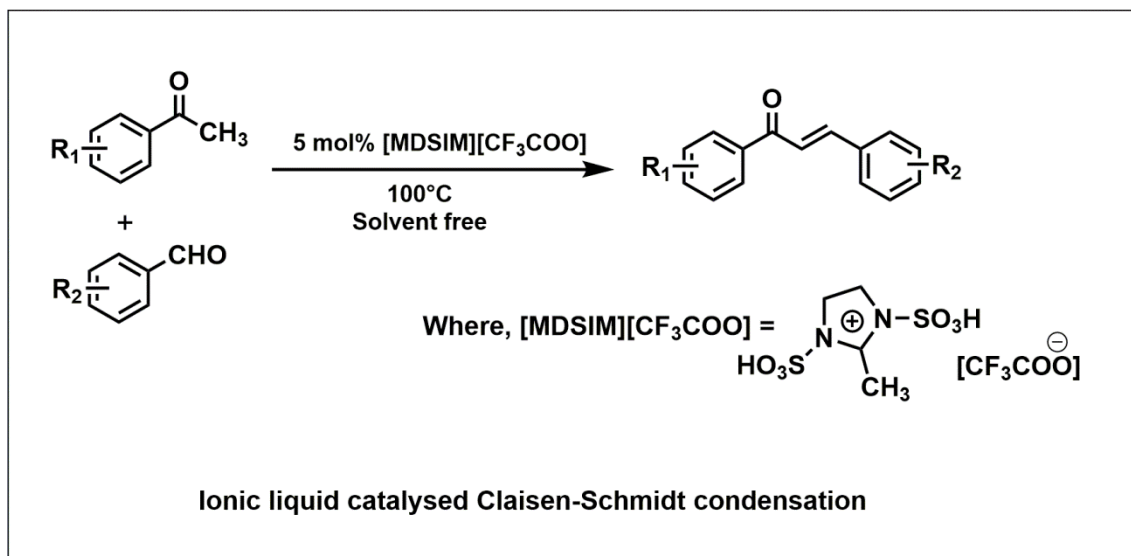
ILs Used As Catalysts in Organic Reactions.



Scheme 2 and **3** shows the use of IL catalysts in Claisen-Schmidt condensation and Michael addition reaction.

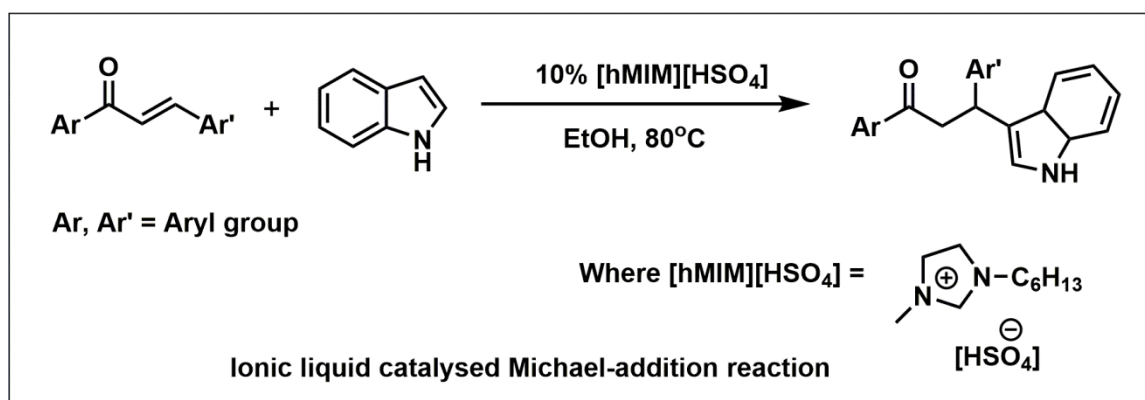
Scheme 2

Ionic liquid catalysed Claisen-Schmidt condensation.



Scheme 3

Ionic liquid catalysed Michael addition reaction.



The use of ILs supported on solid frameworks like zeolites, clay, graphene etc. as catalysts have also been reported (Saikia et al. 2019; Luo et al. 2018; Kim & Chi, 2004). The supported ILs act as heterogeneous catalysts and thus, leading to their easy recovery and better recyclability. It has been observed that the use of ILs in organic reactions has proved to be advantageous in terms of high product selectivity, elimination of organic solvents as reaction media, reusability of the IL as solvent/catalyst, simple work-up procedures, minimization of waste generation, etc.

ILs express high thermal stabilities, which make them eligible to be used in heat conversion devices, batteries and in high temperature reactions (Das et al. 2020; Mysyk et al. 2010; Van Valkenburg et al. 2005; Mayrand-Provencher et al. 2009). The wide electrochemical windows and high conductivities of RTAILs provides a wider scope for their uses as electrolytes in fuel cells, in batteries and capacitors (Mysyk et al. 2010; Yasuda & Watanabe, 2013; Menne et al. 2013; Gunawan et al. 2012). Their ability to dissolve a vast range of solutes in a viscous state has made them potential

candidates for separation and extraction media, biomass conversion etc (Tian et al. 2019; Ho et al. 2014; Xu et al. 2016). The surfactant-like properties of ILs paves the way for them to be successfully used in micellar catalysis. The limitation of experimental works often caused by the higher viscosities or lower conductivities of RTAILs can be overcome by mixing them with appropriate molecular solvents (Das et al. 2019). Such binary mixtures of ILs in molecular solvents have been gaining sufficient research interest in the recent years.

4. CONCLUSION

Ionic liquids have gathered generous interests across several research disciplines, owing to their unique and diverse physicochemical properties. This article provides a comprehensive review on the history of ionic liquids, followed by their different classifications, distinctive physicochemical properties and finally their versatile applications. At present, we have many research studies documented which indicate many promising industrial applications of ILs. However, their fulfilment remains dependent on their wide-scale and cost-effective production. It is expected that with the development of newer technologies, we will be able to gain a better insight into the intrinsic properties of the ionic liquids. This knowledge is ought to enrich us with ideas for their different their modifications and applications in the future.

List of abbreviations

IL: Ionic liquids

RTIL: Room-temperature ionic liquids

BAIL: Brønsted acidic ionic liquids

LAIL: Lewis acidic ionic liquids

TSIL: Task-specific ionic liquids

TEPO: Triethylphosphine oxide

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