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IONIC LIQUIDS: PREPARATIONS AND LIMITATIONS

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Abstract

Ionic liquids are considered as an ideal alternative to volatile organic solvents and chemical industries in the future, because they are non-volatile. Ionic liquids are also considered as new novel chemical agents and widely regarded as a greener alternative to many commonly used solvents. Ionic liquids have been studied for a wide range of synthetic applications and have attracted considerable interest for use as electrolytes in the areas of organic synthesis, catalysis, solar cell, fuel cells, electrodeposition and supercapacitors. However, some ionic liquids suffer from more or less some drawbacks such as toxicity, preparation and high cost in the process for use. Most recently, three types of ionic liquids are attracted much attentions specifically traditional ionic liquid, protic ionic liquid and deep eutectic solvent, where their preparation, mechanism and limitation were differentiated. However, those liquids are having their own advantages and limitations based on applications. Traditional ionic liquid and protic ionic liquid are highly cost and toxic for applied engineering research, but they consist of micro-biphasic systems composed of ionic compounds which have more varieties in the applications. The deep eutectic solvent is very economic for large-scale possessing but there are only limited ionic mixtures to certain application such as electrochemistry.

Keywords: deep eutectic solvent, ionic liquids, protic ionic liquids, volatile organic solvents

1. Introduction

The term ionic liquids (ILs) has been used to describe salts that melt below 100 °C. Whereas, the term room-temperature ionic liquids (RTILs) is usually reserved for ILs melts with melting points below room temperature. ILs are electrolytes forming liquids that consist only of cations and anions. ILs extremely low vapour pressure being non-volatile, highly polar, miscible with certain organic solvents and/or water and good solubility of organic and inorganic materials, chemically inert. They are reusable (residual reagents, reaction products and catalysts are separated by suitable procedures e.g., removal under reduced pressure or extraction), and can be designed, non-inflammable and thermally stable as well (high thermal stability and liquid range up to about 300 °C) [1-3].

ILs are usually characterized by a wide electrochemical window of stability, a reasonable ionic conductivity (similar to most non-aqueous electrolytes). ILs typically consists of organic nitrogen-containing heterocyclic cations and inorganic anions [4]. ILs are promising

environmentally benign, numerous of reaction media which are expected to provide an attractive alternative to conventional volatile organic solvents (VOSs) in current synthetic organic chemistry since their growing use does not lead to air pollution [5]. Nevertheless, in the last few years they have become more attractive in other fields such as catalysis [6], in basic electrochemical studies of organic compounds and inorganic compounds [7], formation of metal nanostructures [8], analytical chemistry [9] including sensors [10], bioanalytical chemistry [11], and for electrochemical biosensors [12].

ILs have been hailed as the green alternative to VOSs in chemistry due to their novel properties, while maintaining the ability to dissolve a wide range of organic and inorganic compounds for example, 1-allyl-3-methylimidazolium chloride could be dissolved cellulose up to 39% without derivatization [13] and 1-butyl-3-methylimidazolium chloride have been shown to stabilize proteins [14]. Since VOSs nature consists of relatively small molecules, they have weak intermolecular forces between them and making them highly volatile. They

are also flammable and often toxic, consequently there has been much interest in finding non-volatile solvents as replacements. Therefore, unlike VOSs, ILs do not vaporise into the air, effectively eliminating one of the major routes of environmental contamination [15], making its operations safer and environmentally acceptable.

Among these, ILs have recently classified to three types namely traditional ionic liquid, protic ionic liquid and deep eutectic solvent. Nonetheless, during our investigations we have found that the reported compilations of three types of ILs were comparatively scarce. This paper focused on ILs in order to gain an in-depth understanding of its mechanism of synthesis reaction, so as to pave the way to the production of better ILs.

2. Preparations of Traditional Ionic Liquid, Protic Ionic Liquid and Deep Eutectic Solvent

Preparation of traditional ionic liquid. The methylimidazolium and pyridinium ions have proven to be good starting points for the development of ILs [16]. The structure of a common ILs precursor based on alkyl imidazolium and pyridinium ions is given in Figure 1.

Preparation of traditional ILs by use of N-alkylimidazole has been shown in Figure 2. Reaction, in particular metathesis reaction is prepared by the reaction of 1-methylimidazole with butyl chloride in the present of acetonitrile as catalyst usually was applied towards the end of the last century [17]. They are, however, quite difficult to make, very expensive, and their toxicity has not yet been ascertained.

Preparation of protic ionic liquid. Several researchers have reported an alternative method to produce ILs through acidic reactions using strong acids as protonator. Because strong acids have high proton activity, they have become increasingly alternative to metathesis reaction. For example, sulfuric acid is used for reactions involving N-alkylimidazoles [18]. Scheme of synthesized protic ionic liquid has been shown in Figure 3.

Preparation of deep eutectic solvent. Another ILs that is receiving interest is deep eutectic solvents (DES) which are a type of ILs. Its similar ILs have been made using a wide variety of quaternary ammonium salts, most notably imidazolium cations [19]. Best of all, they are easy to make simply take the two solids, mix them together with gentle heating, until they melt, and when they cool they remain liquid. In this case, DES, particularly choline chloride, has currently received widespread attention as a hydrogen bond receiver for complexation reactions [20]. The use of choline chloride,

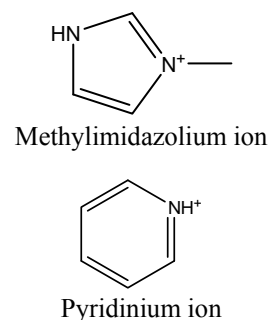


Figure 1. Example of Ionic Liquid Cations

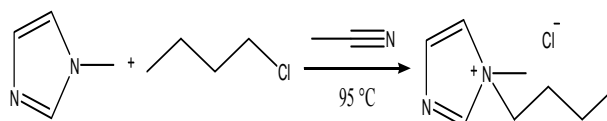


Figure 2. 1-methylimidazole Reacts with Butyl Chloride to Produce 1-butyl-1-methylimidazolium Chloride

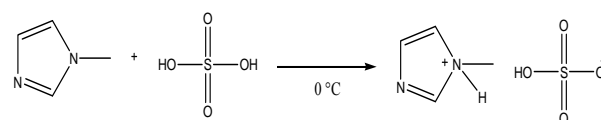


Figure 3. 1-methylimidazole Reacts with Sulfuric Acid to Produce 1-Methylimidazolium Hydrogen Sulfate

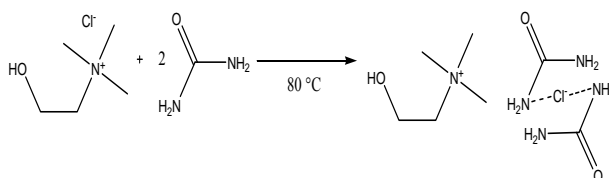


Figure 4. Choline Chloride (2-hydroxyethyl-trimethylammonium chloride) Reacts with Urea to Produce Deep Eutectic Solvent

chloride, as shown in Figure 4, is interesting because this quaternary ammonium salt forms a liquid with complexing agent in a same phase, making eutectic liquid.

3. Mechanism of Ionic Liquids

Traditional ionic liquid. It must be emphasized that ILs are not ions in solution but are pure compounds and they are conceptually similar to table salt Na⁺Cl⁻(l) not Na⁺Cl⁻(aq). As NaCl melts at approximately 800 °C but 1-butyl-3-methylimidazolium tetrafluoroborate for instance melts at approximately -80 °C. This pure ionic character gives them unusual properties compared with

electrolytic solutions or polar organic solvents. In the NaCl phase, the Coulomb interactions between cations and anions are generally stronger. As a result, compounds in these structures tend to have higher melting points [21].

The first-order description of ILs is that they are simple charged species in a liquid state, as shown in Figure 2. While Coulombic interactions are the dominant force between the ions, the ions are not simply spheres of charge but have shape and chemical functionality that impose subtle changes in the physical properties. Thus, dipole, hydrogen-bonding, and dispersive forces are important to the interactions between constituents in the ILs [22] however, these forces are weak enough to keep them liquid at room temperature. These properties and others are modified by the variation in the ILs composition.

Protic ionic liquid. The reasons why those compounds changes be converted into protic ILs are after a strong acid was added to N-alkylimidazole; mostly the nitrogen constituent was protonated with hydrogen ions to be nitrogen ions and bound with hydrogen itself, as shown in Figure 3. In protonation the nitrogen constituent phenomenon by strong acid is to neutralize the compound and it created positive and negative ions corresponding protic ILs. In addition, protic ILs melting points also decrease with the larger more asymmetric nitrogen cations, which the highest melting points are observed with the more symmetric nitrogen cations, owing to the larger size of cations providing greater degrees of freedom and asymmetry.

Deep eutectic solvent. Quaternary ammonium halide salts can form complexes with hydrogen bond donors and in at least one extreme case, choline chloride and urea as shown in Figure 4 with a molar ratio of 1 : 2, form a non-volatile DES, with a melting point of 12 °C. In the DES phase, it consists of nitrogen cations and anions complex, in these structures, the weak interactions of the nitrogen cations with the anions complex, and the large radius ratios, make possible break away of cation from anion relation, and cation motion quantities can turn out to be greater. For the reason that its form a eutectic mixture due to hydrogen bonding interactions between the complexing agent (such as urea) and chloride ions. In nitrogen cations and anions, complex species the increased stabilization of the liquid state also depresses the kinetics of the crystallization process and in this systems leads to the possibility of lowering melting points given low temperature molten salts solutions [23].

Apart from that, when a complexing agent was added, basically the endothermic shifted to lower temperature. As the appropriate of complexing agent molar ratio, the melting point rapidly shifted to lower room temperature.

In other words, the highest of the melting point may suggest the existence of strong ion coupling in the mixture. Improved chemical stability for the liquid is possible because of the increased thermodynamic stability of the anion complexes, which are generally held together by strong chemical bonds (typically ionic-covalent). Furthermore, it has been proposed that the anion in DES entity is the chloride ions complexed by the hydrogen bond donor that leads to a charge delocalization effectively decreases the freezing point [24]. Additionally, the hydrogen groups of the two hydrogen bond donor complexing agents are attached to a relatively electronegative atom than the chloride ion of choline chloride, this should favour their complexation. Complexation of choline chloride, actually, is driven by relatively strong hydrogen bonding between the chloride ion and the hydrogens in the urea.

4. Limitations of Ionic Liquids

Traditional ionic liquid. The majority of investigations have concentrated on N-alkylimidazolium, N-alkylpyridinium, N-alkylthiazolium, N,N-dialkylpyrazolium, tetraalkylammonium cations, etc. with weakly coordinating inorganic bulky anions such as BF_4^- , PF_6^- , F_3CSO_3^- and $(\text{F}_3\text{CSO}_2)_2\text{N}^-$, ZnCl_3^- , CF_3SO_3^- , etc. [25-26]. There are several simulations and experimental studies concerning mainly the structure of imidazolium based ILs and the main conclusions are that those liquids are micro-biphasic systems composed of polar and non-polar domains [27]. However, the use of this type of ILs have several disadvantages such as toxicity because of possible release into the soil or water-courses ILs could become persistent pollutants and pose environmental risks and also cost making them somewhat impractical for larger industrial applications such as metal electroplating, electrodeposition and biocatalyst. Therefore, the key challenges in the application research of traditional ILs has been the availability and cost issues. Myriad issues such as toxicity and availability will limit their practical use for larger scale applications of other metals and biomaterials. Although a multitude of recipes has been published to carry out the synthesis of traditional ILs, not all laboratories focused on applied research have the expertise, work practices and equipment necessary to carry out synthesis work due to complicated synthetic processes. In addition, to prepare pure, dried traditional ILs or to execute post synthesis purification steps is often challenging. On the other hand, commercial availability of some traditional ILs is restricted to small volumes or the cost of many liquids is still unacceptable for applied engineering research [28]. The physical and chemical properties of traditional ILs can be influenced significantly by small amounts of impurities. The catalytic activity and the electrochemical behaviour are highly dependent on the purity level of the traditional ILs. The quality of traditional ILs has become an

important consideration in their use. Commercial producers try to make traditional ILs of the highest quality achievable at reasonable cost. Typical impurities are colours, organic starting materials and other volatiles, halide impurities, protic impurities, other ionic impurities from incomplete metathesis reactions and water. Analysis and trace analysis of impurities in ILs is still a field of ongoing fundamental research [29]. Moreover, concerns about their toxicity have raised questions about their use in large-scale industrial applications, especially those that involve the creation of large amounts of waste. Eventhough ultrasonic irradiation ostensibly can break down traditional ILs into more environmentally benign non-toxic compounds (such as biurea and acetoxyacetic acid) [30] but, its consumed very high frequency sound waves on solutions of hydrogen peroxide and acetic acid to implement and merely for dialkylimidazolium based ILs.

Protic Ionic Liquid. On the other hand, proton transfer from a Bronsted acid to a Bronsted base can also form ILs [31]. It was recently reported that the protonation of 1-alkyl imidazoles by strong acids provided salts, which act as ILs and considered as protic ILs. One would expect protic ILs to provide good proton conductivity compared to inorganic media because of their higher mobility. The idea exploited here is using strong acid as proton-rich electrolytes for proton carrying medium. In fact, some protic ILs have been shown to be more conductive than aqueous electrolytes at room temperature [32]. Protic ILs have the additional advantage that the proton activity (PA) can be adjusted by the choice of Bronsted base and Bronsted acid used in their formation. In the absence of solvent, the PA plays the role of pH in ordinary solutions [33]. Protic ILs, which constitute a subgroup of the ILs family, are currently under intense study in a variety of applications, including fuel cells, where their ability to transport protons between electrodes has been a recent discovery [34]. Example of protic ILs is 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIm][HSO₄]), which could be prepared by ion exchange between [BMIm]Cl and H₂SO₄ or NaHSO₄, has been used as acidic catalysts for the esterification [35] and alkylation [36]. Furthermore, some inorganic or organic acids, such as HCl, HBF₄ and CF₃COOH, could react directly with N-alkylimidazoles to form a new class of protic ILs, which bear an acidic proton on nitrogen of the imidazolium ring. Recently, the protic ILs have been used as protection reaction of aldehyde carbonyls [37], Mannich reaction [38], Biginelli condensation [39] and Friedlander annulation [40]. The advantage of protic ILs is the high yield that can be obtained economically with this method (>99 wt%), but this is at the expense of a reduced protic ILs quality. This quality reduction is caused by the extensive strong acid protonation processes that are necessary and the fact that the excess

of hydrogen ions from strong acid are undesired components from the protic ILs. Especially for high value strong acid, this quality reduction is unacceptable, limiting the production process. The traditional process uses sulfuric acid, which is not only extremely hazardous to use but it is also very inefficient. In the series of such protic ILs, then again, it is still a challenge for the large-scale applications of ILs in commerce, owing to the expensive costs of precursor (N-alkylimidazoles), potentially toxicological and purity issues [41].

Deep eutectic solvent. To differentiate them from the wide range of ILs that are available they have been given the name deep eutectic solvents (DES) with special properties composed of a mixture forming a eutectic with a melting point much lower than either of the individual components. The approach for making DES is to start with a simple quaternary ammonium halide. They possessed low vapour pressure, high stability, wide liquid-range, non-flammability, wide-range electrochemical window and tunable solvency, which show similar properties to those of traditional ILs [42]. These eutectic mixtures have some superior characters in the preparation procedure exhibited as following; firstly, the preparation procedure of these eutectic mixtures is very simple, only needs to mix two different compounds mechanically and requires no medium; secondly, 100% reaction mass efficiency and zero emission in the synthesis are achieved, and which is relatively environmentally benign. Lastly, substance density and energy density in the preparation process is the lower [43]. All these advantages of the eutectic mixtures have best answer the industrial requirement for large-scale production compared to the traditional and protic ILs synthesized by metathesis and ion exchange respectively [44,45]. DES can be successfully employed in electropolishing, electroplating and metal oxide processing. Recently, they have also shown that choline chloride (as the quaternary ammonium salt) and either urea or ethylene glycol (as hydrogen bond donors) based DES can be employed in the electrodeposition of zinc, tin and zinc-tin alloys. However, there are only several successfully DES related to low melting point ILs were claimed as be composed of choline chloride or choline iodide [46] that can complexed with hydrogen bond donor including amides, carboxylic acids and alcohols. For choline chloride or iodide, only those compounds form hydrogen bonds with metal chlorides or hydrogen bond donors produced a homogeneous liquid with a significant decrease in the freezing point. Compounds with greater ability to form hydrogen bonds display an enhanced freezing point depression when choline chloride and a hydrogen bond donor are mixed [47]. Their applications and variations were narrow due to limited sorts of quaternary ammonium salt that consumed merely choline based. Accordingly, for choline chloride and urea this compound has been

registered as Reline [48]. However, these are precursor for the agriculture product used in the manufacture of an additive for chicken feed industries and this currently limits their wide-scale use. These industries make use of choline chloride as the basic raw material. As a result, demands for choline chloride have been on the increase without any appreciable profit margin to the producers due to higher competition, hence, the dwindling production of chicken feed additive. On the other hands, as electrolytes DES may be limited by the electrochemical reactions are rather slow due to the high viscosity of the electrolytes. This, in turn, reduces the mass transfer of the electro-analyte due to low diffusion coefficients [49]. In addition, owing to the higher relative viscosity of DES, compared to those of traditional ILs, the chemical reaction rates are decrease; it can slow down mass diffusion transfer-limited reactions. Although, the physical and chemical properties of DES are congruent to those of the traditional ILs but the range of structure of DES is likely to be different from that of traditional ILs constituted only by discrete ions. The liquids were found to be homogeneous mixtures of the two components are actually to be precise no covalent bonds were formed via side reactions through complexation [50]. Moreover, to drive the reaction a base is easier, but separating the impurities of reactants is difficult for the DES produced.

5. Conclusion

There are many of the available routes to obtain some materials with the typical ILs properties by a low-cost synthetic method. Hence, certain approach can be economically applied for large-scale possessing for commercial inexpensive ILs and consequently industrial application. Without a doubt, ILs are potential candidates to be used as non-volatile solvent based electrolytes of syntheses since they possess many benefits than those solvent based on VOSS. Therefore, the ILs future and its potential is still widely open.

Regarding DES, they are simple to synthesize, the components of the eutectic can be easily mixed and converted to ILs without further purification. They are also very cheap due to the low cost of raw materials. For this reason, several study indicated the feasibility of using the eutectic mixture for developing ILs. The main advantages of eutectic mixture of quaternary ammonium over heterocyclic nitrogen cations, such as N-alkylimidazoles, are economic and it can speed up production of ILs.

The most important features, which make DES a suitable ILs for large-scale applications, are its low cost and ease in preparation compared with other air and water stable ILs based on traditional and protic ILs. Probably this is the last century for metathesis reaction usage in this field. Moreover, compared to conventional

ILs, DES share many characteristics and are known to be less toxic, air and moisture stable, biodegradable and economically viable to large-scale processes, but there are only ionic mixtures and not ionic compounds. Based on it, almost limitless varieties of liquids still to be discovered with a wide range of possible applications without limitation. For that reason, better alternatives are necessary for practical applications for the future.

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