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Synthesis and Structural Characterization of Imidazolium-Based Dicationic Ionic Liquids †

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Abstract: Dicationic ionic liquids present a novel class of ionic liquids composed of dication and two monoanions; the latter have shown an increasing interest in recent years and are used in many applications. Compared to conventional ionic liquids, the physicochemical properties of dicationic ionic liquids can be set by modifying the languor and the type of chains linking the cationic heads as well as the type of cation. In this work, we present the synthesis of three dicationic ionic liquids based on imidazolium with two steps; the first of which is a quaternization reaction leading to the formation of dicationic ionic liquids with the iodide ion. The characterization of these organic salts was carried out by magnetic resonance spectroscopy, allowing a better identification of the products obtained.

Keywords: ionic liquids; dicationic ionic liquids; imidazolium; quaternization

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1. Introduction

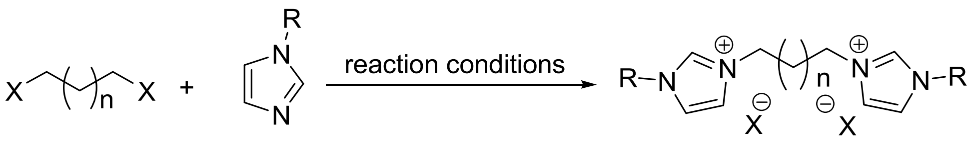
Ionic liquids may be considered as a new and impressive class of solvents or as a type of materials that possess a long and useful history [1]. Ionic liquids (ILs) are organic salts [2] comprised of organic cations in combination with organic and/or inorganic anions, which exhibit a myriad of remarkable and interesting properties [3,4]. The physicochemical properties of ILs, such as their high thermal stability, their good electronic conductivity, their reasonable viscosity, their wide liquid range, their low vapor pressure, and their high thermal conductivity, make them an interesting reaction medium for green chemistry. In particular, this allows them to work at a high temperature with good heat dispersion [5]. ILs are capable of dissolving a large number of organic or inorganic compounds [6], or organometallic compounds and provide a polar coordinating medium for transition metal catalysts. In this case, the ILs are used as inert solvents or co-catalysts [7]. The properties of ILs, such as their very wide electro-activity range, their high conductivity and their high thermal stability, have made these new media prime candidates in the search for new energy systems (photovoltaic cell, battery, etc.) [8,9]. They can also be used as battery electrolytes [10].

Recently, many studies have focused on the development of a new subclass of ILs known as dicationic ionic liquids (DILs), which typically comprise of two cationic head groups linked by a rigid or flexible spacer that are associated with two counteranions [11]. Since the number of possible combinations of cations and anions in DILs is greater than that of monocationic ILs, a greater variability in the properties of LIDs would be possible [12]. Compared to monocationic ILs, multicationic ones can have a higher melting point, surface tension, viscosity, wide liquid range, thermal stability and tenability of chemical and physical properties [13,14]. Therefore, they have good potential to be used in a wide range of applications, including solar cells [15]. DILs are studied in detail with improved photovoltaic properties for solar cells sensitized to dyes [16,17].

DILs are promoter catalysts for the esterification reaction. They have also been widely used in various scientific fields due to their high thermal stability, wide range of liquid state temperatures, and biological activities such as antiviral, antifungal and anticancer activities [18]. DILs have proven to be essential in the fields of catalysis [19]. More recently, improving the isomerization degree of *n*-pentane and electrolytes for photo-harvesting [20–22]. However, they are also referred to as organic ionic plastic crystals due to their property of solid-state electrolytes [23,24].

The property of being sufficiently stable at melting points above 200 ° C gives them superior lubricating properties, which allows them to be used in high temperature lubricants [25,26]. They have shown promising results in the separation of oils. aromatic fractions of the extracts, thereby replacing aromatic solvents [27]. In addition, they have been successfully studied in zeolite beta applications, which have given promising results [28–30]. Many researchers have described the synthesis of imidazolium-based LIDs by various methods with their advantages and disadvantages. After remarking on various methods, the major limitation is the time spent on the synthesis and the tedious procedure [31]. In 2007, Ding and coworkers synthesized an imidazolium-based DIL containing a substituted alkyl group 14 carbons long, and where it had been synthesized by an elimination reaction of substituted quaternary ammonium salts; the synthesis process involves four consecutive steps [32]. Recently, a series of dicationic imidazolium-based ionic liquids containing incorporated Br^-, BF_4^-, PF_6^-, NTf_2^- anions were synthesized by Zhang et al. [33], in order to improve the thermal stability of these compounds and enhance the thermal storage density. More recently, Kuhn and his group [34] used the synthesized imidazolium-based dicarboxylate dicationic ionic liquids to study their thermal properties and showed that the dicarboxylate's spacer length has no effect on the melting point.

Herein, we present the synthesis of three dicationic ionic liquids based on imidazolium (Scheme 1). The synthesis takes place through two steps; the first one is a quaternization reaction where the first DIL was obtained with iodide ion. The second step would be an ion exchange, in order to obtain the two last DILs. The characterization of the dicationic ionic liquidss was carried out by nuclear magnetic resonance spectroscopy (NMR ^1H and NMR ^{13}C, allowing for a better identification of the products obtained.



Scheme 1. General synthesis of dicationic ionic liquids based on imidazolium.

2. General Experimental Procedure

The synthesis of three different ionic liquids, composed of 1,1-Bis(3-imadazoilum-1-yl) methane [$C_4(Mim)_2$] cation and three different anions, were synthesized using the already reported approaches [35,36]. Initially, Imidazole (0.1 mol) and diiodomethane (0.05 mol) were charged into a round bottom flask contain acetonitrile (10 mL) and was stirred for 6 h at 50 °C. The synthesized white crystalline intermediate, 1,1-Bis(imadazoilum-1-yl) methylene iodide ([$C_1(Mim)_2$]2I), was washed with ethyl acetate and toluene to remove unreactive residues. In the second step, [$C_1(Mim)_2$][2I] (0.025 mol) was dissolved in water

(20 mL) and then respective acids (0.05 mol) were added dropwise under the cooling conditions for 30 min. After dropwise addition, the temperature of the mixture was increased to 50 °C and stirred for 12 h. The desired ionic liquids were washed with water and toluene to remove the unreacted materials.

3. Results and Discussion

Nuclear Magnetic Resonance ^{1}H and Nuclear Magnetic Resonance ^{13}C (Bruker 300 MHz spectrometer) spectra were used to confirm the structure of synthesized dicationic ionic liquidss using methanol (CH_3OH) as an internal solvent.

4. Conclusions

In summary, we have synthesized three dicationic ionic liquidss based on imidazolium composed of 1,1-Bis(3-imadazoilum-1-yl) methane dication and three different anions through two steps. The first is a quaternization reaction and the first dicationic ionic liquids was obtained with iodide ion. The characterization of the dicationic ionic liquids was carried out by magnetic resonance spectroscopy, allowing for better identification of the obtained products.

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