# **RSC Advances**



View Article Online

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# PAPER



Cite this: RSC Adv., 2016, 6, 26386

# Synthesis and hypergolic activity evaluation of some new ammonium-imidazolium based ionic liquids<sup>†</sup>

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In this study, a new class of dicyanamide-based ionic liquids containing mono and dicationic counterparts was synthesized and characterized. Results demonstrate that the physical properties of these salts, including thermal stability, melting point, density and viscosity, are highly dependent on the structure of cation and type of anion. It was observed that the thermal stability of dicationic ionic liquids is higher for the monocationic ones. Furthermore, droplet tests were used to investigate the hypergolic properties of these ionic liquids. All of the synthesized compounds showed hypergolic activity upon contact with white fuming nitric acid, suggesting that some may have potential for application as bipropellants or energetic additives.

Received 16th January 2016 Accepted 29th February 2016

DOI: 10.1039/c6ra01364c www.rsc.org/advances

## Introduction

A hypergolic rocket propellant is a propellant that spontaneously ignites when a fuel and an oxidizer come into contact with each other.<sup>1,2</sup> Traditional hypergolic propellants (such as hydrazine and its derivatives) are extremely toxic and/or carcinogenic.<sup>3</sup> They also have less energy density than such cryogenic propellant combinations as liquid hydrogen/liquid oxygen.<sup>4</sup> As a result, a launch vehicle, which uses a hypergolic propellant, must carry a greater mass of fuel than one using these cryogenic fuels. Hence, there is considerable interest in the development of suitable alternatives for hydrazine family of hypergolic fuels.<sup>5-7</sup>

Recently, ionic liquids (ILs) have received considerable attentions as energetic materials for propellant applications.<sup>8-12</sup> Hypergolic ILs have become paragons of environmental friendliness, green chemistry and low vapour toxicity materials, which exhibit energetic performances comparable to hydrazine. They have shown great potential to meet the requirements of developing non-toxic, high performance propellant formulations; especially for space propulsion applications.<sup>13-16</sup>

Such liquid salts tend to have low volatilities and viscosities and high thermal and chemical stabilities, and often exhibit wide liquid ranges, all of which allow their application as bipropellant fuels in a variety of conditions.

In comparison with monocationic ILs, dianionic ILs have the potential to exhibit superior physical properties<sup>17–20</sup> in terms of

greater thermal stability, lower volatility, and more flexibility in tuning/varying their physicochemical properties.

The tunability of dianionic ILs has been enhanced by cationic moieties.<sup>20</sup> Although many dianionic ILs exhibit melting points higher than 100 °C, they are still referred to as "ionic liquids" for convenience<sup>20,21</sup> since they are liquids at temperatures at which they are employed.

On the basis of the advantages of the dianionic ILs, some applications of these compounds have been explored, such as high temperature lubricants,<sup>22,23</sup> solvents in high temperature reactions,<sup>22–24</sup> additives in dye-sensitized solar cells,<sup>25</sup> extraction liquids<sup>26</sup> in chromatography<sup>27–29</sup> and mass spectroscopy,<sup>30</sup> and as electrolytes for secondary batteries.<sup>22</sup>

Despite much effort, most of the research work has thus far focused on monocationic type energetic ionic liquids. To gain further understanding of structure-property relations and extend the applications of ILs as energetic and hypergolic components, it is incumbent to explore new dicationic IL structures.

In the current study and in continuation of our previous study on ILs we would like to introduce the synthesis of unsymmetrical monocationic salts have been synthesized based on imidazolium and ammonium cations. Furthermore, asymmetrical dicationic compounds have been synthesized by combination of imidazolium and ammonium cations and their properties have been compared with those of the new synthesized monocationic ILs (Scheme 1).

Regarding the selection of the energetic anion, dicyanamide anion provides a combustible organic structure and gives ILs with low viscosities and wide liquid ranges.<sup>8</sup> On the other hand, the introduction of fuel-rich amine groups as well as vinyl and allyl substitutents into the cations can increase the energy density and hypergolic reactivity of the resultant energetic ILs.<sup>10</sup> Therefore, open-chain amines, vinyl and allyl substitutents, and

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra01364c



dicyanamide anion were chosen for the preparation of a new series of monocationic and dicationic ILs. Thermophysical and hypergolic properties of the newly synthesized compounds were investigated to evaluate their potential use in bipropellant systems.

## **Experimental section**

#### **Reagents and instruments**

All the solvents and chemicals were purchased from Sigma-Aldrich Chemical Company and used without further purification. All the synthesized compounds were characterized by <sup>1</sup>H and  $^{13}C$  NMR spectroscopies using a Bruker DRX-300 instrument. Chemical shifts were reported relative to TMS as the internal standard. FTIR spectra were obtained on a Nicolet 800 spectrophotometer. Elemental analyses were obtained using a Heraeus CHN analyzer (Germany) instrument. Thermal gravimetric analyses (TGA) were recorded using a thermal analysis Perkin Elmer (Pyris Diamond model) instrument, with  $\pm 0.1~^\circ\text{C}$  and  $\pm 0.2~\mu\text{g}$  precisions in temperature and mass measurement, respectively.

Densities,  $\rho$ , were measured using an Anton Paar DMA 5000 vibrating tube densimeter and viscosities,  $\eta$ , were measured using an Anton Paar MCR 300 rheometer.

#### Synthesis procedures

General procedure for synthesis of imidazolium-based compounds (1a and 2a). To a vigorously stirred solution of 1methylimidazole or 1-vinylimidazole (30 mmol) in toluene (20 mL) at 0 °C was added 3-chloro-1-propene (2.85 mL, 35 mmol). The solution was heated to reflux at 110 °C for 24 hours, after which the toluene was decanted and the remaining viscous liquid washed with *n*-hexane and dried under vacuum to give a yellow or red viscous liquid (1a or 2a) in approximately 90% yield.

General procedure for synthesis of ammonium-based compounds (4a–7a). 2-Azido-*N*,*N*-dimethylethyl amine (DMAZ) was prepared according to a literature method in which 2-chloro-*N*,*N*-dimethyl ethanol amine hydrochloride was reacted with sodium azide in water, followed by ether extraction to get a good yield.<sup>10</sup>

Ammonium-based salts (4a–7a) were prepared by alkylation of DMAZ (3) with alkyl or allyl halides such as methyl, ethyl, butyl iodide and 3-chloro-1-propene according to the following method.

To a vigorously stirred solution of DMAZ (3.42 g, 30 mmol) in acetonitrile (20 mL) at 0 °C was added alkyl or allyl halide (35 mmol). The solution was heated to reflux at 60 °C for 24 hours, after which the precipitate was filtered, washed with *n*-hexane and dried under vacuum to give a white or cream oil/semi-crystalline product (93% yield).

General procedure for synthesis of halide-functionalized ammonium-based salts (8b and 9b). To a stirred solution of 2-(dimethylamino) ethanol (3.00 mL, 30 mmol) in acetonitrile (20 mL) at 0 °C was added methyl iodide (1.86 mL, 35 mmol) or 3chloro-1-propene (2.85 mL, 35 mmol). The solution was heated to reflux at 60 °C for 12 hours, after which the precipitate was filtered, washed with *n*-hexane and dried under vacuum to give a white or cream solid product (8a and 9a, 93% yield).

Compounds **8b** and **9b** were prepared by reaction of **8a** and **9a** with thionyl chloride. A solution of the ammonium-based salt (**8a** or **9a**) (30 mmol) in chloroform (20 mL) was cooled in an icewater bath and a solution of thionyl chloride (4.41 mL, 37.5 mmol) in chloroform (20 mL) was added dropwise with stirring. After the mixture was left at reflux for 3–4 hours, the precipitate was filtered. The crude product was purified by dissolving it in boiling ethanol and then the impurities were separated by filtration. The product was dried under vacuum to give a yellow (**8b**, 86% yield) or light brown (**9b**, yield: 81%) solid. General procedure for synthesis of ammonium-imidazolium based compounds (10a–13a). 1-Methylimidazole or 1-vinylimidazole (30 mmol) was slowly added into a stirred solution of halide-functionalized ammonium salt (8b or 9b) (35 mmol) in acetonitrile (30 mL). The reaction mixture was heated to reflux at 110 °C for 24 hours to give a semi-crystalline liquid. The product was washed with a mixture of acetonitrile and ethyl acetate (50 : 50) and dried under vacuum at 80 °C to give a yellow viscous (10a and 11a) or dark red (12a and 13a), semicrystalline liquid in approximately 90% yield.

General procedure for synthesis of dicyanamide-based ILs. Silver dicyanamide was prepared by mixing equal molar amounts of silver nitrate and sodium dicyanamide in aqueous solutions followed by filtration. The dicyanamide-based ILs were prepared by metathesis of corresponding salts with silver dicyanamide according to a literature method.<sup>31</sup>

#### Results and discussion

In this study, the ammonium and imidazolium mono and dicationic based ionic liquids were synthesized using a multistep synthetic route (Scheme 1).

The structures of these ionic liquids were elucidated using NMR spectroscopy, FTIR spectrometries and elemental analysis. The compounds **1b**, **2b**, and **4b** were previously reported in the literature.<sup>32–34</sup> However, these salts were synthesized and their properties were studied under the same experimental conditions for the sake of comparison.

The energetic performance of ILs in practical applications is determined by their properties such as melting or decomposition point, density, viscosity, detonation properties or even sensitivity, which vary by different substituents and energycontaining groups in their structures. Thus, some important properties of synthesized DCHILs were measured and the results are discussed below.

# Density and viscosity of the synthesized dicyanamide-based ILs

The first part of this work consisted of density and viscosity measurements at atmospheric pressure. The densities and viscosities of all the synthesized dicyanamide-based ILs were measured under the same experimental condition and the results are presented in Table 1.

Density reflects the energy performance of energetic materials. Generally, compounds with higher density have higher energy contribution due to a higher mole number that can be packed into a limited volume. Moreover, the cationic and anionic structures of the energetic ILs have direct effects on the density of the salts. The density of ILs containing the same anion structure depends on three different aspects of cation structure:<sup>35</sup> (i) the length of the substituted alkyl chain, (ii) the functionalization of the chain with hydrophilic groups, and (iii) the head group of the cation. In addition, the presence of the energetic groups such as  $-NO_2$ ,  $-N_3$ , and -CN increase strong H-bond interactions in molecules and as a result the density of the compound can increases.

Table 1 Properties of the synthesized hypergolic ionic liquids

Entry	Compound	T <sub>onset</sub> (°C)	ho (g cm <sup>-3</sup> )	η (cP)	ID (ms)	Ref.
1	1b	211.12	1.13	112.9	16	32
2	2b	208.23	1.15	30.3	13	33
3	4b	182.20	1.19	81	35	This work
4	5b	182.34	1.21	93	73	34
5	6b	157.96	1.03	101	51	This work
6	7b	200.60	1.13	71	43	This work
7	10b	252.32	1.23	180	52	This work
8	11b	235.78	1.25		63	This work
9	12b	226.19	1.17	570	41	This work
10	13b	217.66	1.18	368	36	This work

In agreement with this approach, the azide-functionalized ILs (entries 3–6) show higher density compared to imidazolium based salts (entries 1 and 2). As can be seen from Table 1, the densities decreases with increasing length of the hydrocarbon linkage chain (entry 5). It is also clear from table that the density for the dicationic ILs is higher than that for monocationic ILs when the dicationic ILs are compared to the monocationic ILs with the identical anions (entries 7–10). It is depended on the differences in van der Waals volumes for dicationic and monocationic ILs.

The viscosity of energetic ILs is one of the important issues influencing the performance of the compounds. The high viscosity may be caused by the presence of a strong H-bonded network as well as strong interactive forces such as electrostatic or van der Waals interactions. Hence, the viscosities of all the synthesized compounds were measured. The results show that imidazolium-based ILs have lower viscosities compared to azidefunctionalized ones. On the other hand, when the dicationic ILs are compared to monocationic ones having the same anions, the viscosity in the dicationic ILs is much larger than that in the monocationic ones (Table 1, entries 7–10). This may be due to the stronger interionic and interamolecular interactions as well as more bulky cations in the dicationic ILs than monocationic ones, which certainly gives low mobility and high viscosity.<sup>34</sup>

#### Thermal behaviour of the synthesized dicyanamide-based ILs

The thermogravimetric analysis (TGA) of all the synthesized dicyanamide-based ILs was carried out in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The results of TGA are depicted in Fig. 1 and the corresponding values are shown in Table 1. Thermal stability of ILs is directly linked to the nature of the anions and cations. Generally, ILs containing more nucleophilic and coordinated anions decompose at lower temperatures while ILs with poor proton withdrawing anions are more stable to high-temperature decomposition.<sup>36–38</sup> The decomposition temperature of ILs also depends on the type of the cations. Most studies have shown that imidazolium-based ILs are thermally more stable than pyridinium and quaternary ammonium-based ones.<sup>39,40</sup> This may be due to the fact that the imidazolium groups have better positive charge dispersion than does the pyridine group, which give them a stronger attraction



Fig. 1 TGA curves for the synthesized ILs: (A) imidazolium-based ILs, (B) ammonium-based ILs, (C) ammonium-imidazolium-based ILs.

to anions. The dicationic ILs are also thermally more stable than monocationic ones with identical anions.<sup>41,42</sup> The higher thermal stability of dicationic ILs is also associated with the better positive charge dispersion balanced by two separated monoanions, which gives them a stronger attraction to the anions.<sup>41,42</sup> In addition, the observed higher thermal stability of dicationic ILs is attributed to the greater charge and intermolecular interactions, their higher molecular weight, higher density and smaller free volume. TGA results showed that allyl or vinyl functionalized ILs (Table 1, entries 2, 6, 8 and 10) exhibited slightly lower thermal stabilities than common dicyanamide-based ones (Table 1, entries 1, 3–5, 7 and 9), attributed to the rigidity of these groups.<sup>34</sup>

The exact mechanism of thermal ionic liquid degradation is not straightforward since multiple parameters must be taken



Scheme 2 Proposed mechanisms of thermal decomposition of 12b.

into account. Thus, the decomposition mechanisms are subject to multiple simultaneous initiation reactions (hemolytic cleavage and proton transfer), autocatalytic effects and finally, competing reaction pathways with different reaction rates dependent on temperature and the heating rate.<sup>43,44</sup> The suggested decomposition mechanisms and thermal degradation products of **12b** are shown in Scheme 2. It seems that, at the first stage of decomposition, the linkages of dicyanamide anions with corresponding cations are cleavage. Afterwards the cations are dissociated to smaller fragments such as imidazole derivatives, amines, cyanides, ethylene, acetylene and *etc.* 

#### Hypergolic test

To evaluate the potential hypergolic characteristics of the synthesized dicyanamide-based ILs and measure their actual ignition delay (ID) time, the droplet test was used.<sup>2,45</sup>

Using a pipette, the IL sample (10–50  $\mu$ L) was transferred into a vial containing excess (1.5 mL) white fuming nitric acid (WFNA). A high speed camera was used to record the ignition process. The dicationic compounds are semi-crystalline liquids or solids at room temperature (Table 1, entries 7–10), hence, we decided to subject them to drop test while these ILs were heated until clear liquids were obtained. In reality, the melted salts are not classified as hypergolic. Nevertheless, they can be used as additives in hypergolic room temperature IL mixtures to improve their properties. Fig. 2 shows typical observation of the synthesized dicyanamide-based ILs in contact with WFNA. The ID values of the studied ILs are represented in Table 1. The reaction of ammonium and imidazolium-based ILs (Table 1, entries 1, 2 and 3–6) are quite similar to those observed in ammonium-imidazolium based salts (Table 1, entries 7–10).

As previously reported, the unsaturated side chains initiate or promote hypergolic ignition.<sup>9</sup> Therefore, among the synthesized ILs, compounds with allyl or vinyl unsaturated substitute show lower ID times. In general, the dianionic ILs (Table 1, entries 7– 10) showed longer ignition durations than the monocationic ones (Table 1, entries 1, 2 and 3–6), which probably demonstrates the higher energy content of the corresponding salts.



Fig. 2 The ID test processes of ammonium-imidazolium-based ILs shown with high speed camera photos.

## Conclusions

A series of ammonium and imidazolium-based ILs as well as unsymmetrical ammonium-imidazolium based dicationic ILs containing dicyanamide anion were successfully synthesized and their chemical structures were characterized by NMR, FTIR spectroscopies and elemental analysis. Dianionic ILs are more thermally stable than monocationic ones. In addition, the melting points of dianionic ILs are substantially higher than those of monocationic compounds, which is probably due to the better positive charge dispersion in dianionic ILs giving them a stronger attraction to the anions.

The synthesized ILs showed tremendous hypergolic activities with WFNA. In the context of our drop test conditions, the dianionic ILs represent longer ignition duration probably due to the higher energy content of these salts.

The ammonium and imdazolium based ILs are not liquid at room temperature, but they were subjected to the drop tests as heated liquids. These salts cannot be labelled as hypergolic fuels, nevertheless they can be used as additives in hypergolic IL mixtures.

### Acknowledgements

We gratefully acknowledge the financial support by Malek-Ashtar University of Technology (MUT).

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