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# Synthesis and thermal characterization of new ammonium–imidazolium dual dicyanamide-based ionic liquids

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ABSTRACT

Novel dual dicyanamide-based ionic liquids consisting of coupled ammonium–imidazolium cationic structures were synthesized and their thermal properties were studied. The molecular structures of these compounds were identified by NMR, FT-IR and CHN analysis. Viscosity measurements showed that the new ionic liquid with vinylimidazolium group has lower viscosity than the ionic liquid with methylimidazolium group. However, the densities of the new synthesized compounds are almost same.

Thermal behaviors and heat capacities of these ionic liquids were also investigated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). The results suggest that the new ionic liquids have thermal stabilities up to 200 °C, as well as reasonable heat capacities in the range 25 to 100 °C.

## 1. Introduction

Research on ionic liquids (ILs) has been rapidly growing in the past decades, focusing on the development of organic chemistry and chemical technology [1]. Ionic liquids are organic salts that are liquids at room temperature with low vapor pressures. In addition, ILs are also characterized by liquidity over a wide temperature range, high thermal and chemical stability, good ionic conductivity, non-flammability, recyclability and structural design ability [2]. Due to their unique properties, ILs have been widely used in a variety of chemical and industrial applications such as conventional organic solvents in organic synthesis [3], extractions [4], liquid–liquid extractions [5], enzymatic reactions [6], electrochemical studies [7], dye-sensitized solar cells [8], as buffer additives in capillary electrophoresis [9], as stationary phases in gas–liquid chromatography [10], as electrolytes in battery systems, solar cells and electrochemical capacitors [11,12].

Recently, a series of ILs, namely dicationic ILs, in which two monocations are combined into a dication have been developed [13–16]. Dicationic ILs (DCILs) have been shown to possess superior physical properties in terms of thermal stability, and tunability compared to traditional ILs. Consequently, they have been proposed as high temperature lubricants [15,16], solvents in high temperature reactions [15–17], additives in dye-sensitized solar cells [18], extraction liquids [19] in chromatography [20–22], in mass spectroscopy [23], and as electrolytes for secondary batteries [15].

In general, DCILs have been classified as germinal (when the two mono-cations that form the dication are the same) or unsymmetrical (when the mono-cations are different). So, the number of possible combinations of cations and anions in DCILs is greater than that in monocationic ILs.

Actually, DCILs would be rather fascinating research targets. The main reason for this growing interest seems to lie in the opportunity to design their structures with respect to cations, anions, and length of linker chain between the two cations to achieve desired properties according to specific tasks [24–26].

Over the last decade, high temperature applications of ILs have become more attractive, such as in thermal fluids and electrolytes for solar cells or fuel cells [8,11,12]. Accordingly, much attention has been paid to the synthesis of ionic liquids with desired thermal and chemical properties.

Among them, ionic liquids containing the dicyanamide anion, regardless of the cation counterpart, have special properties that make them very attractive [27]. Low viscosities render them easy to handle and facilitate operations such as mixing and filtering [28]. Thermal and electrochemical stabilities allow them to be good alternatives to organic solvents as well as their role as catalysts in some reactions [29,30]. Furthermore, dicyanamide-based ILs have shown special properties in energetic ionic liquids and liquid–liquid extraction of aromatics from aliphatic/aromatic mixtures [31–33]. Since these applications often require high stability at high temperature, it is essential that thermal stability of ILs is determined.

Therefore, thermophysical properties of 1-butyl-3-methylimidazolium dicyanamide, which can be used as energetic ionic liquid or solvent in

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chemical reactions, were investigated and all results confirmed the good thermal stability of this ionic liquid [34–40]. Recent research on some cyano-based ionic liquids showed that these ILs have high thermal stabilities and can be used as new green alternatives to currently used conventional organic extraction solvents, such as sulfolane [41]. In addition, thermal properties of 1-ethyl-3-methylimidazolium dicyanamide and 1-ethyl-4-methylpyridinium bis (trifluoromethyl sulfonyl) imide ionic liquid mixture were investigated and results showed that this mixture can be used as a solvent in separation of aromatic hydrocarbon compounds [31].

Although dicyanamide-based ILs have desirable properties, there have been no reports on the synthesis of dicyanamide-based dicationic ILs.

With regard to this point and in our continued interest in the synthesis and application of ionic liquids [42,43], synthesis and characterization of a new series of dual dicyanamide-based DCILs are reported here. Characterization of synthesized DCILs was carried out by the use of NMR and FT-IR spectroscopies as well as CHN analysis. Their physical properties such as density and viscosity were characterized to qualitatively estimate ion association, polarity, and hydrogen-bonding interaction. Furthermore, their thermal stabilities and heat capacities were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC), allowing for a deeper understanding of these ILs.

## 2. Experimental

### 2.1. Reagents and instruments

All of the solvents and chemicals were purchased from Sigma-Aldrich and were used without further purification. All the synthesized compounds and DCILs were characterized by $^1$H and $^{13}$C-NMR spectroscopy using a Bruker DRX-300 instrument. Chemical shifts were reported relative to TMS as an internal standard. FT-IR spectra were obtained on a Nicolet 800 instrument. Elemental analyses were obtained using a Heraeus CHN analyzer (Germany) instrument. Thermal gravimetric analyses (TGA) were recorded using a thermal analysis instrument, Perkin Elmer (Pyris Diamond model). Runs were carried out in 40 μL alumina pans and under an inert atmosphere of nitrogen. Nitrogen flow was 20 mL · min$^{-1}$. Initial mass introduced in the pan was set at 10 ± 1 mg. Dynamic measurements were conducted at 25 to 500 °C.

The heat capacities of ILs were performed using a differential scanning calorimeter (DSC) in a Perkin Elmer instrument (Pyris 6 DSC model). Same as TGA, the measurements were carried out using 10 ± 1 mg of sample and under an inert atmosphere of nitrogen. The experiments were performed in the range from 25 to 100 °C, with a 20 °C · min$^{-1}$ heating rate.

Densities, ρ, were measured using a Anton Paar DMA 5000 vibrating tube densimeter, whereas viscosities, η, were analyzed using a Anton Paar MCR 300 rheometer with a cp 25-2 fixture (25 mm diameter, 2° cone angle) at 500 1/s constant shear rate. Density and viscosity measurements were carried out at atmospheric pressure and temperature in the range of 25 to 80 °C.

### 2.2. Synthesis procedures

#### 2.2.1. Synthesis of N-(2-hydroxyethyl)-N, N-dimethyl prop-2-en-1-ammonium chloride [I]

To a stirred solution of 2-(dimethylamino) ethanol (10 mmol, 0.89 g) in acetonitrile (20 mL) was added 3-chloropropene (12 mmol, 0.92 g) drop wise at 0 to 5 °C. The reaction mixture was stirred for 12 h at 60 °C. Removal of the solvent under reduced pressure afforded crude ammonium-based salt. The crude product was purified by salting out in mixture of acetonitrile and n-hexane. Finally, the resulting light brown salt was dried under vacuum at 80 °C for 5 h (mp: 48–53 °C and yield: 93%). The first step of Scheme 1 represents the synthesis of ammonium-based salt [I].

Spectroscopic data for salt [I]: $^1$H NMR (300 MHz, $D_2O$): $\delta = 5.76$ (m, 1H; CH), 5.64 (dd, $J = 16.62$ Hz, 1H; CH), 5.46 (dd, $J = 10.81$ Hz, 1H; CH), 3.91 (m, 2H; $CH_2$), 3.72 (t, $J = 7.11$ Hz, 2H; $CH_2$), 3.30 (t, $J = 7.24$ Hz, 2H, $CH_2$), 3.00 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $D_2O$): $\delta =$ 129.12, 124.19, 67.18, 64.49, 55.08, 50.62. IR (KBr, $\mathcal{V}$/cm$^{-1}$): 3404.6, 3067.4, 2848.6, 1636.1, 1488.2, 1334.5, 1188.6, 1050.6, 877.1, and 752.9. Anal. calcd. for $C_7H_{16}ClNO$ (165.5): C, 50.75; H, 9.66; N, 8.45%; found: C, 50.63; H, 9.57; N, 8.36%.

#### 2.2.2. Synthesis of N-(2-chloroethyl)-N, N-dimethyl prop-2-en-1-ammonium chloride [II]

To a stirred solution of ammonium-based salt obtained from previous step (10 mmol, 1.65 g) in chloroform (20 mL) was added thionyl chloride (12.5 mmol, 1.47 mL) drop wise at 0 to 5 °C. The reaction mixture was stirred for 4–5 h at 65 °C. After this step, the product was obtained by evaporation of chloroform under reduced pressure. The crude product was purified by dissolving it in boiling ethanol, and then the impurities were separated by filtering. Ethanol was removed from the mixture by vacuum evaporation at 60 °C. Finally, the resulting brown viscose liquid was dried under vacuum at 80 °C for 3 h (yield: 98%). The second step of Scheme 1 represents the synthesis of compound [II].

Spectroscopic data for compound [II]: $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 6.00$ (m, 1H; CH), 5.68 (dd, $J = 16.84$ Hz, 1H; CH), 5.57 (dd, $J = 10.10$ Hz, 1H; CH), 4.13 (m, 2H; $CH_2$), 4.11 (t, $J = 7.68$ Hz, 2H; $CH_2$), 3.77 (t, $J = 7.31$ Hz, 2H, $CH_2$), 3.13 (s, 6H, $CH_3$).$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta =$ 127.95, 125.84, 65.64, 62.68, 49.90, 38.65. IR (KBr, $\mathcal{V}$/cm$^{-1}$): 3010.3, 2933.4, 1636.1, 1472.5, 1336.4, 1275.3, 1149.1, 1001.3, 758.8, and 701.6. Anal. calcd. for $C_7H_{15}Cl2N$ (184): C, 45.65; H, 8.15; N, 7.60%; found: C, 45.33; H, 8.06; N, 7.51%.

#### 2.2.3. Synthesis of 3-(2-allyldimethylammonio)ethyl-1-methyl-1-H-imidazol-3-ium dichloride [IL-1]

1-Methyl imidazole (12 mmol, 0.98 g) was slowly added to the ammonium-based compound [II] (10 mmol, 1.84 g) in acetonitrile (20 mL). The reaction mixture was stirred for 18–24 h at 70 °C, during this time a reddish viscose liquid was formed. The IL-1 mass was washed three times with a mixture of acetonitrile and ethyl acetate. After being under vacuum at 80 °C for 5 h, the pure product was obtained (yield: 91%). The third step of Scheme 1 represents the synthesis of [IL-1].

Spectroscopic data for [IL-1]: $^1$H NMR (300 MHz, $D_2O$): $\delta = 8.33$ (s, 1H; CH), 7.27 (d, $J = 10.02$ Hz, 1H; CH), 7.24 (d, $J = 10.12$ Hz, 1H; CH), 5.88 (m, 1H; CH), 5.63 (dd, $J = 13.29$ Hz, 1H; CH), 5.57 (dd, $J = 9.52$ Hz, 1H; CH), 3.90 (m, 2H; $CH_2$), 3.77 (s, 3H; $CH_3$), 3.63 (t, $J = 6.59$ Hz, 2H; $CH_2$), 3.37 (t, $J = 6.62$ Hz, 2H, $CH_2$), 3.02 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $D_2O$): $\delta =$ 135.95, 129.16, 123.37, 122.41, 121.77, 66.97, 56.92, 49.96, 41.72, 35.54. IR (KBr, $\mathcal{V}$/cm$^{-1}$): 3097.8, 2933.4, 16,035.9, 1580.1, 1523.7, 1470.9, 1336.4, 1284.9, 1234.0, 1011.0, 832.1, and 799.2. Anal. calcd. for $C_{11}H_{21}C_{l2}N_3$ (266): C, 49.62; H, 7.89; N, 15.78%; found: C, 49.54; H, 7.81; N, 15.68%.

#### 2.2.4. Synthesis of 3-(2-allyldimethylammonio)ethyl-1-vinyl-1-H-imidazol-3-ium dichloride [IL-2]

1-Vinylimidazole (12 mmol, 1.13 g) was slowly added to the ammonium-based salt (10 mmol, 1.84 g) in acetonitrile (20 mL). The reaction mixture was stirred for 18–24 h at 70 °C to form IL-2. The IL-2 mass was washed three times with a mixture of acetonitrile and ethyl acetate. After being under vacuum at 80 °C for 5 h, a reddish viscose liquid was obtained (yield: 88%). The third step of Scheme 1 represents the synthesis of [IL-2].

Spectroscopic data for [IL-2]: $^1$H NMR (300 MHz, $D_2O$): $\delta = 8.38$ (s, 1H; CH), 7.84 (d, $J = 9.69$ Hz, 1H; CH), 7.80 (d, $J = 9.80$ Hz, 1H; CH), 7.02 (m, 1H; CH), 5.92 (m, 1H; CH), 5.64 (dd, $J = 15.70$ Hz, 1H; CH), 5.62 (dd, $J = 8.38$ Hz, 1H; CH), 5.55 (dd, $J = 13.51$ Hz, 1H; CH),