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The effect of counteranion on the physicochemical and thermal properties of 4-methyl-1-propyl-1,2,4-triazolium ionic liquids

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ABSTRACT

Temperature-dependent physicochemical properties such as viscosity, molar conductivity and density, as well as short- and long-term thermal stabilities, as determined by thermogravimetric analysis, are reported for a series of 4-methyl-1-propyl-1,2,4-triazolium ionic liquids where the counteranion was varied ([I], [NO₃], [OMs], [OTs], [BF₄], [OTf] and [NTf₂]). In general, use of the poorly coordinating anions [NTf₂] and [OTf] led to the lowest ionic liquid viscosities and highest molar conductivities. All of the 1,2,4-triazolium ionic liquids studied were classified as 'good' ionic liquids after Walden plot analysis; however use of the [OTs] anion led to the poorest overall ionic liquid performance, presumably due to the introduction of π - π interactions from the aromatic ring. Temperature-ramped TGA experiments revealed that strongly coordinating anions such as [I] and [NO₃] resulted in the lowest T_{onset} values (<210 °C) while poorly coordinating anions such as [NTf₂] and [OTf] led to T_{onset} values in excess of 330 °C. Results from long-term, isothermal TGA analysis indicated that all of the ILs exhibited decomposition well below the observed T_{onset} as reflected in their $T_{0.01/10}$ values.

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1. Introduction

Ionic liquids continue to attract great interest across a wide range of potential applications due to their tunable physicochemical and thermal properties. While the majority of ionic liquid research has focused on the imidazolium, ammonium and phosphonium cations, a strong desire remains to explore other cations in order to achieve a more diversified portfolio for application-specific materials. Towards this end, ionic liquids that are based upon 1,2,3- and 1,2,4-triazolium heterocycles have gained increased interest, especially in energy-rich applications such as explosive and propellant fuels, due to their large, positive heats of formation (compared to the imidazolium cation), reduced melting points, high densities and improved thermal stabilities [1–3].

Much of the work reported to date concerning 1,2,4-triazolium ionic liquids has focused on designing materials specific for electrochemical or other energy-rich applications [3–7]. For example, Shreeve has investigated and reviewed the physical properties of a number of 'energetic' ionic liquids, several of which were derived from amino-, nitro- or azido-substituted 1,2,4-triazolium cations with high energy anions such as nitrate or perchlorate [3,8–10]. Most of these ionic liquids were found to exhibit high combustion energies, good thermal stabilities and high densities (> 1.50 g/mL). More recently, the thermal properties and ignition delays of several 1,2,4-triazolium dicyanamide ionic

liquids were evaluated for their potential use as hypergolic fuels by Rogers [11]. The triazolium ionic liquids were found to have longer ignition delays when compared to analogous imidazolium, pyridinium and pyrrolidinium systems. A series of 1,2,4-triazolium ionic liquids have also been evaluated for carbon dioxide permeability/solubility by Dai and co-workers [12]. Thermal stabilities and carbon dioxide capture capabilities of the triazolium ionic liquids of interest were observed to be similar to imidazolium ionic liquid analogs.

In all of these studies, the ability to appropriately create 'designer' ionic liquids for a specific end application depends upon the ability to successfully correlate physicochemical and thermal properties with changes in cation and anion structure. As a result, gaining a better understanding of the ionicity (the effective fraction of ions available for conduction) for different cation–anion combinations has become paramount. A number of research groups have used Walden plots as a viable method for correlating ionicity and ionic liquid structure [13–17]. The logarithmic Walden plot, which is derived from the classical Walden rule, correlates molar conductivity (Λ_m) with reciprocal viscosity (η^{-1}). The resulting linear relationship for any given ionic liquid is then compared with an 'ideal line' (based upon the properties of a dilute, aqueous solution of KCl) [18,19]. The ionicity of the ionic liquid, as well as the relative classification of the material as 'superionic', 'good ionic' or 'subionic', can then be determined from this comparison. Generally speaking, 'good' ionic liquids are those that consist of poor cation–anion interactions (commonly prepared when bulky, organic cations are combined with bulky and/or non-coordinating anions). These ionic liquids are often characterized by their reduced melting points and viscosities as well as improved conductivities.

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A Walden plot analysis was recently completed in our laboratory to investigate the physicochemical properties of a series of 1-alkyl-4-methyl-1,2,4-triazolium bis(trifluoromethylsulfonyl)imide ionic liquids where the length of the *N*-1 alkyl side chain was varied from ethyl (C2) to dodecyl (C12) [20]. Viscosities of the ionic liquids were found to increase with increasing alkyl chain length; however molar conductivities were found to decrease. Both of these trends were attributed to an increase in van der Waals interactions as the alkyl chain length increased. All of the 1-alkyl-4-methyl-1,2,4-triazolium bis(trifluoromethylsulfonyl)imide ionic liquids were classified as 'good' ionic liquids from the Walden plot analysis, with use of the smaller alkyl chains (ethyl or propyl) resulting in the best overall performance.

Thermal stability is another important property that is commonly attributed to ionic liquids. Temperature-ramped thermogravimetric analysis (TGA) is the most commonly used technique for the determination of thermal stability, allowing for the determination of relative, short-term stability (T_{onset} and/or $T_{\text{d}5\%}$). While T_{onset} values are typically extrapolated from the steepest portion of the resultant thermograph, $T_{\text{d}5\%}$ represents the temperature at which 5% of the ionic liquid has decomposed. Although these thermal properties are widely reported for a large number of ionic liquids, the values differ widely between research groups due to a number of variables that are associated with a temperature-ramped study (ramp rate, gas purity, flow rate, sample mass, etc.) [21,22]. Additionally, T_{onset} and $T_{\text{d}5\%}$ consistently overestimate the thermal stability of ionic liquids since thermal decomposition is known to occur well below these temperatures [23,24].

'Isothermal' TGA experiments have become a more reliable (albeit time consuming) tool to determine and estimate long-term thermal stability. At a constant temperature, weight loss is monitored over a period of time, resulting in a linear correlation that follows pseudo-zeroth-order kinetics. The decomposition of an ionic liquid at any given temperature and time can then be determined and is commonly reported as ' $T_{x/z}$ ', where *x* is the extent of decomposition (typically this is 0.01 or 1%) and *z* is the length of time (e.g., 10 h) [23]. Several research groups have highlighted the utility of $T_{0.01/10}$ for various imidazolium ionic liquids and all of the reported values were found to be well below the corresponding T_{onset} [23–27]. We have also demonstrated the utility of isothermal TGA experiments for the previously mentioned 1-alkyl-4-methyl-1,2,4-triazolium bis(trifluoromethylsulfonyl)imide ionic liquid series [20]. Long-term thermal stability, as defined by $T_{0.01/10}$, was found to generally increase with increasing alkyl chain length.

We have now turned our attention to the effect that the counteranion has on the ionicity and long-term thermal stabilities of 1,2,4-triazolium ionic liquids. In this study, we chose 4-methyl-1-propyl-1,2,4-triazolium as the standard cation in combination with a wide range of commonly used anions: iodide [I], nitrate [NO₃], tetrafluoroborate [BF₄], mesylate [OMs], tosylate [OTs], triflate [OTf] and bis(trifluoromethylsulfonyl)imide [NTf₂]. Temperature-dependent viscosities, densities and molar conductivities have been determined and analyzed using a Walden plot. Thermal properties (DSC) and thermal stability data (short- and long-term TGA experiments) are also reported and the results are discussed.

2. Materials and methods

2.1. General experimental methods

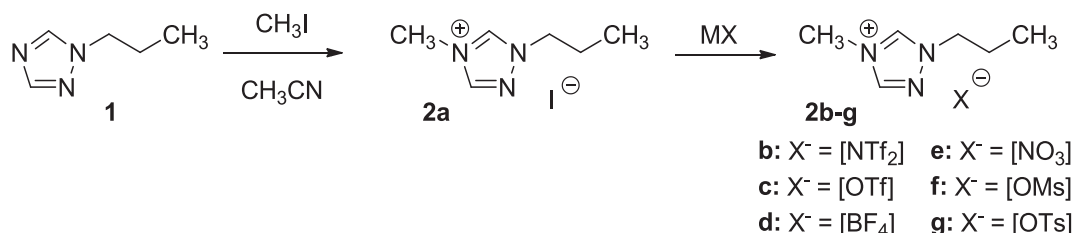
All commercial reagents were used without further purification. All solvents were of reagent or HPLC grade. Water having a resistivity of 18 MΩ-cm was used in all reactions involving ionic liquids. All ionic liquids were stored in a vacuum oven at 40–60 °C for 48 h prior to the determination of any of the physicochemical or thermal measurements reported below. ¹H and ¹³C NMR spectra were obtained on a JEOL 400 MHz spectrometer at ambient temperature and chemical shift values are reported in parts per million relative to using residual solvent signals as internal standards (DMSO-*d*₆: ¹H, 2.50 ppm; ¹³C, 39.52 ppm). Water content was determined by volumetric Karl-Fisher titration and/or thermogravimetric analysis (temperature ramped TGA), the results of which indicated levels below 100 ppm.

2.2. Measurement of physical properties

Temperature-dependent viscosities were measured on a Brookfield LVDV2T-CP cone and plate viscometer with a minimum volume requirement of 0.5 mL. The temperature was controlled to ±0.1 °C with a Brookfield TC-550 circulating water bath and monitored by a thermocouple located inside the plate of the viscometer. The sample was allowed to equilibrate for 5 min at the desired temperature prior to any measurement taken. All viscosity experiments were performed in duplicate, resulting in an average relative standard deviation of 1.85%. Temperature-dependent conductivities were measured using a custom apparatus built in-house which utilized an ET915 miniature Dip-In Conductivity Electrode (eDAQ) [20]. Duplicate conductivity tests resulted in an average relative standard deviation of 1.98%. Temperature-dependent densities were measured using an Anton-Parr DMA 4100M instrument over a range from 25 to 80 °C. Density measurements were found to be reproducible within ±0.001 g/mL.

2.3. Measurement of thermal properties

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 instrument under a nitrogen atmosphere (flow rate of 50 mL/min) using aluminum pans at a heating rate of 2 °C/min on 5–8 mg samples. All thermal transitions reported here were measured on the second heating and experiments were completed in duplicate (error of ±2 °C). Temperature-ramped thermal stabilities (T_{onset} and $T_{\text{d}5\%}$) were studied under a constant nitrogen flow (flow rate of 35 mL/min) using a thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min on 4–8 mg samples using platinum pans. Samples were first heated to 100 °C and held for 2 h prior to the beginning of the experiment to ensure that the samples were dry. All experiments were completed in duplicate (error of ±2 °C). Isothermal TGA experiments were conducted on a TA Instruments Q500 under a constant nitrogen flow on 6–8 mg samples. Samples were first heated to 100 °C and held for 2 h for drying purposes. The temperature was then increased to the desired isothermal temperature at a rate of 5 °C/min.



Scheme 1. Synthesis of 4-methyl-1-propyl-1,2,4-triazolium ionic liquids 2a-g.

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