THE JOURNAL OF
PHYSICAL CHEMISTRY B

Article

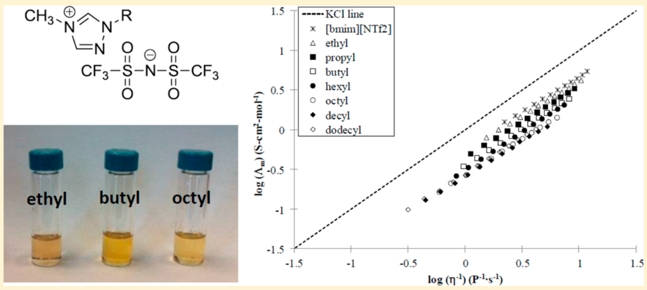
pubs.acs.org/JPCB

Physicochemical and Thermal Properties for a Series of 1-Alkyl-4-methyl-1,2,4-triazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids

Andreah T. De La Hoz, Ulises G. Brauer, and Kevin M. Miller*

Department of Chemistry, Murray State University, Murray, Kentucky 42071, United States

S *Supporting Information*



ABSTRACT: Physicochemical properties and long-term thermal stabilities are reported for a series of 1-alkyl-4-methyl-1,2,4-triazolium $[NTf_2]$ ionic liquids, and a Walden plot analysis was conducted in order to determine the ionicity of these materials. In general, viscosities were found to increase with increasing alkyl chain length while densities and molar conductivities were found to decrease. The 1,2,4-triazolium ionic liquids were classified as "good" ionic liquids after analysis of the Walden plot; however, they did not perform as well as the standard imidazolium ionic liquid $[bmim][NTf_2]$. Thermal properties from DSC and TGA experiments were also completed. 1,2,4-Triazolium ionic liquids with an alkyl chain length of octyl (C8) or less exhibited a single T_g transition below −70 °C; however, the decyl (C10) and dodecyl (C12) systems exhibited a T_m value. No correlation between T_{onset} or $T_{d5\%}$ and alkyl chain length was observed during short-term, temperature-ramped TGA experiments. However, long-term, isothermal TGA studies indicated a general increase in $T_{0.01/10}$ value as the alkyl chain length increased. Both short- and long-term TGA studies indicated that the 1,2,4-triazolium ionic liquids were not as thermally stable as the model imidazolium ionic liquid $[bmim][NTf_2]$.

■ INTRODUCTION

Research in ionic liquids (ILs) has grown exponentially over the past decade because of their tunable physicochemical properties and wide range of potential applications. Properties that have drawn attraction to ILs have included reduced volatility and flammability, wide electrochemical window, and increased thermal stability.[1−5] While the imidazolium cation remains a benchmark for a number of these desirable characteristics, there remains a strong desire to explore ionic liquid classes that are based upon other heterocycles in order to satisfy specific application requirements.[6,7] Nitrogen-rich ionic liquids, such as those based upon the 1,2,3- or 1,2,4-triazolium ring, have gained increased interest due to their potential applicability in energy-rich applications. The triazolium ring has been found to exhibit large, positive heats of formation (compared to the imidazolium ring) as well as enhanced densities, improved thermal stabilities, and reduced vapor pressures, all attributes of which are considered to be advantageous over nonionic "energetic" materials currently used.[8,9]

Despite the ease in which the 1,2,4-triazole heterocycle can be alkylated at the *N*-1 and *N*-4 positions, research on 1,2,4-triazolium ionic liquids has been rather limited, and reports have primarily focused on materials specifically designed for energetic or electrochemical applications.[8,10,11] For example, Shreeve and co-workers have generated a number of "energy-rich" ionic liquids where 1,2,4-triazolium cations substituted with amino, nitro, or azido functional groups were matched with high energy anions such as perchlorate or nitrate.[12] Thermal properties and miscibilities of a number of fluorinated 1,2,4-triazolium ionic liquids have also been reported by Shreeve.[13] More recently, Strasser has explored the tunability of arylated or alkylated 1,2,4-triazolium ionic liquids.[14]

We have also been active in the area of 1,2,4-triazolium ionic liquids. Recently, we reported fundamental correlations between the thermal properties (melting point (or glass transition) and thermal stability) and structural changes (alkyl chain length and/or counteranion) of a series of 1-alkyl-4-methyl-1,2,4-triazolium ionic liquids.[15] As part of this structure−activity study, we determined that T_g/T_m values generally increased with longer alkyl chain lengths at N-1 but generally decreased when larger counteranions were employed. Counteranions that were weakly basic were found to provide the greatest resistance to thermal degradation (highest $T_{d5\%}$ values). While this study provided several valuable trends between structure and thermal properties, we wanted to conduct a more comprehensive analysis of these materials by investigating their temperature dependent physicochemical properties (conductivity, viscosity, and density) as well as their long-term thermal stability.

Received: June 5, 2014
Revised: July 30, 2014
Published: July 31, 2014

dx.doi.org/10.1021/jp505592t | *J. Phys. Chem. B* 2014, 118, 9944−9951

The classical Walden rule has been increasingly used as a method for evaluating the ionicity of ionic liquids as well as the classification of these materials as “superionic”, “good ionic”, or “subionic”.[16−21] The Walden plot allows for determination of the ionicity of an ionic liquid by correlating molar conductivity (Λ_m) with viscosity (η) and comparing the resulting linear relationship with an “ideal line” which is based upon the properties of a dilute, aqueous solution of KCl.[22,23] Ionic liquids that exhibit properties near this ideal line are considered to be “good”, where the cations and anions are described as being in a loose, quasi-lattice arrangement.[16] If the properties of the IL result in behavior above the ideal line, it is considered “superionic”, an example of which is liquid $LiAlCl_4$ (T_m = 145 °C).[21] “Subionic” liquids exhibit properties well below the ideal line, resulting from stronger cation−anion pair interactions. While a variety of imidazolium ionic liquids have been analyzed using this methodology, there are no published reports to date that apply the Walden rule to 1,2,4-triazolium ionic liquids.

Thermal stability is another important property that is commonly attributed to ionic liquids; however, care must be taken because most reported values are highly dependent upon the type of experimental conditions that are employed.[24] Thermogravimetric analysis (TGA) is the most widely used instrument for the determination of thermal stability of ionic liquids, and the majority of decomposition temperatures have been determined from “temperature-ramp” experiments. In these experiments, weight loss is monitored as a function of temperature (typically at a rate of 5−20 °C/min) and T_{onset} values are extrapolated from the steepest portion of the thermograph.[25−27] Alternatively, we and others have used $T_{dx\%}$ nomenclature to represent the temperature at which x% of the material has decomposed.[15,28−30] While both of these interpretations are suitable for the determination of relative, short-term thermal stability, the temperature-ramp method is highly dependent upon a number of variables, including heating rate, carrier gas, sample quantity, and the composition of the pan, all of which have contributed to ranges of reported T_{onset} values for several ionic liquids.[31,32] Additionally, the temperature ramp method fails to provide an accurate representation of long-term thermal stability, since degradation typically begins at temperatures significantly lower than T_{onset} or $T_{d5\%}$.[24,33]

“Isothermal” TGA experiments have been used to more accurately portray the long-term stability of ionic liquids and to allow for estimations of degradation rates at temperatures lower than T_{onset}. In this method, weight loss is monitored over a period of time at a constant temperature, yielding a linear correlation that follows pseudo-zeroth-order kinetics. A “$T_{x/z}$” parameter can then be determined for each ionic liquid, 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).[24] There have been several recent reports that highlight the utility of $T_{0.01/10}$ for various imidazolium ionic liquids.[24,25,34,35] Reported $T_{0.01/10}$ values for all examples were found to be well below the corresponding T_{onset}, meaning that the use of isothermal TGA methods may be a more accurate way to determine long-term IL stability.

We report the physicochemical properties and long-term thermal stabilities for a series of 1-alkyl-4-methyl-1,2,4-triazolium ionic liquids. The counteranion bis(trifluoromethylsulfonyl)imide [NTf_2^-] was chosen for all of the ILs studied to ensure that the materials would exist in the liquid range at (or close to) room temperature. As part of this structure−activity study, a variety of alkyl chain lengths were explored, ranging from ethyl (C2) to dodecyl (C12). Conductivity, viscosity, and density measurements of each ionic liquid were determined over a temperature gradient (room temperature to 80 °C), and the Walden rule was applied to determine the ionicity of these materials. Additionally, temperature-ramp and isothermal thermogravimetric experiments were completed for each ionic liquid and a comparative analysis of short- and long-term thermal stability is provided.

EXPERIMENTAL SECTION

General Experimental Methods. All commercial reagents were used without further purification. All solvents were 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 (<0.1 mmHg) at 60 °C for 48 h prior to the determination of any of the physicochemical or thermal measurements reported below. Water content was determined by volumetric Karl Fischer titration or thermogravimetric analysis (temperature ramped TGA), the results of which indicated levels below 100 ppm for all ionic liquids. ^1H and ^{13}C 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; ^{13}C, 39.52 ppm). Elemental analyses were conducted by Atlantic Microlab, Inc.

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 was monitored using an electronic 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 0.68%. Temperature-dependent conductivities were measured using a custom apparatus built in-house which utilized an ET915 miniature dip-in conductivity electrode (eDAQ). A description and schematic of the apparatus can be found in the Supporting Information. Duplicate conductivity tests resulted in an average relative standard deviation of 1.20%. 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.

Measurement of Thermal Properties. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 instrument under a nitrogen atmosphere at a heating rate of 2 °C/min on 5−8 mg samples, using aluminum pans. All reported thermal transitions were measured on the second heating, and experiments were completed in duplicate (error of ±2 °C). Temperature ramped thermal stabilities ($T_{d5\%}$) were studied under a constant nitrogen flow 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 samples did not absorb any residual moisture as the experiment was being prepared. T_{onset} values were extrapolated from the steepest portion of the resultant thermograph, while $T_{d5\%}$ represents the temperature at which 5% of the ionic liquid had decomposed.

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 isothermal temperature at a rate of 5 °C/min. Data acquisition began after a 10 min temperature equilibration period. The values reported for $t_{0.01/10}$ and E_a represent the average taken from duplicate runs at each temperature.

Preparation 1-Alkyl-4-methyl-1,2,4-triazolium Iodides 1a−g. 1-Alkyl-4-methyl-1,2,4-triazolium iodides **1a−e** and **1g** have been previously reported.[13,15] 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf$_2$]) was prepared according to a previously reported procedure.[36]

*Preparation of 1-Decyl-4-methyl-1,2,4-triazolium Iodide **1f**.* 1-Decyl-1,2,4-triazole[13] (5.00 g, 23.9 mmol) was dissolved in acetonitrile (75 mL) in a 250 mL round-bottomed flask. Iodomethane (5.08 g, 35.8 mmol) was added, and the resulting stirred solution was warmed to 40 °C and held for 48 h. The solution was then concentrated in vacuo, resulting in a light orange solid, which was recrystallized from acetonitrile, affording a white solid (7.85 g, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 1 H), 9.12 (s, 1 H), 4.36 (t, J = 7.3 Hz, 2 H), 3.89 (s, 3 H), 1.82 (m, 2 H), 1.26 (m, 14 H), 0.85 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.5, 142.9, 51.4, 34.1, 31.3, 28.9, 28.8, 28.7, 28.4, 28.1, 25.4, 22.1, 14.0. Anal. Calcd for $C_{13}H_{26}N_3I$: C, 44.45; H, 7.46; N, 11.96. Found: C, 44.73; H, 7.51; N, 12.02.

Preparation of 1-Alkyl-4-methyl-1,2,4-triazolium Bis(trifluoromethylsulfonyl)imides 2a−g. 1-Alkyl-4-methyl-1,2,4-triazolium [NTf$_2$] ionic liquids **2a−g** were prepared following a previously reported procedure.[13,15] Representative examples are provided below for ionic liquids **2a** and **2b**. Reaction yields and characterization data for the remaining ionic liquids **2d−g** can be found in the Supporting Information. Full characterization of ionic liquid **2c** has been previously reported.[15]

*1-Ethyl-4-methyl-1,2,4-triazolium Bis(trifluoromethylsulfonyl)imide **2a**.* To a 100 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1-ethyl-4-methyl-1,2,4-triazolium iodide **1a** (2.37 g, 9.91 mmol) in DI water (20 mL). To this stirred solution was added a solution of lithium bis(trifluoromethylsulfonyl)imide (2.87 g, 10.0 mmol) in DI water (20 mL). After several minutes, a biphasic mixture was observed. After 24 h of stirring at room temperature, chloroform (40 mL) was added and the resulting mixture was transferred to a separatory funnel. The organic phase was separated, washed twice with DI water (20 mL each) and the solvent removed under reduced pressure, resulting in **2a** as a clear yellow oil (3.58 g, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1 H), 9.11 (s, 1 H), 4.39 (t, J = 7.3 Hz, 2 H), 3.88 (s, 3 H), 1.45 (q, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.2, 142.6, 119.5 (q, J = 327 Hz, CF_3), 46.9, 33.8, 13.6. Anal. Calcd for $C_7H_{10}N_4F_6O_4S_2$: C, 21.43; H, 2.57; N, 14.28. Found: C, 21.44; H, 2.56; N, 14.34.

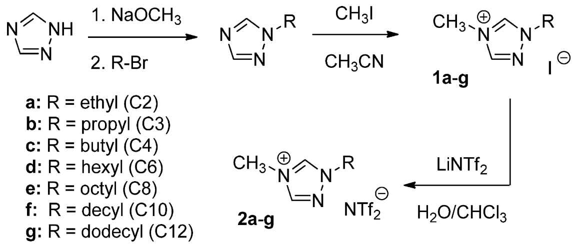
*1-Propyl-4-methyl-1,2,4-triazolium Bis(trifluoromethylsulfonyl)imide **2b**.* To a 100 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1-propyl-4-methyl-1,2,4-triazolium iodide **1b** (3.00 g, 11.9 mmol) in DI water (15 mL). To this stirred solution was added a solution of lithium bis(trifluoromethylsulfonyl)imide (3.45 g, 12.0 mmol) in DI water (15 mL). After several minutes, a biphasic mixture was observed. After 24 h of stirring at room temperature, chloroform (50 mL) was added and the resulting mixture was transferred to a separatory funnel. The organic phase was separated, washed twice with DI water (20 mL each) and the solvent removed under reduced pressure, resulting in **2b** as a light yellow oil (4.49 g, 93% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1 H), 9.13 (s, 1 H), 4.33 (t, J = 6.9 Hz, 2 H), 3.88 (s, 3 H), 1.87 (m, 2 H), 0.89 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.6, 142.8, 119.4 (q, J = 327 Hz, CF_3), 52.9, 34.0, 21.7, 10.4. Anal. Calcd for $C_8H_{12}N_4F_6O_4S_2$: C, 23.65; H, 2.98; N, 13.79. Found: C, 23.72; H, 3.00; N, 13.69.

Residual Iodide Content. The quantity of residual iodide [I$^-$] in ionic liquids **2a−g** was determined by ion chromatography (ICS-110, Dionex) under the following conditions: 4.5 mM CO_3^{2-}/1.4 mM HCO_3^- eluent concentration, 1.2 mL/min flow rate, 31 mA suppressor current. After chromatographic calibration via aqueous standards prepared by serial dilution of 1000 ppm [I$^-$] stock (from sodium iodide, Aldrich, >99.5%), 10−15 mg of each ionic liquid was dissolved in 1 mL of acetonitrile and injected.[37] The amount of residual iodide in each ionic liquid was determined to be less than 0.01% w/w.

RESULTS AND DISCUSSION

Synthesis. Preparation of the desired 1-alkyl-4-methyl-1,2,4-triazolium [NTf$_2$] ionic liquids **2a−g** is shown in Scheme 1. Briefly, commercially available 1,2,4-triazole was functionalized at the N-1 position by allowing it to react first with sodium methoxide followed by addition of the appropriate 1-bromoalkane.[13,15] Quaternization at the N-4 position was then accomplished through the addition of iodomethane, resulting in the corresponding 1-alkyl-4-methyl-1,2,4-triazolium iodides **1a−g**, the majority of which were off-white solids under ambient conditions, the exception being R = propyl, which appeared as a clear, light yellow oil. Anion exchange reactions using lithium bis(trifluoromethylsulfonyl)imide provided the targeted ionic liquids **2a−g** as a series of clear, light yellow oils. Purity of the ionic liquids was determined by NMR spectroscopy and elemental analysis. Residual iodide content was determined to be less than 0.01% w/w by ion chromatography.

Scheme 1. Synthesis of 1-Alkyl-4-methyl-1,2,4-triazolium [NTf$_2$] Ionic Liquids 2a−g



Physicochemical Properties. As illustrated in Figure 1, the viscosity for each ionic liquid was found to decrease with increasing temperature over the temperature range studied (room temperature to 80 °C). Given a constant temperature, viscosity was found to increase with increasing alkyl chain length, with the 1-dodecyl-4-methyl-1,2,4-triazolium [NTf$_2$] **2g** exhibiting the highest overall viscosity (227 mPa·s at 30 °C). This observed trend is analogous to previously reported 1-alkyl-3-methylimidazolium ionic liquids and is attributed to an increase in van der Waals forces between the alkyl chains of the

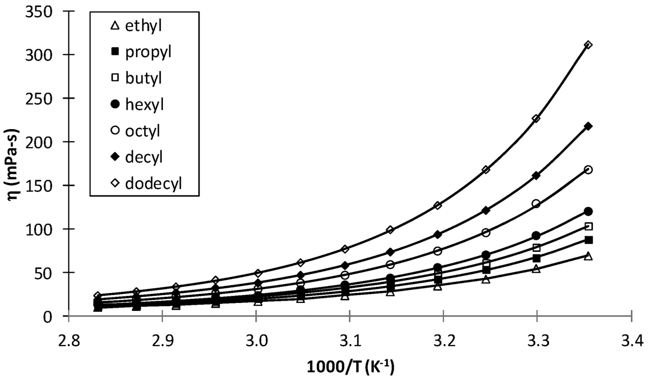


Figure 1. Temperature-dependent viscosity curves for 1-alkyl-4-methyl-1,2,4-triazolium $[NTf_2]$ ionic liquids **2a–g**.

ionic liquid cations as the chain length increases.[38,39] In general, viscosities of the 1,2,4-triazolium ILs were higher than values previously reported for the analogous imidazolium systems. For example, 1-butyl-4-methyl-1,2,4-triazolium $[NTf_2]$ **2c** was found to exhibit a viscosity of 79.2 mPa·s at 30 °C compared to 41.3 mPa·s for freshly prepared $[bmim][NTf_2]$.[39]

Temperature-dependent viscosities and conductivities of ionic liquids generally exhibit non-Arrhenius behavior.[16,23,38,39] As a result, the empirical Vogel–Fulcher–Tammann (VFT) relationship,

$$\eta = \eta_o \exp[B/(T - T_0)] \tag{1}$$

was applied to the experimental viscosity data, where η_o (mPa·s) is the viscosity at the temperature limit, B (K) is a quantity related to the activation barrier, and T_0 (K) is the absolute or "ideal glass transition" temperature.[40–43] VFT fitted curves (solid curves) are provided in Figure 1, while the best-fit parameters are tabulated in Table 1.

Table 1. VFT Equation Parameters for Viscosity Data

ionic liquid	η_o (mPa·s)	B (K)	T_0 (K)
2a (ethyl)	0.191	659	186
2b (propyl)	0.112	807	177
2c (butyl)	0.091	889	172
2d (hexyl)	0.053	1031	165
2e (octyl)	0.026	1294	151
2f (decyl)	0.060	1071	167
2g (dodecyl)	0.057	1108	169

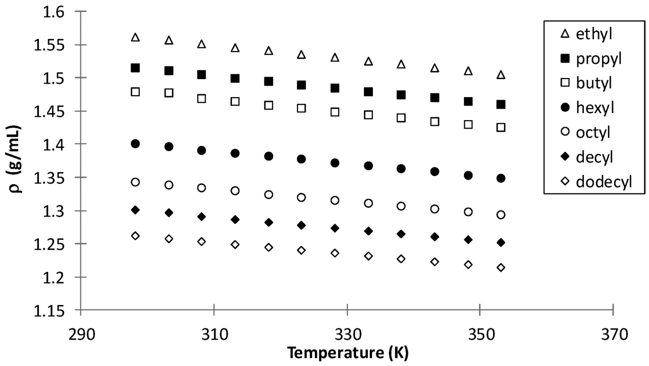


Figure 2. Temperature-dependent densities for 1-alkyl-4-methyl-1,2,4-triazolium $[NTf_2]$ ionic liquids **2a–g**.

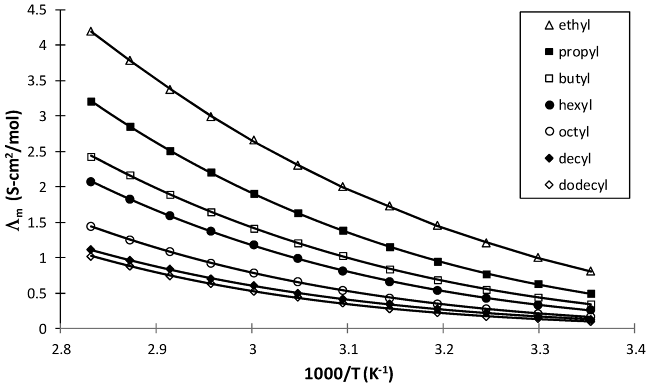


Figure 3. Temperature-dependent molar conductivity curves for 1-alkyl-4-methyl-1,2,4-triazolium $[NTf_2]$ ionic liquids **2a–g**.

Table 2. VFT Equation Parameters for Conductivity Data

ionic liquid	Λ_m ($S{\cdot}cm^2{\cdot}mol^{-1}$)	B (K)	T_0 (K)
2a (ethyl)	134.3	592	182
2b (propyl)	155.5	652	185
2c (butyl)	120.5	638	189
2d (hexyl)	118.4	649	196
2e (octyl)	130.2	755	186
2f (decyl)	147.5	879	173
2g (dodecyl)	209.7	952	174

Temperature-dependent densities of ionic liquids **2a–g** were found to be generally higher than those reported for analogous imidazolium $[NTf_2]$ ionic liquids.[39] As expected, the density of each ionic liquid decreased with increasing temperature (Figure 2). Increasing the alkyl chain length led to a decrease in density with the C12 (dodecyl) analogue exhibiting the lowest density profile (ρ = 1.26 g/mL at 30 °C).

Temperature-dependent molar conductivity (Λ_m) data are presented in Figure 3 (data points) along with the VFT fitted curves (solid curves) which follow the equation

$$\Lambda_m = \Lambda_o \exp[B/(T - T_0)] \tag{2}$$

where Λ_o ($S{\cdot}cm^2{\cdot}mol^{-1}$) is the molar conductivity at the temperature limit and B (K) and T_0 (K) are variable constants. The best-fit parameters from the VFT fitted molar conductivity curves are provided in Table 2. Molar conductivity was generally found to increase with increasing temperature, presumably because of the improved mobility of the cations and anions. However, molar conductivity was observed to decrease with increasing alkyl chain length, given a constant temperature. This was anticipated, since longer alkyl chain lengths should theoretically reduce mobility because of increased van der Waals interactions. In general, the 1,2,4-triazolium ionic liquids were found to exhibit lower molar conductivities than the analogous imidazolium ionic liquids.[38,39] For example, the molar conductivity of 1-butyl-4-methyl-1,2,4-triazolium $[NTf_2]$ **2c** was found to be 0.44 $S{\cdot}cm^2{\cdot}mol^{-1}$ at 30 °C compared to 1.28 $S{\cdot}cm^2{\cdot}mol^{-1}$ for $[bmim][NTf_2]$. It is believed that this finding is directly related to the increased Lewis acidity of the 1,2,4-triazolium ring, which would result in stronger cation–anion interactions.[44,45]

The relationship between the viscosity and conductivity of an ionic liquid can be demonstrated by constructing a logarithmic plot based upon the Walden rule:

$$\log \Lambda_m = \log C + \alpha \log \eta^{-1} \tag{3}$$

where Λ_m is the molar conductivity, η is the viscosity of the ionic liquid, and C is a constant that represents the deviation from a standard set of parameters.[16,23] The standard or "ideal line" is commonly represented by a completely dissociated ion pair (dilute KCl solution) where the slope is $\alpha = 1$ and the intercept ($\log C$) travels through the origin. As mentioned in the Introduction, ionic liquids have been classified as "good", "poor", or "superionic" based upon a comparison with the ideal line; however, the use of dilute KCl as a standard has been recently questioned.[21,23]

Figure 4 shows the Walden plot for ionic liquids **2a**−**g**. Data for a freshly prepared sample of [bmim][NTf_2] were also acquired and are provided for comparative analysis. Upon inspection of the Walden plot, it is apparent that the fitted data are grouped relatively close together, with an average standard deviation of ~0.1% and $R^2 > 0.999$ for each individual data set. Linear fit parameters are provided in Table 3. Overall, the 1,2,4-triazolium ionic liquids studied performed well and could be classified as "good" ionic liquids based upon literature comparison.[21] However, all of the 1,2,4-triazolium ionic liquids were found to deviate from the ideal line to a greater extent than [bmim][NTf_2], as evidenced by an increase in log C. As previously hypothesized, this finding could be the result of stronger overall cation−anion interactions due to the more acidic 1,2,4-triazolium ring. Within the 1,2,4-triazolium ionic liquid series, increasing the alkyl chain length resulted in a decrease in performance. Once again, longer chain lengths are believed to increase van der Waals interactions between cations, resulting in an increase in viscosity and a decrease in molar conductivity.

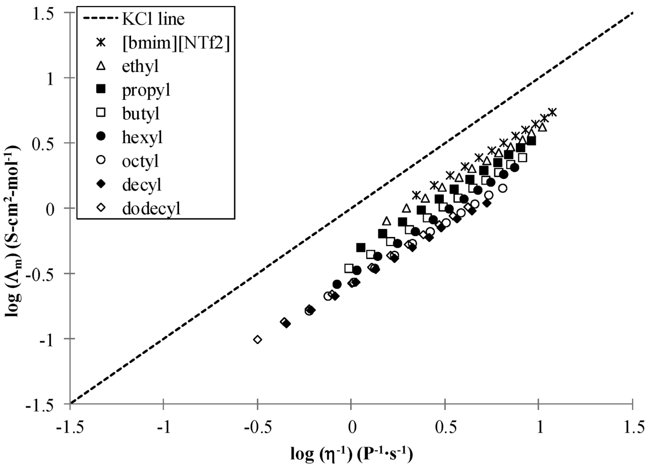


Figure 4. Walden plot for 1-alkyl-4-methyl-1,2,4-triazolium [NTf_2] ionic liquids **2a**−**g** and [bmim][NTf_2].

Table 3. Linear Fit Parameters from the Walden Plot

ionic liquid	α	log C ($S{\cdot}cm^2{\cdot}mol^{-1}$)
[bmim][NTf_2]	0.936	−0.205
2a (ethyl)	0.865	−0.258
2b (propyl)	0.896	−0.345
2c (butyl)	0.922	−0.449
2d (hexyl)	0.949	−0.505
2e (octyl)	0.949	−0.510
2f (decyl)	0.884	−0.506
2g (dodecyl)	0.912	−0.557

Thermal Properties. Thermal transitions of 1-alkyl-4-methyl-1,2,4-triazolium [NTf_2] ionic liquids **2a**−**g** were determined using differential scanning calorimetry (DSC), the results of which are provided in Table 4. All DSC experiments were completed in duplicate (error ± 2 °C), and reported measurements are from the second heating event. All ionic liquids with an alkyl chain length of C8 (octyl) or less exhibited a single glass transition temperature (T_g) below −70.0 °C. 1-Dodecyl-4-methyl-1,2,4-triazolium [NTf_2] **2g** exhibited a single melting point transition (T_m) at 19.8 °C, while 1-decyl-4-methyl-1,2,4-triazolium [NTf_2] **2f** displayed a solid−solid phase transition at −45 °C in addition to a melting point transition at 2.9 °C. Thermal properties for [bmim][NTf_2] were also acquired, and the experimental results were in agreement with previously published values; however, a melting point transition (T_m of −3.5 °C) was only observed during the first heating event.[26,46]

Table 4. Thermal Properties of 1-Alkyl-4-methyl-1,2,4-triazolium [NTf_2] Ionic Liquids 2a−g

ionic liquid	T_g (°C)	T_m (°C)	T_{onset} (°C)	$T_{d5\%}$ (°C)	$T_{0.01/10}$ (°C)	E_a (kJ/mol)
[bmim][NTf_2]	−85.5	−3.5	418	385	196	130.7
2a (ethyl)	−72.8		355	327	164	102.5
2b (propyl)	−71.6		365	337	175	110.3
2c (butyl)	−70.2		350	327	177	114.7
2d (hexyl)	−71.3		345	318	178	119.1
2e (octyl)	−72.2		346	318	178	123.6
2f (decyl)		2.9	357	331	183	127.7
2g (dodecyl)		19.8	354	326	194	131.6

Thermal stabilities of 1-alkyl-4-methyl-1,2,4-triazolium [NTf_2] ionic liquids **2a**−**g** were determined using both "temperature ramp" (short-term stability) and "isothermal" (long-term stability) methods. Each temperature-ramped TGA experiment was completed in duplicate, and T_{onset} and $T_{d5\%}$ values were found to be reproducible within ±2 °C. All of the ionic liquids were found to exhibit generally high T_{onset} (≥345 °C) and $T_{d5\%}$ (≥315 °C) values; however, they were less stable than [bmim][NTf_2] or other analogous imidazolium [NTf_2] ionic liquids.[46] No correlation between T_{onset} or $T_{d5\%}$ and alkyl chain length was observed.

As mentioned in the Introduction, T_{onset} or $T_{d5\%}$ values are known to overestimate the thermal stability of ionic liquids. Thus, isothermal TGA experiments have become a more reliable (albeit time-consuming) tool to determine and estimate long-term stability.[24,35] Since the decomposition of the ionic liquid generates volatile degradants, the concentration of the cations and anions in the bulk ionic liquid is assumed to remain unchanged, leading to pseudo-zeroth-order kinetics. Thus, the rate constant k_{obs} can be determined from the slope of a line that plots weight loss against time (min). Furthermore, the activation energy (E_a) for decomposition can be determined using the Arrhenius equation for each set of isotherms:

$$k_{obs} = A \exp[-E_a/(RT)] \tag{4}$$

where the slope of a plot of ln k_{obs} versus $1/T$ (K^{-1}) is equal to $-E_a/R$ and the intercept of the y-axis is ln A.

Ionic liquids **2a**−**g**, as well as [bmim][NTf_2], were subjected to isothermal TGA experiments. Each set of isotherms was completed in duplicate and zeroth-order rate constants were determined. Subsequent Arrhenius plots gave linear regressions with $R^2 > 0.995$, and the derived activation energy (E_a) values from eq 4 are provided in Table 4. Sample isothermal graphs and Arrhenius analysis for 1-butyl-4-methyl-1,2,4-triazolium [NTf_2] **2c** are provided in Figures 5 and 6, respectively. Similar plots for the remaining ionic liquids are provided in the Supporting Information. Comparison of the activation energy data provided in Table 4 indicated a general rise in E_a as the alkyl chain length was increased from ethyl (102.5 kJ/mol) to dodecyl (131.6 kJ/mol). For comparison, the activation energy of [bmim][NTf_2] was determined to be 130.7 kJ/mol. In general, the 1,2,4-triazolium ionic liquids appear to be less thermally stable than imidazolium [NTf_2] ionic liquids, as previously determined from T_{onset} and $T_{d5\%}$ comparisons.

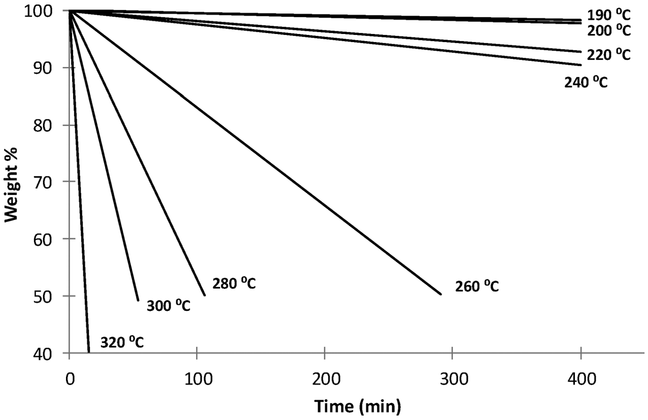


Figure 5. TGA isotherms for 1-butyl-4-methyl-1,2,4-triazolium [NTf_2] **2c**.

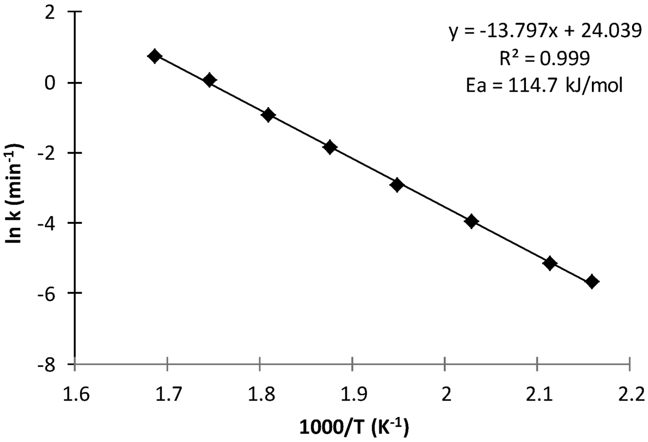


Figure 6. Arrhenius plot for 1-butyl-4-methyl-1,2,4-triazolium [NTf_2] **2c** from thermal decomposition analysis.

From each set of isothermal experiments, a value for $T_{0.01/10}$ was also determined, following the methods employed by MacFarlane and Welton.[24,35] A plot of $t_{0.99}$ versus temperature (K) for 1-butyl-4-methyl-1,2,4-triazolium [NTf_2] **2c** is shown in Figure 7, where $t_{0.99}$ represents the time necessary for 1% of the ionic liquid to decompose at each isothermal temperature. Extrapolation of the exponential curve to a time of 600 min (10 h) provided a value of 177 °C for the $T_{0.01/10}$ of **2c**. Additional data and graphical analysis for the remaining ionic liquids can be found in the Supporting Information. For all ionic liquids studied, the $T_{0.01/10}$ value was found to be significantly below the observed T_{onset} or $T_{d5\%}$ value, an observation that is in agreement with previously reported experimental values.[23,34,35]

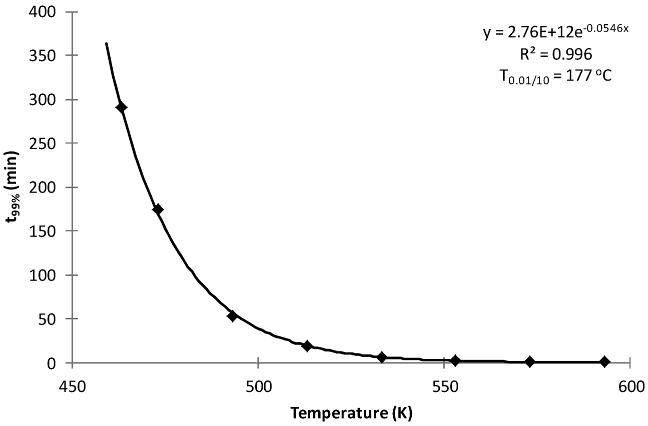


Figure 7. Long-term thermal stability $t_{0.99}$ plot for 1-butyl-4-methyl-1,2,4-triazolium [NTf_2] **2c**.

From a comparison of the long-term thermal stability of the 1,2,4-triazolium ionic liquid series, a general increase in $T_{0.01/10}$ as the length of the alkyl chain increased (164−194 °C) was observed; however, they were all found to be generally less stable than the model imidazolium ionic liquid [bmim][NTf_2] ($T_{0.01/10}$ of 196 °C). This is once again attributed to the increased Lewis acidity of the 1,2,4-triazolium ring, leading to stronger cation−anion interactions. These findings further emphasize the importance of isothermal TGA studies as an accurate measure for the long-term stability of ionic liquids as well as for the estimation of thermal stability at processing temperatures that are below the T_{onset} or $T_{d5\%}$ value.

■ CONCLUSIONS

In summary, a series of 1-alkyl-4-methyl-1,2,4-triazolium [NTf_2] ionic liquids were prepared. Temperature-dependent physicochemical properties such as viscosity, density, and conductivity were determined, and a Walden plot was constructed in order to determine the ionicity of the ionic liquids. Viscosity (η) and density (ρ) were found to decrease with increasing temperature, while molar conductivity (Λ_m) was found to increase. Increasing the alkyl chain length from ethyl (C2) to dodecyl (C12) led to increased viscosity (η) measurements given a constant temperature but decreased densities (ρ) and molar conductivities (Λ_m). In general, the 1,2,4-triazolium ionic liquids can be classified as "good" ionic liquids when compared with published data; however, they did not perform as well as the standard imidazolium ionic liquid [bmim][NTf_2] with respect to the "ideal" KCl line.

Thermal properties from DSC and TGA experiments were also reported. 1,2,4-Triazolium ionic liquids with an alkyl chain length of octyl (C8) or less exhibited a T_g below −70 °C; however, the decyl and dodecyl systems exhibited a T_m value. No correlation between T_{onset} or $T_{d5\%}$ and alkyl chain length was observed during short-term, temperature-ramped TGA experiments. However, long-term, isothermal TGA studies indicated a general increase in $T_{0.01/10}$ value as the alkyl chain length increased. Both short- and long-term TGA studies indicated that the 1,2,4-triazolium ionic liquids were not as thermally stable as the model imidazolium ionic liquid [bmim][NTf_2].

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **1f** and **2a−g**; reaction yields and spectroscopic data for ionic liquids **2d−g**; schematic and description of the conductivity apparatus built in-house; representative DSC and TGA thermograms for ionic liquids **2a−g**; plots of isothermal TGA experiments for ionic liquids **2a−g**; [bmim][NTf$_2$] and activation energy and $t_{0.99}$ plots. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 270-809-3543. E-mail: kmiller38@murraystate.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support for this project was provided by the Petroleum Research Fund of the American Chemical Society (PRF Grant 53097-UNI7) and the Department of Chemistry at Murray State University, KY. The authors thank Dr. R. Daniel Johnson (Department of Chemistry, Murray State University) for his assistance in the acquisition and interpretation of the conductivity data. All thermal measurements (DSC and TGA) were conducted in the Polymer and Materials Characterization Laboratory at Murray State University.

■ REFERENCES

(1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH, Weinheim, Germany, 2002.

(2) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071−2084.

(3) Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, A. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(4) Rogers, R. D.; Seddon, K. R. *Ionic Liquids as Green Solvents: Progress and Prospects*; American Chemical Society: Washington DC, 2003.

(5) Wasserscheid, P.; Keim, W. Ionic Liquids—New "Solutions" for Transition Metal Catalysis. *Agnew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(6) *Ionic Liquids IIIA: Fundamentals, Progress, Challenges and Opportunities*; Rogers, R. D., Ed.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2005.

(7) Smiglak, M.; Metlen, A.; Rogers, R. D. The Second Evolution of Ionic Liquids: From Solvents and Separations to Advanced Materials—Energetic Examples from the Ionic Liquid Cookbook. *Acc. Chem. Res.* **2007**, *40*, 1182−1192.

(8) Ang, H. G. *Energetic Polymers: Binders and Plasticizers for Enhancing Performance*; Wiley-VCH: New York, 2012.

(9) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; Mckay, M.; Vij, A.; Ismail, I. Energetic, Low-Melting Salts of Simple Heterocycles. *Propellants, Explos., Pyrotech.* **2003**, *28*, 174−180.

(10) Swain, P. K.; Singh, H.; Tewari, S. P. Energetic Ionic Salts Based on Nitrogen-Rich Hetereocycles: A Prospective Study. *J. Mol. Liq.* **2010**, *151*, 87−96.

(11) Vestergaard, B.; Bjerrum, N. J.; Petrushina, I.; Hjuler, H. A.; Berg, R. W.; Begtrup, M. Molten Triazolium Chloride Systems as New Aluminum Battery Electrolytes. *J. Electrochem. Soc.* **1993**, *140*, 3108−3113.

(12) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. Energetic Nitrogen-Rich Salts and Ionic Liquids. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584−3601.

(13) Mirzaei, Y. R.; Twamley, B.; Shreeve, J. M. Syntheses of 1-Alkyl-1,2,4-triazoles and the Formation of Quaternary 1-Alkyl-4-polyfluoroalkyl-1,2,4-triazolium Salts Leading to Ionic Liquids. *J. Org. Chem.* **2002**, *67*, 9340−9345.

(14) Meyer, D.; Strassner, T. 1,2,4-Triazole-Based Tunable Aryl/Alkyl Ionic Liquids. *J. Org. Chem.* **2011**, *76*, 305−308.

(15) Daily, L. A.; Miller, K. M. Correlating Structure with Thermal Properties for a Series of 1-Alkyl-4-methyl-1,2,4-triazolium Ionic Liquids. *J. Org. Chem.* **2013**, *78*, 4196−4201.

(16) Angell, C. A.; Anasari, Y.; Zhao, Z. Ionic Liquids: Past, Present, and Future. *Faraday Discuss.* **2012**, *154*, 9−27.

(17) Xu, W.; Cooper, E. I.; Angell, C. A. Ionic Liquids: Ion Mobilities, Glass Temperatures, and Fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170−6178.

(18) Yoshizawa, M.; Xu, W.; Angell, C. A. Ionic Liquids by Proton Transfer: Vapor Pressure, Conductivity, and the Relevance of ΔpK_a from Aqueous Solutions. *J. Am. Chem. Soc.* **2003**, *125*, 15411−15419.

(19) MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. On the Concept of Ionicity in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962−4967.

(20) Ueno, K.; Tokuda, H.; Watanabe, M. Ionicity in Ionic Liquids: Correlation with Ionic Structure and Physicochemical Properties. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1649−1658.

(21) Lee, S.-Y.; Ueno, K.; Angell, C. A. Lithium Salt Solutions in Mixed Sulfone and Slone-Carbonate Solvents: A Walden Plot Analysis of the Maximally Conductive Compositions. *J. Phys. Chem. C* **2012**, *116*, 23915−23920.

(22) Walden, P. Über Organische Lögsungs-und Ionisierungsmittel. III. Teil: Innere Reibung und deren Zusammenhang mit dem Leitvermögen. *Z. Phys. Chem.* **1906**, *55*, 207−246.

(23) Schreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the So-Called Ideal KCl Line for the Walden Plot. *J. Chem. Eng. Data* **2010**, *55*, 1784−1788.

(24) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. Thermal Degradation of Ionic Liquids at Elevated Temperatures. *Aust. J. Chem.* **2004**, *57*, 145−147.

(25) Maton, C.; De Vos, N.; Stevens, C. V. Ionic Liquids Thermal Stabilities: Decomposition Mechanisms and Analysis Tools. *Chem. Soc. Rev.* **2013**, *42*, 5963−5977.

(26) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−964.

(27) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase Transition and Decomposition Temperatures, Heat Capacities and Viscosities of Pyridinium Ionic Liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559−568.

(28) Noack, K.; Schultz, P. S.; Paape, N.; Kiefer, J.; Wasserscheid, P.; Leipertz, A. The Role of the C2 Position in Interionic Interactions of Imidazolium Based Ionic Liquids: A Vibrational and NMR Spectroscopic Study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14153−14161.

(29) Shirota, H.; Mandai, T.; Fukazawa, H.; Kato, T. Comparison between Dicationic and Monocationic Ionic Liquids: Liquid Density, Thermal Properties, Surface Tension, and Shear Viscosity. *J. Chem. Eng. Data* **2011**, *56*, 2453−2459.

(30) Green, M. D.; Schreiner, C.; Long, T. E. Thermal, Rheological, and Ion-Transport Properties of Phosphonium-Based Ionic Liquids. *J. Phys. Chem. A* **2011**, *115*, 13829−13835.

(31) Kosmulski, M.; Gustafsson, J.; Rosenholm, J. B. Thermal Stability of Low Temperature Ionic Liquids. *Thermochim. Acta* **2004**, *412*, 47−53.

(32) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. Thermal Properties of Imidazolium Ionic Liquids. *Thermochim. Acta* **2000**, *357−358*, 97−102.

(33) Seeberger, A.; Anderson, A.-K.; Jess, A. Prediction of Long-Term Stability of Ionic Liquids at Elevated Temperatures by Means of Non-Isothermal Thermogravimetric Analysis. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9375−9381.

(34) Wooster, T. J.; Johanson, K. M.; Fraser, K. J.; MacFarlane, D. R.; Scott, J. L. Thermal Degradation of Cyano Containing Ionic Liquids. *Green Chem.* **2006**, *8*, 691−696.

(35) Clough, M. T.; Geyer, K.; Hunt, P. A.; Mertes, J.; Welton, T. Thermal Decomposition of Carboxylate Ionic Liquids: Trends and Mechanisms. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20480−20495.

(36) Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. The Large Scale Synthesis of Pure Imidazolium and Pyrrolidinium Ionic Liquids. *Green Chem.* **2007**, *9*, 449−454.

(37) Villagrán, C.; Deetlefs, M.; Pitner, W. R.; Hardacre, C. Quantification of Halide in Ionic Liquids Using Ion Chromatography. *Anal. Chem.* **2004**, *76*, 2118−2123.

(38) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation. *J. Phys. Chem. B* **2005**, *109*, 6103−6110.

(39) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.

(40) Ikeda, M.; Aniya, M. Understanding the Vogel−Fulcher−Tammann Law in Terms of the Bond Strength-Coordination Number Fluctuation Model. *J. Non-Cryst. Solids* **2013**, *371*−*372*, 53−57.

(41) Vogel, H. Das Temperaturabhängigkeitsgesetz der Viskosität von Flüssigkeiten. *Phys. Z.* **1921**, *22*, 645−646.

(42) Fulcher, G. S. Analysis of Recent Measurements of the Viscosity of Glasses. *J. Am. Ceram. Soc.* **1952**, *8*, 339−355.

(43) Tammann, G.; Hesse, W. Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245−257.

(44) Massey, R. S.; Collett, C. J.; Lindsay, A. G.; Smith, A. D.; O'Donoghue, A. C. Proton Transfer Reactions of Triazol-3-ylidenes: Kinetic Acidities and Carbon Acid pK_a Values for Twenty Triazolium Salts in Aqueous Solution. *J. Am. Chem. Soc.* **2012**, *134*, 20421−20432.

(45) Alder, R. W.; Allen, P. R.; Williams, S. J. Stable Carbenes as Strong Bases. *J. Chem. Soc., Chem. Commun.* **1995**, *12*, 1267−1268.

(46) Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X. Physical Properties of Ionic Liquids: Database and Evaluation. *J. Phys. Chem. Ref. Data* **2005**, *35*, 1475−1517.