

Thermophysical Properties of Imidazolium-Based Ionic Liquids

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Ionic liquids (ILs) are salts that are liquid at low temperatures, usually including the region around room temperature. They are under intense investigation, especially as replacement solvents for reactions and separations, since they exhibit negligible vapor pressure and would not, therefore, contribute to air pollution. Clearly, basic thermophysical properties are vital for design and evaluation for these applications. We present density as a function of temperature, melting temperatures, glass-transition temperatures, decomposition temperatures, and heat capacities as a function of temperature for a series of 13 of the popular imidazolium-based ILs. The ionic liquids investigated here are 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium dicyanamide, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 2,3-dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide, 2,3-dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate. The properties follow quite reasonable trends. For instance, density decreases as the length of the alkyl chain on the cation increases. For a given cation, the density increases as the molecular weight of the anion increases for the anions studied here. Many of the ILs tend to subcool easily, forming glasses at very low temperatures rather than exhibiting crystallization or melting transitions. The thermal stability increases with increasing anion size, and heat capacities increase with temperature and increasing number of atoms in the IL.

Introduction

Organic salts that have low melting points (usually defined as below 100 °C) have come to be known collectively as ionic liquids (ILs). Since they are salts, they tend to have extremely low vapor pressures and it is this feature that has garnered them much recent attention as potential solvents to replace volatile organic solvents in a wide variety of chemical reaction, separation, and manufacturing processes. For example, ILs have been considered as solvents for reactions, as absorption media for gas separations, as the separating agent in extractive distillation, as heat transfer fluids, for processing biomass, and as the working fluid in a variety of electrochemical applications (batteries, solar cells, etc.).^{1–4}

A large number of different classes of ILs have been investigated. Examples include imidazolium, pyridinium, phosphonium, quaternary ammonium, pyrrolidinium, quindinium, and triazolium salts. Within any one of these classes, the choice of anion and substituents on the cation can yield a large number of different compounds. In this work, we will focus on the popular imidazolium-based salts. The compounds investigated are shown in Table 1, which includes the abbreviations (1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][dca]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][triflate]), 1-butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide ([bmim][methide]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]), 2,3-dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide ([emmim][Tf₂N]), 2,3-dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide ([pmmim][Tf₂N]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bmim][BF₄]), and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bmmim][PF₆])) for the ILs that will be used throughout this manuscript.

Understanding basic thermophysical properties of ILs is vital for design and evaluation. For instance, melting points, glass-transition temperatures, and thermal decomposition temperatures are needed to set the feasible temperature operating range for a particular fluid. Density (as a function of temperature) is needed for equipment sizing. Heat capacities are needed to estimate heating and cooling requirements as well as heat-storage capacity.

Since the synthesis and investigation of water-stable ILs is relatively recent, information on pure-component physical properties is somewhat limited or incomplete. For instance, for the imidazolium salts investigated here, we are aware of only three publications that report density as a function of temperature ([emim][Tf₂N],⁵ [bmim][Tf₂N],⁶ and [bmim][BF₄]).⁷ Other reports only include room-temperature values ([bmim][BF₄],^{8–10} [bmim][Tf₂N], and [emim][Tf₂N]).¹¹ Previously, we have reported the densities both as a function of temperature and pressure for [bmim][PF₆], [C₈mim][PF₆], [C₈mim][BF₄], and [NBuPy][BF₄].¹²

Melting points (T_m) and glass-transition temperatures (T_g) of imidazolium-based ILs, as measured by differential

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Table 1. List of Imidazolium-Based Ionic Liquids Investigated with CAS Registry Numbers

compound	CAS no.	structure	abbreviation
1- <i>n</i> -butyl-3-methylimidazolium tetrafluoroborate	174501-65-6		[bmim][BF ₄]
1- <i>n</i> -butyl-3-methylimidazolium hexafluorophosphate	174501-64-5		[bmim][PF ₆]
1- <i>n</i> -butyl-3-methylimidazolium chloride	79917-90-1		[bmim][Cl]
1- <i>n</i> -butyl-3-methylimidazolium bromide	85100-77-2		[bmim][Br]
1- <i>n</i> -butyl-3-methylimidazolium dicyanamide	44824-52-1		[bmim][dca]
1- <i>n</i> -butyl-3-methylimidazolium trifluoromethanesulfonate	174899-66-2		[bmim][triflate]
1- <i>n</i> -butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide			[bmim][methide]
1- <i>n</i> -butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	174899-83-3		[bmim][Tf ₂ N]
1- <i>n</i> -ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	174899-82-2		[emim][Tf ₂ N]
2,3-dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide	174899-90-2		[emmim][Tf ₂ N]
2,3-dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide	169051-70-1		[pmmim][Tf ₂ N]
1- <i>n</i> -butyl-2,3-dimethylimidazolium hexafluorophosphate	227617-70-1		[bmmim][PF ₆]
1- <i>n</i> -butyl-2,3-dimethylimidazolium tetrafluoroborate	402846-78-0		[bmmim][BF ₄]

scanning calorimetry (DSC), are somewhat more available.^{5,6,8,9,13–16} This is also true for thermal decomposition temperatures, as measured by thermogravimetric analysis (TGA).^{8,13,15,17,18} There is evidence that the presence of an oxidizing atmosphere (O₂), rather than an inert one (N₂), does not have a significant effect on the decomposition temperature of some imidazolium salts.¹³ However, there is also evidence that some imidazolium salts decompose at lower temperatures in the presence of O₂.¹⁷ Here we include values of T_m , T_g , and thermal decomposition temperatures for completeness and comparison with the various literature values.

By contrast, information on heat capacities of imidazolium-based ILs is more seriously lacking. Magee and co-workers have studied the heat capacity (C_p) of [bmim][PF₆] as a function of temperature.¹⁹ Holbrey and co-workers report the heat capacity of [bmim][PF₆], [bmim][Cl], and [bmim][Tf₂N] as well as 1-ethyl-3-methylimidazolium PF₆

and 1-*n*-hexyl-3-methylimidazolium PF₆ as a function of temperature.²⁰ Otherwise, we know of only three other reported values for C_p . These are for [bmim][BF₄], [pmmim][Tf₂N], and [emim][BF₄], all at a single temperature of 100 °C.²¹

Thus, there is certainly a need for thermophysical property data of ionic liquids. In particular, we seek to gain an understanding of how the anion and the choice of substituents on the cation affect thermophysical properties. Therefore, below we present density as a function of temperature, melting temperatures, glass-transition temperatures, decomposition temperatures and heat capacities as a function of temperature for the series of imidazolium-based ILs shown in Table 1.

Experimental Section

Materials. The list of chemicals used in the synthesis of ILs in this study, including CAS number, source and

grade, and purification method (if any), is as follows: 1-methylimidazole (616-47-7, Aldrich 99%, redistilled over KOH), 1-butylimidazole (4316-42-1, Aldrich 98%, redistilled over KOH), 1-bromobutane (109-65-9, Aldrich 99%, washed with concentrated sulfuric acid and distilled over P_2O_5),²² 1-chlorobutane (109-69-3, Aldrich 99.5%, redistilled), ammonium tetrafluoroborate (13826-83-0, Aldrich 97+%, used without purification), tetrafluoroboric acid (16872-11-0, Aldrich, 48 wt % solution in water, used without purification), methyl trifluoromethanesulfonate (333-27-7, Aldrich 99+%, used without purification), silver nitrate (7761-88-8, Aldrich 99+%, used without purification), and sodium dicyanamide (1934-75-4, Aldrich 96%, used without purification). Solvents used include deionized water from a Millipore purification unit and redistilled Fisher 99.9% grade dichloromethane.

Several ionic liquids were purchased or received from commercial vendors and other research groups. [bmim]-[PF₆] was purchased from Sachem, Inc., and was purified by washing with water to remove acid and by mixing with activated carbon to remove colored compounds. The [bmim]-[PF₆] from Sachem is reported to contain less than 3 ppm chloride. [bmim][Tf₂N], [emim][Tf₂N], [emim][Tf₂N], [pmmim][Tf₂N], and [bmim][methide] were obtained from Covalent Associates, Inc., and are all electrochemical grade (>99% purity). [bmmim][PF₆] and [bmmim][BF₄] were obtained from the research group of Professor Tom Welton, Imperial College, London. Because of the small amounts of these samples available, the halide content of these two ILs was not measured. However, it is expected that the values are quite low.²³ All ionic liquids purchased or received from other groups were dried before use, and the water content was determined by Karl Fisher titration (EM Science Aquastar V-200 Titrator) prior to use. These values are reported below in the section on density measurements. While we make every attempt to keep the samples as dry as possible (e.g., storage in a glovebox or desiccator), a recent report indicates that significant decomposition of ILs containing PF₆ and BF₄ anions (e.g., through hydrolysis) can take place even at room temperature.²⁴ Thus, we recognize that the PF₆ and BF₄ ILs studied could contain some decomposition products. For the T_m , T_g , thermal decomposition, and C_p measurements, the IL samples were dried further in situ, as described below.

Synthesis. Five of the ionic liquids were synthesized, using previously published methods.^{11, 23, 25}

[bmim][Cl] and [bmim][Br]. 1-Methylimidazole was reacted with an excess of a butyl halide (1-chlorobutane or 1-bromobutane) in a round-bottom flask under a nitrogen atmosphere to produce the 1-butyl-3-methylimidazolium halide ([bmim][Cl] or [bmim][Br]).

[bmim][BF₄]. The 1-butyl-3-methylimidazolium halide was reacted with an excess of either ammonium tetrafluoroborate in a dichloromethane solution or HBF₄ in an aqueous/dichloromethane biphasic solution, and the ionic liquid [bmim][BF₄] was formed. Product ammonium halide and any residual ammonium tetrafluoroborate, or the hydrochloric acid and any residual tetrafluoroboric acid, were removed from the ionic liquid by washing with water.

[bmim][triflate]. 1-Butylimidazole was reacted directly with methyl trifluoromethanesulfonate in an ice bath, forming [bmim][triflate].

[bmim][dca]. Equimolar amounts of sodium dicyanamide and silver nitrate were mixed in an aqueous solution, with solid silver dicyanamide precipitating from the solution. The solid was filtered and washed with water to remove any sodium nitrate. Excess silver dicyanamide was

reacted with 1-butyl-3-methylimidazolium bromide in aqueous solution to form the ionic liquid [bmim][dca]. The aqueous solution was then filtered to remove all solid precipitate (silver bromide and excess silver dicyanamide).

[bmim][BF₄], [bmim][triflate], and [bmim][dca] were cleaned with activated carbon to remove any colored compounds and dried under vacuum for 48 h to remove organic solvents (e.g., dichloromethane) and water. The water contents of [bmim][BF₄], [bmim][triflate], and [bmim][dca] were measured using a EM Science Aquastar V-200 Karl-Fisher Titrator. These values are reported below in the section on density measurements. All five ionic liquids were analyzed by proton NMR spectroscopy to ascertain the lack of any major impurities. Halide (Cl⁻ and Br⁻) and ammonium ion content were measured using an Oakton Ion 510 Series pH/mV/Ion/°C meter with Cole-Parmer Ion Specific Probes (27502-13 for Cl⁻, 27502-05 for Br⁻, and 27502-03 for NH₄⁺). Two different samples of [bmim][BF₄] were used for these investigations. For the density measurements, the [bmim][BF₄] was synthesized via the acid route. Its halide content was less than 10 ppm chloride. For the other measurements, the [bmim][BF₄] was synthesized via the ammonium tetrafluoroborate route. It contained less than 8 ppm bromide and less than 18 ppm ammonium. The [bmim][triflate] contains neither halide nor ammonium impurities since it was synthesized by direct metathesis. The [bmim][dca] contains less than 293 ppm bromide.

Density Measurements. Densities were measured with 1 mL pycnometers from Thomas Scientific. The pycnometers were heated in an airbath (Varian 1400 Series Auto-graph GC oven) with a circulation fan to ensure uniform heating. The precision of the balance used in these experiments was 0.0002 g. The pycnometers were calibrated using water and were found to give values to within $\pm 0.5\%$ using acetonitrile. Each density measurement was replicated four times, with the standard deviation being reported as the uncertainty in the results section below. We did not correct any of the measurements for buoyancy effects since the magnitude of this correction is significantly less than the uncertainties reported.

Because of the small amounts of sample available, the densities of [bmmim][PF₆] and [bmmim][BF₄] were measured using a 50- μ L airtight syringe equipped with a push-button valve (Series A-2, Vici Valco Instruments Co. Inc.). The syringe volume was calibrated using acetonitrile, and the calibration was verified by measuring the density of toluene and [bmim][PF₆]. The calibration experiments indicated the accuracy of the measurements to be within 0.4%. Heating was achieved using a Varian 3400Cx GC oven. Each density measurement was replicated five times, with the standard deviation being reported as the uncertainty in the results section below.

As mentioned above, the ILs were dried with stirring at 70 °C for 48 h under a vacuum of approximately 0.01 Pa. They were then sealed and stored in a desiccator. When in use, the ILs were constantly under a nitrogen atmosphere to prevent absorption of water from the atmosphere. In the best cases, we were able to reduce the water content to a couple hundred parts per million. However, some ILs, such as [bmim][triflate] and [bmim][dca], are extremely difficult to dry unless one uses excessive heating and is willing to accept the subsequent degradation. Therefore, some of our samples still contained several tenths of a percent of water. Water contents, as determined by Karl Fisher titration, were as follows: [emim][Tf₂N] contained 230 ppm, [emim][Tf₂N] contained 220 ppm, [pmmim]-

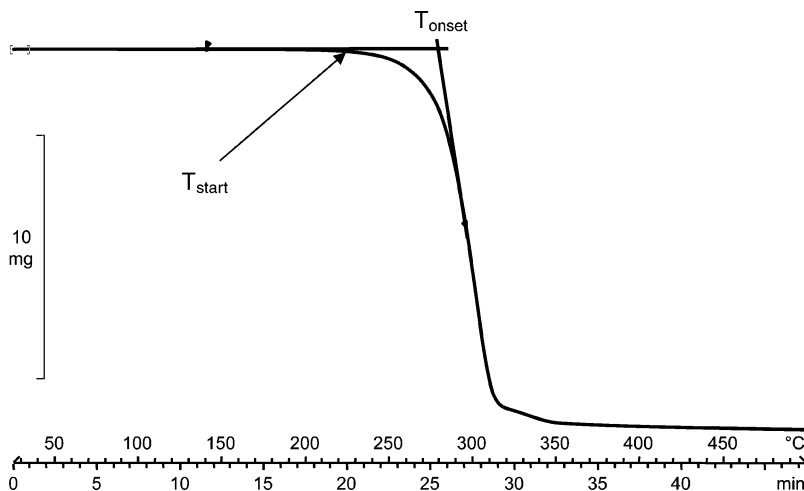


Figure 1. Characteristic decomposition curve, determined by TGA, for imidazolium ILs, indicating the start and onset temperatures.

[Tf₂N] contained 820 ppm, [bmim][Tf₂N] contained 460 ppm, [bmim][triflate] contained 2800 ppm, [bmim][BF₄] contained 1900 ppm, and [bmim][dca] contained 5150 ppm (0.515 wt %). The water content of [bmim][methide], [bmmim][PF₆], and [bmmim][BF₄] was not measured (due to limited amounts of sample), although they were dried as described above. We believe that the water content of the [bmim][methide] and [bmmim][PF₆] should be less than 1000 ppm. The [bmmim][BF₄] may be a bit higher, similar to [bmim][BF₄].

Melting Temperature, Glass-Transition Temperature, and Heat Capacity Measurements. Measurements of phase-transition temperatures and heat capacities were done with a Mettler-Toledo differential scanning calorimeter, model DSC822^e, and the data were evaluated using the Mettler-Toledo STAR^e software version 7.01. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler-Toledo. Samples were placed in a 40- μ L hermetically sealed aluminum pan with a pinhole at the top of the pan. An empty aluminum pan was used as the reference. The samples inside the differential scanning calorimeter furnace were exposed to a flowing N₂ atmosphere. Samples were dried in situ on the differential scanning calorimeter by holding the sample at 130 °C for 1–3 h. This is important because the presence of volatiles, especially water, can affect the glass transition and melting temperatures. Samples were dried repeatedly until the results were unchanged from before to after a drying step.

Measurements for melting, crystallization, and glass-transition temperatures were determined by cooling the samples from 130 °C to –120 °C, followed by heating from –120 °C to 130 °C, both at a rate of 10 °C/min. The glass transition was determined to be the midpoint of a heat capacity change, whereas the melting and crystallization temperatures were determined as the onset of the transition. The main sources of uncertainty in the temperature measurements come from instrument variability for a sample that has not been removed from the instrument and uncertainties resulting from inexact placement of the sample in the furnace that yields slightly different thermal contact with instrument thermocouples. The variability in the temperature measurements as determined by three replicate scans of the same sample was ± 0.2 °C, while the uncertainty associated with varying thermal contact, as determined by removing the pan and then replacing it, was found to be ± 0.3 °C. The melting point of a standard sample of tin with a purity of 99.999% was measured to

be within 0.1 °C of its literature value. Thus, we estimate that the total uncertainty of the melting, crystallization, and glass-transition temperatures is ± 0.3 °C. Nonetheless, we only report the values to the nearest 1 °C, since we recognize that slight impurities in one sample of IL to the next are likely to produce greater uncertainty than inherent instrument uncertainty. It should be also pointed out that the results may depend somewhat on the scan rate. For example, we have observed samples that solidify in the laboratory at room temperature only after very long times (e.g., months). We would not expect these transitions to be observed during a DSC run that is performed over a short period of time (e.g., several hours).

The heat capacities of the compounds were determined relative to an α -alumina (sapphire) sample. The main source of uncertainty for these measurements was the uncertainty in the weight of the sample and the reference. Most samples were between (20 and 50) mg, with an uncertainty of ± 0.5 mg. The combined uncertainty of the sample mass and the sapphire reference mass corresponds to an uncertainty of $\pm (2.5$ to $4)\%$ in C_p , as indicated in the results section. The heat capacity of Sn and NaCl reference samples were measured to be within 1% of the published values.

Decomposition Temperatures. The decomposition temperatures were measured with a Mettler-Toledo TGA/SDTA 851e/SF/1100 °C thermal gravimetric analyzer, using a nitrogen atmosphere. The Mettler-Toledo STAR^e Version 7.01 software was used to determine the onset and start temperature. The onset temperature (T_{onset}) is the intersection of the baseline weight, either from the beginning of the experiment or after the drying step, and the tangent of the weight vs temperature curve as decomposition occurs. The start temperature (T_{start}) is the temperature at which the decomposition of the sample begins. An example of the onset and start temperatures is shown in Figure 1. All samples were run in aluminum pans under a nitrogen atmosphere at a heating rate of 10 °C/min. When necessary, samples were dried in situ at 130 °C for 30 min. There was no observable difference in decomposition temperature for samples dried in situ vs samples dried to the water contents listed in the section on density measurements. Three replicates for each ionic liquid were run to verify reproducibility. The largest uncertainty is from manually determining the tangent point for the onset temperature, which results in an uncertainty in the thermal decomposition temperatures of ± 2 °C. However,

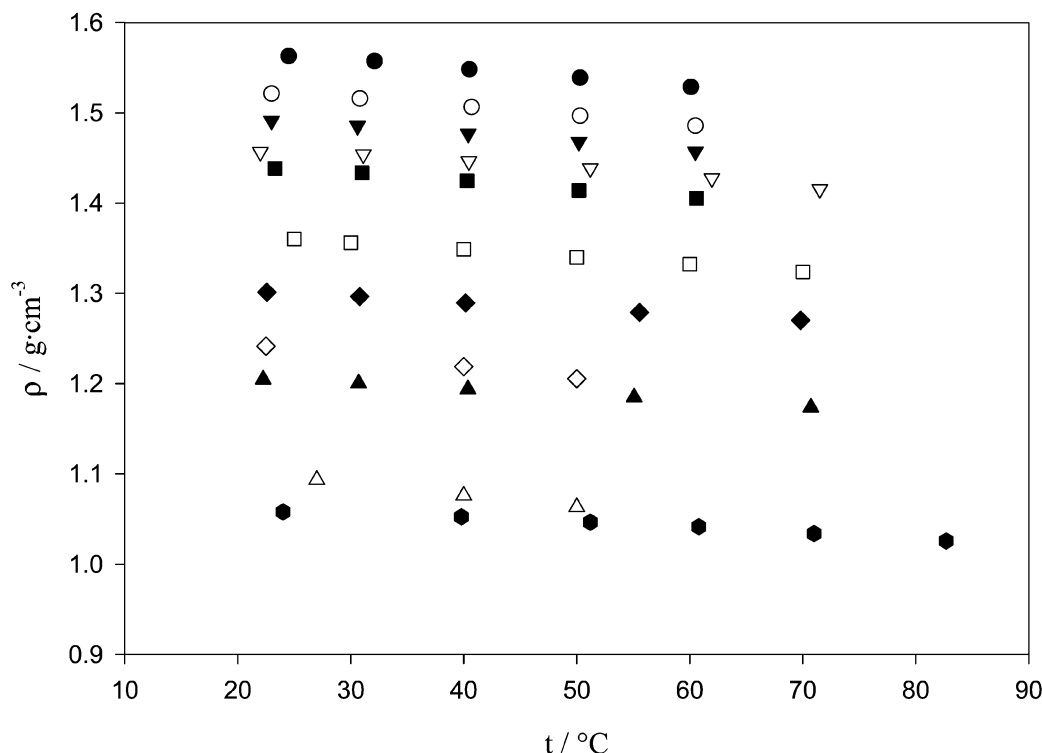


Figure 2. Densities of imidazolium-based ionic liquids as a function of temperature. ●, [bmim][methide]; ○, [emim][Tf₂N]; ▼, [emmim][Tf₂N]; ▽, [pmmim][Tf₂N]; ■, [bmim][Tf₂N]; □, [bmim][PF₆]; ◆, [bmim][triflate]; ◇, [bmmim][PF₆]; ▲, [bmim][BF₄]; △, [bmmim][BF₄]; ●, [bmim][dca].

the uncertainty in the replicates for each ionic liquid is about an order of magnitude less than this uncertainty.

Results and Discussion

Densities. The densities of [bmim][PF₆],¹² [bmim][BF₄],²⁶ [bmim][triflate], [bmim][methide], [bmim][dca], [bmim][Tf₂N], [emim][Tf₂N], [emmim][Tf₂N], [pmmim][Tf₂N], [bmmim][PF₆], and [bmmim][BF₄] are shown as a function of temperature in Figure 2. Densities decrease slightly with an increase in temperature. All the ILs studied exhibited a similar degree of volume expansion with temperature. All of the ILs are more dense than water, ranging in values from 1.0258 g/cm³ for [bmim][dca] at 82.7 °C to 1.5630 g/cm³ for [bmim][methide] at 24.5 °C. The density values, along with the experimental uncertainties, are shown in Tables 2–4. We did not measure the liquid densities of [bmim][Cl] and [bmim][Br]. Although they remain as liquids below room temperature when fully dried (see the Melting, Crystallization, and Glass-Transition Temperatures section below), they readily crystallize at room temperature when exposed to even small amounts of water vapor. Also note that in the section below the melting points of [emmim][Tf₂N] and [bmmim][BF₄] are reported as 25 °C and 37 °C, respectively. The numbers reported here for the liquid densities at temperatures below these values are for the subcooled liquids. These compounds can remain as liquids for long periods of time (i.e., months) at temperatures well below the melting points.

Our data compares remarkably well with literature values for which temperature-dependent densities are available. These comparisons are shown in Figure 3 for [emim][Tf₂N],⁵ [bmim][Tf₂N],⁶ and [bmim][BF₄].⁷ This good agreement provides additional confidence in the data presented here. Also included in Tables 2–4 are the other available literature values, which are around room temperature. For [bmim][BF₄], there is significant scatter in

Table 2. Densities of [bmim][BF₄],²⁶ [bmim][triflate], [bmim][dca], and [bmim][methide] as a Function of Temperature

<i>t</i> /°C	ρ /g·cm ⁻³	ρ (lit)/g·cm ⁻³
		[bmim][BF ₄]
22.3 ± 0.1	1.2048 ± 0.0024	1.12 (25 °C) ⁸ (4530 ppm H ₂ O) 1.26 (25 °C) ¹⁰ (1.8–3.7 ppm H ₂ O) 1.17 (30 °C) ⁹ (H ₂ O content not reported) 1.2077 (20 °C) ⁷ (307 ppm H ₂ O)
30.7 ± 1.1	1.2005 ± 0.0025	
40.4 ± 0.1	1.1940 ± 0.0014	
55.1 ± 0.3	1.1850 ± 0.0027	
70.7 ± 0.8	1.1737 ± 0.0022	
		[bmim][triflate]
22.6 ± 0.1	1.3013 ± 0.0015	
30.8 ± 0.4	1.2965 ± 0.0014	
40.2 ± 0.1	1.2894 ± 0.0012	
55.6 ± 0.5	1.2790 ± 0.0023	
69.8 ± 0.9	1.2700 ± 0.0038	
		[bmim][dca]
24.0 ± 0.1	1.0580 ± 0.0010	
39.8 ± 0.1	1.0525 ± 0.0011	
51.2 ± 0.1	1.0466 ± 0.0011	
60.8 ± 0.1	1.0415 ± 0.0010	
71.0 ± 0.1	1.0340 ± 0.0010	
82.7 ± 0.1	1.0258 ± 0.0010	
		[bmim][methide]
24.5 ± 0.1	1.5630 ± 0.0012	
32.1 ± 0.2	1.5573 ± 0.0014	
40.5 ± 0.1	1.5484 ± 0.0012	
50.3 ± 0.1	1.5390 ± 0.0019	
60.1 ± 1.3	1.5288 ± 0.0013	

the various reported values. The Suarez and co-workers⁹ value is 3% lower than the value obtained here and by Seddon and co-workers.⁷ Since water content was not reported for this sample, this somewhat lower value may be due to a higher water content. Seddon and co-workers⁷ have shown that increased water content can decrease the

Table 3. Densities of [bmim][Tf₂N], [emim][Tf₂N], [emmim][Tf₂N], and [pmmim][Tf₂N] as a Function of Temperature

<i>t</i> /°C	ρ /g·cm ⁻³	ρ (lit)/g·cm ⁻³
	[bmim][Tf ₂ N]	
23.3 ± 0.4	1.4386 ± 0.0003	1.429 (22 °C) ¹¹ 1.436 (25 °C) ⁶
31.0 ± 0.3	1.4336 ± 0.0008	
40.3 ± 0.1	1.4247 ± 0.0013	
50.2 ± 0.4	1.4142 ± 0.0008	
60.6 ± 0.1	1.4054 ± 0.0010	
	[emim][Tf ₂ N]	
23.0 ± 0.1	1.5213 ± 0.0023	1.518 (25 °C) ⁵ 1.520 (22 °C) ¹¹ 1.56 (20 °C) ²⁵
30.8 ± 0.1	1.5159 ± 0.0018	
40.7 ± 0.3	1.5065 ± 0.0018	
50.3 ± 0.1	1.4967 ± 0.0015	
60.5 ± 0.4	1.4858 ± 0.0021	
	[emmim][Tf ₂ N]	
23.0 ± 0.1	1.4913 ± 0.0008	
30.6 ± 0.1	1.4855 ± 0.0007	
40.4 ± 0.1	1.4769 ± 0.0008	
50.2 ± 0.1	1.4680 ± 0.0008	
60.5 ± 0.4	1.4572 ± 0.0010	
	[pmmim][Tf ₂ N]	
22.0 ± 1.4	1.4567 ± 0.0032	
31.1 ± 0.2	1.4542 ± 0.0029	
40.5 ± 0.1	1.4464 ± 0.0040	
51.2 ± 0.9	1.4386 ± 0.0049	
62.0 ± 0.1	1.4275 ± 0.0040	
71.5 ± 0.8	1.4155 ± 0.0037	

Table 4. Densities of [bmmim][PF₆] and [bmmim][BF₄] as a Function of Temperature

<i>t</i> /°C	ρ /g·cm ⁻³
	[bmmim][PF ₆]
22.5 ± 0.1	1.2416 ± 0.0018
40.0 ± 0.1	1.2190 ± 0.0073
50.0 ± 0.1	1.2055 ± 0.0104
	[bmmim][BF ₄]
27.0 ± 0.1	1.0935 ± 0.0034
40.0 ± 0.1	1.0762 ± 0.0034
50.0 ± 0.1	1.0634 ± 0.0070

density significantly. The other two values, with reported water content of 4530 ppm and 1.8–3.7 ppm, respectively, are 9% lower and 6% higher, respectively, than the values reported here. While these discrepancies may be due entirely to water content, we note that it is our experience that it is not possible to achieve extremely low water content for ILs containing the BF₄ anion without serious heating, which can result in significant degradation of the IL. For all other compounds where data is available, i.e., [bmim][Tf₂N], [emim][Tf₂N], and [bmim][dca], our room-temperature values are in good agreement with literature values,^{5,6,11,25} except for one measurement for [emim][Tf₂N],²⁵ which is a bit high.

The effect of having different substituents on the imidazolium cation is shown in Figure 4 for a series of ILs with the [Tf₂N] anion. The density decreases as the alkyl-substituted chain length on the cation increases. For instance, the density of [emim][Tf₂N] is significantly greater than that of [bmim][Tf₂N]. In addition, the introduction of a third alkyl substituent on the imidazolium ring at the C2 position reduces the density (e.g., comparing [emim][Tf₂N] with [emmim][Tf₂N] and [bmim][BF₄] with [bmmim][BF₄]). The effect of the anion is shown in Figure 5 for a series of ILs with the common [bmim] cation. It is clear that the density of these compounds increases with increasing molecular weight of the anion: the larger the

anion, the higher the density. The molecular weights of the dca, BF₄, PF₆, triflate, Tf₂N, and methide anions are (66.0, 86.8, 145.0, 149.1, 280.1, and 411.2) g/mol, respectively. This trend is most likely due to the nature of the anions studied. Since none of the anions have a particularly long or awkward chain, it is possible that they all can occupy favorable, relatively close-approach positions around the cation, resulting in the high densities. However, one would not expect the observed trend to hold for anions with very long alkyl chains, such as those proposed by Wasserscheid and co-workers.²⁷

Melting, Crystallization, and Glass-Transition Temperatures. Melting, crystallization, and glass-transition temperatures were measured using DSC. The results are presented in Table 5 showing the melting temperature (*T*_m), the freezing temperature (*T*_f), the glass-transition temperature (*T*_g), and the cold crystallization temperature (*T*_{cc}), where appropriate. Here, the melting and freezing temperatures are taken to be the onset of an endothermic peak on heating and the onset of the exothermic peak on cooling, respectively. The glass-transition temperature is the midpoint of a small heat capacity change on heating from the amorphous glass state to a liquid state. The cold crystallization temperature is defined as the onset of an exothermic peak on heating from a subcooled liquid state to a crystalline solid state. This behavior is well known in polymers and other amorphous materials.^{28, 29}

In general, three types of behavior are observed for the imidazolium-based ionic liquids studied. The first group of ILs has a distinct freezing point on cooling and a distinct melting point on heating. While subcooling of ILs is common,¹³ these particular ILs readily crystallize and do not form glasses. The DSC scan of [bmim][triflate] in Figure 6 shows this type of behavior. Note that the scan, as read from left to right, indicates cooling from 20 °C down to -100 °C, followed by heating from -100 °C to above 20 °C. The compounds studied that show this behavior are [bmim][triflate] and [emmim][Tf₂N].

The second type of behavior is characterized by no true phase transitions but only the formation of an amorphous glass on cooling and reformation of the liquid on heating. These ILs have no melting or freezing points, but only glass-transition temperatures. The heating branch of a typical DSC scan that shows this behavior is presented for [bmim][BF₄] in Figure 7. The compounds studied that show this behavior are [bmim][Cl], [bmim][Br], [bmim][BF₄], [bmim][methide], [bmmim][PF₆], and [pmmim][Tf₂N].

The third group of ILs is characterized by the liquid subcooling to a glass state, as is observed for the second group. However, upon heating, the compound passes from the glass to a subcooled liquid phase, and then a cold crystallization occurs, followed by a melting transition. In other words, at temperatures higher than *T*_g, the subcooled liquid actually *crystallizes upon heating*. Then, as the sample is heated further, it melts at *T*_m. The heating branch of a typical DSC scan for [bmim][Tf₂N] shows this behavior in Figure 8. As mentioned above, this third type of behavior is typical for many polymers and other amorphous compounds.^{28,29} The compounds studied that show this behavior are [bmim][PF₆], [bmim][Tf₂N], [bmim][dca], [emim][Tf₂N], and [bmmim][BF₄].

Many of the compounds listed in Table 5 have been studied by other groups and the literature values for *T*_m, *T*_f, and *T*_g are shown in the table. No transitions have been identified as cold crystallization previously. The data presented here shows good agreement with literature values with a few exceptions. For [emim][Tf₂N], our *T*_m

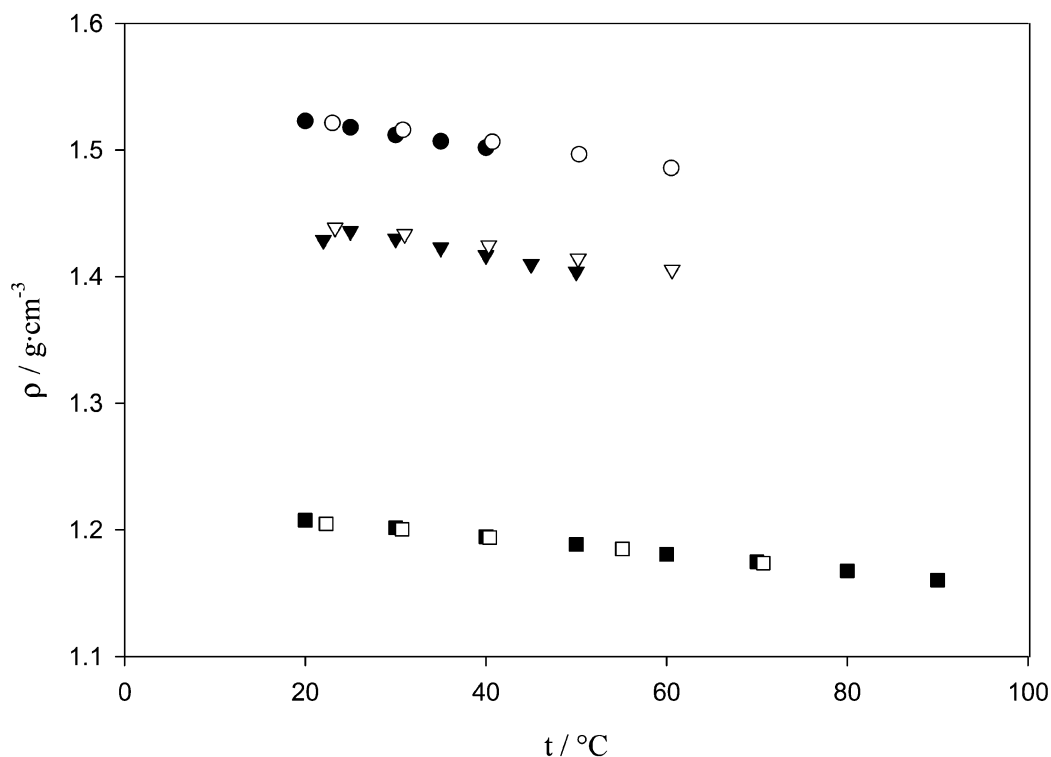


Figure 3. Comparison of densities of [emim][Tf₂N], [bmim][Tf₂N], and [bmim][BF₄] with literature values.⁵⁻⁷ [emim][Tf₂N]: ○, this work; ●, Noda et al.⁵ [bmim][Tf₂N]: ▽, this work; ▼, Dzyuba and Bartsch.⁶ [bmim][BF₄]: □, this work; ■, Seddon et al.⁷

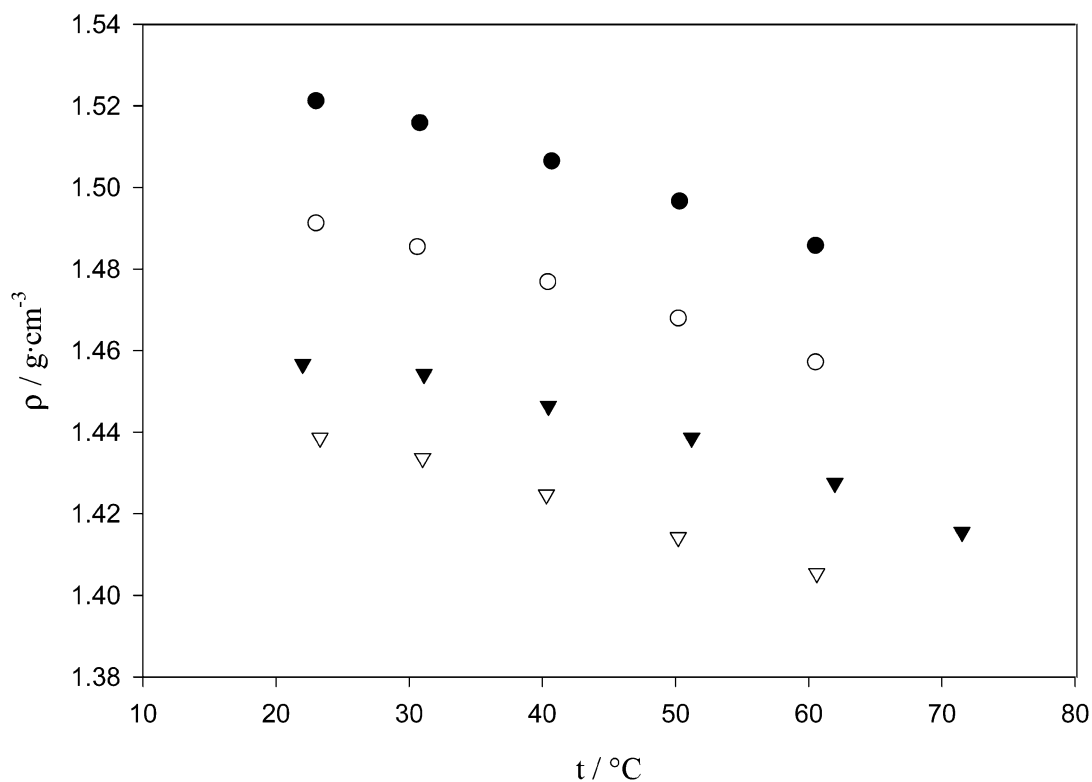


Figure 4. Effect of different cation substituents on the density for ILs containing the [Tf₂N] anion. ●, [emim][Tf₂N]; ○, [emmim][Tf₂N]; ▼, [pmmim][Tf₂N]; ▽, [bmim][Tf₂N].

value agrees well with the two literature values.^{6,13} However, the T_g values differ somewhat,⁶ and no T_{cc} has been previously identified for this compound, but this could correspond to what was listed as T_f .¹³ Differences in scanning rate, water content, and the definition of a transition (i.e., using the transition peak rather than the transition onset, as was done here) all can affect the

reported temperatures. Although melting transitions are reported for [bmim][Br], [bmim][Cl], and [pmmim][Tf₂N] in some sources,^{8,13} no melting peaks were observed in the current work after in situ drying. One can observe melting peaks for the two halides in the presence of water, but after drying to remove the water, crystallization appears to be inhibited. Finally, the melting temperature (T_m) for [bmim]-

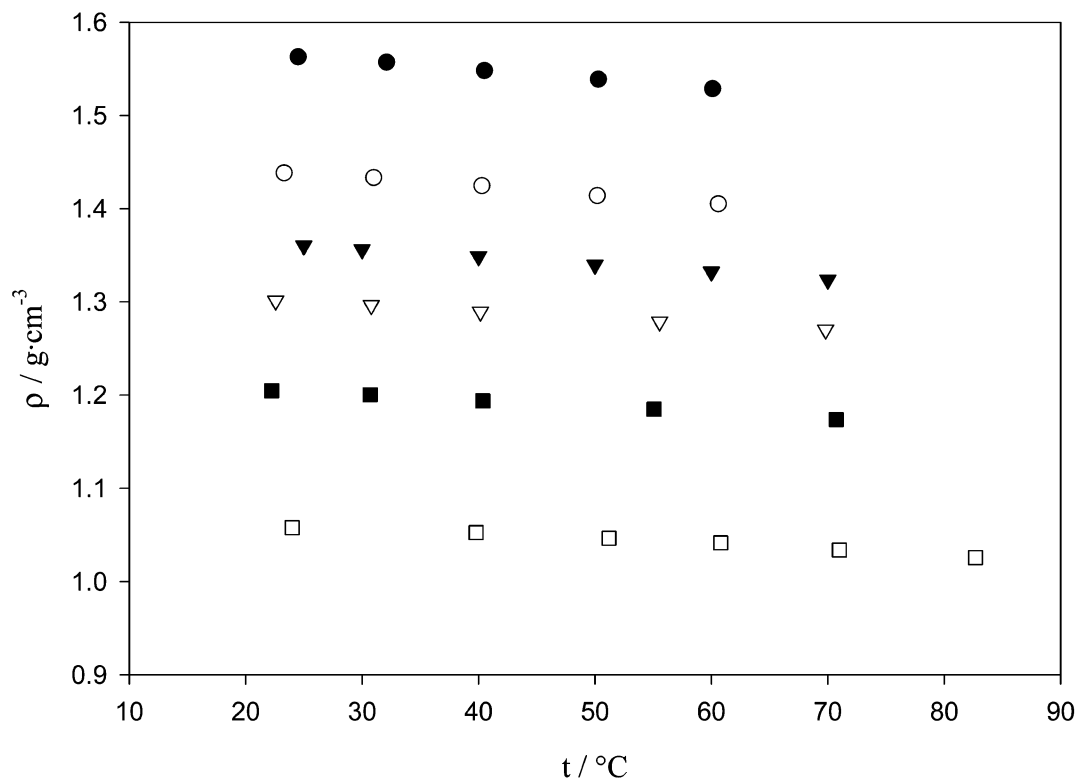


Figure 5. Effect of different anions on the density for ILs containing the [bmim] cation. ●, [bmim][methide]; ○, [bmim][Tf₂N]; ▼, [bmim]-[PF₆]; ▽, [bmim][triflate]; ■, [bmim][BF₄]; □, [bmim][dca].

Table 5. Melting (T_m), Freezing (T_f), Cold Crystallization (T_{cc}), and Glass-Transition (T_g) Temperatures for Imidazolium Ionic Liquids as Determined by DSC (Literature Values Are Included in Parentheses)

compound	$T_m/^\circ\text{C}$	$T_f/^\circ\text{C}^a$	$T_{cc}/^\circ\text{C}$	$T_g/^\circ\text{C}$
[emim][Tf ₂ N]	-17 (-15 ¹³ , -21 ⁶)	(-50 ¹³)	-61	-92 (-78 ⁶)
[emmim][Tf ₂ N]	25 (27 ¹³)	-25 (-18 ¹³)		
[pmmim][Tf ₂ N]	(15 ¹³)			-82 (-82 ¹³)
[bmim][Cl]	(41 ⁸)			-69
[bmim][Br]				-50
[bmim][BF ₄]				-85 (-71 ¹⁵ , -81 ⁹)
[bmim][PF ₆]	11 (10 ⁸)		-37	-76 (-77 ⁶ , -61 ⁹)
[bmim][Tf ₂ N]	-2 (-6 ⁶)		-44	-86 (-87 ⁶)
[bmim][triflate]	13	-19		
[bmim][methide]				-65
[bmim][dca]	-6		-29	-90
[bmmim][BF ₄]	37		-3	-68
[bmmim][PF ₆]				-58

^a All literature values for crystallization are recorded as freezing points.

[PF₆] reported here agrees with the data by Huddleston et al.,⁸ although other researchers have only observed a T_g for this compound.^{6,9} Again, differences in heating rates, water content, and some experimental conditions could explain the discrepancies. The effect of cation and anion structure on T_m , T_f , and T_g have been discussed elsewhere.^{6,13,15} It should be noted that two different crystal structures have been observed for [bmim][Cl].^{30,31} However, the conversion between the two structures is observed to be very slow. Moreover, for [bmim][Cl] and many other [bmim] salts (see group two, above), we do not observe any crystal formation at all. This is due to the relatively short time frame of the DSC experiments (e.g., 10–20 min using a scan rate of 10 °C/min).

Decomposition Temperatures. Figure 1 shows a characteristic curve for the decomposition of the ILs, as measured by TGA. The decomposition curves of all ILs studied were similar to this curve, except for [bmim][dca]. For [bmim][dca], the weight of the sample decreased at the start temperature but leveled off around 330 °C before

decreasing significantly above 400 °C. There were no attempts to analyze the decomposition products of any of the ILs. Table 6 shows the onset and start temperatures for the imidazolium ILs investigated, as well as comparisons to previously published onset temperatures. We note that the relatively fast heating rate used here (10 °C/min) should give a reasonable indication of the relative thermal stability of the various ILs. However, a true understanding of long-term stability with various impurities and in reactive atmospheres would require a more detailed investigation.¹⁸

For those ILs where decomposition temperatures have been previously published in the literature, the onset temperature from this study matched the previously reported values (see Table 6) reasonably well, given the different methods employed to determine T_{onset} . Nonetheless, we should point out the large difference between our value for [bmmim][PF₆] and [bmmim][BF₄] that is reported by Awad and co-workers.¹⁷ This difference may be due to the composition of the pan used in the experiments. Our

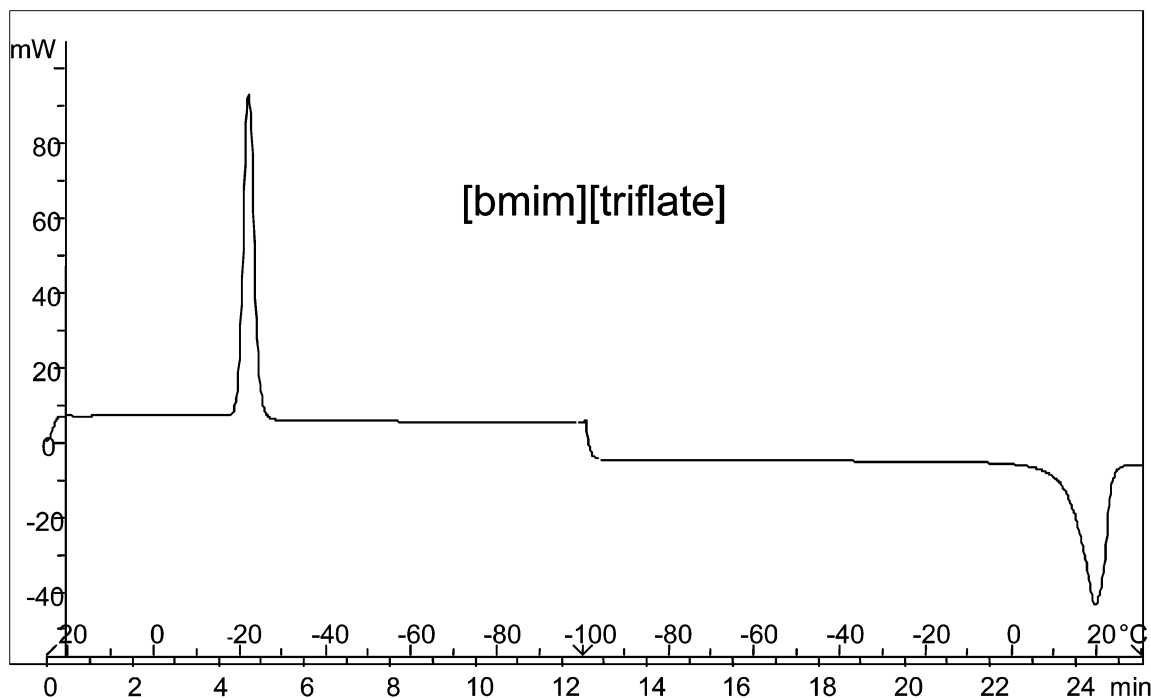


Figure 6. DSC scan for [bmim][triflate], showing a distinct freezing point upon cooling and a distinct melting point upon heating.

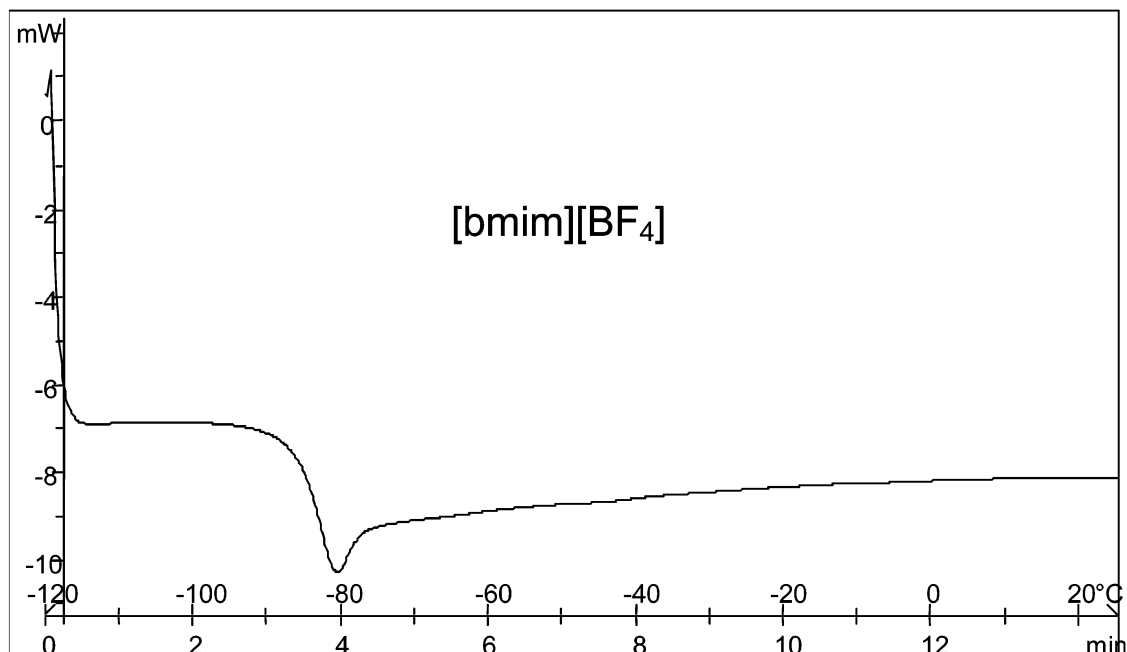


Figure 7. DSC scan for [bmim][BF₄], showing only a glass transition around -85 °C.

samples were examined in aluminum pans, while the decomposition experiments by Awad et al. were conducted in alumina pans. This confirms earlier decomposition results shown by Ngo et al. that PF₆ salts decompose at lower temperatures in aluminum pans as compared to alumina pans.¹³ In addition, there is a wide range of values reported for [bmim][BF₄], with our value more closely matching the value reported by Holbrey and Seddon.¹⁵ From Table 6, it is clear that the relative stability of ILs where various anions are paired with the 1-butyl-3-methylimidazolium cation is Br < dca < BF₄ < triflate < methide < Tf₂N. This is similar to what was observed by Ngo et al.¹³ The one exception is that we find the methide anion to be more thermally stable than BF₄.

Heat Capacities. The heat capacity of a compound is defined as the amount of energy per molecule that the compound can store before the temperature of the compound increases. Generally, the energy can be stored in translational, vibrational, and rotational modes. Therefore, one would expect that a molecule containing more atoms would have more energy storage modes and thus a higher heat capacity. This is the general trend observed in the heat capacities of the compounds as shown in Table 7, where we show values of the heat capacities at two temperatures, along with the estimated experimental uncertainties. For instance, if one compares the series of [bmim] ILs with various anions, it is clear that the larger the anion, the higher the heat capacity. Likewise, longer

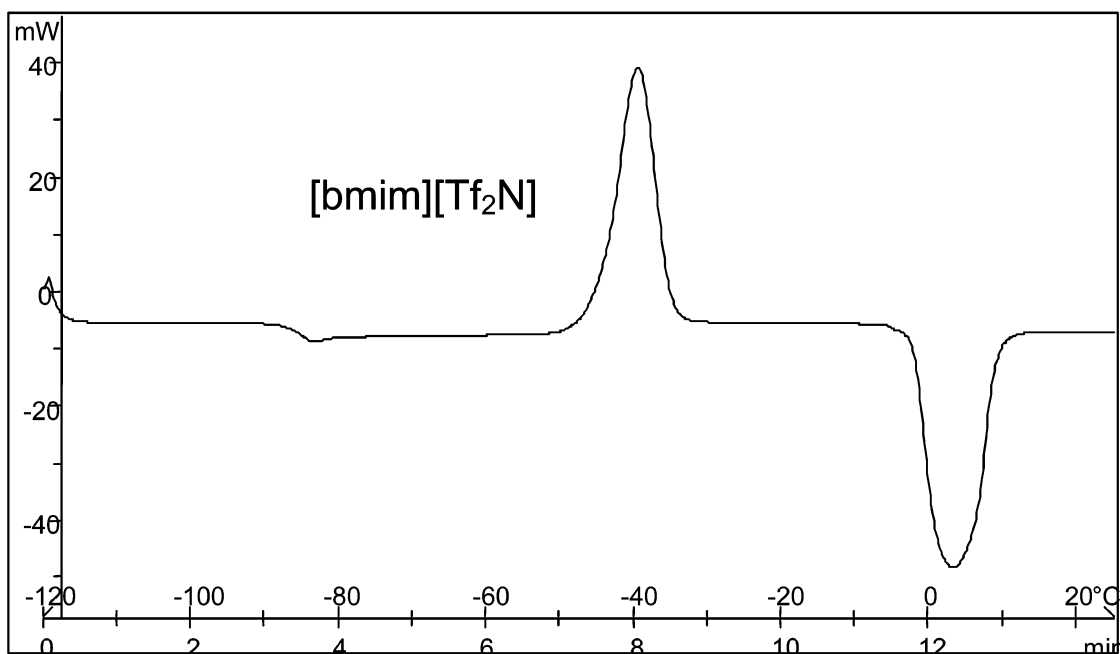


Figure 8. DSC scan for [bmim][Tf₂N], showing a glass-transition temperature, followed by a cold crystallization and a melting transition.

Table 6. Onset and Start Temperatures for Thermal Decomposition of Several Imidazolium ILs

compound	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{start}}/^{\circ}\text{C}$	$T_{\text{onset}}(\text{lit})/^{\circ}\text{C}$
[bmim][Cl]	264	150	254 ⁸ , 234 ¹⁷
[bmim][Br]	273	215	
[bmim][dca]	300	240	
[bmim][BF ₄]	361	290	403 ⁸ , 360 ¹⁵
[bmim][methide]	413	360	
[bmim][triflate]	392	340	
[bmim][Tf ₂ N]	422	330	439 ⁸
[bmmim][PF ₆]	373	235	425 ¹⁷
[bmmim][BF ₄]	380	285	405 ¹⁷
[pmmim][Tf ₂ N]	462	385	462 ¹³

Table 7. Heat Capacities of the Imidazolium ILs at 25 and 50 °C

compound	$C_p(25\text{ }^{\circ}\text{C})$	$C_p(50\text{ }^{\circ}\text{C})$	uncertainty
	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
[emim][Tf ₂ N]	524.3	532.2	±3.9%
[emmim][Tf ₂ N]	492.7 ^a	498.8	±2.6%
[pmmim][Tf ₂ N]	554.5	558.7	±4.3%
[bmim][Cl]	322.7	333.7	±4.1%
[bmim][Br]	316.7	323.6	±3.2%
[bmim][BF ₄]	351.5	358.0	±3.7%
[bmim][PF ₆]	397.6	405.1	±4.4%
[bmim][Tf ₂ N]	536.3	543.9	±3.6%
[bmim][TfO]	417.2	423.1	±4.0%
[bmim][methide]	782.8	802.4	±2.3%
[bmim][dca]	364.6	370.0	±3.8%
[bmmim][BF ₄]	375.3 ^b	406.5 ^c	±3.4%
[bmmim][PF ₆]	433.6	449.1	±2.4%

^a Measurement at 36 °C. ^b Measurement at 57 °C. ^c Measurement at 99 °C.

alkyl substituents on the cation, for a given anion, increases the heat capacity. This is clear from a comparison of [emim]-[Tf₂N] with [bmim][Tf₂N]. Likewise, adding a methyl group on the C2 carbon (e.g., [bmmim][PF₆] compared with [bmim][PF₆]) increases the heat capacity. The one exception is [emmim][Tf₂N], which has a lower heat capacity than [emim][Tf₂N]. We do not have an explanation for this result. In Table 8 we give linear or cubic fits of the heat capacity data as a function of temperature, along with the applicable temperature range for the correlation.

Table 8. Correlations for the Heat Capacities of the Imidazolium ILs as a Function of Temperature Along with the Applicable Temperature Ranges

compound	correlation for $C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	σ	$\Delta T/\text{K}$
[emim][Tf ₂ N]	$0.315(T/\text{K}) + 430.39$	0.43	298.15–327.15
[emmim][Tf ₂ N]	$0.427(T/\text{K}) + 360.72$	0.24	309.15–347.15
[pmmim][Tf ₂ N]	$4.58 \times 10^{-4}(T/\text{K})^3 - 0.428(T/\text{K})^2 + 133.4(T/\text{K}) - 13310$	0.83	298.15–327.15
[bmim][Cl]	$0.406(T/\text{K}) + 202.0$	0.24	298.15–327.15
[bmim][Br]	$0.262(T/\text{K}) + 238.9$	0.30	298.15–327.15
[bmim][BF ₄]	$0.261(T/\text{K}) + 273.65$	0.24	298.15–327.16
[bmim][PF ₆]	$0.302(T/\text{K}) + 307.53$	0.32	298.15–327.17
[bmim][Tf ₂ N]	$4.71 \times 10^{-4}(T/\text{K})^3 - 0.438(T/\text{K})^2 + 136.0(T/\text{K}) - 13555$	0.77	298.15–327.18
[bmim][TfO]	$0.238(T/\text{K}) + 346.19$	0.45	298.15–327.19
[bmim][methide]	$0.784(T/\text{K}) + 549.04$	0.30	298.15–327.20
[bmim][dca]	$0.197(T/\text{K}) + 305.81$	0.41	298.15–327.21
[bmmim][BF ₄]	$0.742(T/\text{K}) + 130.33$	0.57	330.15–372.15
[bmmim][PF ₆]	$0.539(T/\text{K}) + 273.7$	0.55	298.15–327.21

We should reiterate that a number of the ILs do not crystallize readily after they are thoroughly dried in situ, as described in the melting, crystallization, and glass-transition temperatures section above. Rather, these compounds (e.g., [bmim][Cl]) only go through a glass-transition temperature at very low temperatures. Therefore, all of the heat capacities reported here are for liquids, although some of them may be subcooled liquids.

As mentioned previously, literature data for C_p values of ILs is rather scarce. Agreement of limited literature values^{19–21} with the data presented here is mixed. Specifically, the values presented here for [bmim][PF₆] agree with those of Magee and co-workers¹⁹ within experimental uncertainty. Wilkes and co-workers²¹ give C_p values for [emim][BF₄], [bmim][BF₄], and [pmmim][Tf₂N] at 100 °C. Their value for [bmim][BF₄] of 375 J mol⁻¹ K⁻¹ agrees remarkably well with the value obtained by our correlation, even though this represents an extrapolation beyond the temperatures investigated here. However, their value for [pmmim][Tf₂N] of 501 J mol⁻¹ K⁻¹ at 100 °C is significantly less than the value obtained from our correlation and even less than our value measured at 50 °C. Holbrey and co-

workers²⁰ presented values for [bmim][Cl], [bmim][PF₆], and [bmim][Tf₂N] as well as two other ILs. Their values for the three [bmim] salts are consistently (10–15)% lower than the values reported here.

Conclusions

Understanding basic thermophysical properties of ILs is vital for design and evaluation. In this paper, we have presented density as a function of temperature, melting temperatures, glass-transition temperatures, decomposition temperatures, and heat capacities as a function of temperature for the series of 13 imidazolium-based ILs. We find that density decreases as the alkyl-substituted chain length on the cation increases. Moreover, for a given cation, the density increases with increasing molecular weight of the anion for the anions studied here. The ILs tend to subcool easily; in many cases, they do not crystallize but simply form glasses at very low temperatures. A number of them exhibit crystallization, and then melting, upon heating, similar to what is observed for many polymers. The thermal stability increases with increasing anion size. Finally, heat capacities increase with temperature and with increasing number of atoms in the IL.

Acknowledgment

We would like to acknowledge the generous contribution of samples of [pmmim][Tf₂N], [emim][Tf₂N], [emmim][Tf₂N], and [bmim][methide] from Covalent Associates. Finally, we would like to thank the group of Prof. Tom Welton for the [bmmim][PF₆] and [bmmim][BF₄] samples, Dr. Mark Muldoon for synthesis of the [bmim][dca] sample, and Ms. Neha Kamat for measurements of the density of [bmim][dca].

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Received for review December 2, 2003. Accepted April 28, 2004. We acknowledge partial financial support for the project from the National Science Foundation (CTS-9987627), the Department of Education (P200A010448-01 for J.M.C. and D.G.H.), and the State of Indiana 21st Century Research and Technology Fund (#909010455).

JE034261A