Isobaric Heat Capacities of the Ionic Liquids $[C_n mim][Tf_2N]$ ($n = 6, 8$) from (323 to 573) K at 10 MPa[†]

Sebastian Bochmann and Glenn Hefter*

Chemistry Department, Murdoch University, Murdoch WA 6150, Australia

Isobaric volumetric heat capacities (σ_p) of the ionic liquids 1-hexyl (or octyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6mim][Tf_2N]$ and $[C_8mim][Tf_2N]$, have been measured in the temperature range of $323 \le T/K \le 573$ with a Tian-Calvet type differential calorimeter at a pressure of 10 MPa. Isobaric massic (c_p) and molar (C_p) heat capacities were calculated from the σ_p values using densities estimated from literature data. The present C_p values increase approximately linearly with temperature over the investigated range. Where comparison is possible, the present results are in excellent agreement with literature data obtained by adiabatic calorimetry but disagree markedly (by up to 7 %) with those measured by differential scanning calorimetry. Both compounds show evidence of decomposition at $T \gtrsim 535$ K, which is in approximate agreement with recent slow scan thermogravimetric measurements but is about 85 K lower than suggested by previous fast scan data.

Introduction

In recent years room-temperature ionic liquids (ILs) have attracted intense attention because of their many interesting properties. This includes their very low vapor pressure,[1] thermal stability,[2] ability to solubilize both polar and nonpolar substances,[3] and their large liquidus temperature range.[4] A key feature of ILs is that their physical properties can be tailored by judicious selection of cations, anions, and substituents.[5] This makes them promising candidates for a variety of applications, such as reaction and separation media, and for devices like batteries, fuel cells, and solar cells.[5−9] On the negative side, the viscosity of ILs is high compared to that of conventional molecular solvents, which is a disadvantage in industrial applications with respect to reaction rates and engineering design (for example, in relation to pumping costs). The easiest way to deal with such problems is to reduce the viscosity by increasing the temperature. The energy required to do this is directly related to the heat capacity. This quantity is also important for characterizing the nature of these new materials.

Until now, relatively few heat capacities of ILs have been determined, particularly at the higher temperatures that are likely to be of practical importance. Furthermore, most of the reported heat capacity measurements were obtained using commercial differential scanning calorimeters (DSCs). While this technique is convenient and rapid, the accuracy of the results is often hard to determine. A good example of this is provided by the extensive measurements that have been made on the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6mim][Tf_2N]$. This compound has been adopted by IUPAC as a useful reference material to establish the accuracy of common physicochemical measurements on ILs.[10−12] It was selected because it is stable, has a reasonably low viscosity and a low water affinity, and is easily prepared and purified.[11] While most of the physical properties of this compound could be satisfactorily reproduced in independent laboratories, the heat capacity data showed serious discrepancies.[11,13−18] Two independent determinations[13,14] of the molar heat capacity of $[C_6mim][Tf_2N]$ using adiabatic calorimetry, which is usually considered to be the most accurate method for determining the heat capacities of condensed materials, produced values that agreed to about ± 0.5 % over a wide temperature range. On the other hand, the numerous DSC measurements[15−18] differed significantly, by up to ± 7 %, from the adiabatic calorimetry results and from each other. To resolve this unsatisfactory situation the present paper reports the heat capacity of $[C_6mim][Tf_2N]$ over the range of $323 \le T/K \le 573$ using a modified[19] commercial Tian-Calvet calorimeter. In addition, $[C_8mim][Tf_2N]$ has also been studied for comparison.

Experimental Section

Materials. A sample of $[C_6mim][Tf_2N]$ was obtained from a very well-characterized batch prepared by J. A. Widegren at the University of Notre Dame, USA, and distributed through the National Institute of Standards and Technology (NIST), Boulder, USA, as a part of an IUPAC project.[10−12] For convenience this material will be referred to as the "IUPAC sample". The IL $[C_8mim][Tf_2N]$ was provided by K. N. Marsh, University of Canterbury, Christchurch, New Zealand.

Prior to measurement, the ILs were degassed and dried under vacuum ($< 10^{-5}$ MPa) with stirring at room temperature for about 24 h. They were then sealed in Schlenk tubes which were stored under vacuum over freshly dried silica gel in a desiccator. The mass fraction (w) of water in the samples, measured by coulometric Karl Fischer titration was $w(H_2O) = 1.1 \cdot 10^{-4}$ before and $6.5 \cdot 10^{-4}$ after the heat capacity measurement for $[C_6mim][Tf_2N]$ and $1.4 \cdot 10^{-4}$ before and $3.5 \cdot 10^{-4}$ after for $[C_8mim][Tf_2N]$.

Experimental Setup

A Tian-Calvet type differential microcalorimeter (Setaram, Lyon, France, model C-80, sensitivity = 5 μW, resolution = 0.1 μW) was used to determine the isobaric volumetric heat capacities (σ_p) of the ILs between (323 and 573) K at a pressure

---

[†] Part of the "Josef M. G. Barthel Festschrift".

* Corresponding author. E-mail: g.hefter@murdoch.edu.au.

10.1021/je900676b

of 10 MPa. The modifications and experimental protocol have been described in detail by Schrödle et al.,[19] so only brief comments are made here. The pressure within the sample cell was kept constant by a connection to a large (~ 1 L) buffer volume filled with high-purity N_2 (BOC, > 99.9 %) at the target pressure. The pressure was arbitrarily fixed at 10 MPa to facilitate the use of liquid water as a calorimetric reference up to 573 K. Temperature fluctuations in the laboratory, which was thermostatted to ± 3 K, resulted in relative pressure changes of ± 0.3 % during a typical experimental run (due to the thermal mass of the apparatus). This variation has an insignificant effect on the measured heat capacities. Nitrogen (N_2) and water were used as the heat capacity standards.[20,21] Matched nickel cells (low carbon, Ni-201) were used throughout. A preheater was fitted above the calorimetric block to minimize heat loss from the cells through the filling tubes and to reduce convective phenomena within the calorimeter.[22,23]

Sample Preparation and Calorimetric Measurements. Polypropylene syringes and the calorimeter cell were dried at 50 °C and flushed with N_2 before use. The selected sample was drawn slowly from its Schlenk tube into a syringe under a flowing N_2 atmosphere and immediately injected into the cell, which was then pressurized to 10 MPa with N_2.

The calorimetric measurements were performed using the step method. Following initial stabilization for 5 h at 323 K, successive temperature increments (ΔT) were made, followed by isothermal equilibration for (1.5 to 2) h between each step. Alternating increments of (5 and 20) K with scan rates of (0.25 and 1.0) $\mathrm{K \cdot min^{-1}}$ were used throughout except for the two highest temperature steps which were of 10 K at 0.50 $\mathrm{K \cdot min^{-1}}$. A complete temperature scan therefore required about two days. High purity water and nitrogen were used as calibrants as described below. This method has a reproducibility and uncertainty of ± 0.3 % in σ_p over the entire temperature range.[19]

Results and Discussion

Volumetric Heat Capacities. The volumetric heat capacities were evaluated from temperature $T(t)$ and heat flow $\dot{Q}(t)$ data recorded as function of time (t). As described previously,[19] the average isobaric volumetric heat capacity of a sample, σ_j^{S}, at the average temperature of the increment, $\bar{T}_j = 1/2(T'_j + T_j)$, where $T_j = T(t_j)$, and $T'_j = T(t'_j)$ are respectively the temperature of the sample before and after each temperature increment, was calculated assuming a linear response for the calorimeter as

$$\sigma_j^{\mathrm{S}} = (q_j^{\mathrm{S}} - q_j^{\mathrm{W}})\frac{\sigma_j^{\mathrm{W}} - \sigma_j^{\mathrm{N}}}{q_j^{\mathrm{W}} - q_j^{\mathrm{N}}} + \sigma_j^{\mathrm{W}} \tag{1}$$

where q_j are instrument-specific volumetric heat capacities. The superscripts W and N indicate values for liquid water and gaseous nitrogen, respectively, which were obtained from calibration experiments performed under identical conditions. Volumetric heat capacities for water and nitrogen at the appropriate conditions were taken from standard literature sources.[20,21] Isobaric volumetric heat capacities obtained in this way are summarized in Tables 1 and 2.

Table 1. Experimental Volumetric, Massic, and Molar Heat Capacities of $[C_6mim][Tf_2N]$ in the Liquid State at Constant Pressure (p = 10 MPa)[a]

T / K	σ_{IL} / $\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$	ρ_{IL} / $\mathrm{g \cdot cm^{-3}}$	c_p / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	C_p / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
325.02	1.9518	1.357	1.438	644
337.38	1.9648	1.346	1.460	653
349.75	1.9710	1.335	1.476	661
362.12	1.9813	1.324	1.496	670
374.48	1.9879	1.313	1.514	677
386.84	2.0029	1.302	1.538	688
399.19	2.0088	1.291	1.556	696
411.56	2.0192	1.280	1.578	706
423.91	2.0322	1.269	1.601	717
436.27	2.0346	1.258	1.617	724
448.63	2.0488	1.248	1.642	735
460.99	2.0446	1.237	1.653	740
473.35	2.0450	1.226	1.668	746
485.72	2.0469	1.216	1.683	753
498.09	2.0562	1.205	1.706	763
510.46	2.0535	1.195	1.718	769
522.84	2.0653	1.185	1.743	780
535.20	2.0619	1.175	1.755	785
547.56	(2.0762)	1.166	(1.781)	(797)
554.97	(2.0997)	1.160	(1.810)	(810)
564.85	(2.0326)	1.153	(1.763)	(789)

[a] Densities ρ_{IL} were estimated from literature data as described in the text. Parentheses indicate that the result is probably affected by decomposition.

Table 2. Experimental Volumetric, Massic, and Molar Heat Capacities of $[C_8mim][Tf_2N]$ in the Liquid State at Constant Pressure (p = 10 MPa)[a]

T / K	σ_{IL} / $\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$	ρ_{IL} / $\mathrm{g \cdot cm^{-3}}$	c_p / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	C_p / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
325.02	1.9479	1.304	1.494	710
337.38	1.9625	1.292	1.519	722
349.75	1.9722	1.279	1.542	733
362.12	1.9829	1.267	1.565	744
374.48	1.9920	1.255	1.587	755
386.84	2.0025	1.242	1.612	767
399.19	2.0104	1.230	1.634	777
411.56	2.0164	1.218	1.656	787
423.91	2.0267	1.206	1.681	799
436.27	2.0326	1.194	1.702	809
448.63	2.0453	1.182	1.730	823
460.99	2.0439	1.170	1.747	831
473.35	2.0462	1.159	1.765	839
485.72	2.0479	1.147	1.785	849
498.09	2.0574	1.135	1.813	862
510.46	2.0563	1.124	1.829	870
522.84	2.0685	1.113	1.858	884
535.2	2.0647	1.102	1.874	891
547.51	(2.0791)	1.091	(1.906)	(906)
554.94	(2.0771)	1.085	(1.914)	(910)
564.84	(2.0755)	1.076	(1.929)	(917)

[a] Densities ρ_{IL} were estimated from literature data as described in the text. Parentheses indicate result is probably affected by decomposition.

Density Estimation. Conversion of the experimental isobaric volumetric heat capacities (σ) into the more useful massic values (c_p) requires knowledge of the density of the sample under identical conditions of temperature and pressure. Densities of liquid $[C_6mim][Tf_2N]$ have been reported for the IUPAC sample[19,24−26] and for other preparations.[27−33] A critical examination of the data, especially those for the IUPAC sample, has been given by Chirico et al.[12] The recommended values for $p \approx 0.1$ MPa and $258 \le T/\mathrm{K} \le 373$ were expressed by the linear equation, eq 2.

$$\rho/(\mathrm{g{\cdot}cm^{-3}}) = 1.64095 - 0.9012{\cdot}10^{-3}(T/\mathrm{K}) \tag{2}$$

As no experimental density data were available for $[C_6mim][Tf_2N]$ at $T > 423$ K, eq 2 was used to calculate the densities up to $T = 570$ K.

The pressure dependency of the density of $[C_6mim][Tf_2N]$ was studied on the IUPAC sample for pressures up to 65 MPa at temperatures up to 423 K.[25,26] All data were fit to the following form of the Tait equation:[12]

$$\rho = \rho^\circ/[1 - c\ln\{(b + p/\mathrm{kPa})/(b + 101.3)\}] \tag{3}$$

where ρ° is the density at the reference pressure (101.3 kPa) calculated with eq 2. The calculation of parameters b and c as a function of temperature is described in Chirico et al.[12] Equation 3 was used to transform the calculated densities of $[C_6mim][Tf_2N]$ at $p \approx 0.1$ MPa into values applicable at $p = 10$ MPa.

No density data for $[C_8mim][Tf_2N]$ at high pressures or temperatures were found in the literature. Densities reported by Tokuda et al.[2] at $p \approx 0.1$ MPa and $288 \leq T/\mathrm{K} \leq 313$ were linear with respect to T and could be expressed by eq 4:

$$\rho/(\mathrm{g{\cdot}cm^{-3}}) = 1.62 - 1.00{\cdot}10^{-3}(T/\mathrm{K}) \tag{4}$$

This equation was used to calculate the densities (ρ_B°) of $[C_8mim][Tf_2N]$ at $p \approx 0.1$ MPa over the temperature range of $325 \leq T/\mathrm{K} \leq 570$. Assuming that the differences in densities, $\Delta\rho = \rho - \rho^\circ$, between those at ambient (ρ°) and elevated (ρ) pressures of $[C_8mim][Tf_2N]$ (B) and $[C_6mim][Tf_2N]$ (A) are identical, the densities of $[C_8mim][Tf_2N]$ were adjusted to 10 MPa according to:

$$\rho_\mathrm{B} = \rho_\mathrm{B}^\circ + \Delta\rho_\mathrm{A} \tag{5}$$

The densities of the two ILs estimated in these ways are shown in Tables 1 and 2. Note that the relative density differences between $p = 0.1$ MPa and $p = 10$ MPa are rather small, varying from 0.6 % at 323 K to 1.6 % at 550 K (Figure 1), but large enough to have a significant effect on the massic and molar heat capacities.

Massic and Molar Heat Capacities. The measured isobaric volumetric molar heat capacities of $[C_6mim][Tf_2N]$ and $[C_8mim][Tf_2N]$ were converted to the corresponding isobaric, massic ($c_p/\mathrm{J{\cdot}K^{-1}{\cdot}g^{-1}}$), and molar ($C_p/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) quantities, all at 10 MPa, in the usual way with $c_p = \sigma_p/\rho$ and $C_p = c_p{\cdot}M$, where M is the molar mass of the sample and ρ its density at the appropriate temperature and pressure.

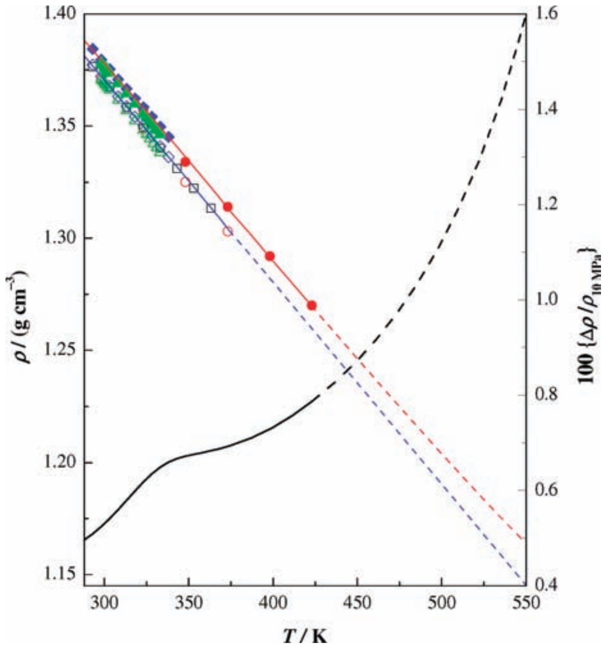

Figure 1. Effect of pressure on densities (ρ, left-hand scale) of $[C_6mim][Tf_2N]$: hollow symbols, $p = 0.1$ MPa; filled symbols, $p = 10$ MPa. Data from: ○, ●, Kandil et al.;[25] □, Marsh et al.;[11] ◇, ◆, Esperança et al.;[26] △, ▲, Azevedo et al.[29] Lines are the recommended values from Chirico et al.[12] for ρ at: blue line, $p = 0.1$ MPa and red line, $p = 10$ MPa. Right-hand scale, full black line: the relative difference in ρ ($\Delta\rho = \rho_{10\mathrm{MPa}} - \rho_{0.1\mathrm{MPa}}$). Dashed lines indicate values extrapolated to higher T.

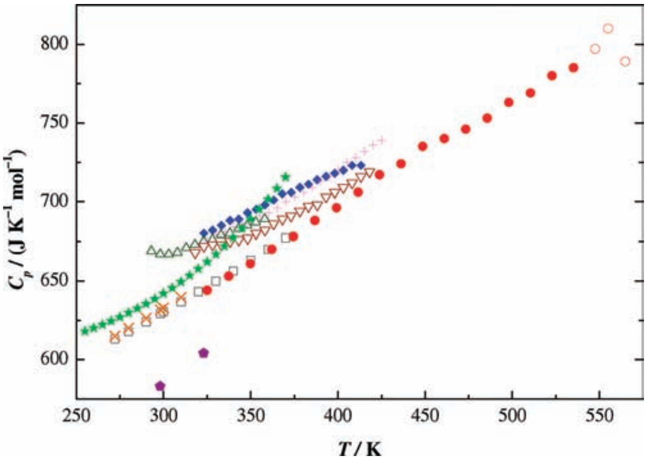

Figure 2. Isobaric molar heat capacities of $[C_6mim][Tf_2N]$ in the liquid state as a function of temperature: ●, this work (Tian-Calvet); □, Blokhin et al.[13] (adiabatic); ×, Shimizu et al.[14] (adiabatic); △, Ge et al.[18] (DSC); ⬠, Crosthwaite et al.[15] (DSC); +, ◆, ▽, Diedrichs and Gmehling[17] (DSC, MDSC, Tian−Calvet, respectively); ★, Archer[16] (DSC). All data at $p = 0.1$ MPa except for the present measurements at $p = 10$ MPa (but see text). Note present data at $T \gtrsim 535$ K (○) are probably unreliable due to partial sample decomposition.

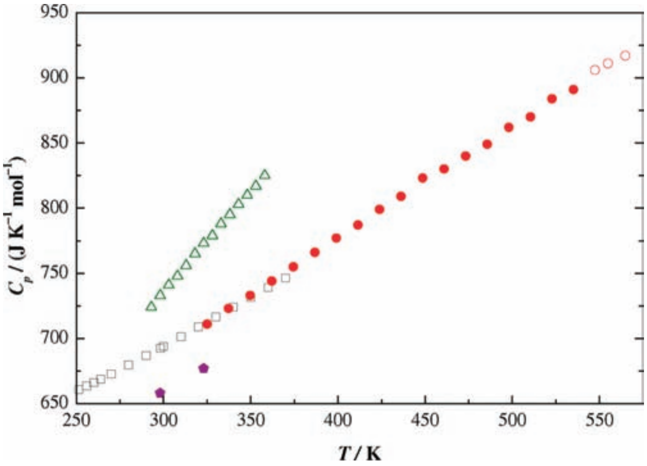

Figure 3. Isobaric molar heat capacities of $[C_8mim][Tf_2N]$ in the liquid state as a function of temperature: ●, this work (Tian-Calvet); □, Paulechka et al.[36] (adiabatic); △, Ge et al.[18] (DSC); ⬠, Crosthwaite et al.[15] (DSC). All data at $p = 0.1$ MPa except for the present measurements at $p = 10$ MPa (but see text). Note present data at $T \gtrsim 535$ K (○) are probably unreliable due to partial sample decomposition.

The pressure dependence of C_p was not determined in this work. However, it can be estimated from the following standard thermodynamic relationship, eq 6.[34]

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{6}$$

As the densities of both the present ILs are linear functions of temperature (eqs 2 and 4), the right-hand side of eq 6 is zero, and thus $C_p(T)$ is independent of pressure over the present experimental range. Hence, the heat capacities determined at 10 MPa can be assumed to be valid also at 0.1 MPa. The C_p values so obtained are summarized in Tables 1 and 2 and are plotted as a function of temperature in Figures 2 and 3, together with the literature data. The experimental methods used to obtain each data set are listed in the captions of Figures 2 and 3.

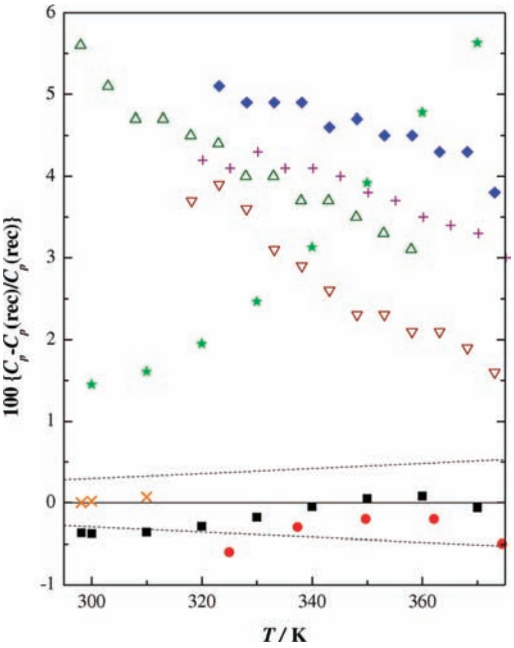

Figure 4. Relative deviation of reported molar heat capacities C_p of [C_6mim][Tf_2N] in the liquid state from the recommended values of Chirico et al.,[12] C_p(rec): ●, this work; ■, Blokhin et al.;[13] ×, Shimizu et al.;[14] △, Ge et al.;[18] +, ◆, ▽, Diedrichs and Gmehling;[17] ★, Archer.[16] The values reported by Crosthwaite et al.,[15] which are about 7 % lower, are not shown. All data at $p = 0.1$ MPa except for the present measurements at $p = 10$ MPa (but see text). The dashed lines show the combined expanded uncertainties for C_p(rec).[12]

Where comparison is possible ($325 \leq T/\mathrm{K} \leq 375$), the heat capacities determined in this work are in excellent agreement with those obtained by adiabatic calorimetry.[13,14,35,36] Thus, for [C_6mim][Tf_2N] in the overlapping temperature range, the present C_p values are ≤ 0.3 % lower than the adiabatic results of Blokhin et al.[13] and Shimizu et al.[14] (Figure 2). Such differences lie within the probable combined uncertainties of the two techniques. In contrast, as noted in the Introduction, the molar heat capacities obtained by DSC for this very well-characterized, stable liquid are in poor agreement with each other and, more importantly, with the present and adiabatic values (Figure 2). The differences between the various independent determinations of C_p for [C_6mim][Tf_2N] are plotted relative to the recommended (reference) values of Chirico et al., which were based on the adiabatic data,[13,14] in Figure 4. With one exception,[15] the DSC values are all more positive than the recommended data, averaging about + 3.5 % (but rising to as much as 6.5 %) higher. These deviations are well outside of the claimed accuracies. In addition, the strong curvature in the C_p values as a function of temperature, observed in some DSC studies (Figure 2), contrasts markedly with the almost linear behavior of the present and adiabatic data. Both of these effects are possibly indicative of inadequate thermal equilibration in the dynamic DSC measurements, perhaps as a result of the relatively high viscosity ($\eta = 0.0694$ Pa·s at 298.15 K)[12] and low thermal conductivity ($\lambda = 0.125$ W·m^{-1}·K^{-1} at 353 K)[37] of [C_6mim][Tf_2N].

The results obtained for [C_8mim][Tf_2N] were broadly similar. While the agreement between the present and the adiabatic data[36] was again very satisfactory, ranging from 0.5 % low to 0.7 % high (Figure 3), the available DSC data[15,18] are in poor agreement with each other and differ markedly from the present results. The more comprehensive DSC data set[18] is, as for [C_6mim][Tf_2N], much higher than the present values and shows a much stronger dependence on temperature (Figure 3).

Table 3. Comparison of Reported Molar Heat Capacities (C_p) at 298.15 K and $p = 0.1$ MPa for the ILs [C_6mim][Tf_2N] and [C_8mim][Tf_2N]

IL	C_p J·K^{-1}·mol^{-1}	method[a]	ref
[C_6mim][Tf_2N]	626 ± 2[b]	TC	this work
	631.6 ± 0.5	AC	14, 42
	629.2 ± 2.5	AC	13
	640.7 ± 7.0	DSC	16
	583 ± 30	DSC	15
	667	DSC	18
[C_8mim][Tf_2N]	687 ± 2[b]	TC	this work
	692.7 ± 2.8	AC	36
	654	DSC	15
	733	DSC	18

[a] Abbreviations: TC, Tian-Calvet calorimetry; AC, adiabatic calorimetry; DSC, differential scanning calorimetry. [b] At $p = 10$ MPa (but see text).

The temperature dependencies of the molar heat capacities of both ILs at $p = 10$ MPa were approximately linear and therefore could be expressed satisfactorily by eq 7 over the range of $325 \leq T/\mathrm{K} \leq 535$.

$$C_p/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = d + e\{[T/\mathrm{K}] - 298.15\} \qquad (7)$$

with adjustable parameters $d = 626 \pm 2$ and $e = 0.706 \pm 0.015$ for [C_6mim][Tf_2N] and $d = 687 \pm 2$ and $e = 0.898 \pm 0.012$ for [C_8mim][Tf_2N], where the uncertainties are 95 % confidence intervals and the maximum relative deviation between the experimental and the calculated values of C_p was 0.5 %.

The extrapolated values of C_p at 298.15 K are compared with the literature values in Table 3. As would be expected (Figures 2 and 3), the present results for both ILs are in excellent agreement with those obtained by adiabatic calorimetry,[13,14,36] differing within or just outside the stated limits of accuracy. Again as expected, the DSC values are very poor in agreement with the present and adiabatic results and differ by up to about 13 % from each other.

Effects of Substituent Chain Length. The molar heat capacity of a liquid is a measure of its ability to store energy. Compounds containing polyatomic ions or molecules mostly store energy in their bonds. The heat capacity *per bond* (i.e., C_p divided by the total number of covalent bonds in the salt, regardless of their nature) of the present ILs is approximately constant at 13.9 J·K^{-1}·mol^{-1} for the C_6 and C_8 compounds, respectively. As might be expected from the strong interionic interactions in ILs, these values are somewhat, but not greatly, different from, for example, the C_6 and C_8 1-alkanols (≈ 12 J·K^{-1}·mol^{-1} per bond)[38] or even the C_6 and C_8 *n*-alkanes (≈ 10 J·K^{-1}·mol^{-1} per bond).[39] Thus, the relatively high C_p values observed for the present ILs (Tables 1 and 2) mostly just reflect their size (number of bonds).

The effect of increasing the chain length of the 1-alkyl substituent of the cation from [C_6mim]$^+$ to [C_8mim]$^+$ was to increase the isobaric molar heat capacity per CH_2 group, $\Delta C_p\{-CH_2\}$, by 34 J·K^{-1}·mol^{-1} at 325 K, rising to almost 54 J·K^{-1}·mol^{-1} at 535 K (Figure 5). The extrapolated difference of $\Delta C_p\{-CH_2\} \approx 31$ J·K^{-1}·mol^{-1} at 298.15 K for the present ILs is similar to those reported at 298.15 K for other 1-alkyl-3-methylimidazolium ILs by Holbrey et al.,[40] Archer et al.,[41] Paulechka et al.,[36] and Ge et al.,[18] who found $\Delta C_p\{-CH_2\} = 40$ J·K^{-1}·mol^{-1} for [$C_n$mim][PF_6], 30 J·K^{-1}·mol^{-1} for [$C_n$mim][BF_4], and (31 and 35) J·K^{-1}·mol^{-1} both for [$C_n$mim][Tf_2N], respectively. Similar results regarding the methylene group contribution to C_p at 298.15 K have been reported by Shimizu et al.[42]

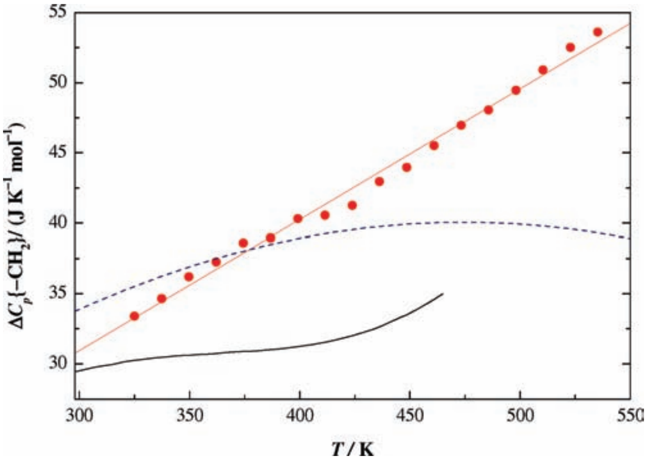

Figure 5. Change in isobaric molar heat capacities per $-CH_2$ group, $\Delta C_p\{-CH_2\}$, for various substances upon increasing the chain length from C_6 to C_8: this work, ILs [$C_n$mim][Tf_2N] at ●, $p = 10$ MPa; red line, assumed linear fit; dashed line, 1-alkanols[38] at $p = 10$ MPa; black line, n-alkanes[39] at $p = p_{sat}$.

Figure 5 also includes for comparison the $\Delta C_p\{-CH_2\}$ values that can be calculated from the C_p values reported for C_6 and C_8 1-alkanols (at $p = 10$ MPa)[38,43] and for C_6 and C_8 n-alkanes[39] (at saturation pressure). While there is some similarity between the present results and the 1-alkanol values at $T \lesssim 450$ K, they diverge at higher temperatures. The behavior of the n-alkanes appears to be rather different probably due to the much weaker interactions between the n-alkane molecules.

Thermal Stability. Following temperature scans, the samples were removed from the calorimeter by syringe. The originally slightly yellow ILs had darkened a little ([C_8mim][Tf_2N]) or a lot ([C_6mim][Tf_2N]). This decomposition is consistent with their erratic thermal behavior at high temperatures ($T \gtrsim 535$ K).

The thermal stability of a range of ILs has been studied by Crosthwaite et al.[4,15] using thermogravimetric analysis (TGA). They reported detectable decomposition starting at about 620 K for both [C_6mim][Tf_2N] and [C_8mim][Tf_2N], which is about 85 K higher than the present calorimetric data suggest. This is almost certainly due to the difference in operating conditions since the TGA was performed in a "dynamic" mode with continuous heating rates $\geq 10\ K\cdot min^{-1}$ without the lengthy equilibration periods used in the present procedure (Section 3.1). This is confirmed by recent TGA measurements[44] at a low heating rate ($1\ K\cdot min^{-1}$) which showed a decomposition temperature (T_d) ≈ 538 K for [C_6mim][Tf_2N] and ≈ 485 K for [C_8mim][Tf_2N]. In contrast, for TGA scans at $10\ K\cdot min^{-1}$ it was found that $T_d \approx 574$ K and $T_d \approx 513$ K respectively which are broadly consistent with the earlier measurements of Crosthwaite et al.[4,15] TGA measurements are of course sensitive only to decomposition involving mass change, which in the context of ILs would probably mean formation of gaseous products.

The present data suggest that the true thermal stability of the present (and by implication many other) ILs is much lower than the apparent decomposition temperatures obtained from fast scan TGA measurements.[4,15] Such considerations may be important in possible industrial applications of ILs at high temperatures.

Acknowledgment

The authors thank Prof. K. N. Marsh, University of Canterbury, Christchurch, New Zealand, for his encouragement of this work and for providing, along with Dr. J. A. Widegren, University of Notre Dame, U.S., and Dr. J. Magee, NIST, Boulder, Co, U.S., samples of the ILs. A. Pinkert is thanked for making available his unpublished TGA results.[44]

Literature Cited

(1) DeSimone, J. M. Practical approaches to green solvents. *Science* **2002**, *297*, 799–803.
(2) 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.
(3) Blanchard, L. A.; Brennecke, J. F. Recovery of organic products from ionic liquids using supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292.
(4) 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.
(5) Brennecke, J. F.; Maginn, E. J. Ionic liquids: innovative fluids for chemical processing. *AIChE J.* **2001**, *47*, 2384–2389.
(6) Wasserscheid, P.; Keim, W. Ionic liquids - new solutions for transition metal catalysis. *Angew. Chem.* **2000**, *39*, 3772–3789.
(7) Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.
(8) Sakaebe, H.; Matsumoto, H. N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI): novel electrolyte base for Li battery. *Electrochem. Commun.* **2003**, *5*, 594–598.
(9) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-pressure phase behavior of ionic liquid/CO_2 systems. *J. Phys. Chem. B* **2001**, *105*, 2437–2444.
(10) Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems, IUPAC Project 2002−005−1-100. http://www.iupac.org/projects/2002/2002-005−1-100.html.
(11) Marsh, K. N.; Brennecke, J. F.; Chirico, R. D.; Frenkel, M.; Heintz, A.; Magee, J. W.; Peters, C. J.; Rebelo, L. P. N.; Seddon, K. R. Thermodynamic and thermophysical properties of the reference ionic liquid: 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (including mixtures). Part 1. Experimental methods and results. *Pure Appl. Chem.* **2009**, *81*, 781–790.
(12) Chirico, R. D.; Diky, V.; Magee, J. W.; Frenkel, M.; Marsh, K. N. Thermodynamic and thermophysical properties of the reference ionic liquid: 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (including mixtures). Part 2. Critical evaluation and recommended property values. *Pure Appl. Chem.* **2009**, *81*, 791–828.
(13) Blokhin, A. V.; Paulechka, Y. U.; Kabo, G. J. Thermodynamic properties of [C_6mim][NTf_2] in the condensed state. *J. Chem. Eng. Data* **2006**, *51*, 1377–1388.
(14) Shimizu, Y.; Ohte, Y.; Yamamura, Y.; Saito, K.; Atake, T. Low-temperature heat capacity of room-temperature ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Phys. Chem. B* **2006**, *110*, 13970–13975.
(15) 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.
(16) Archer, D. G. *Thermodynamic Properties of 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide*, NISTIR 6645; National Institute of Standards and Technology, Gaithersburg, MD, 2006; pp 1−22.
(17) Diedrichs, A.; Gmehling, J. Measurement of heat capacities of ionic liquids by differential scanning calorimetry. *Fluid Phase Equilib.* **2006**, *244*, 68–77.
(18) Ge, R.; Hardacre, C.; Jacquemin, J.; Nancarrow, P.; Rooney, D. W. Heat capacities of ionic liquids as a function of temperature at 0.1 MPa. Measurement and prediction. *J. Chem. Eng. Data* **2008**, *53*, 2148–2153.
(19) Schrödle, S.; Königsberger, E.; May, P. M.; Hefter, G. Heat capacities of aqueous solutions of sodium hydroxide and water ionization up to 300 °C at 10 MPa. *Geochim. Cosmochim. Acta* **2008**, *72*, 3124–3138.
(20) Jacobsen, R. T.; Penoncello, S. G.; Lemmon, E. W.; Span, R. *Multiparameter Equations of State*; Elsevier: Amsterdam, 2000; Vol. 5, p 33.
(21) Harvey, A. H.; Peskin, A. P.; Klein, S. A. *NIST/ASME Steam Properties, 2.11*; National Institute of Standards and Technology: Boulder, CO, 1996.
(22) Coxam, J. Y.; Quint, J. R.; Grolier, J. P. E. Heat capacities of aqueous electrolyte solutions at elevated temperatures and pressures. *High Temp. High Pressures* **1991**, *23*, 575–81.
(23) Bessieres, D.; Saint-Guirons, H.; Daridon, J. L.; Coxam, J. Y. Apparatus for simultaneous determination of the densities and heat capacities of liquids and of liquids with dissolved gas under an extended range of pressure (0.1−100 MPa). *Meas. Sci. Technol.* **2000**, *11*, N69–N72.

(24) Lachwa, J.; Morgado, P.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Canongia Lopes, J. N.; Rebelo, L. P. N. Fluid-phase behavior of {1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [C_6mim][NTf_2], + C_2-C_8 *n*-alcohol} mixtures: liquid-liquid equilibrium and excess volumes. *J. Chem. Eng. Data* **2006**, *51*, 2215–2221.

(25) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Measurement of the viscosity, density, and electrical conductivity of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at temperatures between (288 and 433) K and pressures below 50 MPa. *J. Chem. Eng. Data* **2007**, *52*, 2382–2387.

(26) Esperança, J. M. S. S.; Guedes, H. J. R.; Lopes, J. N. C.; Rebelo, L. P. N. Pressure-density-temperature ($p-\rho-T$) surface of [C_6mim][NTf_2]. *J. Chem. Eng. Data* **2008**, *53*, 867–870.

(27) Fitchett, B. D.; Knepp, T. N.; Conboy, J. C. 1-Alkyl-3-methylimidazolium bis(perfluoroalkylsulfonyl)imide water-immiscible ionic liquids. The effect of water on electrochemical and physical properties. *J. Electrochem. Soc.* **2004**, *151*, E219−E225.

(28) Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F. High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids. *J. Phys. Chem. B* **2004**, *108*, 20355–20365.

(29) Azevedo, R. G. D.; Esperança, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N. Thermophysical and thermodynamic properties of ionic liquids over an extended pressure range: [bmim][NTf_2] and [hmim][NTf_2]. *J. Chem. Thermodyn.* **2005**, *37*, 888–899.

(30) Kato, R.; Gmehling, J. Systems with ionic liquids: Measurement of VLE and γ^∞ data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol). *J. Chem. Thermodyn.* **2005**, *37*, 603–619.

(31) Kumelan, J.; Pérez-Salado Kamps, Á.; Tuma, D.; Maurer, G. Solubility of CO_2 in the ionic liquid [hmim][Tf_2N]. *J. Chem. Thermodyn.* **2006**, *38*, 1396–1401.

(32) 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.

(33) Lopes, J. N. C.; Cordeiro, T. C.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. Deviations from ideality in mixtures of two ionic liquids containing a common ion. *J. Phys. Chem. B* **2005**, *109*, 3519–3525.

(34) McGlashan, M. L. *Chemical Thermodynamics*; Academic Press: London, 1979; p 346.

(35) Blokhin, A. V.; Paulechka, Y. U.; Kabo, G. J. Formation of metastable crystals of [C_4mim][NTf_2] and [C_6mim][NTf_2]. *Thermochim. Acta* **2006**, *445*, 75–77.

(36) Paulechka, Y. U.; Blokhin, A. V.; Kabo, G. J.; Strechan, A. A. Thermodynamic properties and polymorphism of 1-alkyl-3-methylimidazolium bis(triflamides). *J. Chem. Thermodyn.* **2007**, *39*, 866–877.

(37) Ge, R.; Hardacre, C.; Nancarrow, P.; Rooney, D. W. Thermal conductivities of ionic liquids over the temperature range from 293 K to 353 K. *J. Chem. Eng. Data* **2007**, *52*, 1819–1823.

(38) Fulem, M.; Růžička, K.; Růžička, V. Heat capacities of alkanols: Part I. Selected 1-alkanols C_2 to C_{10} at elevated temperatures and pressures. *Thermochim. Acta* **2002**, *382*, 119–128.

(39) Růžička, V. J.; Zábranský, M.; Majer, V. Heat capacities of organic compounds in liquid state. II. C_1 to C_{18} *n*-alkanes. *J. Phys. Chem. Ref. Data* **1991**, *20*, 405–44.

(40) Holbrey, J. D.; Reichert, W. M.; Reddy, R. G.; Rogers, R. D. Heat capacities of ionic liquids and their applications as thermal fluids. *ACS Symp. Ser.* **2003**, *856*, 121–133.

(41) Archer, D. G.; Widegren, J. A.; Kirklin, D. R.; Magee, J. W. Enthalpy of solution of 1-octyl-3-methylimidazolium tetrafluoroborate in water and in aqueous sodium fluoride. *J. Chem. Eng. Data* **2005**, *50*, 1484–1491.

(42) Shimizu, Y.; Ohte, Y.; Yamamura, Y.; Saito, K. Is the liquid or the solid phase responsible for the low melting points of ionic liquids? Alkyl-chain-length dependence of thermodynamic properties of [$C_n$mim][Tf_2N]. *Chem. Phys. Lett.* **2009**, *470*, 295–299.

(43) Somewhat different values are given in Miltenburg, J. C. v.; Gabrielová, H.; Růžička, K. Heat capacities and derived thermodynamic functions of 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol between 5 and 390 K. *J. Chem. Eng. Data* **2003**, *48*, 1323. Zábranský, M.; Růžička, V.; Majer, V. Heat capacities of organic compounds in the liquid state. I. C1 to C18 1-alkanols. *J. Phys. Chem. Ref. Data* **1990**, *19*, 719–62.

(44) Pinkert, A.; Marsh, K. N. University of Canterbury, Christchurch, New Zealand. Private communication, 2009.

Received for review August 11, 2009. Accepted October 19, 2009.

JE900676B