Phase behavior and heat capacities of the 1-benzyl-3-methylimidazolium ionic liquids

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A C T I V E A R C H I V E

Article history:
Received 15 July 2015
Received in revised form 4 April 2016
Accepted 15 April 2016
Available online 16 April 2016

Keywords:
Phase behavior
Benzylimidazolium
Ionic liquids

A B S T R A C T

The thermal behavior, solid and liquid heat capacities of the 1-benzyl-3-methylimidazolium, [Bzmim]+, based ionic liquid series with Cl −, PF6 −, BF4 −, CH3CF2SO3 − and NTf2 − as anions were used to evaluate the effect of the insertion of an aromatic character (benzyl group) and the expected increase of the π–π interactions as well as the impact in the cation–anion hindrance and charge delocalization in the ionic liquid properties. It was found that the molar liquid heat capacities of [Bzmim][X] are in the same order as the 1-pentyl-3-methylimidazolium, [C5C1im][X] analogs. A good correlation between the molar (solid and liquid) heat capacity and the number of atoms of the anion was found. Two different crystalline forms for [Bzmim][BF4] differing by 10 K in the melting temperature and about 10% in the heat capacity were found. The crystallization behavior, melting temperatures, and enthalpies and entropies of fusion show that the insertion of an aromatic character (benzyl group) in the imidazolium cation leads to a significant and systematic change of the thermophysical properties of the ionic liquids associated with an increase of the glass transition and melting temperatures arising from the additional π–π interactions.

1. Introduction

The ionic liquids (ILs) are known for their broad range of viscosities, heat capacities, and electrical and thermal conductivities which can simply be tuned by varying the cation/anion combinations [1]. This is an important feature for both academic and industrial fields because ILs can be easily adjusted to different applications, and the study of different cation/anion combinations contributes for the knowledge about physicochemical properties and the design of new ILs [1]. Another interesting property of ILs is their unique structuration into heterogeneous zones due to the asymmetric ions that have a shielded or delocalized charge, disturbing the anion–cation interaction [4–6]. For many ionic liquids, the cooling of the liquid phase tends to pass through a state of a metastable equilibrium (supercooling) and subsequently a glass formation. The phase behavior of ILs strongly depends on the thermal history as it is an interplay between the kinetically and thermodynamically driven phenomena. The kinetics of the phase transitions can be slow due to a molecular packing arising from the molecular shape, asymmetry, and flat interaction potentials. As a result, long equilibration times and small samples are needed to obtain reliable thermal phase behavior data [7,8].

The most studied IL families are based on the alkyl imidazolium cation and very little is known about the effect of additionally aromatic moieties such as the benzyl on their properties. The insertion of a group with an aromatic character is expected to increase the π–π interactions, cation/anion to aromatic ring interactions, as well as to have an impact on the cation–anion hindrance and charge delocalization. This is supposed to lead to a major impact on the thermal behavior, stability, and thermophysical properties.
The heat capacities and phase transition temperatures of the cation 1-benzyl-3-methylimidazolium,[Bzmim][Cl], IL series are used to explore the effect of the benzyl group and the conjugation effect of different anions on the nanostructuring of this family of ILs.

The 1-benzyl-3-methylimidazolium IL series (Fig. 1) is one of the less studied ionic liquid series, and no data on heat capacities was found in the literature. These derivatives, [Bzmim][Cl], [Bzmim][PF6], [Bzmim][BF4], [Bzmim][CHF2CF2SO3], and [Bzmim][NTf2] were chosen to study the interaction between different cations with an imidazolium derivative. The cation derivative, (a bulky and aromatic benzyl group used to increase the asymmetry), charge dispersion, and increase the aromatic character leading to an enhancement of the π-π, cation/anion to aromatic ring interactions) was tested with highly charged, almost spherical and non-flexible anions (Cl−, BF4− and PF6−) and asymmetrical and flexible anions with dispersed charges (CHF2CF2SO3− and NTf2−). In order to understand the effect of the change between an aromatic ring and an alkyl side chain, a comparison/rationalization between the studied ILs and the [CnCim][X] (X = Cl−, PF6−, BF4− and NTf2−) IL series is presented.

2. Experimental details

2.1. Materials and purification

The five 1-benzyl-3-methylimidazolium derivatives [Bzmim][Cl] (1-benzyl-3-methylimidazolium chloride, [Bzmim][BF4] (1-benzyl-3-methylimidazolium tetrafluoroborate), [Bzmim][PF6] (1-benzyl-3-methylimidazolium hexafluorophosphate), [Bzmim][CHF2CF2SO3] (1-benzyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate), [Bzmim][NTf2] (1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), were acquired from Sigma-Aldrich and IOLITEC. The abbreviations, CAS numbers and stated purities are listed in Table 1. The samples were distributed among the two laboratories (Porto and Prague), and independent purification processes were performed following the same purification and manipulation procedure. All the ionic liquids were purified under vacuum (<10 Pa) at moderate temperature (room temperature to 323 K) and constant stirring to reduce the presence of water or other volatile components. After the drying procedure, the water content was evaluated before, based on the measurements of benzoic acid and hexafluorobenzene [14,17,18]. The masses of the samples were corrected for the buoyancy effect for both calibration and heat capacity measurements of ILs. The relative atomic masses used were those recommended by the IUPAC Commission in 2007 [19].

The uncertainties quoted are twice the standard deviation of the mean and the calibration uncertainty is included.

2.2. Phase behavior measurements

The phase behavior of the studied ILs was studied by DSC. The melting temperatures, Tm, were determined as the onset temperatures of an endothermic peak on heating, the cold crystallization temperature, Tc, as the midpoint of the heat capacity drop calorimeter, Tg, as the onset temperature of an exothermic peak on heating from a subcooled liquid to a crystalline solid and the glass transition temperature, Tg, as the midpoint of the heat capacity change on heating from the glass to a liquid. The Tg, Tc, Tm and the Tg/Tm ratio for each of the studied ILs are presented in Table 2 and the thermograms are presented as Supporting information.

The melting temperature, Tm, fusion enthalpy, ΔHm, and fusion entropy, ΔSm, of the studied ionic liquids are presented in Table 3. A graphical representation of the Tg, Tc and Tm values as function of the molar mass, is depicted in Fig. 2. This figure shows that the phase transition temperatures cannot be easily predicted and related with molar mass or the number of atoms.

3. Results and discussion

3.1. Thermal and phase behavior

The phase behavior of the studied ILs was explored in the temperature range of 183 K to 423 K using two differential scanning calorimeters (DSC, TA Q1000, TA Instruments, USA; DSC, PerkinElmer, model Pyris Diamond) using a heating rate of 5 K min−1, a N2(g) flow of 50 ml min−1 and sealed aluminum crucibles. The temperature and heat flux scales of the calorimeter were calibrated using water, gallium, naphthalene, indium, and tin. During the thermal analysis of the studied ILs, two isothermal delays, in the beginning and in the end of each measurement, were performed to ensure the sample stabilization. The initial isotherm was performed at 183 K to obtain the initial crystalline phase, and before a subsequent measurement, the sample was quenched by fast cooling down to 183 K to induce an amorphous state. The crucibles were weighted using a Denver Instrument analytical balance with a readability of 0.01 mg and the typical sample load was of about 10 mg.

2.3. Heat capacities measurements

2.3.1. Tian-Calvet calorimetry

The heat capacities of condensed phases were measured with a Tian-Calvet type microcalorimeter (Setaram, model μDSCIIIa) in the temperature range from 258 to 358 K using the incremental temperature mode (step method) [9]. Each 5 K step included a heating rate of 0.3 K min−1 followed by an isothermal delay of 2600 s. The combined expanded uncertainty of the heat capacity measurements is estimated to be Uc (Cp,m) = 0.01°C−1 mol−1. A detailed description of the calorimeter and its calibration can be found in the literature [10] and the measuring procedure was previously described in detail [11].

2.3.2. High-precision heat capacity drop calorimetry

The heat capacities of the five studied ILs were measured at T = 298.15 K by a high-precision heat capacity drop calorimeter, already described in the literature [12–14]. Based on a drop temperature step procedure of ΔT = 10 K [9,12–15] and using the respective standard molar heat capacities at 298.15 K reported in literature, the uncertainty of the apparatus for the measurements of the heat capacities of solids and liquids was evaluated before, based on the measurements of benzoic acid and hexafluorobenzene [14,17,18]. The masses of the samples were corrected for the buoyancy effect for both calibration and heat capacity measurements of ILs. The relative atomic masses used were those recommended by the IUPAC Commission in 2007 [19].

The uncertainties quoted are twice the standard deviation of the mean and the calibration uncertainty is included.
Unfortunately, no information about the purity and purification methods are reported. In addition, a drying step to reduce the water content of the sample is not taken into account in the work. The difference observed between this work and literature is most probably related with the questionable purity of the sample synthesized used in the literature work. [20]

**Table 1**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>CAS-Number</th>
<th>Source</th>
<th>Mass fraction purity</th>
<th>Batch/Lot Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bzmim][Cl]</td>
<td>36443-80-8</td>
<td>Sigma–Aldrich</td>
<td>0.996</td>
<td>1369086</td>
</tr>
<tr>
<td>[Bzmim][BF4]</td>
<td>500996-04-3</td>
<td>Iolitec</td>
<td>0.999</td>
<td>F00203.1</td>
</tr>
<tr>
<td>[Bzmim][PF6]</td>
<td>433337-11-2</td>
<td>Iolitec</td>
<td>0.996</td>
<td>F00103.1.1</td>
</tr>
<tr>
<td>[Bzmim][CHF2CF2SO3]</td>
<td>n/a</td>
<td>Iolitec</td>
<td>0.999</td>
<td>H00120.1</td>
</tr>
<tr>
<td>[Bzmim][NTf2]</td>
<td>433337-24-7</td>
<td>Iolitec</td>
<td>0.999</td>
<td>G00103.1.3</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Tg/K</th>
<th>Tcc/K</th>
<th>Tm/K</th>
<th>Tg/Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bzmim][Cl]</td>
<td>264.7 ± 0.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Bzmim][BF4]</td>
<td>235.3 ± 1.2</td>
<td>282.5 ± 0.3</td>
<td>336.5 ± 0.3</td>
<td>0.699</td>
</tr>
<tr>
<td>[Bzmim][PF6]</td>
<td>244.8 ± 0.8</td>
<td>279.2 ± 0.3</td>
<td>399.7 ± 0.4</td>
<td>0.612</td>
</tr>
<tr>
<td>[Bzmim][CHF2CF2SO3]</td>
<td>229.1 ± 0.5</td>
<td>260.1 ± 0.3</td>
<td>315.4 ± 0.3</td>
<td>0.726</td>
</tr>
<tr>
<td>[Bzmim][NTf2]</td>
<td>216.7 ± 1.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Tm/K</th>
<th>ΔHm (T)/kJ mol⁻¹</th>
<th>ΔSm (T)/J K⁻¹ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bzmim][BF4]</td>
<td>336.5 ± 0.3</td>
<td>16.6 ± 1.7</td>
<td>49.3 ± 4.9</td>
</tr>
<tr>
<td>[Bzmim][PF6]</td>
<td>346.2 ± 0.3 b</td>
<td>19.1 ± 1.9 b</td>
<td>55.2 ± 5.5 b</td>
</tr>
<tr>
<td>[Bzmim][CHF2CF2SO3]</td>
<td>397.9 ± 0.4</td>
<td>24.9 ± 2.5 [9.0c]</td>
<td>62.3 ± 6.2</td>
</tr>
<tr>
<td>[Bzmim][NTf2]</td>
<td>315.4 ± 0.3</td>
<td>236 ± 2.4</td>
<td>74.8 ± 7.5</td>
</tr>
</tbody>
</table>

a Literature Erdmenger et al. [21].
b Lower melting temperature “Form A”.
c Higher melting temperature “Form B”.
d Literature Dzyuba et al. [20].
e Literature Jeon et al. [22].
f Literature Tao et al. [23]. Standard pressure (p0 = 0.10 ± 0.01 MPa). Standard uncertainties, u(T), are u(T) = 0.02 K, the 0.95 confidence level (k = 2).

(Table 3), are not in agreement with the one obtained in this work. Unfortunately, no information about the purity and purification methods are reported. In addition, a drying step to reduce the water content of the sample is not taking into account in the work. The difference observed between this work and literature is most probably related with the questionable purity of the sample synthesized used in the literature work. [20]

**Fig. 2**

Thermal behavior temperatures as a function of the molar mass. □ - Tg, △ - Tm, ◊ - Tm of [Bzmim][BF4] higher melting “Form B”. “a” stands for [Bzmim][Cl], “b” stands for [Bzmim][BF4], “c” is the [Bzmim][PF6], “d” is the [Bzmim][CHF2CF2SO3] and “e” is the [Bzmim][NTf2]. The dash and dots view-lines highlight the series trend, which have no physical meaning.
Fig. 2 shows the influence of anion weight and anion-cation pair interactions on the thermal behavior temperatures of the selected \([\text{Bzmim]}^+\) based ionic liquids. According to Matthews et al. [24], for \([\text{C}_1\text{C}_1\text{im}][\text{Cl}]\), the coulomb effects are dominant over the steric contributions which leads to a packing of the aromatic rings and positioning of Cl\(^-\) anions in peripheral positions where they can interact with the highest possible number of C–H groups. This agrees with our results and combining it with the conclusions of Abbott et al. [25], we can predict the higher melting temperature for ILs that possess a better crystallization ability, will be for the intermediate weight/size anions due to the better space combination between imidazolium cation and the anion to fill the crystal vacancies. \([\text{Bzmim}][\text{PF}_6]\) ionic liquid exhibits the highest melting temperature and a relatively high enthalpy of fusion, as expected. This confirms the best packing combination between the PF\(_6\) anion and the benzyliimidazolium cation among the studied ILs. \([\text{Bzmim}][\text{CHF}_2\text{CF}_2\text{SO}_3]\) has the lowest melting temperature (the crystallization of \([\text{Bzmim}][\text{NTf}_2]\) was not achieved) in agreement with expected asymmetrical and flexible anion shape leading to a low enthalpy and high entropy of melting, reflecting indirectly the weaker interactions between these two anions and the benzylimidazolium cation, as well as, the liquid entropy increase arising from the group rotation, and the decrease of crystal entropy due to the asymmetric shape of the anions when compared with the spherical ones. The \([\text{NTf}_2]^+\) anion possesses two bulky groups bonded to the nitrogen atom that can rotate. These characteristics make the interaction between the cation and the anion difficult preventing the easy crystallization as well as an increased liquid stability over the solid form due to the additional liquid entropy arise from the configurational entropy contribution of the group rotation in the \([\text{NTf}_2]^+\) anion. In the case of the \([\text{CHF}_2\text{CF}_2\text{SO}_3]^-\) the inexistence of the two bulky groups with freedom to rotate, leads to the formation of a crystalline form with a low melting point. The big/bulky anions lead to a significant increase of the entropies of melting due to the balance of the crystal interaction potential that, as a consequence of the asymmetrical shape of the anion will contribute to the decrease the crystal entropy. This is in accordance with Abbott et al. [25] who showed that physical properties are affected by the ion size and the hole-size ratio, explaining how \([\text{PF}_6]^−\) seems to fit better in the crystal lattice created by the \([\text{Bzmim]}^+\) cation. To evaluate the effect of the insertion of an aromatic character (benzyl group), an analysis comparing the glass transition temperatures, \(T_g\) of the studied \([\text{Bzmim}]^+\) based ILs with those of their linear alkyl analogs, \([\text{C}_2\text{mim}]^+\), \([\text{C}_3\text{mim}]^+\) and \([\text{C}_5\text{mim}]^+\) based ILs is depicted in Fig. 3. A significant increase of \(T_g\) in the order of (40–60 K) was observed as a consequence of the enhanced aromatic character of the cation and increase of the \(\pi–\pi\) cation/anion to aromatic ring interactions.

During the phase behavior studies of \([\text{Bzmim}][\text{BF}_4]\) two distinguishable crystalline forms (“Form A” and “Form B”) were observed as depicted in Fig. 4. After the first melting, the obtained crystalline phase (“Form A”, metastable form) showed a decrease of about 10 K in the melting temperature and a decrease of about 10% in the heat capacity. It was found that the lower melting point phase (“Form A”) presents the lower molar heat capacity (the differentiation is clear and higher than the uncertainty interval). “Form A” presents as well as, a lower enthalpy and entropy of fusion but the differentiation was initially unclear (according with the assigned uncertainty intervals). Based on that, we decided to re-measure the enthalpy and entropy of fusion using a new power compensated DSC apparatus (DSC PerkinElmer PYRIS) and an independent \([\text{Bzmim}][\text{BF}_4]\) sample. The new data concerning the melting equilibrium (temperature, enthalpies and entropies of melting) was in full agreement with the previous. We found that the “Form B” is thermodynamically more stable than “Form A” at the melting temperature and the two polymorphs are monotropic related. On the other hand, based in the heat capacity phase assignment rule, we have the indication that the two polymorphs are enantiotropic related. This is apparently in contradiction with the heat and entropy of fusion rule. A metastable phase with lower heat capacity than the respective stable phase is very unusual but not impossible [35]. The slightly higher absolute enthalpy and entropy presented by “Form A” (lower enthalpy and entropy of fusion) could be due to a crossover in the molar heat capacity functional (of the two polymorphic forms) at lower temperature.

The relative stability of the two polymorphs could be explained and interpreted based on the shift of the balance in the dominant forces that are ruling the structure stability: temperature dependence of the hydrogen bonding strength; aromatic interactions; steric hindrance [6].

The higher melting form was observed from a slow relaxation of the crystalline phase to a more stable packing at room temperature, suggesting a slow interconverting (between the two monotropic polymorphs) of the low melting phase (obtained at low...
temperatures)”Form A” into the high melting form long the time “Form B”. The high melting form (Form B) was only obtained from the original sample, not being observed after the first melting. For better understanding, Fig. 5 depicts a schematic Gibbs energy phase versus temperature diagram for the two crystalline forms of [Bzmim][BF₄] that was build based on the data obtained for the heat, entropies and heat capacity differentiation between the two crystalline forms (Table 2). The Gibbs energy difference between the two forms is quite small and could be derived at the temperature of the lower melting temperature (336.5 K) as (−0.5 kJ mol⁻¹) in agreement with slow interconverting speed between the two crystalline forms.

“Form B” (more stable) is enthalpically more stable and entropically less stable than “Form A”. This entropic factor together with the stronger intermolecular forces in “Form A” overrides the higher enthalpic factor of “Form B”, explaining how the heat capacity values of “Form B” (stable crystal) are higher than the heat capacity values of “Form A” (metastable crystal). As it can be observed from the DSC (Tian-Calvet) data depicted in Fig. 4 (heat flux baseline detail), the heat capacity of “Form A” is higher than the “Form B”, in agreement with the heat capacity differentiation that will presented further. The two crystalline forms were evaluated by powder X-ray diffraction (XRD) (the results are presented as Supporting information) and no significant differentiation was detected between the two samples, indicating that structural difference should be very small, in agreement with the derived almost identical Gibbs energy (Fig. 5).

3.2. Heat capacities

The obtained heat capacities of the condensed phases at different temperatures are available as Supporting information and are represented in Fig. 6.

The experimental data were fitted by a linear equation:

$$C_{p,m}(T)/J \cdot K^{-1} \cdot mol^{-1} = a + b \cdot (T/K)$$

where, \(a \) and \(b \) are adjustable coefficients listed in Table 4 for each IL.

The temperature dependence of the molar heat capacities could directly be evaluated from the “\(b^*\)” coefficient of Eq. (1). A significantly higher temperature dependence of the molar heat capacities of the solid phase (\(b = [0.9–1.9] \cdot K^{-2} \cdot mol^{-1}\)) than that of the liquid phase (\(b = 0.6 \cdot K^{-2} \cdot mol^{-1}\)) was observed, as a consequence of the progressive structural relaxation of the crystal.

The obtained heat capacities at \(T = 298.15 \text{ K}\) are listed in Table 5. For the studied ILS no previous literature data were found.

As can be seen in Table 5, the heat capacities at 298.15 K obtained by the two calorimetric methods are in excellent agreement, with the lower melting form being lower than the higher melting form. The temperature range of the fitting is also limited to 298.15 K ± 1 K.

Table 4

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Phase</th>
<th>((\Delta T_{\text{min}} - \Delta T_{\text{max}})/K)</th>
<th>(a/J \cdot K^{-1} \cdot mol^{-1})</th>
<th>(b/J \cdot K^{-2} \cdot mol^{-1})</th>
<th>(s,%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bzmim][Cl]</td>
<td>Solid</td>
<td>261 to 289</td>
<td>-219.6</td>
<td>1.7506</td>
<td>0.51</td>
</tr>
<tr>
<td>[Bzmim][Cl]</td>
<td>Liquid</td>
<td>277 to 355</td>
<td>199.9</td>
<td>0.4670</td>
<td>0.14</td>
</tr>
<tr>
<td>[Bzmim][BF₄]</td>
<td>Solid (Form A)</td>
<td>276 to 319</td>
<td>21.2</td>
<td>0.9534</td>
<td>0.22</td>
</tr>
<tr>
<td>[Bzmim][BF₄]</td>
<td>Solid (Form B)</td>
<td>262 to 328</td>
<td>38.3</td>
<td>0.9689</td>
<td>0.11</td>
</tr>
<tr>
<td>[Bzmim][BF₄]</td>
<td>Liquid</td>
<td>346 to 358</td>
<td>199.3</td>
<td>0.6311</td>
<td>0.02</td>
</tr>
<tr>
<td>[Bzmim][PF₆]</td>
<td>Solid</td>
<td>258 to 355</td>
<td>87.1</td>
<td>0.9058</td>
<td>0.20</td>
</tr>
<tr>
<td>[Bzmim][CHF₂CF₂SO₃]</td>
<td>Liquid</td>
<td>335 to 355</td>
<td>305.7</td>
<td>0.6612</td>
<td>0.03</td>
</tr>
<tr>
<td>[Bzmim][CHF₂CF₂SO₃]</td>
<td>Liquid</td>
<td>258 to 355</td>
<td>448.0</td>
<td>0.5357</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\(^{a}\) \(s = 100 \times \left(\frac{\sum_{i=1}^{n} \left|\frac{\mu_i - \mu_i^{\text{cal}}}{\mu_i}\right|^2}{n} \right)^{1/2}\), where \(n\) is the number of fitted data points, and \(m\) is the number of independent adjustable parameters.

\(^{b}\) Lower melting temperature “Form A”.

\(^{c}\) Higher melting temperature “Form B”. Standard pressure \((p^0 = 0.10 \pm 0.01 \text{ MPa})\). Standard uncertainties, \(u\), are \(u(T) = 0.02 \text{ K}\), the 0.95 confidence level (\(k = 2\)).
The obtained molar heat capacities for both liquid and solid phases at 298.15 K were correlated with the number of atoms in the anion (Fig. 7). A good correlation was found with the exception of the chlorine (monoatomic anion) derivatives. Based on the derived correlation (Eqs. (2) and (3)), the molar heat capacity at 298.15 K for [Bzmim][PF6] (liq) and [Bzmim][NTf2] (cr) can be estimated as: $C_{p,m}^o([Bzmim][PF6]_{(\text{liq})}) = 428 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_{p,m}^o([Bzmim][NTf2]_{(\text{cr})}) = 507 \text{ J K}^{-1} \text{ mol}^{-1}$.

It was found that the molar heat capacity contribution of the [Bzmim]$^+$ is similar to [C5mim]$^+$. Fig. 8 shows a comparison of the molar heat capacities of [Bzmim]$^+$, [C5mim]$^+$, [C4mim]$^+$ and [C6mim]$^+$ based ILs. As can be seen, the length/size of the cation contributes to the molar liquid heat capacity of the ILs by a typical increment contribution at 298.15 K of $\approx 30 \text{ J K}^{-1} \text{ mol}^{-1}$ [17] per methylene (–CH2–).

Fitted linear correlation (Eqs. (2) to (6)) for the liquid and crystalline molar heat capacity at 298.15 K in which $[X]$ is the anion

$$C_{p,m}^o([Bzmim][X]_{(\text{cr})})/J \cdot K^{-1} \cdot \text{mol}^{-1} = 234.1 + 18.2 \cdot x \quad (2)$$

$$C_{p,m}^o([Bzmim][X]_{(\text{liq})})/J \cdot K^{-1} \cdot \text{mol}^{-1} = 280.8 + 21.1 \cdot x \quad (3)$$

$$C_{p,m}^o([C5mim][X]_{(\text{liq})})/J \cdot K^{-1} \cdot \text{mol}^{-1} = 267.6 + 19.9 \cdot x \quad (4)$$

$$C_{p,m}^o([C4mim][X]_{(\text{liq})})/J \cdot K^{-1} \cdot \text{mol}^{-1} = 295.4 + 20.0 \cdot x \quad (5)$$

$$C_{p,m}^o([C6mim][X]_{(\text{liq})})/J \cdot K^{-1} \cdot \text{mol}^{-1} = 329.3 + 20.0 \cdot x \quad (6)$$

The chlorine based ILs present an outlier behavior, with a positive deviation from the previous correlation. This can be explained by strong anion–cation interactions, because this anion is a monoatomic anion, leading to a heat capacity contribution different from polyatomic anions. It is interesting to notice that the coefficient related with the number of atoms (in the molar liquid heat capacity equation) are for all cations near the same ($20 \text{ J K}^{-1} \text{ mol}^{-1}$, per atom in the anion, Eqs. (3)–(6). The molar heat capacity contribution per atom in the anion could be interpreted as a fraction of the maximum theoretical statistical contribution of one atom ($3K = 24.94 \text{ J K}^{-1} \text{ mol}^{-1}$, were $K$ is the ideal gas constant) [7] to the molar gas phase heat capacity, being in the present case an average contribution at the temperature of 298.15 K. Based on Eqs. (2) and (3) the molar heat capacity change between the liquid and crystalline phases at 298.15 K, could be derived as:

$$\Delta L_C^o C_{p,m}^o([Bzmim][X], T = 298.15K)/J \cdot K^{-1} \cdot \text{mol}^{-1} = 46.7 + 2.9 \cdot x \quad (7)$$
The derived molar heat capacity change between the liquid and crystalline phases at 298.15 K, \((-\text{from}+50 \text{ to } +80 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\) presents a typical value, identical to the observed in organic compounds [40] with a similar molecular size. It is interesting to notice that Eq. (7), predicts a small and positive increase of the molar heat capacity change with the number of atoms, “x”. It expected that the observed dependence of the molar heat capacity change between the liquid and crystalline phases (2.9 J·K⁻¹·mol⁻¹ per atom) will be similar for other cations. Eqs. (2), (3) and (7) could be used to predict the molar heat capacities of the benzylimidazolium-based ionic liquids with other polyatomic anions.

Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto through the project Pest-C/QUI/UI0081/2011 and PTDC/aac-amb/121161/2010, Marisa A. A. Rocha and Filipe M. S. Ribeiro acknowledges the financial support from FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of their Ph.D. Research Grants, SRHF/BD/60513/2009 and SRHF/BD/94211/2013. Paulo B. S. Serra acknowledges financial support from specific University Research (MSMT No. 20/2015). Thanks are due to the support of the COST Action CM1206.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2016.04.009.

References
