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**Title:** NANOSTRUCTURATION EFFECT ON THE THERMAL BEHAVIOUR OF IONIC LIQUIDS

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NANOCONSTRUCTION EFFECT ON THE THERMAL BEHAVIOUR OF IONIC LIQUIDS

Ana S. M. C. Rodrigues*, Luis M. N. B. F. Santos*

Abstract: This work shows how the nanostructuration of the ionic liquids rules the glass and melting transitions along the [CnC1im][NTf2] and [CnC2im][NTf2] series, highlighting the trend shift occurring at the Critical Alkyl Size, CAS, n=6. An initial increase of $T_g$ (glass temperature) with the alkyl side chain was observed due to the intensification of the dispersive interactions (van der Waals). After CAS, the -CH$_2$- increment has the same effect both in glass and liquid leading to a plateau in the glass transition after nanostructuration. The melting temperatures, $T_m$, of the [CnC1im][NTf2] and [CnC2im][NTf2] series presents a “V” shape profile. For the short alkyl ionic liquids, the -CH$_2$- increment disturbs the packing ability of ILs, leading to a higher $\Delta S_m$ and consequently a decrease of the $T_m$. After CAS, the -CH$_2$- contribution to melting temperature become more regular, as a consequence of the ionic liquids nanostructuration in polar and non-polar domains. The alkyl chain dependence on the temperatures, enthalpies and entropies of melting in the ILs, after CAS, are very similar to those observed in the alkane series, highlighting the weight and the rule of the non-polar alkyl domains in their thermal behaviour.

Introduction

Ionic liquids (ILs) are nanostructured molten salts that have unique properties and functionalities making them promising new materials for high-tech applications (see Supporting Information). The thermal phase behaviour of ILs, in particular the glass transition, $T_g$, melting temperatures, $T_m$, glass transition heat capacity change, $\Delta C_p$, enthalpies, $\Delta H_m$, and entropies, $\Delta S_m$, of melting are expected to reflect the liquid and glass states nanostructuration. The formation and behaviour of a glass are exclusively kinetic events and are characterized by an appropriately defined glass transition temperature, $T_g$. The glass transition is detectable by a step change of the heat capacity $C_p$ on heating or cooling and it can be measured by Differential Scanning Calorimetry (DSC). Within the transition region, many macroscopic properties, which may have great practical importance, change their values (e.g. viscosity, dielectric and especially mechanical properties). During the glass transition, the compound passes through a sequence of non-equilibrium states upon heating and cooling cycles in which there are changes both in the compound and the measurement variables that occur at the same time scale, thus, the measured quantities become time-dependent. Most of the data found in the literature for the thermal behaviour of ILs (measured by DSC or adiabatic calorimetry, AC) is very scattered and inconsistent, which makes the differential analysis between IL series or different ILs families very hard. The reason for this drawback comes from the fact that the thermodynamic parameters determined directly in the apparatus such as ($T_g$, $T_m$, $\Delta H$), and the ones derived (AS) from the results are very sensitive to the adopted methodology. Experimental parameters such as annealing periods and scanning rates highly influence the thermal behaviour results. Additionally, the apparatus should be carefully calibrated in the same conditions that the experiments were carried out. The purity of samples is another important issue. Samples should be as pure as possible and, in the particular case of ILs, they should be kept in vacuum to avoid moisture.

The nanostructuration of the ILs liquid is kept in the glassy state and it is reflected in the glass transition, $T_g$ and heat capacity change. It was found that in the solid-liquid equilibrium, the temperature, enthalpies and entropies of melting are dependent on the degree of the IL nanostructuration. The trend and shape of the thermal behaviour of the ILs is ruled by the alkyl chain length (CAS) and as a consequence the formation of polar and non-polar domains. The increase of the relative cohesive energy of the liquid is due to the predominant contribution of the increase of the van der Waals interaction starting from the point in which the ionic network reaches stationary interaction potential. After the CAS, there is an increase in the liquid disorder (absolute liquid entropy increase) due to the growth of the motion of the alkyl moieties in the non-polar domains.

Results and Discussion

The glass temperatures as a function of n (number of carbons of one alkyl side chain) is depicted in figure 1 for the [CnC1im][NTf2] and [CnC2im][NTf2] ILs series. The comparative analysis of the experimental results, with the data reported in the literature, for the $T_g$ and $T_m$ of the [CnC2im][NTf2] series reveals a maximum deviation between ±(5 – 10) K (see supporting information). This deviation reflects the dispersion in the literature data due to the different methodologies adopted for the thermal studies of ILs. No literature data was found for the [CnC2im][NTf2] series.

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Supporting information for this article is given via a link at the end of the document.
Our experimental results concerning the thermal behaviour of the $[C_{n}C_{1}{\text{im}}][NTf_{2}]$ and $[C_{n}C_{3}{\text{im}}][NTf_{2}]$ series are summarized in table 1. The thermograms and the experimental details are presented as supporting information. For each series the enthalpies and entropies were corrected to the reference temperature of 298.15 K, according to equations (1) and (2) respectively:

\[
\Delta_{\text{f}}H_{\text{m}}^{\circ}(298.15) = \Delta_{\text{f}}H_{\text{m}}^{\circ}(T_{\text{ref}}) + \Delta_{\text{f}}C_{\text{p,m}}^{\circ}(298.15 - T_{\text{ref}}) \quad (1)
\]

\[
\Delta_{\text{f}}S_{\text{m}}^{\circ}(298.15) = \Delta_{\text{f}}H_{\text{m}}^{\circ}(T_{\text{ref}})/T_{\text{ref}} + \Delta_{\text{f}}C_{\text{p,m}}^{\circ}\ln(298.15/T_{\text{ref}}) \quad (2)
\]

The molar heat capacity differences between the liquid and the solid, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, used in the corrections of the enthalpies and entropies of melting transitions, at $T = 298.15$ K, were estimated based on the respective molar heat capacity change, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, at glass transition (typical ratio between both heat capacities changes, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}/\Delta_{\text{f}}C_{\text{p,m}}^{\circ}(\text{glass}) = 0.80$), taking into account our results and the data reported by Pauleska et al. The raw experimental data of the enthalpies of transition, at the transition temperatures, are available as supporting information.

Figure 1. Glass transition temperatures, $T_{g}$, of the series $[C_{n}C_{1}{\text{im}}][NTf_{2}]$ (●) and $[C_{n}C_{3}{\text{im}}][NTf_{2}]$ (●) as a function of the $n$ (number of carbons in one alkyl side chain). ⚪ $[C_{n}C_{3}{\text{im}}][NTf_{2}]$.

The molar heat capacity change associated with the glass transition, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, determined in this work (table 1) corresponds to the difference between the molar heat capacities of the supercooled liquid $C_{\text{p,m}}^{\circ}(l)$, and glass state $C_{\text{p,m}}^{\circ}(gs)$, according to equation (3).

\[
C_{\text{p,m}}^{\circ}(gs) - C_{\text{p,m}}^{\circ}(l) = \Delta_{\text{f}}C_{\text{p,m}}^{\circ} \quad (3)
\]

The reported overall uncertainties are twice the standard deviation of the mean. The uncertainties of the experimental results were assigned on the basis of the extended standard deviation of the experimental and the calibration results. An overall uncertainty of $\pm 10$ J·K$^{-1}$·mol$^{-1}$ was estimated for the $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$. The observed ratio between $T_{g}/T_{m}$ (from 0.61 to 0.70) is in good agreement with the Beaman-Kauzmann rule ($T_g/T_m=2/3$) for the typical one-component glass-forming. In figure 2, the molar heat capacity change at the glass transition temperature is presented for the $[C_{n}C_{1}{\text{im}}][NTf_{2}]$ and $[C_{n}C_{3}{\text{im}}][NTf_{2}]$ ILs series as a function of $N$ (total number of carbons). The observed increase of the heat capacity change $=10$ J·K$^{-1}$·mol$^{-1}$ per "-CH$_2$-" at the glass transition (slope in figure 2) with the increase of the alkyl chain length is in agreement with the expected heat capacity increments arising in the liquid phase from the additional contribution of the the methyl group "-CH$_3$-". From the extrapolation of the $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, draw in the figure 2, to $n=0$, the average contributions of the cation(imidazolium) and anion (NTf$_2$) to the $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$ can be estimate as $45 \pm 10$ J·K$^{-1}$·mol$^{-1}$.

Figure 2. Molar heat capacity change at the glass transition, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, of the series $[C_{n}C_{1}{\text{im}}][NTf_{2}]$ (●) and $[C_{n}C_{3}{\text{im}}][NTf_{2}]$ (●) as a function of the $N$ (total number of carbons). The dash-dot is a guide line with no physical meaning.

Table 1 Glass transition temperatures, $T_{g}$, experimental heat capacity change at the glass transition, $\Delta_{\text{f}}C_{\text{p,m}}^{\circ}$, temperatures and enthalpies of melting corrected at 298.15 K, $\Delta_{\text{f}}H_{\text{m}}^{\circ}$ (298.15 K), for the $[C_{n}C_{1}{\text{im}}][NTf_{2}]$ and $[C_{n}C_{3}{\text{im}}][NTf_{2}]$ series.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$T_{g}/K$</th>
<th>$\Delta_{\text{f}}C_{\text{p,m}}^{\circ}/J\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$</th>
<th>$\Delta_{\text{f}}H_{\text{m}}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$</th>
<th>$\Delta_{\text{f}}S_{\text{m}}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>178.0 ± 0.5</td>
<td>23.1 ± 0.7</td>
<td>79.5 ± 2.4</td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>185.4 ± 0.5</td>
<td>34.7 ± 0.7</td>
<td>132.7 ± 2.6</td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>184.5 ± 0.5</td>
<td>262.6 ± 0.5</td>
<td>141.0 ± 0.7</td>
<td>125.8 ± 2.7</td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>185.4 ± 0.5</td>
<td>146.0 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>273.9 ± 0.5</td>
<td>123.7 ± 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>291.7 ± 0.5</td>
<td>143.2 ± 2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>308.3 ± 0.5</td>
<td>152.5 ± 2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>319.5 ± 0.5</td>
<td>151.3 ± 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>296.5 ± 0.5</td>
<td>113.9 ± 2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>260.0 ± 0.5</td>
<td>132.7 ± 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{1}{\text{im}}][NTf_{2}]$</td>
<td>287.0 ± 0.5</td>
<td>152.5 ± 2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[C_{n}C_{3}{\text{im}}][NTf_{2}]$</td>
<td>308.3 ± 0.5</td>
<td>152.5 ± 2.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The glass and melting temperatures show two different trends along the alkyl side chain. There is an initial increase in $T_g$ (figure 1), indicating a high relative glass stability and a decrease in $T_m$ (figure 3), which indicates a decrease in the solid stability over the liquid. The glass, which is a frozen state of the isotropic liquid, is a statistical representation of all the conformers that were presented in the liquid before the quenching. Thus, the increase of the dispersive interactions (van der Waals) of the alkyl side chain is reflected in the increase of $T_g$ in the glass, there are virtually no packing requirements, so the relative stability of the glass will be driven mostly by the size and the magnitude of the interactions that the bulk IL can establish. A stationary regime is attained at around 185 K, after $n=6$. The effect of an additional -CH$_2$ group seems to be the same both in glass and liquid, leading to a plateau after the nanostructuration. The obtained stationary value of the glass transition temperature after CAS can be associated with the unchangeable polar network grid type after CAS, which seems to rule the relative stability between the glassy and liquid states. This observation is in agreement with the structuration model, derived from several other experimental [25] and computational data [23,24] which have shown for both ILs series, a trend shift at $n=6$, occurred at the so-called CAS (critical alkyl size) [11,25,26] due to an intensification of the nanostructuration of the liquid phase.

The experimental temperatures of melting for the [C$_n$C$_1$im][NTf$_2$] and [C$_n$C$_1$im][NTf$_2$] ILs series as a function of the number of the alkyl side chain length, $N$, are presented in figure 3, together with the available literature data and the alkanes series 1 ≤ $n$ ≤ 24 [27-38] and other imidazolium based-ILs with different anions such as PF$_6$ and BF$_4$. Some ILs from [C$_n$C$_1$im][NTf$_2$] and [C$_n$C$_1$im][NTf$_2$] series, such as: [C$_n$C$_1$im][NTf$_2$], [C$_n$C$_1$im][NTf$_2$], [C$_n$C$_1$im][NTf$_2$], [C$_n$C$_1$im][NTf$_2$], [C$_n$C$_1$im][NTf$_2$] did not crystallize in the experimental conditions adopted in this work. These ILs form glass at relative high cooling rate. They do not easily crystallize because the kinetic “kick” to form crystals requires a molecular dynamic in the undercooled liquid that is surpassed by the melting equilibrium. Some data found in the literature (measured in other apparatus and using different methodologies) was used to complement the phase transitions temperature profile of the studied ILs series. [12,14-16,37,38] In order to simplify figure 3, the global picture of our experimental results and the literature data of some ILs from the [C$_n$C$_1$im][NTf$_2$] series are presented as supporting information.

The uncertainty of the experimental results was taken as the extended standard deviation for the enthalpies of melting, $\alpha$, and was estimated ± 0.5 K for the $T_g$ and $T_m$. $\Delta U_m$ corresponds to the sum of all the enthalpy change from the most stable crystal form to the isotropic liquid. An uncertainty of 10 J K$^{-1}$ mol$^{-1}$ was estimated for $\Delta U^0_m$. The $\Delta U_m^0$ were corrected for $T = 298.15$ K using the $\Delta U^0_m$, estimated. (a) ratio between $T_g/T_m$.

The “V” shape trend depicted in figure 3 for the [C$_n$C$_1$im][NTf$_2$] and [C$_n$C$_1$im][NTf$_2$] series presented in this work is consistent with the trend observed in the PF$_6$ [14,15,37-40] and BF$_4$ [46] imidazolium series. It is interesting to notice (before CAS), a distinguishable difference in the decrease of the melting temperature for the different anions (guide line in figure 3). In that region the electrostatic potential between the ion–pair plays a major role in the melting transition. The PF$_6$ and BF$_4$ anion based ILs, present higher melting points, in agreement with the predicted effect in the crystal packing stability (higher cohesive interactions between the anion-cation) of smaller and more spherical anions, such as PF$_6$ and BF$_4$.

After CAS, all the series seem to converge to the same trend; reaching the alkanes series plateau. The similarity of the thermal behaviour of the ILs and the alkane series is reflected in their odd-even effect. The odd-even effect present in the BF$_4$ anion series could not be shown in the [C$_n$C$_1$im][NTf$_2$] series as only the even series numbers were studied. However, the odd-even is pronounced in the symmetrical [C$_n$C$_1$im][NTf$_2$] series. The odd-even effect seems to be intensified in the [C$_n$C$_1$im][NTf$_2$] series due to the double alkyl chain contribution which enhance the crystal packing stability. A recent report based in quantum chemical calculations and molecular dynamics simulations [24] of imidazolium and trioctylphosphonium ILs families have shown that the principal contribution for the odd-even alternation is the transoid head-to-head conformations of the ILs pairs in liquid phase. These types of conformations that lead to odd-even alternation are also present in solid phase.
For a short alkyl chain size region (before CAS) the differentiation between the solid and the liquid phase is highly dependent on the initial decrease of the electrostatic interaction. Figure 4 depicts the enthalpies and entropies of melting at the same reference temperature, T=298.15K for the [CnCnim][NTf2] and [CnCnim][NTf6] series. In the solid phase, there are packing requirements which lead to a decrease in the entropy (alkyl side chain must be in a specific orientation to maximize the cohesive interactions). Firstly, in the short alkyl ILs zone (highly packed structures: [C2Cnim][NTf6], [C3-Cnim][NTf6] and [C4Cnim][NTf6]), the Tm drops until the [CnCnim][NTf6], n=6 at CAS, creating a “V” shape profile of the melting temperatures. It is interesting to notice that the alkyl chain dependence of the temperatures, enthalpies, and entropies of melting in the ILs after CAS is very similar to the dependence observed in the alkane series (fig 3 and 4), highlighting the weight and the role of the non-polar alkyl domains in their thermal behaviour. The “-CH2-” increment contributes to a decrease of the electrostatic interactions and an increase of the conformation entropy. This effect is more pronounced, as expected, for the PF6 and BF4 anions, due to the anions sphericity. The diminished odd-even alternation effect (in the enthalpies and entropies of melting), depicted in the imidazolium series when compared with the alkane series, may be explained by the partial compensation arising from the preferential head-to-head conformations in the liquid phase due to the IL nanostructuration.

Figure 5 presents an overview of the derived trends of the enthalpy (I), ΔfHm(298.15) and entropy (II), ΔfSm(298.15), of vaporization and sublimation. The enthalpies and entropies of sublimation were derived from the melting and vaporization phase change thermodynamic parameters according to the relation: ΔfHm(298.15)=ΔfHm(298.15) + ΔfHm(298.15). Due to the short temperature correction interval, the dependence of ΔfHm with the temperature was neglected. A significant differentiation between the asymmetric [CnCnim][NTf6] and symmetric ([CnCnim][NTf6]) series at N = 12 (n=11 in the [CnCnim][NTf6]; n=6 in the [CnCnim][NTf6]) is observed for both enthalpies and entropies of sublimation. The differentiation, due to the “-CH2-” increment is related with the change of the crystal packing in the asymmetric series (at long chain length) caused by additional available packing motives. In fact, a much more complex thermal behaviour was found for n=9, with the appearance of multiple reproducible cold crystallization and solid-solid phase transitions, and, in some cases, pre-melting peaks. Detailed data concerning the thermal analysis of both series are available as supporting information.

Conclusions

The differential study of the thermal behaviour of bistriflimide imidazolium-based [CnCnim][NTf2] and [CnCnim][NTf2] ILs series is presented and their trend is interpreted based in the ILs nanostructuration in each phase.
The glass transition, $T_g$, melting, $T_m$, and cold crystallization, $T_{cc}$, temperatures, enthalpies and heat capacity change involved in those transitions were determined with high reproducibility using a high resolution power compensation DSC apparatus and a well-defined methodology. Glass and melting temperatures, enthalpies and entropies of melting present a trend shift at n=6, CAS (critical alkyl size), in agreement with the tendency found in several others physical-chemistry properties, supported by spectroscopic and molecular simulation studies. This experimental study, firmly supports the evidence of the strong capability of ILs to form a nanostructured network with distinguishable polar and non-polar domains in the liquid phase. A significant differentiation of the thermal behaviour before and after CAS was observed due to the change of the cohesive electrostatic potential that rules the network packing both in solid and liquid phases. For the long chain ILs, the thermal behaviour in both series reflects the “-CH2-” increment, such as: the change in solid network packing for the long chain length (after n=9); and a significant change in the dynamics and nanostructuration of the liquid phase after CAS (n=6), which arose from the formation of alkyl non-polar domains very similar with the ones observed in the alkane series.

**Experimental Section**

The studied ILs were acquired from IOLITEC with state purity above 99%. The commercial IL samples were purified under vacuum (0.1 Pa) at moderate temperature (323 K) and constant stirring for 48 h in order to remove traces of water and volatile impurities. Glass transitions, (temperatures and heat capacity change), enthalpies and entropies of melting of the ILs were measured in a power compensation differential scanning calorimeter, PERKIN ELMER model Pyris Diamond DSC. The water mass fraction content was determined in a 151 Metrohm 831 Karl Fischer coulometer, using a Hydranal 831 Karl Fischer coulometer, using a Hydranal.

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**Keywords:** Ionic Liquids • Phase behaviour • Glass • Enthalpy • Nanostructuration • Melting • CAS • Entropy • Solid

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Thermal behaviour of Ionic Liquids reveals a trend shift at the critical-alkyl-size (CAS), $n=6$.

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