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The effect of *n* vs. *iso* isomerization on the thermophysical properties of aromatic and non-aromatic ionic liquids

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ABSTRACT

This work explores the *n* vs. *iso* isomerization effects on the physicochemical properties of different families of ionic liquids (ILs) with variable aromaticity and ring size. This study comprises the experimental measurements, in a wide temperature range, of the ILs' thermal behaviour, heat capacities, densities, refractive indices, surface tensions, and viscosities. The results here reported show that the presence of the *iso*-alkyl group leads to an increase of the temperature of the glass transition, T_g. The *iso*-pyrrolidinium (5 atoms ring cation core) and *iso*-piperidinium (6 atoms ring cation core) ILs present a strong differentiation in the enthalpy and entropy of melting. Non-aromatic ILs have higher molar heat capacities due to the increase of the atomic contribution, whereas it was not found any significant differentiation between the *n* and *iso*-alkyl isomers. A small increase of the surface tension was observed for the non-aromatic ILs, which could be related to their higher cohesive energy of the bulk, while the lower surface entropy observed for the *iso* isomers indicates a structural resemblance between the IL bulk and surface. The significant differentiation between ILs with a 5 and 6 atoms ring cation in the *n*-alkyl series (where 5 atoms ring cations have higher surface entropy) is an indication of a more efficient arrangement of the non-polar region at the surface in ILs with smaller cation cores. The ILs constituted by non-aromatic piperidinium cation, and *iso*-alkyl isomers were found to be the most viscous among the studied ILs due to their higher energy barriers for shear stress.

1. Introduction

Most of the research on the structural property relationships of ionic liquids (ILs) is focus on the effect that major structural variations, such as alkyl side chain length, and the nature of anions and cations, have on their thermophysical properties [1–8]. The complexity and variety of ILs make the rationalization of these relationships hard, yet amenable, and a large number of approaches to predict the properties of ionic liquids has been proposed [8–16]. However, few studies highlight small structural variations on ILs, such as isomerization, or chemical nature differentiation (e.g. aromatic vs. aliphatic and ammonium vs. phosphonium) and their effect on the ILs thermophysical properties [17–30]. However, the understanding and development of structure-property relationships are important from both fundamental and applied standpoints. It allows a rationalization of the molecular level interactions and the development of heuristics and correlations that allow the design of ionic liquids for specific applications.

Previous studies suggested that the branching of the alkyl side chain not affect their density significantly, but when some cycle group (aromatic and non-aromatic) is present in the alkyl chain, the densities increase [20,23,26]. Regarding transport properties, such as viscosity, a small variation of the aliphatic side group may lead to substantial changes in their properties [23,25];as the nanostructuration of ILs becomes highly affected a significant impact

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occurs in the shear stress of ILs. Aromatic ILs with branched and cyclic alkyl side chains were shown to have higher viscosities than their *n*-alkyl homologous [20,23]. For different cyclic groups in the alkyl chain or the cation core, the viscosity is expected to be dependent on the size and structure of the cyclic group and in the magnitude of dispersive intermolecular interactions (van der Waals). The relatively high viscosity for these ILs compared with their *n*-alkyl homologous depends heavily on the reorientation motion on ILs. Maginn and co-workers [28], based on the unpublished data by Xue et al. [31], reported higher viscosities for branched aromatic ILs. According to the simulation study carried by the authors [28] these results were explained by a higher packing stability of the ion pairs in the liquid phase. In summary, the viscosity is highly affected by the specific shape and length of the ILs alkyl side chain.

There are few works concerning the thermal behaviour of isomeric ILs. Quitevis et al. [26] have shown that changing from aromatic to non-aromatic alkyl substituents has a significant effect on the thermal properties of ILs. Generally, ILs with aromatic and branched substituted cations show higher T_g values than their aliphatic analogs, regardless of the anion [29].

In this work, we investigated the structure–property relationships regarding the effect of *n*-butyl versus *iso*-butyl substituents in aromatic (imidazolium and pyridinium) and non-aromatic (pyrrolidinium and piperidinium) cations of $[NTf_2]^-$-based ILs. These ILs were chosen in order to study the effect of a branched alkyl side chain on aromatic and aliphatic cations on several thermophysical properties, such as thermal behaviour, heat capacities, densities, refractive indices, surface tensions, and viscosities.

2. Experimental section

2.1. Materials and purification

All ILs were purchased from IoLiTec with the highest purity available. The ILs samples were maintained dried under vacuum ($p < 0.1$ Pa) at moderate temperature (323 K) and constant stirring up to the measurements, to remove traces of the most volatile impurities and moisture. The purity of each IL was checked by NMR spectroscopy (^{1}H and ^{13}C). For detailed NMR analysis, see Supporting Information. The water mass fraction contents were determined with a Metrohm 831 Karl Fischer coulometer, using the Hydranal-Coulomat AG® from Riedel-de Haën. Table 1 presents the list of the studied ILs, their abbreviation, molar masses, purity, and the water content while Fig. 1 provides a schematic representation of the ILs studied. The relative atomic masses used in this work were those recommended by the IUPAC Commission in 2007 [32].

2.2. Thermal behaviour

Glass transition (temperatures and molar heat capacity change), enthalpies and entropies of melting of the ILs under study were measured in a power compensation differential scanning calorimeter, PERKIN ELMER model Pyris Diamond DSC, previously calibrated with some reference materials [33,34]. The methodology adopted in the phase behaviour study is provided in the Supporting Information. The calibration and the ILs phase behaviour study were performed using the same experimental methodology to improve the resolution of the differential analysis of this study. The $[C_6C_1im][NTf_2]$ ionic liquid was used as a reference test sample for the DSC calibration and methodology adopted in this work. The experimental results for the $[C_6C_1im][NTf_2]$ were compared with the literature values determined by Paulechka et al. [35]' [36] measured with adiabatic calorimetry.

2.3. Heat capacities

The ILs heat capacities at $T = 298.15$ K were measured by a high-precision heat capacity drop calorimeter described in the literature [37–39]. The calorimeter was calibrated with water and sapphire (α-Al_2O_3) [33]. The calibration constant was found to be $\varepsilon = (6.6040 \pm 0.0036)\ \mathrm{W \cdot V^{-1}}$. The ampoules were weighted in a Mettler Toledo AG245 dual range analytical balance (sensitivity of 1×10^{-5} g and repeatability of 2×10^{-5} g) both empty and after filling with the ionic liquid. The accuracy and resolution of the apparatus for measurements of heat capacities of liquids and solids were previously evaluated using hexafluorobenzene, *p*-terphenyl, benzoic acid, and $[C_6C_1im][NTf_2]$ [39]. All uncertainties are given as twice of the standard deviation of the average value and include the calibration uncertainty. The buoyancy effect correction was considered for both the calibration and ILs measurements.

2.4. Densities and viscosities

The density, ρ, and viscosity, η, of the pure ILs were measured using an automated SVM 3000 Anton Paar rotational Stabinger viscometer – densimeter. The apparatus was calibrated in the same experimental conditions of the ionic liquid measurements, using three standard calibration samples: APN7.5 (9.995 $\mathrm{mPa \cdot s^{-1}}$/0.8159 g. $\mathrm{cm^{-3}}$), APN26 (50.02 $\mathrm{mPa \cdot s^{-1}}$/0.8209 $\mathrm{g \cdot cm^{-3}}$), and APN415 (1105 $\mathrm{mPa \cdot s^{-1}}$0.8456 $\mathrm{g \cdot cm^{-3}}$) (values at 293.15 K). The reproducibility of the dynamic viscosity and density measurements is, according to the manufacturer, 0.35% and ± 0.5 $\mathrm{kg \cdot m^{-3}}$, respectively, from 288.15 to 378.15 K, and the uncertainty of temperature is within ± 0.02 K. The measurements were carried out at

Table 1
IUPAC names, abbreviation, molar masses (*MM*) and water content for each studied ionic liquid.

Ionic liquid	Abbreviation	MM/g mol^{-1}	Water content (ppm)	Purity[a]
1-(2-methylpropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$[iC_4C_1im][NTf_2]$	419.366	20	>98% (NMR); <100 ppm Halides (IC)
1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	$[C_4C_1py][NTf_2]$	430.389	62	99% (NMR) <100 ppm Halides (IC)
1-(2-methylpropyl)-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	$[iC_4C_1py][NTf_2]$	430.389	28	98% (NMR) <100 ppm Halides (IC)
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	$[C_4C_1pyrr][NTf_2]$	422.410	55	99% (NMR) <100 ppm Halides (IC)
1-(2-methylpropyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	$[iC_4C_1pyrr][NTf_2]$	422.410	21	98% (NMR) <100 ppm Halides (IC)
1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	$[C_4C_1pip][NTf_2]$	436.437	70	99% (NMR) <100 ppm Halides (IC)
1-(2-methylpropyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	$[iC_4C_1pip][NTf_2]$	436.437	17	98% (NMR) <100 ppm Halides (IC)

[a] Purity from the supplier: ^{1}H NMR (Nuclear magnetic resonance), Ionic chromatography (IC).