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Heat capacities at 298.15 K of the extended [C$_n$C$_1$im][Ntf$_2$] ionic liquid series

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ABSTRACT

High-precision heat capacities at 298.15 K of the [C$_n$C$_1$im][Ntf$_2$] ionic liquid series were measured with an uncertainty of less than ±0.3%, using a drop heat capacity apparatus that was recently updated. The dependence of the c_p^o values on the alkyl side chain length for the extended ionic liquid series [C$_n$C$_1$im][Ntf$_2$] (with n = 2 to 8, 10, and 12) displays a trend shift at [C$_6$C$_1$im][Ntf$_2$], which is taken as an evidence for percolation limit. Above this limit there is an increase in the methylene group contribution to the molar heat capacity which is in agreement with the higher molar absolute entropies change observed from the (liquid + vapor) equilibrium results. The obtained experimental results support the model that the ionic liquids tend to be segregated into a polar network and non-polar domains, being followed by an increase of the entropy contribution of the non-polar domains.

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1. Introduction

Research on ionic liquids (ILs) is growing at a very fast rate, due to their distinctive properties, such as low vapor pressure, stable liquid phase over a wide temperature range, low-flammability and thermal stability at high temperatures [1]. They are nanostructured fluids in which the ion pairs arrange themselves into polar and nonpolar domains. The structural segregation in these systems will depend on the size of the polar and nonpolar regions in each ion may exist as dispersed or continuous microphases. The transition between these two phases is related with the percolation phenomenon, and depends on the relative size of the high-charge and low-charge regions in each ion and the size of the alkyl chain length [2]. These characteristics are the basis for an increasing number of their potential applications in sensors, thermal fluids, batteries, capacitors, lubricants, ionogels, extractants and as solvents in analysis, synthesis, catalysis, and separation [3–5]. At odds with the exhaustive fundamental and applied studies on an extensive number of these systems, only few works are available in the literature providing reliable physicochemical properties for pure ILs [6,7]. For the interpretation of their properties and a successful modeling of ionic liquids, highly accurate data regarding these physicochemical properties are needed, such as heat capacities, vapor pressures, viscosities, densities, refraction index, etc. Heat capacity is one of the most important thermophysical properties of matter, since it is an important thermodynamic link between the fluid structure and dynamics. For a constant pressure process, the heat capacity, C_p, which is an extensive property, is defined as:

$$C_p = \frac{dq_p}{dT}. \tag{1}$$

The specific heat capacity, at constant pressure, is represented by c_p and is defined as the heat capacity per unit mass, or C_p/m, where m is the mass of the substance. Accordingly, the volumic heat capacity, denoted by C_p/V, is defined as the heat capacity per volume. Molar heat capacity, specific heat capacity, and volumic heat capacity are intensive properties, which is characteristic of each system and related with their structure and dynamics. Heat capacity data for a large number of aprotic ionic liquids have been published before [6]. However, a large fraction of the known data presents large uncertainties that are related to the calorimetric methods used as well as to the quality and purity of the samples.

Recently, we reported a thermodynamic study concerning the vaporization of the extended series of ILs [C$_n$C$_1$im][Ntf$_2$] with n = 2 to 8, 10, and 12, where it was possible to detect important trends in the thermodynamic parameters, which would have been impossible to verify with a smaller number of ILs [8].

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TABLE 1

Molar heat capacity values, at T = 298.15 K, for the studied ionic liquids. Calibration constant of the drop calorimeter used in the heat capacity calculation $(6.6329 \pm 0.0046 \; W \cdot V^{-1})$.

Ionic liquid	$M/(g \cdot mol^{-1})$	N_{drop}	$C_{p,m}^o/(J \cdot K^{-1} \cdot mol^{-1})$
$[C_2C_1im][Ntf_2]$	391.313	10	504.8 ± 1.2
$[C_3C_1im][Ntf_2]$	405.340	13	534.9 ± 0.5
$[C_4C_1im][Ntf_2]$	419.366	10	565.9 ± 0.6
$[C_5C_1im][Ntf_2]$	433.393	17	595.6 ± 0.5
$[C_6C_1im][Ntf_2]$	447.420	15	629.4 ± 1.2
$[C_7C_1im][Ntf_2]$	461.446	16	659.2 ± 0.7
$[C_8C_1im][Ntf_2]$	475.473	6	690.2 ± 0.7
$[C_{10}C_1im][Ntf_2]$	503.526	18	754.5 ± 0.9
$[C_{12}C_1im][Ntf_2]$	531.580	18	820.2 ± 0.9

N_{drop} = number of drop experiments; for the $[C_nC_1im][Ntf_2]$, with n = 3, 5, 6, 7, 10, and 12, the number of drops are the sum of the drops that were obtained in two independent experiments.

In order to evaluate the linearity in the heat capacity of the $[C_nC_1im][Ntf_2]$ ionic liquid series as a function of the alkyl side chain length in the cation and any possible shift that could be related with the percolation phenomenon [2,8], high precision heat capacity data at T = 298.15 K have been measured, for the extended alkyl series (odd and even). The heat capacities of the nine ILs were measured by means of a high-precision heat capacity drop calorimeter developed by Wadsö [9,10] and recently modernized at our laboratory [11]. The quality of the heat capacity data, is comparable, in accuracy, with the best literature data measured by adiabatic calorimetry [12–17]. The observed subtle changes in the heat capacity with the length of the cation alkyl side chain was only possible due to the high precision of the heat capacity drop calorimeter.

2. Experimental section

The 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide series, $[C_nC_1im][Ntf_2]$ (n = 2 to 8, 10, and 12), used in this work, were purchased from IOLITEC with a stated purity of better than 99%. All ionic liquids were dried under reduced pressure (<10 Pa) and stirred constantly for a minimum of 48 h at 373 K, in order to reduce the presence of water or other volatile contents. Karl Fischer titration of the degassed samples revealed less than 100 ppm of water.

2.1. High-precision heat capacity drop calorimeter

The heat capacities at 298.15 K of $[C_nC_1im][Ntf_2]$ were measured by a high-precision heat capacity drop calorimeter, developed by Wadsö [9,10] at the Thermochemistry Laboratory, Lund, Sweden, being afterwards transferred to Porto, Portugal, where its temperature sensors and electronics were modernized to enable the use of computer data acquisition in a user-friendly environment [11]. The apparatus comprises two main parts: the furnace and the receiving calorimeter. The receiving calorimeter consists in a twin heat conduction calorimeter of the type used in Lund's instruments. The furnace temperature was 303.15 K and the receiving calorimeter was kept at 293.15 K. The twin calorimeter measures the heat exchange resulting from the ampoule cooling from the initial temperature (T_i = 303.15 K) to the final temperature (T_f = 293.15 K). For the calculation of the heat capacities, the apparatus calibration constant was derived from the sapphire and water calibrations, and the value $(6.6329 \pm 0.0046 \; W \cdot V^{-1})$ was used. The accuracy of the apparatus for the measurements of the heat capacities for liquids and solids was evaluated before, based on the measurements of benzoic acid and hexafluorobenzene [11]. Since the calorimeter was now used to measure the heat capacity of ionic liquids, the accuracy was additionally checked on the basis of the results obtained for $[C_6C_1im][Ntf_2]$ [18]. The determined $C_{p,m}^o$ ($[C_6C_1im][Ntf_2]$, 298.15 K) = (629.4 ± 1.2) $J \cdot K^{-1} \cdot mol^{-1}$ was obtained from the average of two independent experimental runs, using different ampoules, and is in excellent agreement with the recommended value, $C_{p,m}^o$ ($[C_6C_1im][Ntf_2]$, 298.15 K) = (631.6 ± 1.3) $J \cdot K^{-1} \cdot mol^{-1}$ [18].

The relative atomic masses used were those recommended by the IUPAC Commission in 2007 [19]. The molar masses, M $(g \cdot mol^{-1})$, number of drop experiments, N_{drop}, and molar heat capacities at 298.15 K, $C_{p,m}^o$ $(J \cdot K^{-1} \cdot mol^{-1})$, for each studied ionic liquid are presented in table 1. The masses of the samples were corrected for the buoyancy effect, and it was done both for calibration and experiments of ionic liquids. The reported uncertainty is the twice of the standard deviation of the mean and includes the calibration uncertainty.

3. Results and discussion

Table 2 presents heat capacity data for the studied ionic liquids at T = 298.15 K, together with available literature values. The volumic heat capacities (C_p^o/V) were calculated from the determined specific heat capacities, c_p^o, and the available experimental density values published by Tariq et al. [20]. The literature data for the molar heat capacities ($C_{p,m}^o$) here considered for comparison were obtained by adiabatic calorimetry [12–17]. The heat capacities of the studied ILs were measured with an uncertainty of less than ±0.3%

TABLE 2

Derived heat capacity results at T = 298.15 K, for each ionic liquid, together with selected literature data.

| Ionic liquid	$c_p^o/(J \cdot K^{-1} \cdot g^{-1})$	$C_p^o/V/(J \cdot K^{-1} \cdot cm^{-3})$	$C_{p,m}^o/(J \cdot K^{-1} \cdot mol^{-1})$	$C_{p,m}^o/(J \cdot K^{-1} \cdot mol^{-1})$
	This work			Literature
$[C_2C_1im][Ntf_2]$	1.2900 ± 0.0031	1.9608 ± 0.0047	504.8 ± 1.2	506.5 ± 0.5 [14]
				505.7 ± 2.0 [16]
$[C_3C_1im][Ntf_2]$	1.3197 ± 0.0013	1.9473 ± 0.0019	534.9 ± 0.5	
$[C_4C_1im][Ntf_2]$	1.3494 ± 0.0015	1.9399 ± 0.0022	565.9 ± 0.6	565.4 ± 1.1 [13]
				564.1 ± 1.1 [14]
				565.1 ± 2.3 [17]
$[C_5C_1im][Ntf_2]$	1.3743 ± 0.0012	1.9286 ± 0.0017	595.6 ± 0.5	
$[C_6C_1im][Ntf_2]$	1.4067 ± 0.0026	1.9321 ± 0.0036	629.4 ± 1.2	631.6 ± 0.6 [12]
				629.2 ± 2.5 [15]
				631.6 ± 1.3 [18]
$[C_7C_1im][Ntf_2]$	1.4286 ± 0.0015	1.9215 ± 0.0020	659.2 ± 0.7	
$[C_8C_1im][Ntf_2]$	1.4515 ± 0.0015	1.9189 ± 0.0020	690.2 ± 0.7	692.7 ± 2.8 [16]
$[C_{10}C_1im][Ntf_2]$	1.4984 ± 0.0018	1.9187 ± 0.0023	754.5 ± 0.9	
$[C_{12}C_1im][Ntf_2]$	1.5429 ± 0.0018	1.9212 ± 0.0022	820.2 ± 0.9	
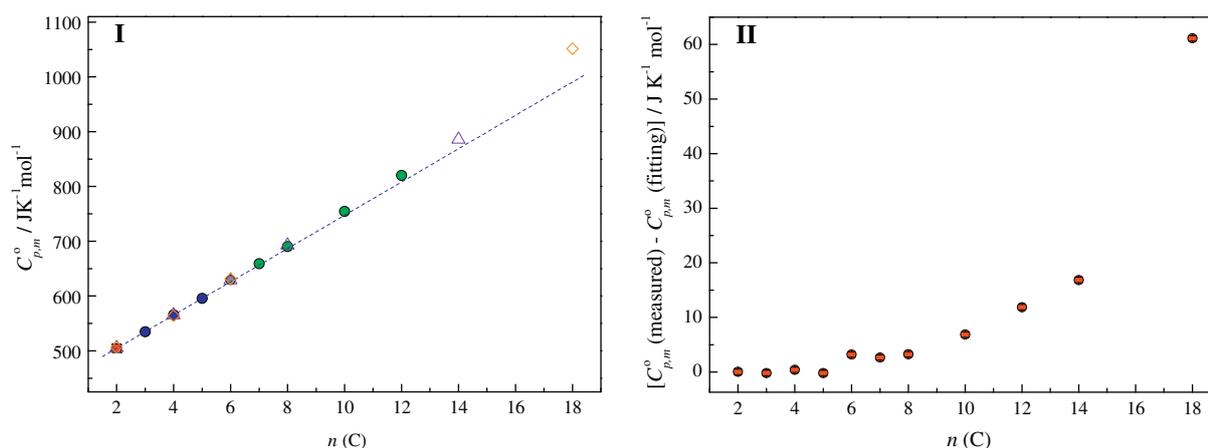
FIGURE 1. Molar heat capacities as a function of the number of carbon atoms in the alkyl side chain of the cation (I); deviation of the $C_{p,m}^o$ (fitting [C$_3$C$_1$im][Ntf$_2$]–[C$_5$C$_1$im][Ntf$_2$]) from the $C_{p,m}^o$ (measured) as a function of the number of carbon atoms in the alkyl side chain of the cation (II). This work: ■, [C$_2$C$_1$im][Ntf$_2$]; ●, [C$_3$C$_1$im][Ntf$_2$]–[C$_5$C$_1$im][Ntf$_2$]; and ●, [C$_6$C$_1$im][Ntf$_2$]–[C$_{14}$C$_1$im][Ntf$_2$]. Literature data: ◇ – [C$_n$C$_1$im][Ntf$_2$], n = 2, 4, 6, 8, 14 [15–17,23] and △ – [C$_n$C$_1$im][Ntf$_2$], n = 2, 4, 6, 18 [12–14].

and the obtained results differ less than 0.4%, from the literature data which is considered in the field an excellent agreement.

Figure 1(I) shows the representation of the molar heat capacity data ($C_{p,m}^o$) against the number of carbon atoms in the alkyl side chain, n(C), of the cation. Figure 1(II) shows the deviation plot derived from the fitting of the data for [C$_3$C$_1$im][Ntf$_2$] to [C$_5$C$_1$im][Ntf$_2$]. An apparent linearity along the IL series is shown in the representation of $C_{p,m}^o$ against the n(C). However, when considering the deviation plot from the line representing the lower members of the series as shown in figure 1(II), we can observe a strong indication of a trend shift starting from [C$_6$C$_1$im][Ntf$_2$], in the direction of higher molar heat capacities. This finding is an indication for an increase of the methylene group, –CH$_2$–, contribution to the heat capacity after n(C) = 6. Despite the excellent agreement between the data obtained in this work and the available in the literature, the fact that before only six ILs (even numbered carbons, n = 2, 4, 6, 8, 14, and 18) of these series were studied [12–17] prevented the detection of the trend shift as found now in this work. The trend shift starting from n(C) = 6 is in agreement with the findings reported on the study of the (liquid + vapor) equilibrium for the extended series of [C$_n$C$_1$im][Ntf$_2$], recently published [8]. The reported trend shift found previously in the enthalpies and entropies of vaporization was related with the structural modifications that occur when the number of alkyl carbon atoms nears six, which corresponds to a kind of limit of the polar network regions and the formation of a continuous non-polar domains. The observed higher –CH$_2$– contribution to the molar heat capacity obtained, also after [C$_6$C$_1$im][Ntf$_2$], is in line with the higher liquid entropy, as well as with the trend shift in the viscosity that was observed for the liquid phase after the limit, n(C) = 6 [8]. The limit at n(C) = 6 is also clearly revealed from the trend of the volumic enthalpies of vaporization, $\Delta_l^g h_V^o$, (derived from literature data [8]) against the n(C) presented in figure 2.

The [C$_2$C$_1$im][Ntf$_2$] shows the highest volumic enthalpies of vaporization in the series, that we relate with its outlier character in the series, due to the proximity of the methylene group to the imidazolium ring, leading to higher density and stronger electrostatic interactions for this IL. From [C$_3$C$_1$im][Ntf$_2$] to [C$_6$C$_1$im][Ntf$_2$], a constant value in the volumic enthalpies of vaporization is observed. This can be explained as the result of a balance between the decrease in density [20] and the increase in specific enthalpies of vaporization per –CH$_2$– group [8]. The limit at n(C) = 6 is clearly observed in figure 2, together with a trend shift in the direction of lower volumic enthalpies of vaporization. The gradual decrease of the volumic enthalpies of vaporization after n(C) = 6, besides being

an evidence for the percolation phenomenon in ionic liquids, it is also in agreement with the expected decrease of the volumic cohesive enthalpies. This decrease arises from the decrease of the electrostatic interactions due to the formation of a larger continuous non-polar domain, and the decrease of the density.

Figure 3 presents the plots of the specific heat capacity (I) and the volumic heat capacity (II) against the number of carbon atoms in the alkyl side chain of the cation. A subtle trend shift at n(C) = 6 in the specific heat capacity is clearly evidenced. There is a gradual increase in the c_p^o along the alkyl side chain of cation, that is explained by an increase in the contribution of the alkyl fraction to the heat capacity of the ionic liquid, which has a higher specific heat capacity (typical value for alkanes is 2.2 J · K^{-1} · g^{-1}) [21].

The volumic heat capacity plot, instead of the constant value previously postulated [22,23] shows from [C$_2$C$_1$im][Ntf$_2$] to [C$_5$C$_1$im][Ntf$_2$] a gradual decrease in C_p^o/V, that reaches a constant value of 1.92 J · K^{-1} · cm^{-3} in [C$_7$C$_1$im][Ntf$_2$] to [C$_{12}$C$_1$im][Ntf$_2$], showing a clear trend shift in this thermophysical property at [C$_6$C$_1$im][Ntf$_2$], in agreement with recent observations concerning the enthalpies and entropies of vaporization, and viscosities, as referred above [8]. The decrease in C_p^o/V from [C$_2$C$_1$im][Ntf$_2$] to [C$_5$C$_1$im][Ntf$_2$] is mainly due to the decrease of the ionic liquid den-
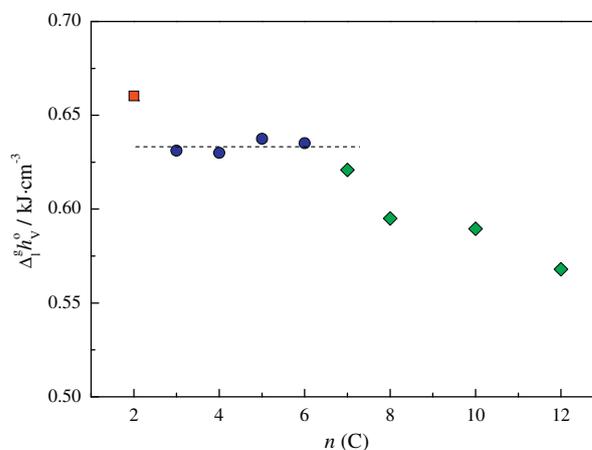

FIGURE 2. Volumic enthalpies of vaporization, $\Delta_l^g h_V^o$, as a function of the number of carbon atoms in the alkyl side chain of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide series, [C$_n$C$_1$im][Ntf$_2$] (n = 2 to 8, 10, and 12). ■, [C$_2$C$_1$im][Ntf$_2$]; ●, [C$_3$C$_1$im][Ntf$_2$]–[C$_6$C$_1$im][Ntf$_2$]; and ●, [C$_7$C$_1$im][Ntf$_2$]–[C$_{12}$C$_1$im][Ntf$_2$].

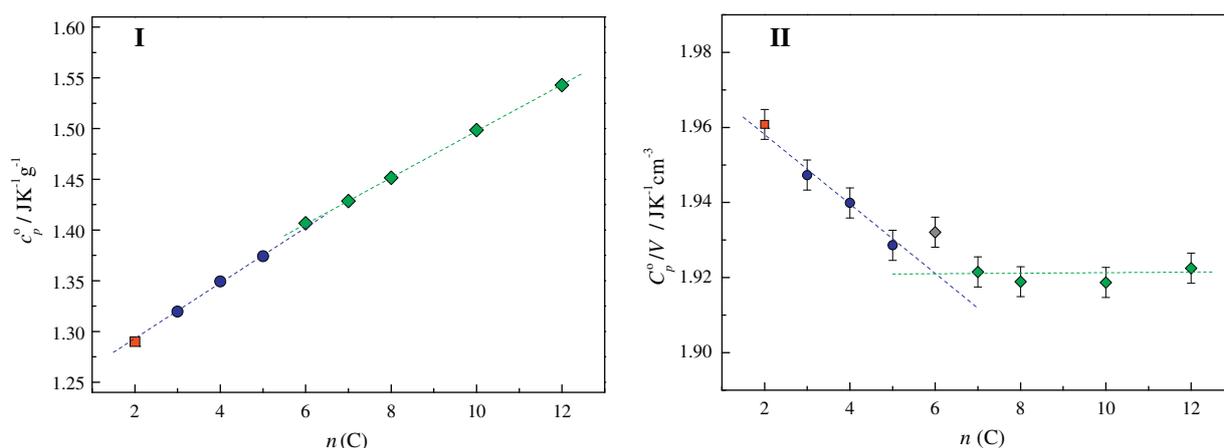*M.A.A. Rocha et al. / J. Chem. Thermodynamics 53 (2012) 140–143*

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FIGURE 3. Specific heat capacities as a function of the number of carbon atoms in the alkyl side chain of the cation (I); volumic heat capacities as a function of the number of carbon atoms in the alkyl side chain of the cation (II). ■, $[C_2C_1im][Ntf_2]$; ●, $[C_3C_1im][Ntf_2]$–$[C_5C_1im][Ntf_2]$; and ●, $[C_6C_1im][Ntf_2]$–$[C_{12}C_1im][Ntf_2]$.

sity along the series [20]. The constant value observed in C_p^o/V from $[C_7C_1im][Ntf_2]$ to $[C_{12}C_1im][Ntf_2]$, could be the result of a balance between the decrease in density and the increase in volumic heat capacity per $-CH_2-$ group. If we take this together with the decrease of the volumic cohesive enthalpy in this region, reflected in the decrease of $\Delta_l^g h_V^o$ (figure 2), one is led to the conclusion that the two phenomena must have the same origin, *i.e.*, the balance between electrostatic and non-polar interactions as the alkyl chain in the IL increases after $n(C) = 6$.

Finally we would like to stress the fact that the trend shift is much clearer when we use the heat capacities or the enthalpies of vaporization on a volumetric basis. This reflects the fact that the trends discussed here in these properties are related to the cohesive strength/energy in the liquid.

4. Final remarks

The heat capacities at 298.15 K of the $[C_nC_1im][Ntf_2]$ ionic liquid series were measured with an uncertainty of less than ±0.3%. A trend shift in the heat capacities with the cation alkyl chain length starting at $n(C) = 6$ was found, providing and additional experimental evidence for the percolation phenomenon in ionic liquids and its impact on their thermophysical properties.

The recently proposed schematic model [8] of the two molecular regions for the $[C_nC_1im][Ntf_2]$ ionic liquids and their different contribution to the thermodynamic properties gives a strong contribution for the interpretation of the percolation phenomenon after a critical number of carbons in the chain and is also supported by the experimental results obtained in this work. Above this limit there is an increase in the methylene group contribution to the molar heat capacity, in agreement with the higher molar absolute entropies change observed from the (liquid + vapor) equilibrium results, as well as the trend shift observed in the viscosity measurements of these compounds.

Acknowledgements

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