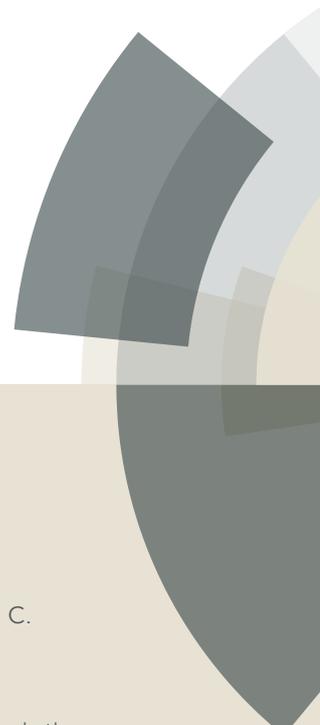


PCCP

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: A. S. Rodrigues, C. F. F. R. A. C. Reis Alves Costa Lima, J. A.P. Coutinho and L. B. Santos, *Phys. Chem. Chem. Phys.*, 2017, DOI: 10.1039/C6CP08451F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Nature of the C2-methylation effect on the properties of imidazolium ionic liquids

Ana S. M. C. Rodrigues,^a Carlos F. R. A. C. Lima,^{a,b} João A. P. Coutinho,^c Luís M. N. B. F. Santos*^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Methylation at the C2 position of 1,3-disubstituted imidazolium-based ionic liquids (ILs) is one of the structural features that has gain attention due to its drastic impact on thermophysical and transport properties. Several hypotheses have been proposed to explain this effect but there is still much discrepancy. Aiming for the rationalization of these structural features on the properties of imidazolium ILs, we present a thermodynamic and computational study of two methylated ILs at the C2 position of imidazolium, [1^C₄²C₁³C₁im][NTf₂] and [1^C₃²C₁³C₁im][NTf₂]. The phase behaviour (glass transition and vaporization equilibrium) and computational studies of the anion rotation around the cation and ion pair interaction energies for both ILs were explored. The results have shown that C2-methylation has no impact on the enthalpy of vaporization. However, it decreases the entropy of vaporization, which is a consequence of the change in the ion pair dynamics that affects both the liquid and gas phases. In addition, the more hindered dynamics of the ion pair are also reflected on the increase of the glass transition temperature, T_g . The entropic contribution of anion-around-cation rotation in the imidazolium [NTf₂] ILs was quantified experimentally by the comparative analysis of the entropy of vaporization, and computationally by the calculation of the entropies of hindered internal rotation. The global results exclude the existence of significant H-bonding in the C2-protonated (non-methylated) ILs and explain the C2-methylation effect in terms of reduced entropy of the ion pair in the liquid and gas phases. On the light of these results, the C2-methylation effect is intrinsically entropic and originates from the more hindered anion-around-cation rotation as the consequence of the substitution of the –H with a bulkier –CH₃ group.

Introduction

The cohesive forces, charge distribution and nanostructuration of ionic liquids (ILs) define their thermodynamic and transport properties and make them very interesting from both fundamental and applied perspectives. Among their structural features, the methylation at the C2 position of the imidazolium ring has been highlighted in the literature due to the enormous impact that this structural change has on viscosities, conductivities, surface tension and phase behaviour.^{1–4} Despite the fact that there are several studies pointing to the existence and importance of this methylation effect, there is still much discrepancy in its explanation.^{3–9} Fumino *et al.*⁷ studied the mid and far-FTIR spectra of two short alkyl imidazolium [NTf₂] ILs and concluded that the substitution of an acidic proton by a methyl group in position C2 of the imidazolium cation blocks the “strong, localized, and highly directional hydrogen bond” between cation and anion, thus explaining why methylated ILs

have higher melting points and higher viscosities. Later on, Hunt⁵ performed computational studies on butyl imidazolium chloride ILs and found a reduced number of stable ion pair conformers in the methylated ILs. Additionally, the calculations have shown that the rotation of the butyl chain is affected by the methyl group, becoming more restricted and with less available conformers. The methylation effect was explained by a significant reduction in the entropy of methylated ILs due, mostly, to loss of configurational space. As pointed out by Hunt, the computational studies of the ion pairs in the gas phase neglect the long-range interactions of the bulk, and therefore it is important to complement these studies with molecular dynamics.⁵ Zahn *et al.*³ investigated, by means of quantum chemical and molecular dynamics simulations, the fluidity of ILs and how methylation affects the thermophysical properties, and concluded that methylation at the C2 position leads to a reduction of the free movement of the anion around the cation. Izgorodina *et al.*⁹ tackled the methylation effect problem by performing experimental and computational studies on imidazolium iodide ILs. They found no significant difference in the conformers’ distribution between methylated and non-methylated ILs. The Boltzmann distribution of the ion pairs for the most stable conformers (anion above and below the ring-plane of the cation) is not affected by methylation and corresponds to a statistical weight of 97%. This result suggests that the number of conformers is not significantly decreased

^a CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Porto, Portugal. E-mail: lbsantos@fc.up.pt

^b Department of Chemistry & QOPNA, University of Aveiro, Aveiro, Portugal.

^c CICECO, Departamento de Química, Universidade de Aveiro, Aveiro, Portugal.

† ASMCR and CFRACL are equally contributing authors.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

by methylation and contradicts the hypothesis that the methylation effect is only due to loss of conformational entropy in methylated ILs. On the other side, the potential energy surface (PES) analysis revealed a significantly higher restriction of the iodide anion movement around the methylated imidazolium cation (an energy barrier of $40 \text{ kJ}\cdot\text{mol}^{-1}$ was reported). In contrast, the protonated imidazolium cation allows a less restricted motion of the anion (energy barrier of only $15 \text{ kJ}\cdot\text{mol}^{-1}$). The explanation proposed by Izgorodina *et al.*⁹ and Zahn *et al.*³ suits better the energy landscape paradigm proposed by Goldstein,¹⁰ which relates the potential energy barrier with the fluidity of a molecular liquid. The liquid cannot flow easily if the barrier separating two minima is much higher than the thermal energy available at a given temperature.

Several works concerning thermophysical properties such as conductivity, viscosity, surface tension and melting point, have pointed out the differences between the C2-methylated ILs and their C2-protonated analogues. However, to the best of our knowledge, there are no reports in the literature dealing with the effect of methylation on the vaporization of ILs. The present work seeks to elucidate the origins of the C2-methylation effect on the properties of imidazolium ILs and distinguish between the H-bond and entropy-based hypotheses. For that, we have explored the phase behavior of the two C2-methylated imidazolium $[\text{NTf}_2]$ ILs presented in figure 1. The effect of C2-methylation was evaluated by comparing the derived thermodynamic properties (glass transition, volatility, and enthalpies and entropies of vaporization) for the methylated ILs with their C2-protonated isomers. The experimental work was accompanied by the computational evaluation of the anion rotation around the cation and the ion pair interaction energies in the C2-methylated and protonated ILs.

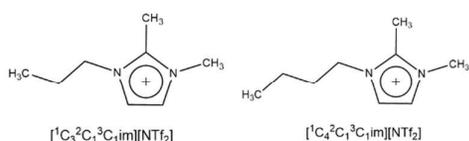


Fig. 1 Schematic representation of the C2-methylated IL cations studied herein.

Experimental section

Materials and purification

The ILs samples were acquired from IOLITEC with the following purity: $[\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ (1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide), CAS RN: 169051-76-7, 99%; $[\text{C}_4^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ (1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide), CAS RN: 350493-08-2, 99%. The ILs were purified under vacuum ($<10 \text{ Pa}$) at moderate temperature (323 K) and constant stirring for 48 hours in order to remove traces of volatile impurities. The mass fraction water content was determined in a 151 Metrohm 831 Karl

Fischer coulometer, using a Hydranal-152 Coulomat AG from Riedel-de Haën. The water content, in all ILs, was below 100 ppm. The relative atomic masses used in this work were those recommended by the IUPAC Commission in 2007.¹¹

Differential scanning calorimetry

The thermal characteristics of $[\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ were studied in a power compensation differential scanning calorimeter, PERKIN ELMER model Pyris Diamond DSC. The temperature and heat flux scales of the DSC were calibrated by measuring the temperature and the enthalpy of fusion of reference materials,^{12,13} namely; benzoic acid, 4-methoxybenzoic acid, triphenylene, naphthalene, anthracene, 1,3,5-triphenylbenzene, diphenylacetic acid, perylene, *o*-terphenyl and 9,10-diphenylanthracene, at different scanning rates (2, 5 and $10 \text{ K}\cdot\text{min}^{-1}$), using hermetically sealed aluminum crucibles and a constant flow of nitrogen ($50 \text{ mL}\cdot\text{min}^{-1}$). Samples of about 15 mg were used in each experiment. Concerning the methodology applied for the thermal behavior study, each sample was firstly heated at $T = 333 \text{ K}$ for 5 minutes, followed by a quenching step consisting of a fast cooling ($\approx 50 \text{ K}\cdot\text{min}^{-1}$) until 173 K. This procedure avoids crystallization on cooling and promotes glass formation. Subsequently, the IL was heated ($5 \text{ K}\cdot\text{min}^{-1}$) until the occurrence of glass transition. This was followed by repeated cooling ($\approx 50 \text{ K}\cdot\text{min}^{-1}$) and heating ($5 \text{ K}\cdot\text{min}^{-1}$) cycles, in which repeatability was observed in the glass transition.

Vapor pressures

The vapor pressures as a function of temperature for the ILs were measured using a Knudsen effusion apparatus combined with a quartz crystal microbalance, KEQCM. The Knudsen apparatus and the methodology applied for these measurements are fully described in the literature.¹⁴ Prior to the vapour pressure measurements, the ILs were purified *in situ* under high vacuum ($<0.001 \text{ Pa}$) in a distillatory chamber, which was developed to purify and collect ultra-pure ILs.

Computational details

All theoretical calculations were performed using the Gaussian 09 software package.¹⁵ The full geometry optimizations and frequency calculations for $[\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ were performed at the M06-2X/6-31+G(d,p) level of theory.¹⁶ These two ILs were used as models for the rotation of the anion $[\text{NTf}_2]$ around the cations. For these two ILs the potential energy surfaces for anion rotation were obtained at the same level of theory, by varying the angle (defined by three atoms, and treated as a frozen variable) between the cation and the anion by increments of 10° and allowing the optimization of the rest of the molecule. A 1D-hindered rotor formalism was applied to the above mentioned vibrational modes, using the formalism introduced by Broadbelt and co-workers and the program CALTHERM.¹⁷⁻¹⁹ In this context the torsional potentials were fitted by a

Fourier series and the hindered rotor Schrödinger equation solved numerically. This was used to calculate the hindered rotor entropy, S_{HR} , associated to anion-around-cation rotation in each IL. The cation-anion electronic interaction energies in the ion pair, $\Delta_{int}E_m$, were calculated for $[^1C_3^2C_1^3C_1im][NTf_2]$ and $[^1C_1^2C_1^3C_1im][NTf_2]$ using M06-2X/6-31+G(d,p) and corrected for BSSE by the counterpoise method.^{20,21} The detailed computational results are presented as the ESI.

Results and discussion

Thermal behaviour

While glass transition was easily observed in $[^1C_3^2C_1^3C_1im][NTf_2]$, crystallization could not be achieved under the experimental conditions used. The experimental results of the glass transition temperatures, T_g , for $[^1C_3^2C_1^3C_1im][NTf_2]$, together with the literature data for $[^1C_4^2C_1^3C_1im][NTf_2]$ and for the C2-protonated isomers, $[^1C_4^3C_1im][NTf_2]$ and $[^1C_5^3C_1im][NTf_2]$, are presented in Table 1.

Table 1 Glass transition temperatures, T_g , for C2-methylated ILs and their C2-protonated analogues

Ionic liquid	T_g / K
$[^1C_3^2C_1^3C_1im][NTf_2]$	189.9 ± 0.5
$[^1C_4^2C_1^3C_1im][NTf_2]$ ²²	191.5 ± 0.5
$[^1C_3^3C_1im][NTf_2]$ ²³	179.3 ± 0.5
$[^1C_4^3C_1im][NTf_2]$ ²³	181.3 ± 0.5
$[^1C_5^3C_1im][NTf_2]$ ²³	183.6 ± 0.5

As can be observed, methylation at the C2 position of the imidazolium cation has a significant effect on T_g . The ΔT_g increment *per* $-CH_2-$ in the $[^1C_{n-1}^3C_1im][NTf_2]$ series, before $n=6$, is of approximately 2 K. However, comparing the methylated ILs, $[^1C_3^2C_1^3C_1im][NTf_2]$ and $[^1C_4^2C_1^3C_1im][NTf_2]$, with their respective isomers, the T_g is \approx 8-9 K higher for the methylated compounds. These results are consistent with the general assumption that higher T_g are observed for more viscous ILs, following the higher energy barrier to flow.^{22,24,25}

Vaporization equilibrium

The results of the vapour pressures for each IL are presented in Table 2. Figure 2 depicts the graphical representations of $\ln(p/Pa) = f[(1/T)/K^{-1}]$ for the C2-methylated ILs measured in this work. The literature results for their C2-protonated isomers are also presented for comparison.²⁶ The results were fitted to the integrated form of the Clausius-Clapeyron equation (1):

$$\ln(p/Pa) = a - b/T \quad (1)$$

where p is the pressure and T is the temperature. From the experimental (p , T) results the a and b coefficients were derived and are presented in Table 3, together with the mean

temperature, $\langle T \rangle$, and the pressure at the mean temperature $p(\langle T \rangle)$.

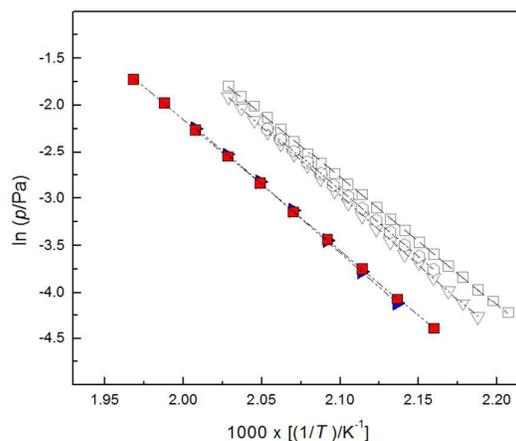


Fig. 2 Graphical representation of $\ln(p/Pa) = f[(1/T)/K^{-1}]$ for the ILs: this work: ■ $[^1C_3^2C_1^3C_1im][NTf_2]$, ► $[^1C_4^2C_1^3C_1im][NTf_2]$; and literature data²⁶ for the C2-protonated isomers: □ $[^1C_3^3C_1im][NTf_2]$, ○ $[^1C_4^3C_1im][NTf_2]$, ▽ $[^1C_5^3C_1im][NTf_2]$.

Table 2 Experimental vapor pressures (p , T) results for the ILs studied

$[^1C_3^2C_1^3C_1im][NTf_2]$			$[^1C_4^2C_1^3C_1im][NTf_2]$		
T / K	p / Pa	Δp / Pa ^a	T / K	p / Pa	Δp / Pa ^a
463.08	0.0124	0.0000	468.09	0.0162	-0.0003
468.08	0.0171	-0.0001	473.08	0.0229	0.0000
473.08	0.0237	0.0001	478.08	0.0319	0.0003
478.07	0.0322	0.0000	483.08	0.0438	0.0006
483.07	0.0433	-0.0004	488.08	0.0593	0.0004
488.07	0.0591	0.0002	493.08	0.0797	0.0000
493.06	0.079	0.0000	498.08	0.1056	-0.0016
498.07	0.1061	0.0008			
503.06	0.1399	0.0005			
508.06	0.1824	-0.0014			

^a $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clausius-Clapeyron equation with the parameters given in Table 3. Standard uncertainties, u , are $u(T) = \pm 0.02$ K, $u(p) = \pm (0.001 + 0.05 \cdot p)$ Pa, at the 95 % confidence level.

Table 3 Coefficients of the Clausius-Clapeyron equation **Error! Reference source not found.** for the ILs studied at the mean temperature, $\langle T \rangle$, and pressure, $p(\langle T \rangle)$, of the experiments

	$[^1C_3^2C_1^3C_1im][NTf_2]$	$[^1C_4^2C_1^3C_1im][NTf_2]$
$a \pm \sigma$	25.89 ± 0.07	27.00 ± 0.24
$b \pm \sigma$ / K	14106 ± 29	14563 ± 114
r^2	0.99997	0.99970
$\langle T \rangle$ / K	485.57	483.09
$p(\langle T \rangle)$ / Pa	0.051	0.043

The standard ($p^0 = 10^5$ Pa) molar enthalpies of vaporization at $\langle T \rangle$, $\Delta_{cr}^g H_m^0(\langle T \rangle)$, are determined by the parameter

ARTICLE

$b = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle)/R$ ($R = 8.3144598 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).²⁷ The molar entropies of vaporization at $\langle T \rangle$ and $p(\langle T \rangle)$, $\Delta_1^{\text{g}}S_m^{\circ}\{\langle T \rangle, p(\langle T \rangle)\}$, are calculated as:

$$\Delta_1^{\text{g}}S_m^{\circ}\{\langle T \rangle, p(\langle T \rangle)\} = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle)/\langle T \rangle \quad (2)$$

The values of $\Delta_1^{\text{g}}H_m^{\circ}$ at the reference temperature, $T = \theta \text{ K}$, were determined by equation (3):

$$\Delta_1^{\text{g}}H_m^{\circ}(\theta) = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle) + \Delta_1^{\text{g}}C_{p,m}^{\circ} \cdot (\theta - \langle T \rangle) \quad (3)$$

where $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ is the standard molar heat capacity of vaporization: $\Delta_1^{\text{g}}C_{p,m}^{\circ} = C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{l})$. The standard molar entropies of vaporization, $\Delta_1^{\text{g}}S_m^{\circ}$, at $T = \theta \text{ K}$, were calculated by equation (4):

$$\Delta_1^{\text{g}}S_m^{\circ}(\theta) = \Delta_1^{\text{g}}S_m^{\circ}(\langle T \rangle, p) + \Delta_1^{\text{g}}C_{p,m}^{\circ} \cdot \ln(\theta/\langle T \rangle) - R \cdot \ln\{p^{\circ}/p(\langle T \rangle)\} \quad (4)$$

where $p^{\circ} = 10^5 \text{ Pa}$. The standard molar Gibbs energies of vaporization, $\Delta_1^{\text{g}}G_m^{\circ}$, at $T = \theta \text{ K}$, were determined using equation (5):

$$\Delta_1^{\text{g}}G_m^{\circ}(\theta) = \Delta_1^{\text{g}}H_m^{\circ}(\theta) - \theta \cdot \Delta_1^{\text{g}}S_m^{\circ}(\theta) \quad (5)$$

The values of $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ used in equations (3) and (4) were estimated as $-(121 \pm 10)$ and $-(127 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $[\text{}^3\text{C}_3\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{}^3\text{C}_4\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$, respectively. These values were determined by considering that $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ is the same for the C2-methylated isomers, $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_5\text{C}_1\text{im}][\text{NTf}_2]$, at $T=388 \text{ K}$, as reported in the literature.^[32] The derived values of $\Delta_1^{\text{g}}G_m^{\circ}$, $\Delta_1^{\text{g}}H_m^{\circ}$ and $\Delta_1^{\text{g}}S_m^{\circ}$ for $[\text{}^3\text{C}_3\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{}^3\text{C}_4\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$, at various temperatures, are presented in Table 4.

Table 4 Standard ($p^{\circ} = 10^5 \text{ Pa}$) molar enthalpies, $\Delta_1^{\text{g}}H_m^{\circ}(\theta)$, entropies, $\Delta_1^{\text{g}}S_m^{\circ}(\theta)$, and Gibbs energies, $\Delta_1^{\text{g}}G_m^{\circ}(\theta)$ of vaporization for the ILs studied

θ / K	$\Delta_1^{\text{g}}G_m^{\circ}(\theta) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_1^{\text{g}}H_m^{\circ}(\theta) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_1^{\text{g}}S_m^{\circ}(\theta) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	$[\text{}^3\text{C}_3\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$		
485.57	58.5 ± 0.3	117.3 ± 0.2	120.4 ± 0.3
298.15	86.3 ± 0.4	140.0 ± 1.9	180.1 ± 4.9
460	61.7 ± 0.3	120.4 ± 0.3	127.6 ± 0.7
	$[\text{}^3\text{C}_4\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$		
483.09	58.9 ± 1.3	121.1 ± 0.9	128.8 ± 1.9
298.15	87.9 ± 1.4	144.6 ± 2.1	190.1 ± 5.2
460	61.9 ± 1.3	124.0 ± 0.9	135.0 ± 2.0

The C2-methylation effect and phase behaviour

Table 5 presents the thermodynamic properties (Gibbs energy, enthalpies and entropies) of vaporization corrected to $T = 460 \text{ K}$, for all ILs considered in this study. This temperature was already considered for other ILs and has the advantage of reducing the weight of the $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ contribution in the derived

thermodynamic values.²⁶ The differential enthalpy and entropy analysis comparing between the methylated ILs and their C2-protonated isomers is schematically depicted in figure 3.

The results presented in table 5 show that methylation at the C2 position of the imidazolium ring has a significant effect on volatility. As indicated by their higher $\Delta_1^{\text{g}}G_m^{\circ}$, methylated ILs are less volatile than their corresponding C2-protonated isomers. The analysis of each contribution individually indicates that the differences in $\Delta_1^{\text{g}}H_m^{\circ}$ between $[\text{}^3\text{C}_3\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{}^3\text{C}_4\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$, and their C2-protonated isomers $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_5\text{mim}][\text{NTf}_2]$, respectively, are negligible. The lower volatility of the methylated ILs is thus entropically driven, as translated by their lower $\Delta_1^{\text{g}}S_m^{\circ}$, $\Delta\Delta S \approx 4\text{--}7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. On the other side, the similar $\Delta_1^{\text{g}}H_m^{\circ}$ between isomers suggests that the different position of the methyl group in the imidazolium ring, either at C2 or in the alkyl chain, has the same effect on the cohesive energy of the liquid (i.e. increasing the van der Waals interactions between ion pairs), and does not affect phenomena like supramolecular structure or reorganization of the ion pairs into significantly different geometries.

Table 5 Standard ($p^{\circ} = 10^5 \text{ Pa}$) molar enthalpies, $\Delta_1^{\text{g}}H_m^{\circ}(460\text{K})$, entropies, $\Delta_1^{\text{g}}S_m^{\circ}(460\text{K})$, and Gibbs energies, $\Delta_1^{\text{g}}G_m^{\circ}(460\text{K})$ of vaporization, at $T = 460 \text{ K}$, for the ILs studied

Ionic liquid	$\Delta_1^{\text{g}}G_m^{\circ}(460\text{K}) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_1^{\text{g}}H_m^{\circ}(460\text{K}) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_1^{\text{g}}S_m^{\circ}(460\text{K}) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$[\text{}^3\text{C}_3\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$	61.7 ± 0.3	120.4 ± 0.3	127.6 ± 0.6
$[\text{}^3\text{C}_4\text{}^2\text{C}_1\text{}^1\text{C}_1\text{im}][\text{NTf}_2]$	61.9 ± 1.3	124.0 ± 0.9	135.0 ± 2.0
$[\text{C}_3\text{mim}][\text{NTf}_2]$ ²⁶	58.5 ± 0.6	114.9 ± 0.4	122.6 ± 0.9
$[\text{C}_4\text{mim}][\text{NTf}_2]$ ²⁶	59.2 ± 0.6	119.6 ± 0.4	131.4 ± 0.8
$[\text{C}_5\text{mim}][\text{NTf}_2]$ ²⁶	59.5 ± 0.6	124.9 ± 0.4	142.1 ± 0.9

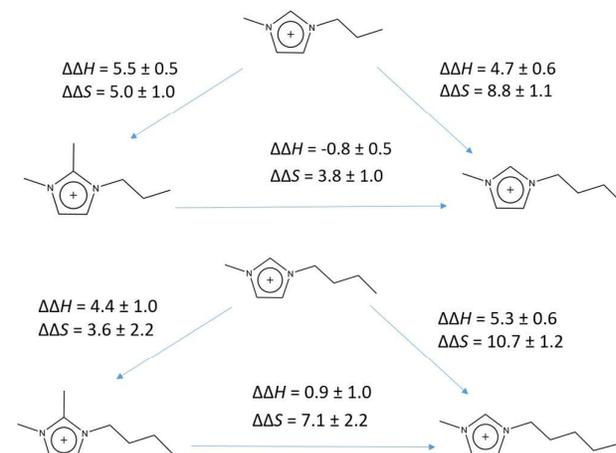


Fig. 3 Schematic enthalpy, $\Delta\Delta H$ (in $\text{kJ}\cdot\text{mol}^{-1}$), and entropy, $\Delta\Delta S$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), diagrams comparing the C2-methylated ILs and their C2-protonated isomers.

In order to elucidate the experimental T_g and volatility results we have evaluated the rotation of the $[\text{NTf}_2]$ anion

around the cation, the full diagram of the potential energy profile for the two representative ILs, ($[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$; $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$) shown in figure 4). These smaller systems constitute a good general model for evaluating the C2-methylation effect by computational chemistry. The influence of a larger alkyl chain in the cation on the anion-cation rotational profile is expected to be small because the alkyl chain has enough flexibility to effectively couple its vibrational motion with anion rotation. Figure 5 illustrates the anion-around-cation rotation in the $[\text{NTf}_2]$ ILs and the angle of rotation used in the calculations. Figure 6 shows the derived M06-2X/6-31+G(d,p) diagram of the potential energy surfaces (PES) for this vibrational motion in both ILs.

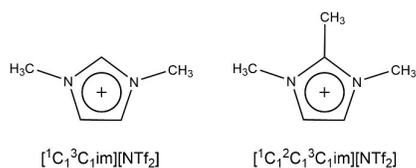


Fig. 4 Schematic representations of the ILs considered in the computational study.

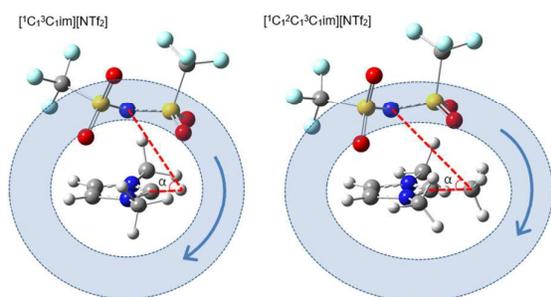


Fig. 5 Schematic representation of the anion-around-cation rotation (α angle) in $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ (left), $\angle\text{C-H-N}$, and $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ (right), $\angle\text{C-C(H}_3\text{)-N}$. The presented structures are the optimized ILs geometries obtained at the M06-2X/6-31+G(d,p) level of theory and correspond to the global minima.

The comparison of the potential energy profiles clearly evidences the higher rotational barrier in the C2-methylated IL $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ – the anion has to surpass an energy barrier of about $80 \text{ kJ}\cdot\text{mol}^{-1}$ to rotate around the cation, whereas in $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ that barrier is of only $30 \text{ kJ}\cdot\text{mol}^{-1}$. Moreover, the shape of the potential for $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ allows for a smoother motion of the anion over a large range in α . In contrast, in $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ the presence of the additional methyl group leads to a significant confinement of the anion over a very limited set of geometries (corresponding to the narrow potential wells around $\alpha = 46^\circ$ and, by symmetry, $\alpha = 314^\circ$). The steric effect of the C2 methyl group on anion rotation was previously investigated by Izgorodina *et al.*⁹ for $[^1\text{C}_3^3\text{C}_1\text{im}][\text{I}^-]$ and $[^1\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{I}^-]$.⁹ Similarly to our results, the authors have found a higher rotational barrier for

the C2-methylated IL. In this case, however, the barrier is significantly lower ($\approx 40 \text{ kJ}\cdot\text{mol}^{-1}$), which may be explained by the smaller size and higher symmetry of the I^- anion, compared to $[\text{NTf}_2]^-$.

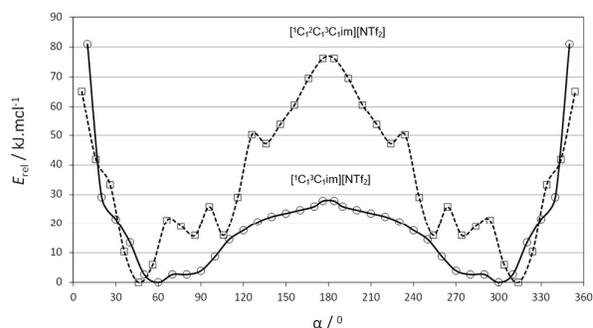


Fig. 6 Full diagram of the potential energy surfaces (PES) for anion-around-cation rotation (C-H-N for $[^1\text{C}_1^3\text{C}_1\text{im}]$ and $\text{C-C(H}_3\text{)-N}$ for $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}]$ – α angle in figure 5) in the two ILs studied, obtained at the M06-2X/6-31+G(d,p) level of theory.

Using the program CALCTHERM,^{17–19} the hindered rotor entropies, S_{HR} , associated to the potential energy profiles presented in figure 6 for anion rotation were found to be of 22 and $18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$, respectively. These calculations then predict lower molecular entropy for the C2-methylated ILs by about $4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Although the theoretical model is just a first approximation to the real dynamics of anion-around-cation rotation, it is consistent with the experimental differentiation observed in $\Delta^{\text{g}}S_{\text{m}}^{\circ}$ between the C2-methylated and protonated isomers (around 4 and $7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, see Figure 3). This indicates that C2 methylation hinders anion rotation and thus decreases the entropy of the ion pair. In the liquid phase the anion-around-cation rotation is further constrained by the surrounding molecules; the potential energy barriers are higher, and this may dilute the difference in S_{HR} . Although there is some differentiation in anion rotation in the liquid phase of the C2-methylated ILs (relative to the protonated isomers), this difference is more pronounced in the gas phase. The net effect is thus to decrease both $S(\text{l})$ and $S(\text{g})$ of the C2-methylated isomers, but $S(\text{g})$ to a greater extent, leading to lower $\Delta^{\text{g}}S_{\text{m}}^{\circ}$.

Another important insight about the C2-methylation effect comes from the calculated M06-2X/6-31+G(d,p) cation-anion interaction energies, $\Delta_{\text{int}}E_{\text{m}}$, for the $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ ion pairs. For both compounds $\Delta_{\text{int}}E_{\text{m}} = -361 \text{ kJ}\cdot\text{mol}^{-1}$ (values corrected for BSSE by the counterpoise method),^{20,21} indicating that methylation at C2 does not affect the cation-anion interaction. Moreover, the PES profiles in figure 6 show that for both ILs the geometries of the absolute minima ($\alpha = 60^\circ$ for $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $\alpha = 46^\circ$ for $[^1\text{C}_1^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$) are similar and do not correspond to a typical H-bonded complex in $[^1\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$. The establishment of an H-bond leads to a different ion pair geometry and in these systems a different orientation of the anion relative to the cation can imply a significant weakening

of the strong orientation dependent electrostatic forces. Since electrostatic interactions between opposite charges are often stronger than H-bonds, ILs will most likely prefer to adopt geometries that maximize the former. These facts are also in accordance with the experimental results of $\Delta_1^{\text{E}}H_m^{\circ}$, which indicate no enthalpic differentiation in the vaporization process of the C2 methylated ILs and their protonated isomers (figure 3). However, since ILs vaporize as ion pairs, the existence of the H-bond is not expected to be fully reflected on the cohesive energy of the bulk, and hence on $\Delta_1^{\text{E}}H_m^{\circ}$. This interaction, being intrinsic to the ion pair, would not be disrupted in the vaporization process. If the H-bond exists it could partially affect $\Delta_1^{\text{E}}H_m^{\circ}$ because the different geometry of the H-bonded ion pairs would in principle affect the organization of the bulk around the ion pair and the specific interactions with the neighbouring cations and anions. Nevertheless, the experimental $\Delta_1^{\text{E}}H_m^{\circ}$ results cannot be a straightforward indication of the existence or not of the H-bond. Notwithstanding, together with the indications provided by the computational results and the entropic analysis discussed above, and considering the good agreement between experiment and theory, it can be concluded that states corresponding to H-bonded ion pairs in $[\text{C}_n\text{C}_1\text{im}][\text{NTf}_2]$ ILs are not statistically significant. Hence, the most probable explanation for the C2 methylation effect, and its implications on physical-chemical properties like viscosity and volatility, is the reduced entropy of the liquid that arises from a more hindered motion of anion-around-cation rotation (as a note, it should be remembered that this is a vibrational degree of freedom and not a typical molecular rotation).

This result can also explain the variation observed in the glass transition temperatures, T_g , (table 1) and the melting points, T_m , of imidazolium ILs with various anions, as reported in the literature.³ The methylated ILs have higher T_g and T_m than the C2-protonated isomers due to the hindrance effect of the $-\text{CH}_3$ group, which restrains the movement of ions in the liquid phase. This lowers the entropy of the liquid, destabilizing it and consequently increasing the temperature range at which the glass and the solid phases can exist before changing into a liquid. The decrease of T_m for C2-protonated imidazolium ILs is easier to explain by the higher entropy of the liquid (and thus higher entropy of fusion) than by the establishment of an H-bond at C2 of the imidazolium ring. These H-bonds would stabilize both solid and liquid phases, although the liquid to less extent. The translational and rotational motions in the more dynamic liquid phase, and consequent randomization of molecular orientations, would reduce the statistical weight of the H-bonded states, resulting in a weaker interaction. This would, as already pointed out by several authors,^{3,5,9} destabilize the liquid relative to the solid, increase the enthalpy of fusion and, contrary to what is observed; increase T_m of the C2-protonated ILs. This follows the general idea that strong intermolecular forces promote the less disordered states. In particular, the establishment of intermolecular H-bonds is generally associated with an increase of the melting and boiling points.

Additional evidence was found in the case of ethyl substituted ILs at C2 of the imidazolium ring.³⁰⁻³² The IL with this bulkier group has an even higher T_m than its C2-methylated analogue, which also goes in line with the entropy hypothesis: apart from the increased molar mass, the energy barrier for anion rotation is even higher and probably contributes to further decrease the entropy of the liquid. Moreover, FTIR-ATR studies by Cammarata *et al.*³³ for imidazolium ILs in water have shown no evidence of H-bonding involving the proton at C2 of the imidazolium ring.

Altogether, these results are a strong indication that the hydrogen at C2 of imidazolium does not participate in H-bonding to any considerable extent and that C2-methylation lowers the entropy of the ion pair; an effect that, although more pronounced in the gas phase, also affects the properties of the liquid.

Conclusions

Herein, we present a thermodynamic study (thermal behaviour and vapour pressures) of two imidazolium ILs, $[\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_4^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$. The purpose of this study was to explain the effect of methylation in position C2 of the imidazolium ring, by analysing its influence on thermodynamic properties like T_g and the enthalpies and entropies of vaporization. Methylation at C2 was found to have a significant effect on T_g , with the $[\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_4^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ ILs presenting higher T_g than their C2-protonated isomers. The vapor pressures at various temperatures were measured using a Knudsen effusion apparatus coupled to a quartz crystal microbalance. These measurements have shown that $[\text{C}_3^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_4^2\text{C}_1^3\text{C}_1\text{im}][\text{NTf}_2]$ are less volatile than their C2-protonated isomers. The enthalpies of vaporization have shown no differentiation between the isomers, and the lower volatility of the C2-methylated ILs was found to be entropically driven. In agreement with the experimental results, the calculated hindered rotor profiles for anion-around-cation rotation, and associated hindered rotor entropies, have shown that this vibrational motion is more restricted in the C2-methylated isomers, which decreases the entropy of the ion pair. Moreover, the calculated geometries and interaction energies of the ion pairs are similar for both methylated and protonated ILs and are not consistent with the establishment of H-bonds between cation and anion in the C2-protonated isomers. From the several hypotheses reported in the literature to explain the C2-methylation effect on thermodynamic and transport properties, our results follow the rationale proposed by Izgorodina *et al.*⁹ On the light of these results the C2-methylation effect is intrinsically entropic and originates from the more hindered anion-around-cation rotation as the consequence of substituting an $-\text{H}$ with a bulkier $-\text{CH}_3$ group.

Acknowledgements

We thank Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and the European Social Fund (ESF) for financial support to CIQUP, University of Porto (Projects: PEst-C/QUI/UI0081/2013, FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065). This work was partly developed in the scope of the project CICECO-Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013), financed by national funds through the FCT/ MEC. A.S.M.C.R and C.F.R.A.C.L. also thank FCT for the award of the Research Grants SFRH/BD/81261/2011 and SFRH/BPD/77972/2011, respectively.

Notes and references

- 1 T. Nishida, Y. Tashiro and M. Yamamoto, *J. Fluor. Chem.*, 2003, **120**, 135–141.
- 2 V. Strehmel, A. Laschewsky, H. Wetzels and E. Görnitz, *Macromolecules*, 2006, **39**, 923–930.
- 3 S. Zahn, G. Bruns, J. Thar and B. Kirchner, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6921–6924.
- 4 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.
- 5 P. A. Hunt, *J. Phys. Chem. B*, 2007, **111**, 4844–53.
- 6 K. Noack, P. S. Schulz, N. Paape, J. Kiefer, P. Wasserscheid and A. Leipertz, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14153–61.
- 7 K. Fumino, A. Wulf and R. Ludwig, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 8731–4.
- 8 K. Fumino, A. Wulf and R. Ludwig, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 3830–4.
- 9 E. I. Izgorodina, R. Maganti, V. Armel, P. M. Dean, J. M. Pringle, K. R. Seddon and D. R. MacFarlane, *J. Phys. Chem. B*, 2011, **115**, 14688–97.
- 10 M. Goldstein, *J. Chem. Phys.*, 2003, **3728**, 3728–3739.
- 11 M. E. Wieser and M. Berglund, *Pure Appl. Chem.*, 2009, **81**, 2131–2156.
- 12 C. Sabbah (France R., A. Xu-wu (China), J. S. Chickos (USA), M. L. P. Leitão (Portugal), M. V Roux (Spain), L. A. Torres (México), R. Sabbah, A. Xu-wu, J. S. Chickos, M. L. P. Leitão, M. V. Roux and L. A. Torres, *Thermochim. Acta*, 1999, **331**, 93–204.
- 13 M. V. Roux, M. Temprado, J. S. Chickos and Y. Nagano, *J. Phys. Chem. Ref. Data*, 2008, **37**, 1855.
- 14 L. M. N. B. F. Santos, L. M. S. S. Lima, C. F. R. A. C. Lima, F. D. Magalhães, M. C. Torres, B. Schröder and M. A. V. Ribeiro da Silva, *J. Chem. Thermodyn.*, 2011, **43**, 834–843.
- 15 M. H. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, Gaussian, Inc.: Wallingford, CT, 2009.
- 16 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2007, **120**, 215–241.
- 17 J. Pfaendtner, X. Yu and L. J. Broadbelt, *Theor. Chem. Acc.*, 2007, **118**, 881–898.
- 18 X. Yu, J. Pfaendtner and L. J. Broadbelt, *J. Phys. Chem. A*, 2008, **112**, 6772–6782.
- 19 X. R. Yu, S. E. Levine and L. J. Broadbelt, *Macromolecules*, 2008, **41**, 8242–8251.
- 20 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
- 21 F. B. van Duijneveldt, J. G. C. M. van Duijneveldt-van de Rijdt and J. H. van Lenthe, *Chem. Rev.*, 1994, **94**, 1873–1885.
- 22 A. S. M. C. Rodrigues, M. A. A. Rocha, H. F. D. Almeida, C. M. S. S. Neves, J. A. Lopes-Da-Silva, M. G. Freire, J. A. P. Coutinho and L. M. N. B. F. Santos, *J. Phys. Chem. B*, 2015, **119**, 8781–8792.
- 23 A. S. M. C. Rodrigues and L. M. N. B. F. Santos, *ChemPhysChem*, 2016, **17**, 1512–1517.
- 24 M. A. A. Rocha, C. M. S. S. Neves, M. G. Freire, O. Russina, A. Triolo, J. A. P. Coutinho and L. M. N. B. F. Santos, *J. Phys. Chem. B*, 2013, **117**, 10889–10897.
- 25 A. S. M. C. Rodrigues, H. F. D. Almeida, M. G. Freire, J. A. Lopes-da-Silva, J. A. P. Coutinho and L. M. N. B. F. Santos, *Fluid Phase Equilib.*, 2016, **423**, 190–202.
- 26 M. A. A. Rocha, C. F. R. A. C. Lima, L. R. Gomes, B. Schröder, J. A. P. M. Coutinho, I. M. Marrucho, J. M. S. S. Esperança, L. P. N. Rebelo, K. Shimizu, J. N. C. J. Lopes and L. M. N. B. F. Santos, *J. Phys. Chem. B*, 2011, **115**, 10919–26.
- 27 P. J. Mohr and B. N. Taylor, *J. Phys. Chem. Ref. Data*, 1999, **28**, 1–7.
- 28 M. A. A. Rocha, M. Bastos, J. A. P. Coutinho and L. M. N. B. F. Santos, *J. Chem. Thermodyn.*, 2012, **53**, 140–143.
- 29 Y. U. Paulechka, G. J. Kabo and V. N. Emel'yanenko, *J. Phys. Chem. B*, 2008, **112**, 15708–17.
- 30 P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.
- 31 C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954–964.
- 32 H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa and Y. Miyazaki, *Chem. Lett.*, 2000, **29**, 922–923.
- 33 L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192–5200.