

Surface tensions of ionic liquids: Non-regular trend along the number of cyano groups



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ABSTRACT

Ionic liquids (ILs) with cyano-functionalized anions are a set of fluids that are still poorly characterized despite their remarkably low viscosities and potential applications. Aiming at providing a comprehensive study on the influence of the number of –CN groups through the surface tension and surface organization of ILs, the surface tensions of imidazolium-based ILs with cyano-functionalized anions were determined at atmospheric pressure and in the (298.15–343.15) K temperature range. The ILs investigated are based on 1-alkyl-3-methylimidazolium cations (alkyl = ethyl, butyl and hexyl) combined with the [SCN][−], [N(CN)₂][−], [C(CN)₃][−] and [B(CN)₄][−] anions. Although the well-known trend regarding the surface tension decrease with the increase of the size of the aliphatic moiety at the cation was observed, the order obtained for the anions is more intricate. For a common cation and at a given temperature, the surface tension decreases according to: [N(CN)₂][−] > [SCN][−] > [C(CN)₃][−] > [B(CN)₄][−]. Therefore, the surface tension of this homologous series does not decrease with the increase of the number of –CN groups at the anion as has been previously shown by studies performed with a more limited matrix of ILs. A maximum in the surface tension and critical temperature was observed for [N(CN)₂]-based ILs. Furthermore, a minimum in the surface entropy, indicative of a highly structured surface, was found for the same class of ILs. All these evidences seem to be a result of stronger hydrogen-bonding interactions occurring in [N(CN)₂]-based ILs, when compared with the remaining CN-based counterparts, and as sustained by cation-anion interaction energies derived from the Conductor Like Screening Model for Real Solvents (COSMO-RS).

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1. Introduction

In recent years, ionic liquids (ILs) have attracted large interest from both academic and industrial researchers based on the premise that their outstanding properties would allow the development of more environmentally friendly and sustainable chemical products and/or processes. A large number of ILs can be prepared by the simple combination and chemical structure rearrangement of their ions [1]. Their ionic nature is the primary characteristic responsible for the preeminent properties displayed by most ILs, namely a negligible vapor pressure, high ionic conductivity, non-flammability, high thermal and chemical stabilities, and an

enhanced solvation ability for a large array of compounds [1–6]. Furthermore, the possibility of tuning their properties, through the simple combination of different ions, allows the design of specific ILs for target applications. As a result of their tailoring ability and unique properties, ILs have been studied for various applications, such as lubricants [7], gas storage media [8,9], solvents in multiphase homogeneous catalytic reactions [5,10], solvent media and catalysts in heterogeneous reactions [11], extraction solvents of compounds of biotechnological and analytical interest [12,13], potential solvents in extractive distillation processes to separate water–ethanol mixtures [14], enhanced candidates to dissolve and process biomass [15], among many other exploratory purposes. Notwithstanding their academic interest, ILs have caught the industry interest and are currently being used in some industrial processes and products [16,17].

While many ILs present high viscosity values, the cyano-based

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ILs possess relatively low values, and thus, appearing as more advantageous for many chemical reactions and processes. The first synthesis of ILs containing a cyano-based anion (dicyanamide, $[\text{N}(\text{CN})_2]^-$), was reported by MacFarlane et al. [18]. The authors [18] demonstrated that these ILs are remarkable fluids with low melting temperatures and viscosities. Since then, a large interest on their application has emerged, comprising the application of cyano-based ILs as fluoro-free alternatives in the development of lithium-conducting electrolytes [19,20], and in organic dye-sensitized solar cells [21]. Cyano-based ILs have also been studied as alternative solvents in separation approaches, namely in the extraction of aromatics from aromatic/aliphatic mixtures [22], in the extraction of phenolic compounds from biomass [23], in the selective separation of CO_2 and N_2 (using supported IL membranes) [24], and in the separation and recovery of alcohols from aqueous media [14,25]. For a better design of related processes, the solvation capacity and ability to establish hydrogen bonds with water and ethanol [26,27], the volumetric properties of binary mixtures composed of benzene and cyano-based ILs [28], and thermophysical properties, such as densities, viscosities and refractive index [29] of these CN-based fluids, have been evaluated.

The knowledge of interfacial tensions is of key importance for the development of target applications and for the understanding and development of structure-property relationships. Despite their inherent interest, surface tensions are not widely and extensively reported as densities and viscosities [30]. In fact, consistent and accurate measurements of surface tensions of ILs are not easy to achieve, mainly due to the presence of surface active impurities that may lead to large deviations in the surface tension values. Moreover, most ILs are highly hygroscopic and the control of their water content at low values during the measurements, known to influence the surface tension [30,31], is not an easy task.

In this work, and aiming at better characterizing cyano-based ILs, the surface tensions of seven imidazolium-based ILs composed of cyano-based anions were experimentally determined. The ILs under study are based on 1-alkyl-3-methylimidazolium cations (alkyl = ethyl, butyl and hexyl) combined with the $[\text{SCN}]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{C}(\text{CN})_3]^-$ and $[\text{B}(\text{CN})_4]^-$ anions. The selected matrix of cation/anion combinations provided a detailed and comprehensive investigation of the influence of the $-\text{CN}$ group through the analysis of the surface tension data. To better understand the cyano-contribution to the surface tension values, electrostatic-misfit, E_{MF} , hydrogen bonding, E_{HB} , and van der Waals energies, E_{vdW} , were determined by the Conductor Like Screening Model for Real Solvents (COSMO-RS). Furthermore, the related surface thermodynamic properties, such as surface entropy and surface enthalpy, were determined. The critical temperatures of the ILs investigated were also estimated by means of the Etövos [32] and Guggenheim [33] equations.

2. Experimental section

2.1. Chemicals

Surface tensions of seven imidazolium-based ILs, namely 1-butyl-3-methylimidazolium thiocyanate (mass fraction purity > 98%), $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$, 1-butyl-3-methylimidazolium dicyanamide (mass fraction purity > 98%), $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$, 1-hexyl-3-methylimidazolium dicyanamide (mass fraction purity > 98%), $[\text{C}_6\text{C}_1\text{im}][\text{N}(\text{CN})_2]$, 1-ethyl-3-methylimidazolium tricyanomethane (mass fraction purity > 98%), $[\text{C}_2\text{C}_1\text{im}][\text{C}(\text{CN})_3]$, 1-butyl-3-methylimidazolium tricyanomethane (mass fraction purity > 98%), $[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$, 1-ethyl-3-methylimidazolium tetracyanoborate (mass fraction purity > 98%), $[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$, and 1-hexyl-3-methylimidazolium tetracyanoborate (mass fraction purity >

98%), $[\text{C}_6\text{C}_1\text{im}][\text{B}(\text{CN})_4]$, were determined at atmospheric pressure and in the (298.15–343.15) K temperature range. All ILs were acquired from Iolitec, with the exception of the $[\text{C}(\text{CN})_3]^-$ and $[\text{B}(\text{CN})_4]^-$ -based fluids that were kindly supplied by Merck. Their chemical structures, molecular weight and water content are presented in Table 1. The ILs 1-ethyl-3-methylimidazolium thiocyanate and 1-ethyl-3-methylimidazolium dicyanamide were also considered and used in this work for comparison purposes, although their surface tension data were taken from a previous work [34]. The cation–anion matrix of the studied ILs is depicted in Fig. 1.

To remove traces of water and volatile compounds, individual samples of each IL were dried at moderate temperature (≈ 323 K) and at high vacuum (≈ 1 Pa), under constant stirring for a minimum of 48 h. After this purification procedure, the purity of all ILs was further checked by ^1H and ^{13}C NMR. Furthermore, the water content of each IL, after the drying procedure and immediately before the measurements, was determined by Karl Fischer titration using a Metrohm 831 Karl Fischer coulometer. The reagent employed was Hydranal[®] - Coulomat AG from Riedel-de Haën. The water content of all ILs is below 0.04 wt% as shown in Table 1.

2.2. Apparatus and procedure

2.2.1. Surface tension

The surface tension of each sample was determined through the analysis of the shape of a pendant drop and measured using a Dataphysics contact angle system OCA-20. Drop volumes of (10 ± 1) μL were obtained using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminium air chamber. The temperature was attained by circulating water in a double jacketed aluminium cell by means of a Julabo F-25 water bath. The temperature inside the aluminium chamber was measured with a Pt100 within ± 0.1 K, placed at a distance of approximately 2 cm to the liquid drop. After reaching each temperature, the drop was formed and the measurements were carried out after 30 min, to guarantee its thermal stabilization. Silica gel was kept inside the air oven to assure a dry environment and to avoid moisture absorption during the equilibration period. For the surface tensions determination, at each temperature and for each IL, at least 5 drops were formed and measured. For each drop, an average of 200 images was captured. The analysis of the drop shape was performed with the software module SCA 20 where the gravitational acceleration ($g = 9.8018 \text{ m s}^{-2}$) and latitude ($\text{lat} = 40^\circ$) were used according to the location of the assay. The density values required for the calculation of the surface tensions from the drop image data were taken from literature [29]. Further details on the equipment and its validity to measure surface tensions of ILs can be found in previous publications [34–37].

2.2.2. COSMO-RS

The COSMO-RS methodology proposed by Klamt and Schüürman [38] is a well-known method for *a priori* prediction of thermophysical properties and phase behavior on the basis of unimolecular quantum chemical calculations. The standard procedure of COSMO-RS calculations consists of two major steps. In the first step, the continuum solvation COSMO calculations of electronic density and molecular geometry, was performed using TURBOMOLE 6.1 program package at the density functional theory level, using the BP functional B88–P86 with a triple- ζ valence polarized basis set (TZVP) and the resolution of identity standard approximation [39]. In the second step, the cation–anion pair interaction energies were generated solely using the *COSMOTHERM*X program with parameter file BP_TZVP_C30_1301 (COSMOlogic GmbH & Co KG, Leverkusen, Germany) [40]. In the molecular approach, COSMO-RS focuses on three specific types of

Table 1
Chemical structures, description, molecular weight and water content of the studied ILs.

ILs	Chemical structure	
1-butyl-3-methylimidazolium thiocyanate [C ₄ C ₁ im][SCN] (197.30 g.mol ⁻¹ ; water wt% = 0.0228)		
1-butyl-3-methylimidazolium dicyanamide [C ₄ C ₁ im][N(CN) ₂] (205.26 g.mol ⁻¹ ; wt% = 0.0225)		
1-hexyl-3-methylimidazolium dicyanamide [C ₆ C ₁ im][N(CN) ₂] (233.31 g.mol ⁻¹ ; wt% = 0.0406)		
1-ethyl-3-methylimidazolium tricyanomethane [C ₂ C ₁ im][C(CN) ₃] (201.23 g.mol ⁻¹ ; wt% = 0.0331)		
1-butyl-3-methylimidazolium tricyanomethane [C ₄ C ₁ im][C(CN) ₃] (229.28 g.mol ⁻¹ ; wt% = 0.0266)		
1-ethyl-3-methylimidazolium tetracyanoborate [C ₂ C ₁ im][B(CN) ₄] (226.05 g.mol ⁻¹ ; wt% = 0.0210)		
1-hexyl-3-methylimidazolium tetracyanoborate [C ₆ C ₁ im][B(CN) ₄] (282.15 g.mol ⁻¹ ; wt% = 0.0214)		

Cation – Anion Combination	 [SCN] ⁻	 [N(CN) ₂] ⁻	 [C(CN) ₃] ⁻	 [B(CN) ₄] ⁻
 [C ₂ C ₁ im] ⁺	✓	✓	✓	✓
 [C ₄ C ₁ im] ⁺	✓	✓	✓	✗
 [C ₆ C ₁ im] ⁺	✗	✓	✗	✓

Fig. 1. Ionic structures and cation–anion matrix of the studied ILs: ✓, ILs studied; ✗, ILs not studied.

interactions. The electrostatic–misfit energy, E_{MF} , and hydrogen bonding energy, E_{HB} , are the most relevant and are described as a function of the polarization charge of the two interacting segments (σ , σ') or ($\sigma_{acceptor}$, σ_{donor}). A third interaction, the van der Waals energy, E_{vdW} , only depends on the atoms composing each molecule or ion. These energies are described according to Eqs. 1–3:

$$E_{MF} = a_{eff}^{\alpha} (\sigma + \sigma')^2 \quad (1)$$

$$E_{HB} = a_{eff} c_{HB} \min(0; \min(0; \sigma_{donor} + \sigma_{HB}) \times \max(0; \sigma_{acceptor} - \sigma_{HB})) \quad (2)$$

$$E_{\text{vdW}} = a_{\text{eff}}(\tau_{\text{vdW}} + \tau'_{\text{vdW}}) \quad (3)$$

where there are five adjustable parameters fitted to the individual atoms properties, namely, the effective contact area between two surface segments, a_{eff} ; the interaction parameter, α ; the hydrogen bond strength, c_{HB} ; the threshold for hydrogen bonding, σ_{HB} ; and τ_{vdW} and τ'_{vdW} , which are elements of specific parameters in van der Waals interactions. These parameters, required to determine each cation–anion interaction energy, are available in the COSMOthermX software package for each pair of ions or IL.

3. Results and discussion

3.1. Surface tension

The surface tension of the ILs investigated was determined at atmospheric pressure in the temperature range from (298.15–343.15) K. Surface tension data for imidazolium-based ILs with anions functionalized with cyano groups present considerable discrepancies among different authors [41–49]. The average relative deviations between the data collected in this work and those already reported [41–49] are depicted in Fig. 2. The absolute average relative deviations between the data collected in this work and those reported in the literature are 2.7% [42], 6.0% [43] and 3.8% [44] for $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$; 5.8% [44] and 10.1% [41] for $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$; 2.1% [49] and 3.4% [48] for $[\text{C}_2\text{C}_1\text{im}][\text{C}(\text{CN})_3]$; 2.2% [49] and 1.0% [48] for $[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$; 2.2% [45], 13.0% [46] and 2.5% [49] for $[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$; and 1.1% [47] and 2.6% [49] for $[\text{C}_6\text{C}_1\text{im}][\text{B}(\text{CN})_4]$. In general, it is well-known that the surface tension of ILs is highly affected by the presence of small amounts of impurities. Moreover, the use of different techniques and experimental procedures may also lead to variations on the surface tension data [30]. Therefore, higher deviations always exist among different authors when comparing surface tension data [30] – a trend that is less evident, for instance, in density data. Overall, the relative deviations on the surface tension data for CN-based ILs, obtained by different authors, range between –6.6% and 18.3%. Nevertheless, a good agreement is observed between the data acquired in this work and those already published, namely for $[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$ [48] and $[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$ [45].

The surface tension values obtained in this work are depicted in Fig. 3 and reported in Table 2. The surface tensions of $[\text{C}_2\text{C}_1\text{im}][\text{SCN}]$ and $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ were previously reported by us [34] and are represented alongside with the new experimental data. For all ILs, the surface tension presents a quasi-linear dependence with temperature. At a given temperature, the surface tension of the studied ILs decreases in the following sequence: $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{CN})_2] > [\text{C}_2\text{C}_1\text{im}][\text{SCN}] > [\text{C}_2\text{C}_1\text{im}][\text{C}(\text{CN})_3] \approx [\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2] > [\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3] > [\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4] > [\text{C}_4\text{C}_1\text{im}][\text{SCN}] > [\text{C}_6\text{C}_1\text{im}][\text{N}(\text{CN})_2] > [\text{C}_6\text{C}_1\text{im}][\text{B}(\text{CN})_4]$. In general, at a fixed temperature and for a common cation, the surface tension decreases according to: $[\text{N}(\text{CN})_2]^- > [\text{SCN}]^- > [\text{C}(\text{CN})_3]^- > [\text{B}(\text{CN})_4]^-$; while for a common anion the surface tension decreases according to the rank: $[\text{C}_2\text{C}_1\text{im}]^+ > [\text{C}_4\text{C}_1\text{im}]^+ > [\text{C}_6\text{C}_1\text{im}]^+$. While this study focused on the impact of cyano groups at the anion, it is also interesting to mention their influence when attached to the cation. In general, ILs containing cyano groups at the cation display lower surface tensions, for instance when comparing the surface tension data between 1-butylpyridinium bis(trifluoromethylsulfonyl)imide and 3-cyano-1-butylpyridinium bis(trifluoromethylsulfonyl)imide [50]. These overall results reveal that the addition of cyano groups, either at the cation or anion, can be used to fine-tune the surface tensions of ILs.

The decrease of the surface tension with the increase of the alkyl side chain length (at least up to an alkyl chain with 6 carbons) is a well-established trend for imidazolium-based ILs [37], and which reflects the magnitude of the entropy increase associated with the surface assembling. This trend was also shown to be extensible to the IL anion alkyl side chain length [51]. On the other hand, the surface tension of cyano-based ILs has been reported to decrease with the number of cyano groups present at the anion [49]. However, these studies [49] were performed with a more limited matrix of ILs, and thus, a more complete evaluation of the effect of the number of –CN groups was not previously addressed. Even so, and although only studying $[\text{SCN}]^-$ and $[\text{N}(\text{CN})_2]^-$ -based ILs, Sanchez et al. [44] demonstrated an increase in the surface tension occurring from $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$ to $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$. From this work, with a more complete matrix of ILs, we provide new evidences on the surface tension decrease from $[\text{N}(\text{CN})_2]^-$ to $[\text{C}(\text{CN})_3]^-$ to $[\text{B}(\text{CN})_4]^-$, whereas the opposite behavior is observed between $[\text{N}(\text{CN})_2]^-$ and $[\text{SCN}]^-$. The surface tension at a given temperature and for the fixed

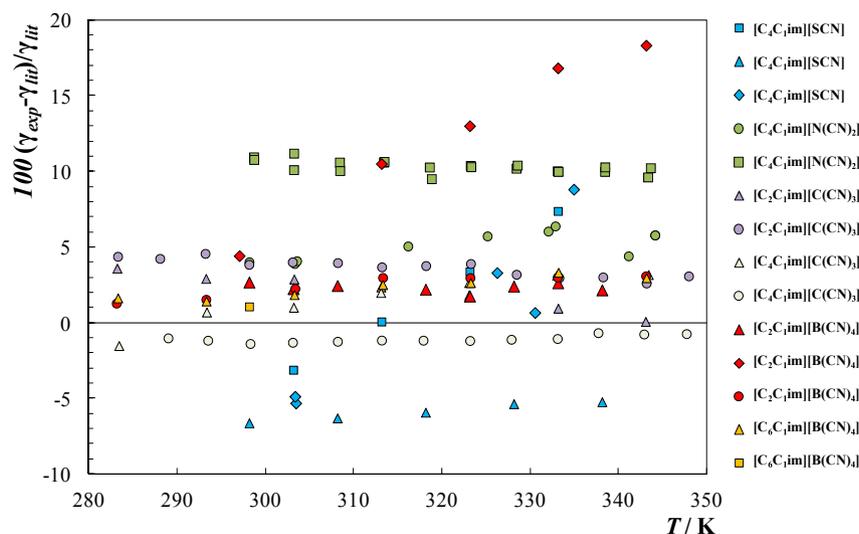


Fig. 2. Relative deviations between the experimental (γ_{exp}) and literature (γ_{lit}) surface tension data: different symbols represent different literature sources while the same color corresponds to the same IL [41–49].

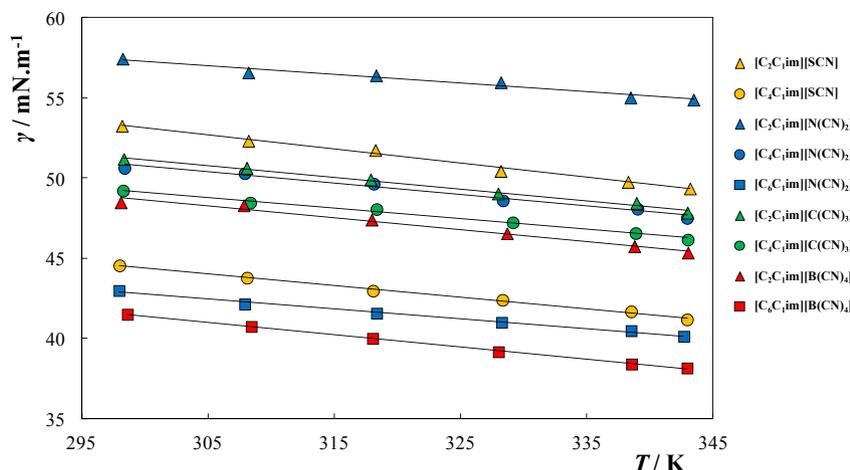


Fig. 3. Surface tension as a function of temperature. Symbols with the same shape represent the same cation core: Δ , $[\text{C}_2\text{C}_1\text{im}]^+$; \circ , $[\text{C}_4\text{C}_1\text{im}]^+$; \square , $[\text{C}_6\text{C}_1\text{im}]^+$. $[\text{C}_2\text{C}_1\text{im}][\text{SCN}]$ and $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ surface tension data were taken from a previous work [34].

Table 2

Experimental surface tension, γ , as function of temperature, T , and at atmospheric pressure for the studied ionic liquids.^a

$[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$		$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$		$[\text{C}_6\text{C}_1\text{im}][\text{N}(\text{CN})_2]$		$[\text{C}_2\text{C}_1\text{im}][\text{C}(\text{CN})_3]$	
T/K	$\gamma/(\text{mN m}^{-1})$						
298.1	44.6	298.4	50.6	298.0	43.0	298.3	51.1
308.2	43.5	307.9	50.3	307.9	42.2	308.1	50.7
318.1	43.0	318.1	49.7	318.4	41.6	317.9	49.9
328.3	42.4	328.4	48.6	328.2	41.0	328.0	49.1
338.5	41.9	339.0	48.1	338.5	40.5	338.9	48.5
342.9	41.6	342.9	47.5	342.7	40.2	343.0	47.9
$[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$		$[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$		$[\text{C}_6\text{C}_1\text{im}][\text{B}(\text{CN})_4]$			
T/K	$\gamma/(\text{mN m}^{-1})$	T/K	$\gamma/(\text{mN m}^{-1})$	T/K	$\gamma/(\text{mN m}^{-1})$		
298.3	49.2	298.1	49.1	298.6	41.5		
308.3	48.5	307.8	48.3	308.4	40.8		
318.3	48.1	318.0	47.4	318.0	40.0		
329.1	47.3	328.7	46.6	328.0	39.2		
338.9	46.6	338.8	45.8	338.5	38.4		
343.0	46.2	343.0	45.4	342.9	38.2		

^a Standard uncertainties u are $u(T) = 0.1$ K and the combined expanded uncertainty U_c is $U_c(\gamma) = 0.3$ mN m^{-1} , at the 95% confidence level ($k \approx 2$).

$[\text{C}_2\text{C}_1\text{im}]^+$ cation as a function of the number of $-\text{CN}$ groups is depicted in Fig. 4. Additional representations for the remaining ILs comprising different cations are provided in the Supporting Information. In fact, and for all $[\text{C}_r\text{C}_1\text{im}]$ -based ILs, a maximum in surface tension occurs for ILs composed of $[\text{N}(\text{CN})_2]^-$.

To better understand this peculiar behavior, and since the surface tension values are related with the force required to break the air/liquid interface, and thus with ion–ion interactions, the atomic orbitals of the central atom of each anion were taken from literature [52]. Electronegativity, firstly introduced by Pauling, is a measure of the attraction of electrons by a particular atom [53]. According to Allen [52], ^{16}S , ^7N , ^6C , and ^5B atoms present an electronegativity (χ) of 2.589, 3.066, 2.544 and 2.051 (Pauling units), respectively. The electronegativity of the central atom of each cyano-based anion (^{16}S , ^7N , ^6C , and ^5B atoms) is depicted in Fig. 4 together with the surface tension data at 298.15 K. A similar trend is observed, with a maximum at $[\text{N}(\text{CN})_2]^-$, meaning that the electronegativity of the central atom of the cyano-based anion plays a significant role in defining the ion–ion interactions at the surface and thus through the liquid surface organization and surface tension values. This maximum in electronegativity occurring at $[\text{N}(\text{CN})_2]^-$ is in good agreement with the observations reported by Batista et al. [26,27]. The authors [26,27] studied the activity coefficients of water in

$[\text{SCN}]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{C}(\text{CN})_3]^-$ and $[\text{B}(\text{CN})_4]^-$ -based ILs, demonstrating a decrease in the activity coefficients of water from $[\text{SCN}]^-$ to $[\text{N}(\text{CN})_2]^-$, and then an increase from $[\text{C}(\text{CN})_3]^-$ to $[\text{B}(\text{CN})_4]^-$. Batista et al. [26,27] supported this trend based on radial and spatial distribution functions along with coordination numbers obtained by molecular dynamics (MD) simulations. The authors [26,27] found that amongst the different CN-based anions, $[\text{N}(\text{CN})_2]^-$ displays the higher ability to establish favorable hydrogen-bonding interactions, *i.e.*, to act as a hydrogen-bond acceptor. Therefore, the stronger cation–anion interactions in $[\text{N}(\text{CN})_2]$ -based ILs, and as a result of cation–anion hydrogen-bonding, seem to be responsible for their higher surface tension values when compared with the remaining members of the series.

Based on the possibility that hydrogen-bonding plays a major role in defining each cation–anion pair attractions and further surface ordering and surface tension values, COSMO-RS was further used to estimate the electrostatic-misfit, E_{MF} , hydrogen-bonding, E_{HB} , and van der Waals energies, E_{vdW} , at 298.15 K, of the different ILs investigated in this work. In general, the relative orientation of the cations and anions at the surface is also a reflection of the cohesive forces between the ions occurring at the bulk. The hydrogen-bonding energy as a function of the number of CN-groups at the IL anion is depicted in Fig. 4. The representation for the remaining ILs and

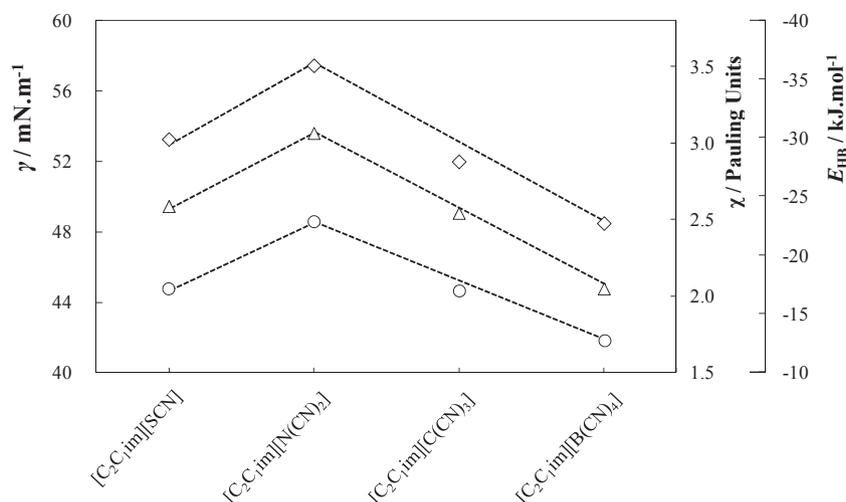


Fig. 4. Surface tension at 298.15 K (◇), electronegativity of the central atom of the cyano-based anion (Δ) [52], and hydrogen bonding energy at 298.15 K, E_{HB} (○), of 1-ethyl-3-methylimidazolium-based ILs. [C₂C₁im][SCN] and [C₂C₁im][N(CN)₂] surface tension data were taken from a previous work [34]. The dashed lines have no physical meaning and are guides for the eyes.

energies, as well as the respective detailed data, are provided in the Supporting Information. Although not so evident with the electrostatic and van der Waals interactions, a similar and clear trend is observed when plotting the hydrogen-bonding energies of each cation–anion pair along the number of –CN based groups at the anion, with a maximum appearing at [N(CN)₂]-based ILs. Nevertheless, it should be remarked that the remaining energies (misfit and van der Waals) also play a role since a maximum also appears at [N(CN)₂]-based ILs, although in a smother way. In summary, it seems that hydrogen-bonding plays a primary role in defining the surface organization and surface tension values of cyano-based ILs (at least for imidazolium-based with alkyl side chains no longer than hexyl). In a previous work [37] we demonstrated that the surface tension largely depends on the sum of all interaction energies occurring in each cation–anion pair by investigating the gas phase fragmentation of isolated aggregate ions. It was found that the experimental collision energies required to dissociate 50% of each adduct linearly correlate with the surface tension data [37]. Therefore, it is expected that all energies contribute to the surface organization of ILs, although hydrogen-bonding appears as the main energy ruling the surface organization of CN-based ILs.

3.2. Surface thermodynamics properties and estimated critical temperature

The surface thermodynamic properties, specifically the surface entropy and the surface enthalpy, were derived using the quasi-linear dependence of the surface tension with temperature. The surface entropy, S^γ , can be calculated according to [54,55]:

$$S^\gamma = -\left(\frac{d\gamma}{dT}\right) \quad (4)$$

while the surface enthalpy, H^γ , according to [54,55]:

$$H^\gamma = \gamma - T\left(\frac{d\gamma}{dT}\right) \quad (5)$$

where γ stands for the surface tension, and T for the temperature.

Values of the thermodynamic functions of the investigated ILs with the respective standard deviations [56], derived from the

curve $\gamma = f(T)$, are presented in Table 3. As previously observed for other ILs [6,31,34–36,57], imidazolium-based fluids combined with cyano-based anions display low surface enthalpies and entropies when compared with molecular organic compounds. This low surface enthalpy and entropy reflect a high surface organization as well as a highly structured liquid phase.

Fig. 5 depicts the surface tension and surface entropy of 1-ethyl-3-methylimidazolium-based ILs combined with cyano-functionalized anions. It is clear that the surface entropies follow the opposite behavior observed for the surface tensions, with a minimum appearing at [N(CN)₂]-based ILs. Thus, [N(CN)₂]-based fluids display a higher organization of the surface when compared with the remaining ILs. On the other hand, no major differences are observed among the surface enthalpies for the different CN-based ILs – cf. the Supporting Information.

The critical temperature of fluids, T_c , is a commonly used property in corresponding states correlations connecting equilibrium and transport properties [58]. However, the determination of the critical temperatures of ILs is a main challenge due to their lower decomposition temperatures. Rebelo et al. [59] proposed the use of the Eötvös [32] and Guggenheim [33] equations to estimate the hypothetical critical temperature of ionic liquids according to

$$\gamma\left(\frac{M_w}{\rho}\right)^{(2/3)} = K_{Eöt}(T_c - T) \quad (6)$$

$$\gamma = K_{Gug}\left(1 - \frac{T}{T_c}\right)^{(11/9)} \quad (7)$$

where T_c is the critical temperature, M_w is the molecular weight, ρ is the density, and $K_{Eöt}$ and K_{Gug} are fitted parameters. Both equations reproduce the fact that the surface tension becomes null at the critical point [58].

As reported in previous works [6,31,34–36,57], the values for critical temperatures of ILs obtained by these approximations must be used with caution. The estimation of critical temperatures using data from a narrow temperature range, and demanding a large extrapolation, are a source of uncertainty. Weiss et al. [60] favored Guggenheim's expression over the Eötvös, as it could yield accurate estimates of T_c and it is capable of describing the behavior in the

Table 3
Surface entropy, S^{γ} , surface enthalpy, H^{γ} , and estimated critical temperature, T_c , using the equations of Eötvös ($(T_c)_{\text{Eot}}$) [32] and Guggenheim ($(T_c)_{\text{Gug}}$) [33], of the studied ILs.^a

Ionic liquid	$(S^{\gamma} \pm \sigma^{\delta}) \cdot 10^{-5} / (\text{J} \cdot \text{m}^{-2} \cdot \text{K}^{-1})$	$(H^{\gamma} \pm \sigma^{\delta}) \cdot 10^{-2} / (\text{J} \cdot \text{m}^{-2})$	$(T_c)_{\text{Eot}}/\text{K}$	$(T_c)_{\text{Gug}}/\text{K}$
$[\text{C}_2\text{C}_1\text{im}][\text{C}(\text{CN})_3]$	7.4 ± 0.4	7.3 ± 0.1	1273 ± 3	1153.4 ± 0.7
$[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$	8.3 ± 0.1	7.38 ± 0.02	1122 ± 5	1018.1 ± 0.7
$[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$	6.2 ± 0.2	6.3 ± 0.5	1352 ± 1	1226.8 ± 0.7
$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$	7.1 ± 0.5	7.2 ± 0.2	1282 ± 5	1171.2 ± 0.7
$[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$	6.7 ± 0.3	6.9 ± 0.1	1356 ± 5	1196.8 ± 0.7
$[\text{C}_6\text{C}_1\text{im}][\text{N}(\text{CN})_2]$	6.1 ± 0.3	6.1 ± 0.1	1256 ± 3	1153.8 ± 0.7
$[\text{C}_6\text{C}_1\text{im}][\text{B}(\text{CN})_4]$	7.7 ± 0.1	6.44 ± 0.04	1012 ± 3	955.0 ± 0.7

^a Expanded uncertainty at the 95% confidence level ($k \approx 2$).

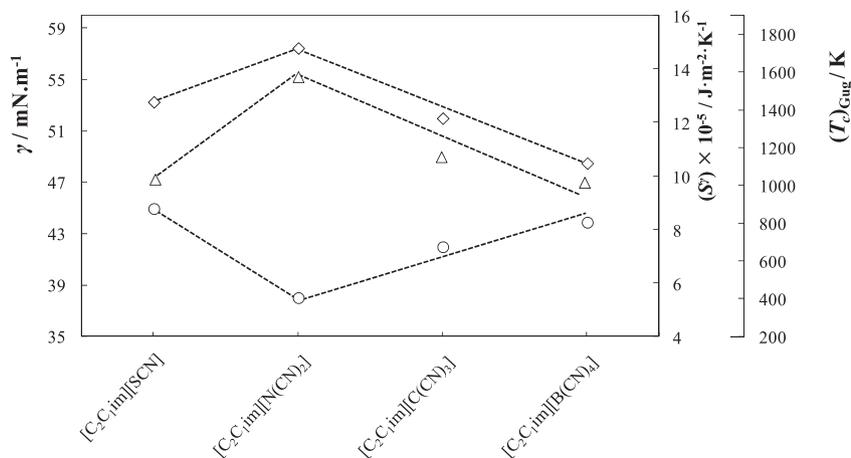


Fig. 5. Surface tension at 298.15 K (\diamond), surface entropy, S^{γ} , (\circ) and estimated critical temperatures (T_c) using the equation of Guggenheim ($(T_c)_{\text{Gug}}$) [33] (Δ), of 1-ethyl-3-methylimidazolium-based ILs. Surface tension data for $[\text{C}_2\text{C}_1\text{im}][\text{SCN}]$ and $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ were taken from a previous work [34]. The dashed lines have no physical meaning and are guides for the eyes.

near-critical region. Also Ghatee et al. [61] determined similar T_c values by these two methods, although the Eötvös equation also depends on the accuracy of the density data. In general, and although not completely accurate due to the inability of determining the critical temperatures of ILs, these values can be used as a first approximation to characterize the volatility of ILs.

The critical temperature values assessed from the surface tension data obtained in this work are reported in Table 3. Fig. 5 depicts the surface tension and estimated critical temperatures (T_c), using the equation of Guggenheim ($(T_c)_{\text{Gug}}$) [33], along with ILs with different anions. A maximum in the critical temperature is observed for $[\text{N}(\text{CN})_2]$ -based ILs, following indeed the same trend verified for the surface tensions at a given temperature. This fact allow us to speculate that $[\text{N}(\text{CN})_2]$ -based fluids are less volatile than the remaining CN-based counterparts – again a result that can be supported by stronger cation–anion interactions occurring in $[\text{N}(\text{CN})_2]$ -based ILs at their liquid state.

4. Conclusions

In the past few years, ionic liquids (ILs) with cyano-based anions have shown to be improved candidates for electrochemical and separation applications. Nevertheless, only scattered surface tension data exist hitherto and a systematic analysis of the effect of the number of –CN groups at the anion was still not attempted. In this work, a comprehensive study on the surface tension and surface thermodynamic properties of a large series of imidazolium-based ILs with cyano-functionalized anions ($[\text{SCN}]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{C}(\text{CN})_3]^-$ and $[\text{B}(\text{CN})_4]^-$) was attempted. New experimental surface tension data in the temperature range from (298–343) K and at atmospheric pressure are here reported. In general, at a fixed

temperature and for a common anion, the surface tension decreases with the increase of the cation alkyl chain length; on the other hand, for a common cation, the surface tension decreases in the following sequence: $[\text{N}(\text{CN})_2]^- > [\text{SCN}]^- > [\text{C}(\text{CN})_3]^- > [\text{B}(\text{CN})_4]^-$. Curiously, amongst the studied ILs series, a maximum in the surface tension and critical temperature is observed for $[\text{N}(\text{CN})_2]$ -based ILs, as well a minimum in the surface entropy indicative of a highly structured surface. All these facts seem to be a result of the stronger cation–anion hydrogen-bonding interactions occurring in $[\text{N}(\text{CN})_2]$ -based ILs, when compared with the remaining CN-based counterparts, and as supported by the ions pair interaction energies derived from COSMO-RS.

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Appendix A. Supporting information

Supporting information related to this article can be found at <http://dx.doi.org/10.1016/j.fluid.2015.10.044>.

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