



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

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