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Thermophysical properties of sulfonium- and ammonium-based ionic liquids

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ABSTRACT

Experimental data for the density, viscosity, refractive index, and surface tension of four sulfonium- and ammonium-based ionic liquids (ILs) with the common bis(trifluoromethylsulfonyl)imide anion were measured in the temperature range between 288.15 and 353.15 K and at atmospheric pressure. The ILs considered include butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{4111}][NTf_2]$, tributylmethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{4441}][NTf_2]$, diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide, $[S_{221}][NTf_2]$, and triethylsulfonium bis(trifluoromethylsulfonyl)imide, $[S_{222}][NTf_2]$. Based on the gathered results and on data taken from literature, the impact of the cation isomerism and of the size of the aliphatic tails, as well as the effect resulting from the substitution of a nitrogen by a sulfur atom as the cation central atom, on the thermophysical properties of sulfonium- and ammonium-based ILs is discussed here. Remarkably, more symmetric cations present a lower viscosity for the same, and sometimes even for higher, alkyl chain lengths at the cation. Additional derivative properties, such as the isobaric thermal expansion coefficient, the surface thermodynamic properties and the critical temperature for the investigated ILs were also estimated and are presented and discussed.

1. Introduction

Ionic liquids (ILs) are a class of neoteric solvents [1] composed of large organic cations and organic/inorganic anions that cannot easily form an ordered crystal and thus remain liquid at or near room temperature. These unique solvents are alluring interest as greener alternatives to customary organic solvents with the aim of supporting more environmentally friendly processes. Room temperature ILs are often referred to as '*designer solvents*' due to the possibility of tuning their physical and chemical properties through a wise combination of cations, anions and/or the introduction of functional groups [1].

Novel applications of ILs continue to be regularly projected based on their excellent properties, such as negligible vapor pressure [2,3], non-flammability [4], high ionic conductivity, high solvation capacity, stability at high temperatures [5], wide liquid electrochemical windows [6], and wide liquid temperature ranges [7]. Based on these interesting properties, ILs are therefore a possible alternative for conventional solvents in separation, engineering and biotechnological processes [8–13], in electrochemistry [14,15], and as catalysts [16], thermo-fluids [17] or sensors [18].

Among different ILs, bis(trifluoromethylsulfonyl)imide-based ILs, $[NTf_2]$-based ILs, have been reported to be convenient for various practical applications, such as in lithium ion batteries [19,20], dye-sensitized solar cells (DSSC) [21–23], and electric double-layer capacitors [24,25]. The weakly coordinating $[NTf_2]$ anion induces a substantial depression in the melting point of the corresponding ILs, partially due to the charge delocalization that extends from the central nitrogen atom to the neighboring sulfur atoms, and, to a less extent, to the oxygen atoms. This adds a shielding effect by the oxygen atoms and the terminal $-CF_3$ groups and reduces the columbic interactions, while increasing the ion mobility. The $[NTf_2]$-based ILs are also appropriate alternatives for apolar organic molecular liquids [26] because of their high hydrophobicity and chemical stability against moisture [27].

To fully optimize the wide range of applications for $[NTf_2]$-based ILs, the knowledge of their thermophysical properties, viz. density, viscosity, refractive index, surface tension, conductivity and critical temperature, are of high importance, especially for any industrial design or lab application. Several studies reporting thermophysical properties for ammonium - and sulfonium-based ILs are

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available in literature [23,28–47]. In particular, sulfonium-based ILs are generating substantial interest as potential alternatives for their ammonium counterparts due to practical benefits including higher chemical and electrochemical stabilities [48,49]. Matsumoto et al. [45] investigated the differences upon densities, viscosities, conductivities, and thermal stability between ammonium- and sulfonium-based ILs. In contrast to most neutral molecular liquids, where the substitution of a constituent atom by a heavier one leads to a viscosity increase, the authors [45] reported lower viscosities and higher conductivities for the sulfonium-based ILs when compared to ammonium-based compounds. Similar observations were made by Lee et al. [23] on the physical and electrochemical properties of sulfonium- and ammonium-based cations combined with the [NTf_2] anion. The authors [23] reported that the sulfonium-based ILs present better performances for DSSCs than those with ammonium-based electrolytes. Another report [50] indicated that trialkylsulfonium salts based on the dicyanamide anion have lower viscosities in comparison with many other ILs, from 20 to 60 mPa s at 293.15 K, which renders sulfonium-based ILs as highly useful for low temperature applications.

This work aims at understanding, using the data measured here and other retrieved from literature, the impact of isomerization, as well as the effect resulting from the substitution of nitrogen by sulfur atom as the cation's central atom on the ILs thermophysical properties. To this end, density, viscosity, refractive index, and surface tension data of four sulfonium- and ammonium-based ILs with the [NTf_2] anion were measured in the temperature range between 283.15 and 353.15 K and at atmospheric pressure. Additional derivative properties, such as the isobaric thermal expansion coefficient, the surface thermodynamic properties, and critical temperature of all ILs studied were also estimated. For the density, viscosity, and refractive index experimental data, further comparisons with the results given by the Gardas and Coutinho group contribution methods [51,52] were carried out and new parameters are proposed here.

2. Materials and methods

2.1. Materials

Four ILs were studied in this work, namely butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, [N_{4111}][NTf_2], tributylmethylammonium bis(trifluoromethylsulfonyl)imide, [N_{4441}][NTf_2], diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide, [S_{221}][NTf_2], and triethylsulfonium bis(trifluoromethylsulfonyl)imide, [S_{222}][NTf_2]. The ionic structures of the studied ILs and corresponding designations are presented in Table 1. The ILs were acquired from IoLiTec with mass fraction purities higher than 99%.

The water content plays an important role in the IL properties, such as surface tension and viscosity [33,53–55], and significant deviations can be found due to small amounts of water. In order to remove traces of water and volatile compounds from the ILs, individual samples of each fluid were dried at moderate temperature (≈313 K), vacuum (≈1 Pa), and under continuous stirring, for a minimum period of 48 h. After this purification procedure, and after the thermophysical properties measurements, the purity of each IL was checked by ^{1}H, ^{19}F, and ^{13}C NMR to assure that no degradation occurred. The final IL water content, after the drying step and immediately before the measurements, was determined with a Metrohm 831 Karl Fischer coulometer (using the Hydranal–Coulomat AG from Riedel-de Haën as analyte). The average water content and the molecular weight of each IL are presented in Table 1.

2.2. Experimental section

2.2.1. Density and viscosity

Density (ρ) and dynamic viscosity (η) measurements were carried out using an automated SVM 3000 Anton–Paar rotational Stabinger viscometer-densimeter in the temperature range from 283.15 to 353.15 K and at atmospheric pressure (≈ 0.1 MPa). The absolute uncertainty in density is $\pm 5 \times 10^{-4}$ g cm^{-3}, and the relative uncertainty in dynamic viscosity is ±1%. The relative uncertainty in temperature is within ±0.02 K. Further details about the use of the equipment and methodologies for the determination of densities and viscosities can be found elsewhere [53,56].

2.3. Refractive index

Measurements of refractive index (n_D) were performed at 589.3 nm using an automated Abbemat 500 Anton Paar refractometer, able to measure either liquid or solid samples. Refractive index measurements were carried out in the temperature range from 283.15 to 353.15 K and at atmospheric pressure. The Abbemat 500 Anton Paar refractometer uses reflected light to measure the refractive index, where the sample on the top of the measuring prism is irradiated from different angles by a light-emitting diode (LED). The maximum deviation in temperature is ±0.01 K, and the maximum uncertainty in the refractive index measurements is $\pm 2 \times 10^{-5}$ n_D. The validity of the equipment to determine accurate refractive indices of IL samples is supported by the previously measured data for other ILs published elsewhere [57–59].

2.4. Surface tension

The surface tensions of each IL were determined through the analysis of the shape of a pendant drop using a Data physics contact angle system, OCA-20 (Data Physics Instruments GmbH, Germany). Pendant drops were created using a Hamilton DS 500/GT syringe connected to a Teflon-coated needle placed inside an aluminum air chamber capable of maintaining the temperature within ±0.1 K. The temperature was attained by circulating water in the double-jacketed aluminum cell by means of a Julabo F-25 water bath. The temperature inside the aluminum chamber was measured with a Pt100 within ±0.1 K which is at a distance of approximately 2 cm of the drop. The surface tension measurements were performed in the temperature range from 293 to 344 K and at atmospheric pressure. After reaching a specific temperature, the measurements were carried out after 30 min to guarantee the thermal equilibrium. Silica gel was kept inside the air chamber to avoid the absorption of moisture. For the surface tension determination, at each temperature and for each IL, at least three drops were formed and analyzed. For each drop, an average of 100 images was additionally captured. The analysis of the drop shape was achieved with the software modules SCA 20. The required density data which are used in the surface tension measurements were those determined in this work. The equipment was previously validated through the measurement of the surface tension of ultra-pure water, decane, and dodecane, as well as with a large variety of ILs [59,60].

3. Results and discussions

3.1. Density

The density measurements for the studied ILs were carried out in the temperature range from 283.15 to 353.15 K, at atmospheric pressure, and the respective values are reported in Table 2 and illustrated in Fig. 1. Similar to what is observed for other tetraalkylammonium [23,28,31,33–35,41] and trialkylsulfonium [23,42,46,47] ILs, the density decreases with the cation alkyl chain