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Densities, viscosities and derived thermophysical properties of water-saturated imidazolium-based ionic liquids

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ABSTRACT

In order to evaluate the impact of the alkyl side chain length and symmetry of the cation on the thermophysical properties of water-saturated ionic liquids (ILs), densities and viscosities as a function of temperature were measured at atmospheric pressure and in the (298.15–363.15) K temperature range, for systems containing two series of bis(trifluoromethylsulfonyl)imide-based compounds: the symmetric $[C_nC_n\text{im}][NTf_2]$ (with n = 1–8 and 10) and asymmetric $[C_nC_1\text{im}][NTf_2]$ (with n = 2–5, 7, 9 and 11) ILs. For water-saturated ILs, the density decreases with the increase of the alkyl side chain length while the viscosity increases with the size of the aliphatic tails. The saturation water solubility in each IL was further estimated with a reasonable agreement based on the densities of water-saturated ILs, further confirming that, for the ILs investigated, the volumetric mixing properties of ILs and water follow a near ideal behavior. The water-saturated symmetric ILs generally present lower densities and viscosities than their asymmetric counterparts. From the experimental data, the isobaric thermal expansion coefficient and energy barrier were also estimated. A close correlation between the difference in the energy barrier values between the water-saturated and pure ILs and the water content in each IL was found, supporting that the decrease in the viscosity of ILs in presence of water is directly related with the decrease of the energy barrier.

1. Introduction

Over the last years, ionic liquids (ILs) have been the subject of intensive investigations as a new class of neoteric solvents. ILs consist of large organic cations, with various alkyl substituents and/or functionalized groups, and inorganic or organic anions. The bulky and asymmetric characteristics of their ions are the major reasons behind the ILs' low melting temperatures [1]. Due to their ionic nature, most ILs are known to present interesting properties, such as a negligible vapor pressure [2], non-flammability [3], high thermal stability [4], and high conductivity [5]. Nevertheless, one of the most important features associated to ILs is the possibility to tune their properties for a given task by adjusting the chemical structure of the constituting ions. Actually, the tuning of ILs is even broader, and in addition to the different combinations of their cations and anions in pure compounds, a relevant attention has been given recently to ionic liquids mixtures [6–8].

Due to their unique solvent properties, ILs have been widely investigated in a large range of processes in the chemical industry [9], including separations processes, reactions and biomass processing [1]. It is well-known that the ILs phase equilibrium and their thermophysical properties are significantly influenced by the presence of water [10,11]. Thus, in the last years, a significant number of works has been addressing the thermophysical and thermodynamic properties of water-saturated ILs, in particular for densities and viscosities [10–17]. Rodríguez and Brennecke [17] studied the density and viscosity of aqueous solutions of imidazolium-based ILs with the anions ethylsulfate,

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Table 1
Investigated ionic liquids: chemical name, abbreviation, source, molecular weight (M_w) and purity.

Chemical name	Abbreviation	Source	M_w (g mol^{-1})	Purity (wt%)
1-Ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_2C_1im][NTf_2]$	IoLiTec	391.31	>99
1-Methyl-3-propyllimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_3C_1im][NTf_2]$	IoLiTec	405.34	>99
1-Butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_4C_1im][NTf_2]$	IoLiTec	419.37	>99
1-Methyl-3-pentylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_5C_1im][NTf_2]$	IoLiTec	433.39	>99
1-Heptyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_7C_1im][NTf_2]$	IoLiTec	461.45	>99
1-Methyl-3-nonylmethylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_9C_1im][NTf_2]$	IoLiTec	489.50	>99
1-Methyl-3-undecylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_{11}C_1im][NTf_2]$	IoLiTec	517.55	>99
1,3-Dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_1C_1im][NTf_2]$	IoLiTec	377.29	>99
1,3-Diethylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_2C_2im][NTf_2]$	IoLiTec	405.34	>99
1,3-Dipropylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_3C_3im][NTf_2]$	IoLiTec	433.39	>99
1,3-Dibutylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_4C_4im][NTf_2]$	IoLiTec	461.45	>99
1,3-Dipenthylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_5C_5im][NTf_2]$	IoLiTec	489.50	>99
1,3-Dihexylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_6C_6im][NTf_2]$	IoLiTec	517.55	>99
1,3-Diheptylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_7C_7im][NTf_2]$	IoLiTec	545.60	>99
1,3-Dioctylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_8C_8im][NTf_2]$	IoLiTec	573.66	>99
1,3-Didecylimidazolium bis((trifluoromethyl)sulfonyl)imide	$[C_{10}C_{10}im][NTf_2]$	IoLiTec	629.76	>99

trifluoroacetate and trifluoromethanesulfonate. Both properties were found to decrease with an increase in either temperature or in mole fraction of water. The same behavior was observed by Ge et al. [13] and by Carvalho et al. [12] with additional imidazolium-based ILs, and by Neves et al. [11] with phosphonium-based compounds. In all situations it was found that the water content has a strong effect on the viscosity of the ILs, while the effect is less significant on their densities [10–17].

Viscosity is one of the most important physical properties when considering the scale-up of IL-based applications. Generally, while higher viscosities may be advantageous for lubrication [1,9], a low viscosity is desired for solvent applications in order to increase the mass transfer rates and to minimize pumping costs. The viscosities of ILs are widely dependent on the type of cation and anion and are relatively high when compared to those of common molecular solvents. Density has also been widely studied with ILs [18]. Usually, density is found to largely depend on the IL anion and cation [10,11,15]. Like with molecular solvents, the densities are closely related to the molar mass of the fluid and ILs containing heavier atoms are usually more dense [1,19].

Despite the importance on the knowledge of the ILs' physicochemical properties, few works have systematically studied the relationships between the structures of ILs and their fundamental properties [20–23]. On the other hand, systematic studies on the effect of water through the ILs' densities and viscosities are still scarce [12,13,17,24–28]. On the basis of the described scenario, the densities and viscosities of binary mixtures of water and ILs, namely for ILs saturated with water at 298.15 K, and composed of the common anion bis(trifluoromethylsulfonyl) imide, $[NTf_2]^-$, were measured at atmospheric pressure and in the (298.15–363.15) K temperature range. The selected ILs comprise two types of cations: (i) a symmetric series of 1,3-dialkylimidazolium cations; and (ii) an asymmetric series of 1-alkyl-3-methylimidazolium-based ILs. The isobaric thermal expansion coefficient and the energy barrier of the water-saturated ILs investigated were also derived from the experimental density and viscosity data, respectively.

2. Experimental

2.1. Materials

The densities and viscosities of water-saturated ILs were measured for the following bis(trifluoromethylsulfonyl)imide-based compounds: 1,3-dialkylimidazolium, $[C_nC_nim][NTf_2]$ (with n = 1–8 and 10); and 1-alkyl-3-methylimidazolium, $[C_nC_1im][NTf_2]$ (with n = 2–5, 7, 9 and 11). The ILs investigated in this work are displayed in Table 1 and their chemical structures are depicted in Fig. 1. In general, two series of fluids were investigated: (i) ILs with symmetric alkyl side chains at the imidazolium cation; and (ii) a group of ILs with alkyl side chains of different length at the cation and where one aliphatic moiety is always a methyl group. All ILs were purchased from IoLiTec with mass fraction purities higher than 99%. To reduce the impurities, all ILs were dried and purified under vacuum (1 Pa) and at moderate temperature (353 K) for a minimum period of 48 h before the experimental measurements. The purity of each IL was further confirmed by us by ^{1}H, ^{13}C, and ^{19}F NMR. Ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus was used. It presented a resistivity of 18.2 MΩ cm, a TOC (total organic content) smaller than 5 μg dm^{-3} and was free of particles >0.22 μm.

2.2. Apparatus and procedure

Densities and viscosities measurements of water-saturated ILs (of the IL-rich phase) were carried out at atmospheric pressure and in the (298.15 and 363.15) K temperature range using an automated

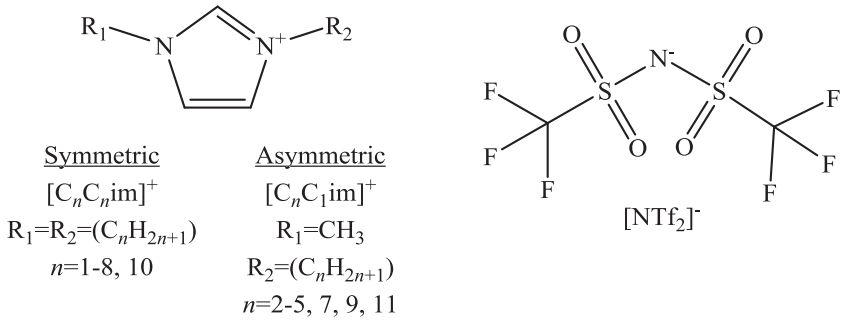

Fig. 1. Schematic representation of the chemical structure of the studied imidazolium-based ILs.

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