



Effect of the relative humidity and isomeric structure on the physical properties of pyridinium based-ionic liquids



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ABSTRACT

In this work, the effect of the relative humidity (water coming from the atmosphere and pure water) and isomeric structure on the physical properties of pyridinium-based ionic liquids (ILs) was studied. For that purpose, physical properties (density, speed of sound, refractive index and viscosity) of dried and hydrated ILs were measured as a function of temperature at atmospheric pressure. The hydration process was carried by two ways: (a) leaving the pure ILs for several days in open Petri dishes under controlled temperature and humidity conditions; and (b) experimental determination of the liquid–liquid equilibrium of binary mixtures {pure water + ionic liquid} at $T = 298.15$ K. From these data, the influence of the humidity coming from the atmosphere and pure water on the physical properties of ILs was studied. The density, speed of sound and refractive index data were properly fitted to a linear equation, while viscosity data were fitted to Vogel–Fulcher–Tamman (VFT) equation. Besides, these data were used to calculate the thermal expansion coefficient, the isentropic compressibility and the molar refraction. Moreover, the effect of the number and position of the alkyl substituents of the ionic liquid on the physical properties was also analyzed and discussed. Finally, a comparison with literature data reported for the studied ILs was also carried out.

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1. Introduction

Ionic liquids (ILs) are salts that are in liquid state at temperatures below to 100 °C, and which are obtained from a combination of big ions; generally, organic cations combined with organic or inorganic anions. The knowledge of their physical properties is required in order to apply these substances in future industrial applications. As instance, density and viscosity are very important from an engineering point of view. Both properties play a crucial role in stirring, mixing and pumping operations [1], being usually required for the design of processing units and to study heat and mass transfer processes. On the other hand, refractive index, although it is a less studied property, can be interpreted as a measure of the electronic polarizability of a molecule and provides interesting information about the intermolecular forces or the behavior of the molecules in solution. This property is also related to certain chemical properties despite providing a bulk property description [2]. Finally, from speed of sound data is possible to

calculate other derived properties such as the isentropic compressibility. Moreover, the knowledge of these properties is useful and needed to develop theoretical models, which are a powerful tool to predict the behavior of these pure compounds and their mixtures.

As was well documented [1–9], the presence of water dramatically modifies the physical properties of ILs. In general, density, viscosity and refractive index usually decrease with the water content because these properties for pure ILs are usually higher than those obtained for water. Furthermore; the presence of water may have a remarkable effect on the reactivity in many reactions in which ILs are used as media [2]. Nevertheless, the presence of water in ILs is not always a handicap; it can improve some physical properties such as viscosity (which decreases in water saturated-ILs, enhancing the flow and pumping in any industrial process) or increase the field of some chemical reaction such as Knoevenagel reaction [10].

Under normal conditions, high levels of moisture in the workplaces are common, while an inert atmosphere is not always feasible. Therefore, the knowledge of the physical properties of hydrated ILs must be also known in order to facilitate their use in future industrial processes.

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In this work, density, speed of sound, refractive index and viscosity of four pyridinium-based ILs with bis(trifluoromethylsulfonyl)imide, $[\text{NTf}_2]^-$, anion were experimentally measured from $T = (293.15 \text{ to } 343.15) \text{ K}$ and atmospheric pressure ($p = 1013 \text{ hPa}$). These physical properties were not determined at higher temperatures in order to avoid changes in the composition of the samples by water vaporization. According to Jacquemin *et al.* [1], below $T = 343 \text{ K}$, the vapor pressure of water is sufficiently low to consider this change in composition as negligible.

The ILs studied in this work were 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide, $[\text{Epy}][\text{NTf}_2]$, 1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide, $[\text{}^1\text{E}^2\text{Mpy}][\text{NTf}_2]$, 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, $[\text{}^1\text{E}^3\text{Mpy}][\text{NTf}_2]$, and 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide, $[\text{}^1\text{E}^4\text{Mpy}][\text{NTf}_2]$. This work was focused on pyridinium ILs because they are considered as more environmentally friendly, concerning their biodegradation ability, than imidazolium-based ILs. Moreover, the NTf_2^- anion is more stable in water than other anions such as tetrafluoroborate, $[\text{BF}_4]^-$, hexafluorophosphate, $[\text{PF}_6]^-$ or allylsulfate, $[\text{R-SO}_4]$, which show hydrolytic instability in presence of water under extreme conditions (high quantity of water and high temperature) [11–13]. Moreover, the selected ILs allow to assess the effect of the alkyl substituents of the cation (number and position) on the physical properties.

The above mentioned properties were determined for both dried and hydrated ILs. Temperature dependence of the viscosity data was correlated using the Vogel–Fulcher–Tamman (VFT) equation [14–16] while density, speed of sound and refractive index data were fitted to a linear equation. The physical properties obtained in this work for dried ILs were compared to those found in the literature for the same ILs [17–24].

As is well known, the presence of water in the air (relative humidity, RH) has a strong effect on the physical properties of the ILs; moreover, this behavior is observed for both hydrophobic and hydrophilic ILs. Nevertheless, to our knowledge, a systematic study concerning the effect of the relative humidity on the amount of water absorbed and, therefore, on the physical properties of the ILs, was not published up to now. In order to analyze the effect of the relative humidity (RH) on the physical properties, the ILs were hydrated following two different procedures: (a) exposing of the pure ILs into open Petri dishes at $T = 298.15 \text{ K}$ and under two different levels of relative humidity (60% RH and 80% RH); and (b) experimental determination of the liquid–liquid equilibrium (LLE) of binary mixtures {pure water + ionic liquid} at $T = 298.15 \text{ K}$ (which was assumed as 100% RH). Then, the physical properties of the hydrated ILs were measured from $T = (298.15 \text{ to } 343.15) \text{ K}$ and atmospheric pressure. From these data, the effect of the water coming from the air and pure water on the physical properties of ILs was compared and discussed.

Finally, the experimental LLE data for {water + ionic liquid} binary mixtures, measured at $T = 298.15 \text{ K}$, were used to analyze the effect of the number and position of the alkyl substituent of the cation on the solubility of water in the studied ILs.

2. Experimental section

2.1. Chemicals

All the ILs included in this study, whose structures are shown in figure 1, were supplied by IOLITEC (Germany) with a purity higher than 0.99. As one of the aims of this work is the experimental determination of the physical properties of the dried ILs, prior their use, each of them were dried under vacuum ($p = 0.2 \text{ Pa}$) and moderate temperature ($T = 343 \text{ K}$) for several days, until their density values were constant. Then, the dried ILs were stored in bottles under an inert gas within a glove box. The CAS number, purity, molar mass, M , water content, w_w , and halide content, w_{halide} , of the studied ILs are reported in table 1.

Milli-Q water (Millipore) was used in the experimental determination of the liquid–liquid equilibrium for the binary mixtures {water + ionic liquid}.

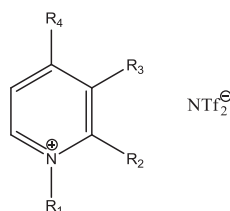
The cathodic and anodic tritrants used to determine the water content by KF Titration were Coulomat CG and Coulomat AG, respectively, and both were supplied by Sigma–Aldrich.

2.2. Material and methods

2.2.1. Physical properties

An Anton Paar DSA-5000M digital vibrating-tube densimeter was used to measure the densities and speeds of sound of both pure and hydrated ILs. This equipment determines the density and speed of sound of a sample ($f = 300 \text{ MHz}$) in one cycle and at the same sample conditions. An internal temperature controller keeps the samples at working temperature with an accuracy of $\pm 0.01 \text{ K}$. The uncertainties in the measurements of the density and the speed of sound were estimated to be within $\pm 3 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ and $\pm 0.3 \text{ m} \cdot \text{s}^{-1}$, respectively. More detailed information about this equipment can be found in a previous work [25].

Dynamic viscosities were measured using a microviscosimeter Lovis 2000/ME which is connected to the Anton Paar DSA-5000M densimeter with hoses, where both instruments are



R ₁	R ₂	R ₃	R ₄	Ionic liquid	Acronym
C ₂ H ₅	H	H	H	1-ethylpyridinium bis(trifluoromethylsulfonyl)imide	$[\text{Epy}][\text{NTf}_2]$
C ₂ H ₅	CH ₃	H	H	1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	$[\text{}^1\text{E}^2\text{Mpy}][\text{NTf}_2]$
C ₂ H ₅	H	CH ₃	H	1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	$[\text{}^1\text{E}^3\text{Mpy}][\text{NTf}_2]$
C ₂ H ₅	H	H	CH ₃	1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	$[\text{}^1\text{E}^4\text{Mpy}][\text{NTf}_2]$

FIGURE 1. Structures of the pyridinium based-ILs studied in this work.

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