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Quantification of the impact of water as an impurity on standard physico-chemical properties of ionic liquids

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The objective of this work was to quantify the effect of the presence of water as impurity in ionic liquids. First, density and viscosity of five ionic liquids as well as their aqueous solutions were measured. For hydrophobic dried ionic liquids, traces of water (50 ppm) have measurable impact neither on the density nor on the viscosity values. In the concentration range studied (up to 5000 ppm), a linear evolution of the molar volume of the mixture with the mole fraction composition is observed. Practically, this allows to estimate the density of an neat ionic liquid provided (i) the water quantity and (ii) the density of the undried sample are known. This is particularly useful for hydrophilic ionic liquids that are difficult to dry. In the studied concentration range, a linear evolution of the relative viscosity was also depicted as a function of the mass fraction composition. It is thus possible to evaluate the viscosity of the pure ionic liquid knowing the water quantity and the viscosity of the undried sample. The comparison of the results obtained using two viscosimeters confirms that a Stabinger viscosimeter is appropriate to precisely measure ionic liquids viscosities. Second, NMR and IR spectroscopies were used to characterize the pure ionic liquids and their solutions with water. The sensitivity of IR spectroscopy does allow neither the quantification nor the detection of water below 1 mol%. With NMR spectroscopy, water can be quantified using either the intensity or the chemical shift of the water proton peak for mole fractions as low as 200 ppm. It is even possible to detect water in the dried hydrophobic ionic liquids, few ppm of water, as long as the water peak does not overlap the ionic liquid signal.

1. Introduction

Ionic liquids are a family of promising liquids that find applications in processes and devices in various domains ranging from synthesis, catalysis, separation or electrochemistry. These salts, with melting points below 100 °C, are liquids over a broad range of temperature including ambient and have no measurable vapor pressure. A feature of these components is that some of them exhibit a nano-structuration with polar and apolar regions [1]. For example, in some imidazolium-based ionic liquids with sufficiently long alkyl chain on the cation, two kinds of domain are present, one formed by aggregates of the non-polar side chains, and the other by a three-dimensional network of the charged head groups. Some of their unusual properties, in particular their solvation properties, are the result of this peculiar molecular structuration [2,3].

One of the limitation when working with ionic liquids is to obtain these components with a high and known purity. Impurities are mainly coming from the synthesis: in most cases an alkylation followed by ion exchange then purification by solvent extraction and drying [4]. Typical impurities are unreacted components, solvents and halide ions. The most problematic are those that have high affinities with ionic liquids or high boiling points (imidazole, pyridine, halide ions). They cannot be correctly removed by liquid extraction or by treating the nonvolatile ionic liquids under vacuum [4]. Water is also a particular concern as ionic liquids are often hygroscopic and the absorption of the water present in air under normal conditions is not negligible [5,6]. For example, after only 20 min in contact with atmospheric air 1-butyl-3-methyl imidazolium trifluoromethanesulfonate, $[C_1C_4Im][TfO]$ will absorb more than 1% w/w of water [7]. To avoid such a contamination, a careful handling of the samples is necessary (work under dry atmosphere, in glove boxes, measurement of the water quantity before and after use) which is not always systematically done. After drying, a hydrophobic ionic liquid will typically contain

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50 ppm (mass) while an hydrophilic one could contain 1000 ppm (mass).

Impurities remaining in the samples have an impact on their particular molecular structuration and will strongly modify their physico-chemical properties even more than in usual organic solvents [8]. The most striking example is the viscosity that dramatically decreases with only traces of water [9]. For instance, the viscosity of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_1C_2Im][NTf_2]$ decreases by more than 30% with the addition of only 1.2% (in mass) of water [10]. As it changes its properties, the presence of impurities will also limit the application of the ionic liquid. For instance, modifications of the selectivity, yield or rate were observed for reactions in ionic liquid medium containing impurities [11,12]. Another example of the effect of impurities is the modification of the solvation in ionic liquids. Unlike usual organic solvents, some ionic liquids can efficiently dissolve cellulose, a potential renewable raw material for chemical industry. This is a promising application of ionic liquids. Nevertheless, the presence of small quantities of water can prevent the cellulose dissolution, water acting as an antisolvent [13,14].

Literature on ionic liquids often shows non reproducible values or important deviations between different sets of data for a number of properties, in particular viscosity and density. As an example, the viscosity of [C1C4Im][NTf2] was measured at $T = 298.15$ K and atmospheric pressure in dozen publications. The typical uncertainty of viscosity measurements cannot explain the observed standard deviation of this set of data (10% of the viscosity value). These discrepancies result mainly from (i) the purity of the samples, (ii) inappropriate measurement methods [15]. Analytical tools are available to quantify the typical impurities in ionic liquids [16] but practically they are often not implemented. Even though, the purity of the sample is frequently used as an argument to explain deviations higher than expected.

In 2009, because of the large discrepancies observed in literature, a IUPAC project was implemented to produce reference data on several physico-chemical properties for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[C_1C_6Im][NTf_2]$. At the same time, these data allow to estimate the expected deviations for the techniques used. In this work, the effect of the presence of water was also studied. From a comparison with literature data, the authors conclude that many of the observed deviations can be explained by water contamination. Diogo *et al.* [17] also highlighted the problem of ionic liquid purity and of water absorption when handling the samples, in the case of viscosity measurement.

A first work on the effect of impurities was proposed in 2000 by Seddon *et al.* [18] who reported the impact of the presence of water, chloride and organic solvents on some physico-chemical properties namely density, viscosity and NMR shifts of several ionic liquids. This work was a first attempt to illustrate the importance of the modification of physico-chemical properties due to the presence of impurities in ionic liquids. Since then, a lot of papers have been published on ionic liquid + water binary systems with the measurement of physico-chemical properties (viscosity, density, infrared or NMR spectra...) as a function of the composition [19–22]. In most cases, the ionic liquids chosen are fully miscible with water the objective being to investigate the whole concentration range. Only very few articles really focus on the characterization of the low water concentrations regions [4,10].

In this work, we choose to focus on the impact of low concentrations of water in ionic liquids and estimate the influence of these traces on some usual physico-chemical properties. Our objective is to help in discriminating between deviations from literature data that are due to sample purity and those due to the experimental technique. Second, the aim is to be able to estimate physico-chemical properties of a pure ionic liquid even if the available sample is contaminated with water provided its quantity is measured.

Densities and viscosities are commonly used to characterize ionic liquids and highly impacted by the presence of impurities. In the first part, these properties were experimentally determined on several samples containing traces of water, up to 10 mol% (this corresponding to the average quantity that can be absorbed by a hygroscopic ionic liquid in contact with air). In a second step, infrared and NMR spectroscopies of the same samples had been investigated in order to estimate the detection limits as well as the impact of water impurity on the spectra of ionic liquids.

In this study, five ionic liquids have been selected. On one side, we choose three ionic liquids with the common imidazolium cation 1-butyl-3-methylimidazolium (C_1C_4Im) and three different anions: bis(trifluoromethylsulfonyl)imide, NTf_2; tetrafluoroborate, BF_4; triflate, OTf. NTf_2-based ionic liquids are hydrophobic while the one with OTf and BF_4 anions are hydrophilic. On the other hand, three ionic liquids with the same anion (NTf_2) with three types of cations (imidazolium, methylpyridinium and tetraalkylammonium) were chosen.

2. Experimental methods

2.1. Chemicals and samples preparation

The ionic liquids were purchased from Iolitec with a minimum stated purity of 0.99. After treating them for 24 h under vacuum (circa 10^{-1} mbar), at room temperature (20 °C), they were considered as dried. Their purity was then checked by NMR and their water and chloride content measured by coulometric Karl-Fisher titration (Mettler Toledo DL31) and ion chromatography respectively. The five ionic liquids are given in table 1 together with their water and chloride contents after the purification step.

All the mixtures were prepared by weighing with an accuracy of ±0.1 mg. For each composition, a volume of (8 to 10) ml was prepared for all measurements at once. The vials were always nearly totally filled to minimize the vapor phase and thus an uncontrolled change in the liquid phase composition. The estimated uncertainty on the mole fraction composition is ±0.0002. The ionic liquids in which no water is added will be called "dry", it corresponds to a quantity of water around or below 50 ppm. Six concentrations were tested for each ionic liquid: dry, 0.5, 1.0, 2.0, 5.0 and 10.0 mol%. In the most water-concentrated solutions, water cannot be considered as an impurity but these mixtures are helpful to vizualise tendencies. The mixtures, once prepared, are kept under nitrogen atmosphere. The quantification of water was performed by Karl-Fisher titration on the prepared mixtures before and after the viscosity and density measurements. The water concentrations measured before and after the experiments are similar (within the precision of the analysis) and correspond to the concentrations calculated from the masses introduced, taking into account the water in the dry samples. The values presented in the results section are the ones obtained from the weights. Since several units for the concentration of water in ionic liquid can be found in the literature, examples of conversion between mole fraction (x_{water}), molar concentration (mol_{water}/kg) and mass fractions (ppm (mass)) are given in table 2.

2.2. Density

The liquid density, ρ, was measured using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 5000) according to a procedure previously described. [23] All the density measurements were performed at 298.15 ± 0.01 K. The sample kept in a bottle under inert atmosphere is introduced using a syringe avoiding