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Thermophysical properties of ionic liquids: Do we know how to measure them accurately?[☆]

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ABSTRACT

Low temperature ionic liquids (LTILs) are innovative fluids for chemical and materials processing, and the recent explosion on their measurement, molecular interpretations and property prediction, allied to the first industrial processes that start to use them as environmentally friendly solvents and reaction fluids, raises a very important point to all the scientific and industrial community, for those that have been involved in the measurement of thermophysical properties of liquids. A careful analysis, assessing its quality, shows that there are discrepancies between data from different laboratories, and sometimes, from samples of different synthesis batches. Therefore a fundamental question must be raised: Do we know enough about the molecular constitution and properties of these fluids, to measure correctly their properties? And if we think we know, which types of care have we to take a priori?

It is the purpose of this paper to analyze the main problems in the measurement of some thermophysical properties of RTILs (density, heat capacity; viscosity, thermal conductivity, and electrical conductivity), calling the attention to the uses and misuses of traditional equipment, with or without handling care.

1. Introduction

Low temperature ionic liquids (LTILs) are innovative fluids for chemical and materials processing, and the recent explosion on their measurement, molecular interpretations and property prediction, allied to the first industrial processes that start to use them as environmentally friendly solvents and reaction fluids, raises a very important point to all the scientific and industrial community, for those that have been involved in the measurement of thermophysical properties of liquids. A careful analysis, assessing its quality, shows that there are discrepancies between data from different laboratories, and sometimes, from samples of different synthesis batches. Therefore a fundamental question must be raised: Do we know enough about the molecular constitution and properties of these fluids, to measure correctly their properties? And if we think we know, which types of care have we to take a priori?

There are several characteristics that can affect the measurement of ionic liquids that will be analyzed in this paper as most of the properties, namely thermophysical properties like viscosity and thermal conductivity have been measured using other liquids approach. People usually have forgotten about the structure and properties of ionic liquids and their impact in methods of measurement (sample preparation and handling, mathematical modeling, chemical reactivity, and gas/liquid absorption). ILs have low to high viscosity, the ions are not mutual independent and can form aggregates, they are electrically conducting, cations and anions have completely different sizes, the reaction with atmospheric water or its solution in ILs is possible, and their heat capacity per unit volume is rather high.

The use of available instrumentation, without a careful consideration of ionic liquid properties, can therefore constitute a serious bad contribution to databases and process designers [1,2]. Our recent papers showed that the actual situation of measurement accuracy is not acceptable, and results for heat capacity of several ionic liquids can be as far as 20% off at room temperature, depending on the samples used, their reported (or not) handling care and their purity [3,4]. Additionally an IUPAC project on the thermophysical properties of one chosen fluid, produced a complete analysis on the determination of properties from the same batch of synthesized liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonylimide, $[C_6mim][NTf_2]$), making a critical evaluation and proposing reference values for heat capacities, density, vapor pressure, viscosity, electrolytic conductivity, speed of sound and relative permittivity [5,6]. When comparing data previously obtained by different authors and different methods, namely for viscosity, discrepancies at room temperature could easily reach 30% for $[C_6mim][NTf_2]$ [6]. Our own measurements of viscosity and electrical conductivity [7] showed that all the reported data for viscosity agreed within 3% in the temperature range of 290 to 370 K, while for electrical conductivity the deviations could be as big as 44% at 263 K. However, good agreement between measurements made in different laboratories can be achieved, if careful control of water (and purity) before and during the

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measurements, is maintained (2% for electrical conductivity and 0.5% for viscosity) and the quality of the samples used is similar. Therefore, any careful measurement of physico-chemical properties of ionic liquids must follow a strategy of control of purity of the samples before, and after the measurements, as well as a careful choice of experimental methods and procedures [1].

It is the purpose of this paper to analyze the state of art in the measurement of thermophysical properties of RTILs (density, heat capacity, viscosity, thermal conductivity, and electrical conductivity), analyzing the main problems that exist, calling the attention to the uses and misuses of traditional equipment, with or without handling care.

2. What can affect thermophysical property measurement

From the knowledge already obtained, several factors can affect the measurements, having a direct influence on the uncertainty of the data obtained. These factors can be divided in two main categories, one directly influenced by the structure and properties of ionic liquids, like the sample and its chemical reactivity/solubility power, and the other, directly dependent on the quality of the mathematical modeling of the instrumentation used (know how to measure!). Other problems like temperature and pressure ranges, although important in many regions of the phase diagram, can be tackled in the same way we use for molecular liquids, and therefore will not be discussed here. Also, some special properties like the paramagnetism of some ionic liquids will also not be discussed, although current research in this area is challenging and we hope to report about this in a near future [8].

2.1. Factors influenced by the structure and properties of ionic liquids

In the first place, if we want to measure properties, we have to use ionic liquids (ILs). Having a tremendous advantage for many applications as the almost non-existing volatility, they have properties that recommend the use of careful methodologies in sample preparation, sample handling and sample characterization, namely the guaranty of purity. The race to IL supported research in the last decade, namely up to 2007, shows the need for fast and multiple property data, patented in the number of publications and patents filed, that have grown exponentially up to 2008 [9]. However, the pressure to publish new data masked the difficulties in obtaining samples of high purity, and less care in the handling of those samples.

We shall considerer first the dissolution/reaction of environmental or synthesis water with the samples. Only around 2005 [10,11], Magee and coworkers could quantify the effect of the presence of water (a very small molecule, prone to hydrogen bonding in the liquid state), in the viscosity and electrical conductivity of some ionic liquids, although it was known before the effect qualitatively. They have prepared water-free[1] samples and water doped mixtures, with ppm concentrations up to 1.5%. Their results demonstrated that, for [C_6mim][NTf_2], the addition of 1% (mass) water decreases the kinematic viscosity by 47%, while the same addition of water would increase the electrical conductivity by 45% [11]. Similar results were obtained for viscosity of [C_2mim][NTf_2], [C_4mim][NTf_2], although the effect is bigger for [C_4mim][PF_6] (0.2% of water cause a decrease in viscosity of 17%, a sensitivity coefficient two times bigger). These results were confirmed in our laboratory and used to correct for the presence of about 200 ppm in the samples used to obtain water free values of viscosity and electrical conductivity [2,7].

Is there any molecular explanation for this effect being so big, much bigger than in any molecular liquid of similar relative molecular mass? Computational determination of molecular structures in *ab initio* calculations has the advantage of showing the molecular geometry and, more importantly, of showing the charge distribution across molecular structures. This additional information makes polarity for the first time visible and thus facilitates the understanding of the role of electrostatic forces in intermolecular interactions ranging from weak attractions to hydrogen bonds, associations and ionic bonds. Fig. 1 helps us to visualize the molecular sizes, shapes, and charge distributions in [C_4mim][PF_6], which demonstrate the difference in size for the positively charged "anion" (top image) and the negatively charged "cation" (bottom left) that combine to ionic liquid. It is a mystery how the much smaller water molecule (right) can have such a large effect on the viscosity of such ionic liquids. Similarly, and discussing only the pure ionic liquids, Weingärtner [12] says "because it is impossible to experimentally investigate even a small fraction of the potential cation–anion combinations, a molecular-based understanding of their properties is crucial. However, the unusual complexity of their intermolecular interactions renders molecular-based interpretations difficult, and gives rise to many controversies, speculations, and even myths about the properties that ILs allegedly possesses".

However, after obtaining your sample free of water, it is also necessary to monitor the increase in water content during sample handling, measuring cell filling and during the measurements. The sample must avoid contact with air (that contains moisture) as many ionic liquids are hygroscopic, and suggestions have been made to use glove chambers or dry nitrogen blankets above the IL. Actually the water content increased during our measurements (from 119.3 to 196.4 ppm) of viscosity of [C_6mim][NTf_2], while further care in all the operations necessary for the measurement of electrical conductivity, like good dying of the electrolytic cell, lead to variations from 21 to 41 ppm [7].

Characterization of ionic liquids is extremely important, not only because of possible presence of water, but also of other compounds, namely ions that are present from the chemical synthesis used to produce the compounds. In our recent paper [4] we have described the care that has to be taken to characterize several ionic liquids, using accepted methods described in the literature. After the synthesis all the ionic liquids were allowed to stay several days in high vacuum ($P \approx 1$ mbar) to remove any excess organic solvents. The ionic liquids were characterized using NMR spectroscopy, elemental analysis, mass spectrometry with electrospray ionization source (ESI), the chloride ion content determined by ion chromatography and the water content by coulometric Karl-Fisher titration. This type of procedure involves a panoply of analytical instrumentation not available in most

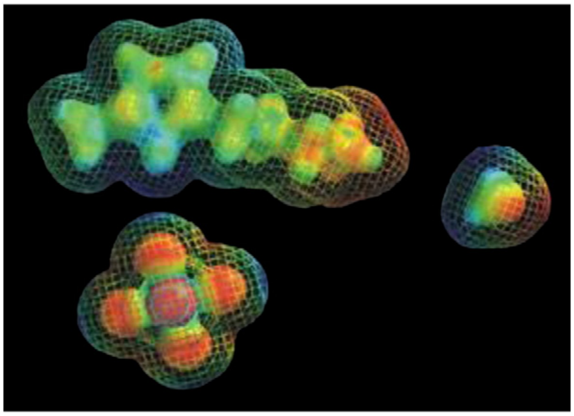

Fig. 1. Comparison of molecular size, shape, and charge distribution of ionic liquid 1-n-butyl-3-methylimidazolium [C4mim]$^+$, hexafluorophosphate [PF6]$^-$, and water. The electrostatic potential is color-mapped onto electron density isosurfaces at the level of 0.002 electrons au^{-3} (outer mesh) and 0.08 electrons au^{-3} with 1 atomic unit (au) = 5.292 nm being the Bohr radius of hydrogen. The meshed surface represents approximately 99% of each molecule. The solid inner surface is intended to indicate the core of a molecule. The color scale ranges from red (negative charge) to blue (positive charge).
Image courtesy of Dr. Arno Laesecke, NIST, Boulder, Colorado, USA, based on equilibrium geometry calculations in the Hartree-Fock approximation with 6-31G* basis sets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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[1] In fact the water content was smaller than 10 ppm.