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

C.A. Nieto de Castro *

Departamento de Química e Bioquímica e Centro de Ciências Moleculares e Materiais, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

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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.

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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$_6$mim][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$_6$mim][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
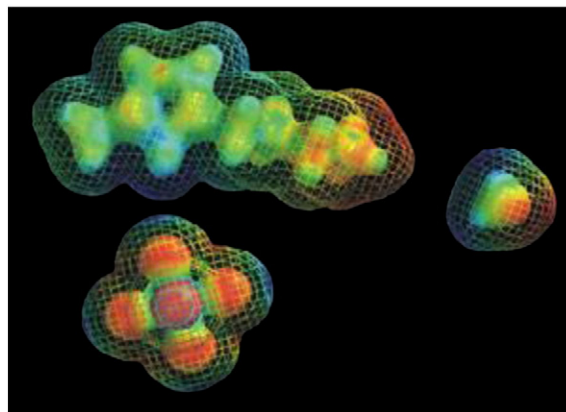

Fig. 1. Comparison of molecular size, shape, and charge distribution of ionic liquid 1-n-butyl-3-methylimidazolium $[C4mim]^+$, hexafluorophosphate $[PF6]^-$, and water. The electrostatic potential is color-mapped onto electron density isosurfaces at the level of 0.002 electrons au^{-3} (outer mesh) 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.

departments. In addition the "true" composition and structure of some of the cations is sometimes not well defined. As an example we cite the cation usually referred as [aliquat]. The designation *Aliquat* refers not to a pure cation, methyltrioctylammonium dicianamide, but to a complex mixture of cations, where three of the alkyl chains have different number of carbon atoms. Following the work that inspired the synthesis performed in this work [13], the precursor used is Aliquat 336®, referred to as 2:1 mixture of methyl trioctyl- and methyl tridecylammonium cations, with an average molecular weight of 396.55 g mol⁻¹. The characterization of this compound by mass spectrometry, was performed at my department, and the results are reported in the Supplementary Information (SI) of reference [4]. However, the MS data have shown that the sample contains a five-component mixture of methyl(n-hexyl)di(n-octyl)ammonium (0.8%), methyltri(n-octyl)am-monium (29.8%), methyldi(n-octyl)decylammonium (43.6%), methyl (n-octyl)di(n-decyl)ammonium (21.9%), and methyltri(n-decyl)am-monium (3.8%), a result that agrees qualitatively with previous publications, in 1981 (GC) and 1998 (ESMS) [14,15]. This corresponds to an average molecular weight of the cation of 396.04 g mol⁻¹, a value which is very close to the value reported in reference [13]. Nonetheless it expresses a markedly different chemical and thermodynamic reality, which can affect several thermophysical properties. Although in the literature the designation [aliquat] appears for different cations, we recommend to designate our compound as [Aliquat 336®-derived][dca] or [*Aliquat*][dca] as a short name.

Other factors are known to affect the determination of experimental values, not strictly dependent of the instrumental methods used. They are their chemical reactivity (important in designing measuring cells, as the material compatibility with seals, gaskets and metals is very important), the fact that anions and cations can be very different in size and most of the existing information, having been obtained for imidazolium cations, is difficult to generalize, ions are not mutual independent, and can form aggregates and complicate structures in the liquid phase. In addition the viscosity is moderate to high, the liquids are electrical conducting and the heat capacity per unit volume is rather high. All these factors condition heat and mass transfer in the transport properties determination and must be known "a priori" to avoid systematic errors.

2.2. Instrumentation problems

Thermophysical properties cannot be obtained without instruments. Measurement of the thermophysical properties (thermodynamic and especially transport) is done in many laboratories, not always with the best qualification for the method of measurement and procedure to be used. The use of available instrumentation in a laboratory, without a careful consideration of ionic liquid properties, can constitute a serious bad contribution to databases and process designers.

It is completely out of scope of this paper to make any comprehensive discussion about the best existing methods for measuring this properties, and some work has been presented before [1] for viscosity, thermal conductivity (thermal diffusivity), electrical conductivity, electrical permittivity and diffusion coefficients. This work suggested the best experimental methods, their classification as primary and secondary, or absolute and relative, the actual attainable accuracy and their adaptability to ILs, namely low-temperature. From a similar analysis to that presented before [1] it can be concluded that:

a) For viscosity, for which a recent review discusses its metrological importance [16], we have recommended the use of quasi-primary instruments,² such as the oscillating body (disk, cup, cylinder, and

sphere) and the vibrating wire for high quality work (these viscometers are expensive, as they need a very accurate body machining, and should be used mostly for measuring the viscosity of well chosen reference liquids), and surface light scattering spectroscopy methods, and capillary flow viscometers for current laboratory work. In this last case, the users must be aware of all the problems about calibrating liquids and traceability chain to SI units. This is a property that has been extensively measured for the ionic liquids, and the feeling about the actual situation can be seen in Fig. 2. Here we have plotted the viscosity of one of the ionic liquids with more available data, [C₄mim][BF₄], between 270 and 360 K, taken from 14 authors form ILThermo Database [17,18–30]. The agreement between the different sets of data, published between 2000 and 2008, is highly distressing, for a property that the scientific community thinks that can be measured with uncertainties of 2% or better. At room temperature there discrepancies of the order of 120%, and if we select data, with current selection criteria, namely those used by IUPAC to establish standard reference data [6,31], deviations can amount to 20%. The situation at lower temperatures, where the number of data sets is smaller, is qualitatively the same.

b) For thermal conductivity the situation is not very different. However, as the thermal conductivity of ionic liquids is less dependent of impurities, the major errors came from the measuring errors, namely from the inadequacy of the experimental methods. From the methods discussed in [1], only the transient hot wire can be considered a primary instrumentation, but with cells adapted for electrically conducting liquids, namely those used before for polar solvents like chlorobenzene and fluoroethanes, water, electrolyte solutions and molten salts. In these applications, the wire was electrically insulated from the conducting media, either by using an electrically insulating film coating or by DC polarization against the cell wall. There are not yet many determinations of the thermal conductivity of ionic liquids and all have been done with transient hot-wire probes [3,32,33], with claimed uncertainties between 2 and 5%. Fig. 3 shows the deviations between our data and those obtained by these authors, for several ionic liquids, for which the amount of water was similar (less than 100 ppm). Although the deviations are within the mutual uncertainty of the measurements (6%), Tomida et al. data was obtained with bare platinum wires. Ge et al. data are more or less systematic (+4–6%) and can be attribute to deficient probe
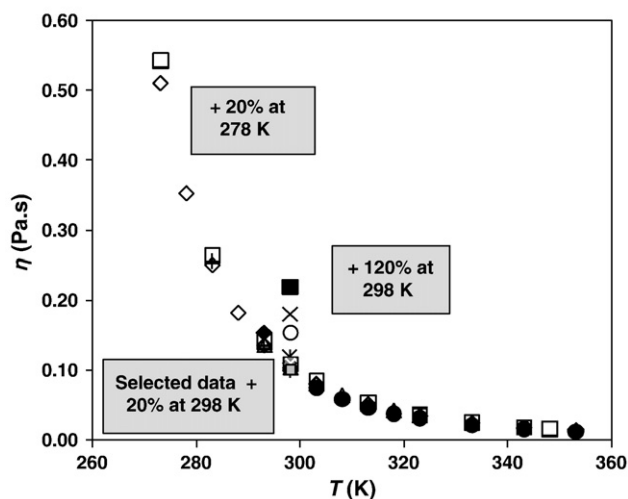

Fig. 2. Viscosity of [C₄mim][BF₄] as a function of temperature. Data from ILThermo [17]. ♦–Seddon et al. [18]; ■–Huddleston et al. [19]; ▲–Wang et al. [20]; ✕–Nishida et al. [21]; ✖–Van Valkenburg et al. [22]; ●–Zhou et al. [23]; +–Tokuda et al. [24]; ○–Liu et al. [25]; ▭–Tomida et al. [26]; ◇–Harris et al. [27], S1; □–Harris et al. [27], S2; △–Sanmamed et al. [28]; ▨–Tian et al. [29]; ▣–Malham et al. [30].
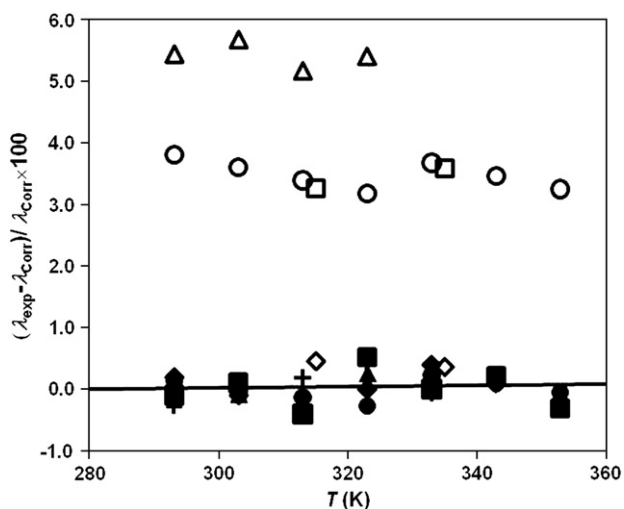
Fig. 3. Deviations of the thermal conductivity of several ionic liquids from de Castro et al. correlation [3], as a function of temperature. ●—[C6mim][BF4] [3]; +—[C4mim][CF3SO3] [3]; ▲—[C4mpyrr][(CF3SO2)2 N] [3]; ♦—[C4mim][PF6] [3]; ■—[C6mim][PF6] [3]; △—[C4mpyrr] [(CF3SO2)2 N], [19]; ○—[C4mim][CF3SO3], [19]; ◇ —[C4mim][PF6] [20]; □—[C6mim][PF6], [20].
Adapted from [3].

Fig. 4. Existing values of the heat capacity for [C4mim][BF4] as a function of temperature. ●—de Castro et al. [3]; △—Van Valkenburg et al. [25]; ○—Rebelo et al. [26]; □—Kim et al.[27]; ♦—Fredlake et al. [28]; +—Waliszewski et al. [29]; ✳—Garcia-Miaja et al. [30]; ▲—Garcia-Miaja et al. [31].

insulation (electrical current leakage) or to the presence of small levels of water or halides, which are common impurities from the synthesis of ionic liquids, and both increase the thermal conductivity of ionic liquids. Current measurements in our laboratory will explain the reason for these discrepancies, as the instrument used in the measurement was the same [3].

c) For density measurements the agreement is also distressing for several liquids, were deviations up to 3% can be found, especially at high pressures. An example is the density of [C6mim][Cl], a common precursor of many ionic liquids containing the some cation, but different anions, at 298.15 K. Three data sets were encountered, two obtained with vibrating tube instruments (relative) [34,35] and on by pycnometry [19], all relative measurements. This compound has a density very close to water (about 1040 kg m⁻³), but the uncertainty of the measurements obtained with a digital vibrating densimeter (Anton Paar DSA-5000) assigned by ILThermo is about 2–3% and by pycnometry about 10%. This assignment is done following the rules described by Chirico et al. [36], based on authors information on the experimental methods and procedures. Although the difference between the reported values is less than 1%, it is known than any of the methods can be used with a much better uncertainty, as shown in [6].

d) For heat capacities of the liquid phase the situation is not different. Fig. 4 shows the heat capacity of [C4mim][BF4], obtained using DSC [22,37–42]. A wide variation between the datasets of up to 20% at room temperature is observed. This situation is very uncommon in calorimetry; however it is known that, apart from differences in sample purity, the DSC used must be well calibrated and this may explain the scatter of data. However, it can be seen [3] that 5 sets of data agree within 2%, within their mutual uncertainties [3,22,37,41,42], a result that might be considered excellent for DSC data, the most popular measuring method, due to its speed and excellent repeatability.

e) For electrical conductivity the problem has two major components, namely the experimental methods and the lack of data. Electrical conductivity (also referred to as electrolytic conductivity) is a measure of a material's ability to conduct an electric current, usually used as an indicator of the material's purity. The state of the art primary measurement method uses cells, of parallel or concentric electrodes with variable spacing, which inhibits electrolytic conduction paths other than the direct way between electrodes, and allows
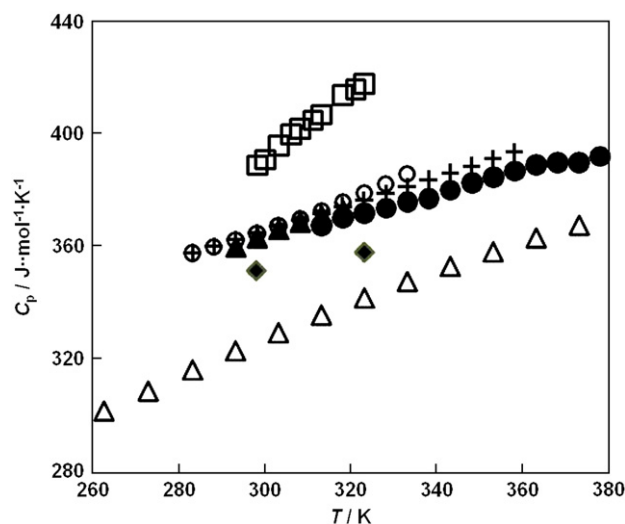
the compensation of fringe effects. Cell materials are currently shifting from the classic pair of glass and platinum to ceramic and platinum thin films on ceramic. Routine measurements (temperatures between 0 °C and 100 °C at atmospheric pressure) still use standard platinum electrodes, and primary measurements are usually done at the metrological institutes. Electrical measurements are done with AC meters or bridges at frequencies of at least 250 Hz, usual values being 1 kHz or 10 kHz. Primary measurements can use several techniques to avoid polarization phenomena at the surface of the electrodes, and measurements must be done as a function of frequency and extrapolated to infinite frequency [1,7], while routine work (end user measurements) will just use the values measured at the standard frequency of the measuring instrument, after having calibrated the measurement cell with secondary reference solutions of electrolytic conductivity [43,44]. As an example, the electrical conductivity of [C2mim][BF4], obtained by different authors is displayed in Fig. 5, for four sets of data [21,44–47], around room temperature. The uncertainties allocated by ILThermo database [17] are, respectively, 2.9%, 9.8%, 20% and 1%. The agreement between the sets of data is worse than 20% at 298.15 K. The data kept in the database shows 34 references and, with viscosity and density, electrical conductivity is one of the most popular properties to measure, although, as explained before for other properties, a careful analysis of the method used and data analysis is strongly recommended, if we want to draw theoretical conclusions on models and structure of ionic liquids. In fact the existing practice, established to deal with the more common ions mostly inorganic and usually small, is suitable to deal with most HTILs but no real experience exists in dealing with the very large ions present in LTILs and the expectable low ionic mobility, that might allow the use of lower measurement frequencies without the occurrence of polarization effects.

Therefore, the method chosen, the cells design and the atmosphere control are fundamental for good quality measurements, in addition to the above mention care on sampling, handling and characterizing. Authors must take care in using instrumentation available "in house" or "in market" that were not developed for ionic liquids systems and that can produce data of bad quality. A good balance between expensive and accurate equipment and cheaper and reliable one, fit for purpose, is therefore a challenge to all users in ionic liquids field.
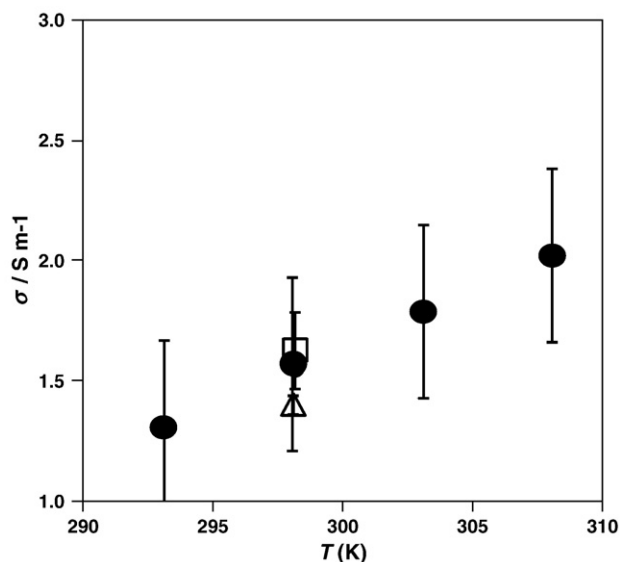
Fig. 5. Electrical conductivity of [C₂mim][BF₄] as a function of temperature. △—Nishida et al. [34]; □—Villa et al. [35]; ●—Villa et al. [36]; ○—Stoppa et al. [37]. Error bars correspond to the assigned accuracy by ILThermo [17].

3. Making good measurements

As mentioned before we think that we can measure the properties of ionic liquids with the same level of accuracy as the molecular liquids, if care is taken in the instrumentation used and in measuring procedures and data analysis. In this section we will demonstrate how well we can measure these properties, to the best level of accuracy attainable.

3.1. Viscosity and electrical conductivity of [C₆mim][NTf₂]

As mentioned in previous section this ionic liquid was chosen as the reference fluid in the IUPAC project 2002-005-1-100 [48] and the conclusions were reported in references [5,6], while our own measurements are shown on reference [7]. The first decision was to produce batches of the liquid, synthesized through the best known synthetic procedure [11], characterized in the origin, and sent to all the participant laboratories, characterized on arrival/measurement initiation and after the measurements, especially on the water content, as this liquid is hygroscopic. The original sample was demonstrated to have a mole
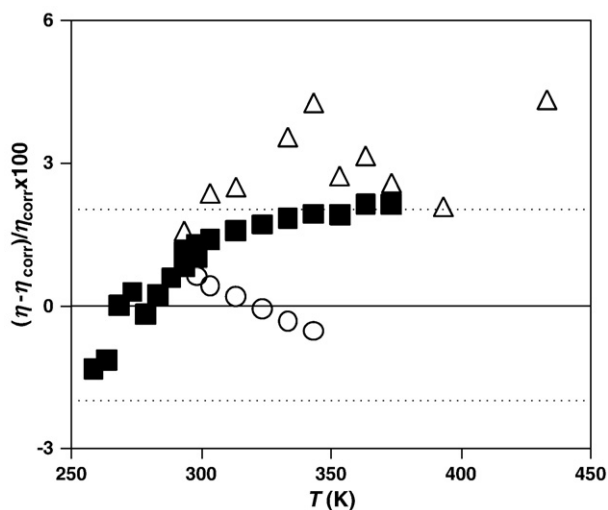

Fig. 6. Deviations of the viscosity of [C₆mim][NTf₂] from the correlation given by Eq. (1). ○—Santos et al. [7]; ■—Widegren and Magee [11]; ♦—Kandill et al. [39].

fraction greater than 0.995 (0.9974 by fractional melting with adiabatic calorimetry) and a water mass fraction less than 10 ppm [6].

The viscosity measurements were taken with vibrating wire viscometer (2% uncertainty) [49], a Stabinger viscometer (rotating concentric cylinder device) (2% uncertainty) [11], a Ubbelohde capillary viscometer (1% uncertainty) [11] and a Ostwald viscometer (0.5% uncertainty) [7]. These data can be considered primary, in the sense of IUPAC standards [31] and were fitted by Chirico et al. [6] to a quadratic equation in powers of temperature:

$$\ln\left(\frac{\eta}{\eta_0}\right) = -13.391 + 6721.88(T/K)^{-1} - 2.24584 \cdot 10^6 (T/K)^{-2} \quad (1)$$
$$+ 3.70841 \cdot 10^8 (T/K)^{-3}$$

where $\eta_0 = 1$ Pa s, for $258 < (T/K) < 433$. Fig. 6 shows the deviations between this correlation and all the data, corrected to water free values by using the equations presented in [10]. It can be seen that, the data of Widegreen and Magee [11] and that of our laboratory [7] agree within ± 1.5%, the agreement being of the order of 0.3% at 298.15 K. The data of Kandill et al. [49] deviates from the correlation given by Eq. (1) by more than 2% above 303 K, the error increasing to 4% at higher temperatures. We must note that the recommended value in the IUPAC project for the viscosity of [C₆mim][NTf₂] at 298.15 K is 69.4 ± 1.4 mPa s, while the value found using only the data of referenced [8,11] is slightly higher (water free values, less than 10 ppm), 70.07 ± 0.23 mPa s. From this analysis we can conclude that capillary viscometry is still an excellent method for liquid viscosity determination, but some of the discrepancies found can probably be solved using "quasi-primary" instruments, as explained in reference [16].

The electrical conductivity of [C₆mim][NTf₂] was measured by Kandill et al. [49] with an impedance bridge, between 0.5 and 10 kHz, and the results were extrapolated for infinite frequency, with an estimated uncertainty of 2%. The water content in the samples was not determined. Widegreen et al. [11,50] used an ac impedance bridge technique, with a commercial conductivity cell and the results were also extrapolated for infinite frequency, with an estimated uncertainty of 2%. Measurements were made as a function of water content. Santos et al. [7] used an impedance analyzer, the capacitance and conductance of the cell measured as a function of frequency between 20 Hz and 300 kHz and the infinite values at infinite frequency of capacitance and conductance C_∞ and G_∞ were obtained by plotting those values for frequencies between 600 Hz and 20 kHz as a function of $f^{-1/2}$ and extrapolating to zero. The cell constant is described in the paper, and its cell constant was determined from the G_∞ values with a standard solution (0.01 mol/kg of solution). The uncertainty of the data was estimated to be 0.5%. The values obtained were corrected to water free values [10]. From the data sets published previously, the IUPAC project report [6] used only the data sets of reference [47,49,50] to propose a correlation for the dependence of the electrical conductivity on temperature. We have recently reanalyzed the problem with our data included and we have obtained Eq. (2):

$$\kappa\left(S \cdot m^{-1}\right) = 1.3598 \cdot 10^{-4}(T/K)^2 - 7.1208 \cdot 10^{-2}(T/K) + 9.3599 \quad (2)$$

with a RMS deviation of 0.8%, for $278.15 < T < 333.15$. Fig. 7 shows the deviations of the four sets of data from Eq. (2) and it can be seen that all the measurements made using the IUPAC sample are in close agreement within their mutual uncertainties for all temperatures, in a much better case than for viscosity. The value of the electrical conductivity at 298.15 K is 0.2173 ± 0.0068 S m⁻¹, a value that agrees very well with the IUPAC study, 0.2167 ± 0.0043 S m⁻¹. This agreement suggest that standard reference values for the electrical conductivity of [C₆mim][NTf₂] can be proposed in a near future.
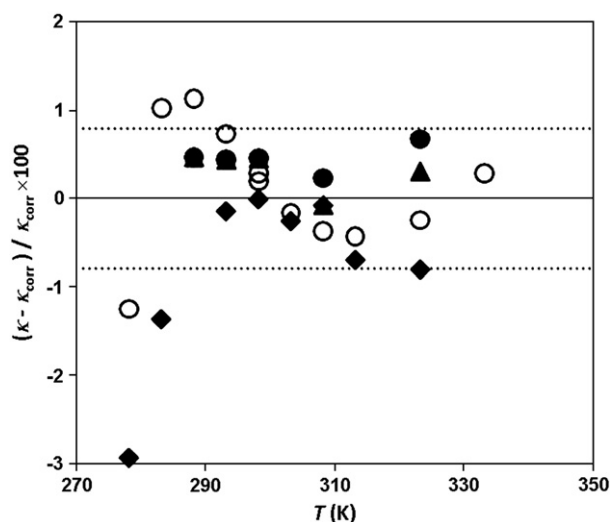
Fig. 7. Deviations of the electrical conductivity of [C6mim][NTf2] from the correlation given by Eq. (2). ○—Santos et al. [7]; ▲—Widegren et al. [10]; ●—Widegren and Magee [11]; △—Kandill et al. [39].

Fig. 8. Deviations of the density at atmospheric pressure of [C4mim][dca] from Eq. (3). ○—de Castro et al. [4]; ◇—Stoppa et al. [37]; ●—Fredlake et al. [41].

3.2. Density of [C4mim][dca]

[C4mim][dca], 1-n-butyl-3-methyl-imidazolium dicyanamide, is an ionic liquid that bridges the gap between different ionic liquid generations, and being a new liquid it has only a few measurements published. In the case of density at atmospheric pressure there are only 3 data sets available, one set using pycnometry [39], and two using vibrating tube densimetry. Both are relative methods that need calibration with reference fluids [4,47]. Our data can be expressed by Eq. (3):

$$\ln\left(\rho / kg\cdot m^{-3}\right) = 7.1587 - 6.8939\cdot 10^{-4}(T/K) + 1.5030\cdot 10^{-7}(T/K)^2 \quad (3)$$

with a RMS of 5.79×10^{-6} kg m^{-3}, for $293.15 < T < 363.15$ K. Fig. 8 shows the deviations of the three data sets from our correlation [4] and it can be seen that no data point departs from it by more than 0.3%, with our data not departing more than 2 parts in 10^5. We can conclude that the methods were used very well and that, even for the sample measured in 2004, where the deviations have an s-shape, it can easily attributed top some purity problems. This fact is totally different from the case reported in Section 2.2 for [C6mim][Cl]. Recent advances in vibrating tube densimetry, show that this method, if a careful choice of calibrants and a correct application of the method equations is done, it will be transformed in a reference method (although secondary) for density measurements in wide ranges of temperature and pressure [51].

3.3. Heat capacity of [C2mim][EtSO4]

[C2mim][EtSO4], 1-ethyl-3-methyl-imidazolium ethylsulphate, is an archetypal stable ionic liquid, for which there is a tremendous number of data points available for many thermophysical properties, and heat capacity at constant pressure is not different. Eight data sets were found in ILThermo database, and two more, yet in press. From these we have selected, after the analysis presented in reference [4], seven references, which we consider with better accuracy, obtained adiabatic calorimetry [52,53] and DSC [4,41,42,54,55]. Our data [4] can be reproduced by Eq. (4):

$$C_P\left(J\cdot mol^{-1}\cdot K^{-1}\right) = 107.40 + 1.3099(T/K) - 1.2339\cdot 10^{-3}(T/K)^2 \quad (4)$$

with a RMS of 0.5206 J mol^{-1} K^{-1} or 0.13%, for $308.16 < T < 358.25$. Fig. 9 shows the deviations of the seven data sets from our correlation [4] and it can be seen that no data point departs from
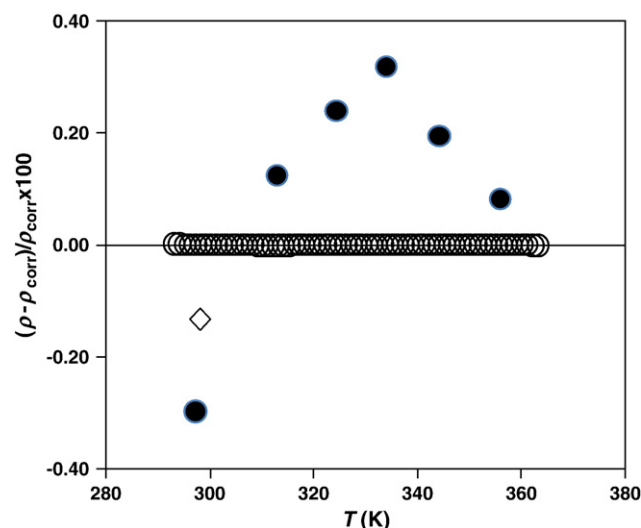
it by more than 3%, with our data not departing more than 0.8%. In reality the data obtained by DSC is bound to have a minimum uncertainty of 1.5% if the calorimeter is well calibrated, around 3–5% in routine applications. Adiabatic calorimetry is more accurate, but it depends on the care taken in using the instrumentation, and the accuracy can be of the order of 0.4% [53] or 1.5% [52]. Our data agrees very well with the adiabatic calorimetry data of Paulechka et al. [53], and within their mutual uncertainty with DSC Garcia-Miaja et al. [41,42] data to within 1.6%, Ge et al. data [55] to within 0.7% up to 320 K, increasing up to 6.8% at 360 K. Greater deviations are found with Ficke et al. [54] data (2–3% lower), and with the adiabatic calorimetry data of Zhang et al. [52], 3.6% lower at 310 K, but deviates up to 6.4% at 360 K. This type of agreement can be found for other ionic liquids, which proves, that currently we can trust all heat capacity data that is obtained using the primary techniques like pure adiabatic calorimetry, and those obtained with DSC that are correctly calibrated, especially in enthalpy by Joule effect (see discussion in [3]), that can provide accuracies of the order of 1.5%.

4. Conclusions

The current state of the measurement of thermophysical properties of ionic liquids is far from being comparable to those actually found for molecular liquids [1]. The situation is a bit equivalent to that found for these liquids three decades ago, when the contribution of electronics and data storage and acquisition increased the instrumental capabilities by orders of magnitude in repeatability and reproducibility of the measurements. However, as we have tried to show in this paper, the situation in the ionic liquids thermophysical property measurement is still far from what can be achieved, but only if the sample handling and characterization and measurement procedure are dealt with professional level. I believe that we can obtain most of the properties of the ionic liquids with the same level of accuracy now found for molecular liquids. However, all those end users of instrumentation have to interiorize that the "game" is different, that the structure and properties of ionic liquids (including high temperature ionic liquids or molten salts) are just different and this fact is still not accommodated in many commercial instruments.

Many years ago, an international team working under the auspices of IUPAC, and charged with the task of proposing reference data for the thermal conductivity of (normal) liquids [56] "discovered" that the thermal conductivity of liquid toluene had a new dependence, not on a state variable, but on time (see Fig. 1 of [56]), between 1900 and 1980. This was of course explained not only in the electronic quality of the
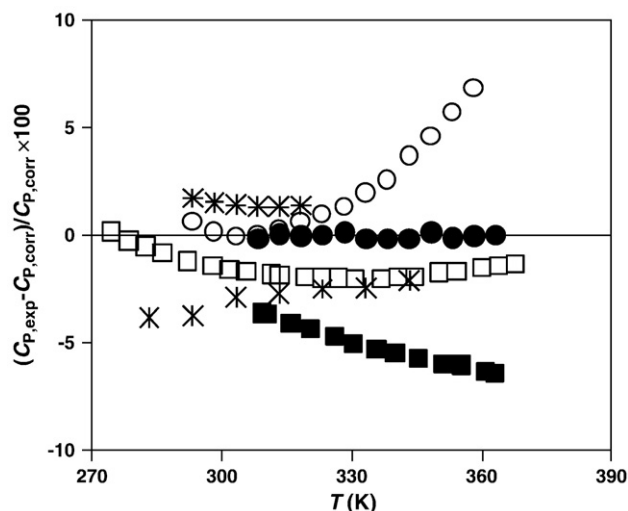
Fig. 9. Deviations of the heat capacity of [C₂mim][EtSO₄] from Eq. (4). ●—de Castro et al. [4]; ○—Ge et al. [19]; +—Garcia-Miaja et al. [30,31]; ■—Zang et al. [43]; □—Paulechka et al. [44]; ✳—Ficke et al. [45].

measurements, but on the existence of additional ways of heat transfer (convection and radiation) simultaneous with the thermal conduction, only started to resolve around 1950 and further improved by the development of the transient hot-wire in the 70s and 80s. However at that time, polar liquids and electrically conducting liquids were not a problem for the thermophysicists, because they never thought that the molecular constitution of the liquids could affect the measurements. Fortunately the problem was resolved and now this technique is a primary technique, capable of measuring thermal conductivity of all type of liquids with uncertainties better than 1%, for state of art instruments, and 2–5% for commercial equipments [3,56–62]. Instead of publishing data without resolving the additional problem posed by the instrumentation and/or the samples, those involved in this evolution (and also on viscosity) decided to develop the correct mathematical modeling of the instrumentation, eliminate or at least minimize additional effects (like convection, radiation, polarity, electrical conduction from the metal wires to the liquids, etc.), quantifying them whenever possible.

I would like to strongly recommend to all those that want to measure thermophysical properties of ionic liquids to measure them well, because the errors in their measurement can produce a tremendous effect on the upcoming design of heat and mass transfer equipments for chemical and energy plants, as demonstrated by the work of França et al. [63]. This attitude will pave the way for the correct development of alternatives today in all important fields for economic development and sustainability. And ionic liquids can be key chemicals for the future.

Acknowledgements

References

[1] M.B. Nunes, M.J.V. Lourenço, F.J.V. Santos, M.M.S. Matos Lopes, C.A.N. de Castro, Accurate measurements of physico-chemical properties on ionic liquids and molten salts, in: K.E. Seddon, M. Gaune-Escard (Eds.), Ionic Liquids and Molten Salts: Never the Twain, John Wiley, 2010, ISBN: 978-0-471-77392-4.
[2] C.A.N. de Castro, F.J.V. Santos, Chimica Oggi/Chemistry Today 25 (6) (2007) 20–23.
[3] C.A.N. de Castro, M.J.V. Lourenço, A.P.C. Ribeiro, E. Langa, S.I.V. Vieira, P. Goodrich, C. Hardacre, J. Chem. Eng. Data 55 (2010) 653–661.
[4] C.A.N. de Castro, E. Langa, A.L. Morais, M.L.M. Lopes, M.J.V. Lourenço, F.J.V. Santos, M.S.C.C.S. Santos, J.N. Canongia Lopes, H.M. Veiga, M. Macatrão, J.M.S.S. Esperança, L.P.N. Rebelo, C.S. Marques, C.A.M. Afonso, Fluid Phase Eq. 294 (2010) 157–179.
[5] K.N. Marsh, J.F. Brennecke, R.D. Chirico, M. Frenkel, A. Heintz, J.W. Magee, C.J. Peters, L.P.N. Rebelo, K.R. Seddon, Pure and Appl. Chem. 81 (2009) 781–790.
[6] R.D. Chirico, V. Diky, J.W. Magee, M. Frenkel, K.N. Marsh, Pure and Appl. Chem. 81 (2009) 791–828.
[7] F.J.V. Santos, C.A.N. de Castro, P.J.F. Mota, A.P.C. Ribeiro, Electrical conductivity and viscosity of 1-hexyl-3-methylimidazolium bis(trifluorosulfonyl)imide, [C₆mim][(CF₃SO₂)₂N] (CAS-RN# 382150-50-7). Int. J. Thermophys. (2009) doi: 10.1007/s10765-009-0584-4, published on-line 08-05-2009.
[8] M.M. Cruz, R.P. Borges, M. Godinho, M.J.V. Lourenço, C.A.N. de Castro, J.M.S.S. Esperança, J.N. Canongia Lopes, L.P.N. Rebelo, Magnetic properties of ionic liquids, JEMS 2010, Joint European Magnetic Symposia, Kraków, Poland, August 23 - 28, 2010.
[9] N.V. Plechkova, K.R. Seddon, Chem. Soc. Rev. 37 (2008) 123–150.
[10] J.A. Widegren, A. Laesecke, J.W. Magee, Chem. Comm. (2005) 1610–1612.
[11] J.A. Widegren, J.W. Magee, J. Chem. Eng. Data 52 (2007) 2331–2338.
[12] H. Weingärtner, Angew. Chem. Int. Ed. 46 (2007) 2–19.
[13] J.P. Mikkola, P. Virtanen, R. Sojholm, Green Chem. 8 (2006) 250–255.
[14] G. Argiropoulos, R.W. Cattrall, I.C. Hamilton, R. Paimin, Anal. Chim. Acta 360 (1998) 167–169.
[15] G.L. Lee, R.W. Cattrall, H. Daud, J.F. Smith, Anal. Chim. Acta 123 (1981) 213–220.
[16] C.A.N. de Castro, F.J.V. Santos, J.M.N.A. Fareleira, W.A. Wakeham, J. Chem. Eng. Data 54 (2008) 171–178.
[17] Ionic Liquids Database - (IL Thermo), NIST Standard Reference Database #147, © 2006, US Secretary of Commerce.
[18] K. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (2000) 2275–2287.
[19] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–164.
[20] J. Wang, Y. Tian, Y. Zhao, K. Zhuo, Green Chem. 5 (2003) 618–622.
[21] T. Nishida, Y. Tashiro, M. Yamamoto, J. Fluorine Chem. 120 (2003) 135–141.
[22] M.E. Van Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochim. Acta 425 (2005) 181–188.
[23] Q. Zhou, L.S. Wang, J. Chem. Eng. Data 51 (2006) 905–908.
[24] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 110 (2006) 19593–19600.
[25] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, J. Solution Chem. 35 (2006) 1337–1346.
[26] D. Tomida, A. Kumagai, K. Qiao, C. Yokoyama, Int. J. Thermophys. 27 (2006) 39–47.
[27] K.R. Harris, M. Kanakubo, L.A. Woolf, J. Chem. Eng. Data 52 (2007) 2425–2430.
[28] Y.A. Sanmamed, D. Gonzalez-Salgado, J. Troncoso, C.A. Cerdeirina, L. Romani, Fluid Phase Equilib. 252 (2007) 96–102.
[29] Y. Tian, X. Wang, J. Wang, J. Chem. Eng. Data 53 (2008) 2056–2059.
[30] I.B. Malham, M. Turmine, J. Chem. Thermodyn. 40 (2008) 718–723.
[31] F.J.V. Santos, C.A.N. de Castro, J.H. Dymond, N.K. Dalaouti, M.J. Assael, A. Nagashima, J. Phys. Chem. Ref. Data 35 (2006) 1–8.
[32] R. Ge, C. Hardacre, P. Nancarrow, D.W. Rooney, J. Chem. Eng. Data 52 (2007) 1819–1823.
[33] D. Tomida, S. Kenmochi, T. Tsukada, K. Qiao, C. Yokoyama, Int. J. Thermophys. 28 (2007) 1147–1160.
[34] E. Gomez, N. Calvar, I. Dominguez, A. Dominguez, Phys. Chem. Liq. 44 (2006) 409–417.
[35] E. Gomez, B. Gonzalez, A. Dominguez, E. Tojo, J. Tojo, J. Chem. Eng. Data 51 (2006) 696–701.
[36] R.D. Chirico, M. Frenkel, V.V. Diky, K.N. Marsh, R.C. Wilhoit, J. Chem. Eng. Data 48 (2003) 1344–1359.
[37] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes da Ponte, J. Szydlowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperanca, H.J.R. Guedes, H.C. de Sousa, Green Chem. 6 (2004) 369–381.
[38] K.-S. Kim, B.-K. Shin, F. Ziegler, Fluid Phase Equilib. 218 (2004) 215–220.
[39] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, J. Chem. Eng. Data 49 (2004) 954–964.
[40] D. Waliszewski, I. Stepniak, H. Piekarski, A. Lewandowski, Thermochim. Acta 433 (2005) 149–152.
[41] G. Garcia-Miaja, J. Troncoso, L. Romani, Fluid Phase Equil. 274 (2008) 59–67.
[42] G. Garcia-Miaja, J. Troncoso, L. Romani, J. Chem. Thermodyn. 41 (2009) 334–341.
[43] F. Brinkmann, N.E. Dam, E. Deák, F. Durbiano, E. Ferrara, J. Fükö, H.D. Jensen, M. Máriássy, R.H. Shreiner, P. Spitzer, U. Sudmeier, M. Surdu, L. Vyskočyl, Accred. Qual. Assur. 8 (2003) 346–353.
[44] R.H. Jameel, Y.C. Wu, K.W. Pratt, Primary standards and standard reference materials for electrolytic conductivity, NIST Special Publication (2000) 260–142.
[45] J. Vila, P. Gines, E. Rilo, O. Cabeza, L.M. Varela, Fluid Phase Equilib. 247 (2006) 32–39.
[46] J. Vila, P. Gines, J.M. Pico, C. Franjo, L.M. Varela, O. Cabeza, Fluid Phase Equilib. 242 (2006) 141–146.
[47] A. Stoppa, J. Hunger, R. Buchner, J. Chem. Eng. Data 54 (2009) 472–479.
[48] Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems, IUPAC project 2002-005-1-100, K.N. Marsh (coordinator).
[49] M.E. Kandil, K.N. Marsh, A.R.H. Goodwin, J. Chem. Eng. Data 52 (2007) 2382–2387.
[50] J. Widegren, E. Saurer, K. Marsh, J. Magee, J. Chem. Thermodyn. 37 (2005) 569–575.
[51] I.M.S. Lampreia, C.A.N. de Castro, A new reliable calibration method for vibrating tube densimeters in wide ranges of temperature and pressure, submitted to J, Chem. Thermodyn., June, 2010.

[52] Z.H. Zhang, Z.C. Tan, L.X. Sun, J.Z. Yang, X.C. Lv, Q. Shi, Thermodynamic investigation of room temperature ionic liquid: The heat capacity and standard enthalpy of formation of EMIES, Thermochimica Acta 447 (2006) 141–146.
[53] Y.U. Paulechka, A.G. Kabo, A.V. Blokhin, G.J. Kabo, M.P. Shevelyova, J. Chem. Eng. Data (2010) Published on-line doi:10.1021/je900974u.
[54] L.E. Ficke, H. Rodriguez, J.F. Brennecke, J. Chem. Eng. Data 53 (2008) 2112–2119.
[55] R. Ge, C. Hardacre, J. Jacquemin, P. Nancarrow, D.W. Rooney, J. Chem. Eng. Data 53 (2008) 2148–2153.
[56] C.A.N. de Castro, S.F.Y. Li, A. Nagashima, R.D. Trengove, W.A. Wakeham, J. Phys. Chem. Ref. Data 15 (1986) 1073–1086.
[57] M.L.V. Ramires, C.A.N. de Castro, Y. Nagasaka, A. Nagashima, M.J. Assael, W.A. Wakeham, J. Phys. Chem. Ref. Data 24 (1995) 1377–1381.
[58] M.J. Assael, C.A.N. de Castro, H.M. Roder, W.A. Wakeham, Transient methods for thermal conductivity, Chapter 7, Experimental Thermodynamics, in: W.A. Wakeham, A. Nagashima, J.V. Sengers (Eds.), Measurement of the transport properties of fluids, Vol. II, Blackwells, Oxford, 1991.
[59] M.L.V. Ramires, J.M.N.A. Fareleira, C.A.N. de Castro, M. Dix, W.A. Wakeham, Int. J. Thermophys. 14 (1993) 1119–1130.
[60] R.A. Perkins, A. Laesecke, C.A.N. de Castro, Fluid Phase Equil. 80 (1992) 275–286.
[61] U.V. Mardolcar, C.A.N. de Castro, Ber. Bunsenges. Phys. Chem. 91 (1987) 152–156.
[62] M.L.V. Ramires, C.A.N. de Castro, J.M.N.A. Fareleira, W.A. Wakeham, J. Chem. Eng. Data 39 (1994) 186–190.
[63] J. França, C.A.N. de Castro, M.M. Lopes, V. Nunes, J. Chem. Eng. Data 54 (2009) 2569–2575.