



Experimental methodology for precise determination of density of RTILs as a function of temperature and pressure using vibrating tube densimeters

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ABSTRACT

A specific calibration procedure that allows the accurate determination of densities of room temperature ionic liquids, RTILs, as a function of temperature and pressure using vibrating tube densimeters is presented. This methodology overcomes the problems of common calibration methods when they are used to determine the densities of high density and high viscosity fluids such as RTILs. The methodology is applied for the precise density determination of RTILs 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄], 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF₄], and 1-octyl-3-methylimidazolium tetrafluoroborate [Omim][BF₄] in the temperature and pressure intervals (283.15 to 323.15) K and (0.1 to 60) MPa, respectively. The viscosities of these substances, needed for the estimation of the viscosity-induced errors, were estimated at the same conditions from the experimental measurements in the intervals (283.15 to 323.15) K and (0.1 to 14) MPa and from a specific extrapolation procedure. The uncertainty in the density measurements was estimated in $\pm 0.30 \text{ kg} \cdot \text{m}^{-3}$ which is an excellent value in the working intervals. The results of these RTILs have demonstrated that viscosity-induced errors are relevant and they must be taken into account for a precise density determination. Finally, an alternative tool for a simpler application of this procedure is presented.

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1. Introduction

Room temperature ionic liquids (RTILs) have been classified as potential 'green' substitutes for the volatile organic compounds commonly used in industry [1]. The 'green' character comes mainly from their facility to be recycled, which has its origin in their almost undetectable vapor pressure [2]. Over the last two decades, most of the research on RTILs has been directed toward the evaluation of their suitability for use in different industrial applications [3–12]. Recently, there has been an increasing interest in the thermophysics of RTILs, producing a great number of publications in the last years (see, for details, reviews of Heintz [13] and Marsh *et al.* [14]). Most of these dealt with experimental measurements of thermophysical properties at atmospheric pressure.

The thermophysical characterization of liquids requires the knowledge of a broad set of properties as a function of temperature and pressure. In this context, the experimental determination of density occupies a central place for several reasons. On the one hand, measurements of density ρ as a function of pressure p and temperature T ($p\rho T$ data) allow to obtain two derived properties,

the isobaric thermal expansivity and the isothermal compressibility [15]. On the other hand, by combining $p\rho T$ data with puT or pC_pT measurements (u is speed of sound and C_p is isobaric heat capacity), the isentropic compressibility and the isochoric molar heat capacity can also be calculated, giving a wide thermodynamic characterization [16,17]. Although $p\rho T$ data can be measured by using a variety of equipments [18], vibrating tube densimeters (VTDs) [19] have been, by far, the most popular in the last decades due to their accuracy and ease of operation. VTD is an indirect measurement technique: the sample density ρ is obtained from the vibration period τ of the hollow U-tube filled with the sample using the relation:

$$\rho = \frac{K}{4\pi^2 V} \tau^2 - \frac{m_0}{V} = A\tau^2 + B, \quad (1)$$

where m_0 is the evacuated tube mass, V is the tube inner volume, and K is the tube stiffness. The parameters A and B are determined by an appropriate calibration using density standards; once A and B are known, by measuring the sample vibration period τ , the density of the sample is readily obtained from equation (1).

Many calibration procedures have been developed for the accurate determination of the density of liquids (see *e.g.*, references [20 and references therein]), however, they must be modified to be used with RTILs, if good precision is desired [21]. This is due to

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both the high density and viscosity values of RTILs. On the one hand, it is well known that conventional calibration methodologies can give imprecise density data for high density fluids having densities between (1300 and 2000) $\text{kg} \cdot \text{m}^{-3}$ due mainly to the absence of good high density standard fluids, especially at high pressure [18]. On the other hand, they do not work well for fluids with viscosities greater than 30 $\text{mPa} \cdot \text{s}$. This fact has its origin in the damping produced by the fluid in the oscillator, which is not taken into account in conventional calibrations, inducing a significant error in the measured density [22]. Errors due to damping are called *viscosity-induced errors*.

In a previous work [21], a calibration method of VTD for precise density measurement of RTILs under atmospheric pressure conditions was presented. This method was applied to the DSA48 densimeter from Anton Paar and it consists of a calibration in two steps. The first step is a conventional calibration for the determination of the *A* and *B* parameters (we shall call this procedure as *A and B calibration*). A 'classical' calibration was chosen using dodecane and tetrachloroethylene as standard fluids (the density standards for the *A and B calibration* are referred to as low viscosity density standards). This procedure overcomes the problem related with the high density of fluids as the densities of standards (i) bound those usually found for RTILs, (ii) are known with high accuracy, and (iii) do not differ from each other to a great extent, fact that assures the linear relation between the sample density and the vibration period to the second power in that density interval. Using this method, the densities of low viscosity fluids are determinable with an uncertainty of $\pm 0.05 \text{ kg} \cdot \text{m}^{-3}$ if the sample density is within the interval (700 to 1600) $\text{kg} \cdot \text{m}^{-3}$. However, for high viscosity samples, due to the damping effect, this procedure overestimates their density. This error directly depends on the viscosity of the sample [22] and can be corrected by using high viscosity density standards for which viscosity and density are known. Thus, the second step (*viscosity-induced errors' calibration*) of our calibration procedure is to estimate the viscosity-induced errors using a set of high viscosity density standards. With the combination of both calibrations, the density at atmospheric pressure of a RTIL can be determined with an uncertainty of $\pm 0.10 \text{ kg} \cdot \text{m}^{-3}$. It should be noted that application of this procedure also requires the determination of the viscosity of the sample to evaluate the viscosity-induced errors.

A specific calibration procedure for the accurate determination of densities of RTILs at pressures higher than atmospheric pressure has yet to be reported. Measurements of the density of RTILs as a function of pressure using VTD have been published by Coutinho et al. [23–25], Rebelo et al. [26–29], and Hoffman et al. [30]. Coutinho et al. [23–25] used as *A and B calibration* a method in which the VTD is modeled by the Niesen equation [31], the parameters of which were determined using water, perfluorohexane, and perfluorononane as low viscosity density standards. In this method, they dealt with the problem of the measurement of high density fluids (the densities of the standards bound those of the RTILs), however, it is only precise within $\pm 1 \text{ kg} \cdot \text{m}^{-3}$. On the other hand, they make an estimation of the viscosity-induced errors but finally they do not make the correction because the error is less than the claimed uncertainty of the densities obtained from the *A and B calibration*. Hoffman et al. [30] used the procedure proposed by Lagourette et al. [32] as *A and B calibration* in which water and vacuum were used as standards, with no viscosity corrections being taken into account. The applicability of this latter procedure has been analyzed in a previous work [20] and it has been demonstrated that it can give good results for liquids with densities close to the standards (in this case, water), however, problems have been detected when the densities are far from that, especially for high pressures. Finally, in the papers of Rebelo et al. [26–29] densities are reported without taking into account viscosity-induced errors although they recognize the existence of the issue.

The aim of the present work is to propose a specific calibration method for the precise determination of densities of RTILs as a function of pressure using VTD. It is also structured in two steps as in the procedure described above [21]. As the *A and B calibration*, we chose a method [33] recently developed in our group that allows the accurate measurement of densities as a function of pressure for liquids in the interval (700 to 1600) $\text{kg} \cdot \text{m}^{-3}$. This procedure, which is based in rigorous mechanical considerations on the behavior of the VTD, uses dodecane, tetrachloroethylene, and water as low viscosity density standards. For the *viscosity-induced errors calibration*, we chose the same procedure as for atmospheric pressure measurements [21]. The proposed methodology was used for the density determination of 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄], 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF₄], and 1-octyl-3-methylimidazolium tetrafluoroborate [Omim][BF₄] in the temperature interval (283.15 to 323.15) K and from 0.1 MPa up to 60 MPa, using the DMA 512P model from Anton Paar. The viscosities for the RTILs were determined using a high-pressure and high-temperature viscometer HPHTV-100 (Stony Brook Scientific) Ltd. The results have been used to analyze the behavior of the viscosity-induced errors for these RTILs as a function of temperature and pressure. Finally, an alternative tool to simpler application of this methodology has been developed.

2. Materials and equipment

The low viscosity density standards, *n*-dodecane, tetrachloroethylene, and those of high viscosity, lube oil 30, lube oil 110, and lube oil A90 were purchased from H&D Fitzgerald Ltd. The viscosity standard S200 of Cannon was obtained from Cole-Parmer. All of them were used as received. The third low viscosity density standard, *i.e.*, water, was supplied by Aldrich and it was degassed under vacuum prior to use. The RTILs, [Hmim][BF₄], and [Omim][BF₄] were purchased from Solvent Innovation with a purity greater than 0.99 in mass fraction. [Emim][BF₄] and [Bmim][BF₄] samples were obtained from Merck with purities higher than 0.98 and 0.99 in mass fraction. In order to reduce the water and volatile compounds of the RTILs, vacuum at moderate temperature (333.15 K) was applied to the RTIL samples for, at least, 3 days prior to use. The water content of the studied samples was determined by Karl-Fischer titration and it was $8 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$, $6 \cdot 10^{-4}$, and $1.7 \cdot 10^{-3}$ in mass fraction for [Emim][BF₄], [Bmim][BF₄], [Hmim][BF₄], and [Omim][BF₄], respectively.

Densities ρ were measured using the Anton Paar DMA512P vibrating tube densimeter, a detailed description of which can be found elsewhere [34]. The temperature and pressure in the measurement vessel (the hollow U-tube) were controlled by a Polyscience thermostatic bath within $\pm 0.01 \text{ K}$ and a Ruska pressure controller model 7610 with an uncertainty of $\pm 0.01 \text{ MPa}$. The calibration procedure will be described in the following section.

Dynamic viscosities η were measured using a HPHTV-100 Stony Brook Scientific falling needle viscometer which is based on the classical falling body type of viscometer. This apparatus can operate at pressures up to 14 MPa and temperatures to 393.15 K. In this type of viscometer, a cylindrical sinker with hemi-spherical ends falls vertically along the symmetrical axis of the device through the sample fluid. The fluid is forced to flow through the annulus between the sinker and the tube. A measurement of the falling body terminal velocity can be used to determine the viscosity $\eta(p, T)$ of the fluid. The time Δt of the fall between two fixed reference points is measured, and the viscosity η of the fluid is calculated using the following equation:

$$\eta = K_{\text{vis}}(\rho_S - \rho_L)\Delta t, \quad (2)$$

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