Influence of the pressure, temperature, cation and anion on the volumetric properties of ionic liquids: New experimental values for two salts

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ABSTRACT

Experimental densities of two ionic liquids (ILs), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Pyrr][NTf_2]$) and 1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$), were measured over a broad temperature and pressure range, *i.e.* from (278.15 to 398.15) K and up to 120 MPa, respectively. The isobaric thermal expansion coefficient of the two ILs was determined from these measurements finding a non-monotonous behaviour over the entire pressure range. The density values obtained were used to analyse the prediction ability of the methods proposed by Gardas and Coutinho and by Jacquemin et al. Furthermore, the influence of the cation and anion structure on the densities and the isothermal compressibilities was analyzed, also considering literature values.

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1. Introduction

Nowadays, environmental concern is leading to the development of more sustainable materials and processes. Ionic liquids (ILs) are one of the products that are attracting more attention during the past few years. Their main properties make them interesting for several applications, such as, electrolytic reactions, electrochemistry and electrolyte systems [1–4], battery technology [5], solvents and/or catalysts for chemical reactions and organic synthesis [6–11], functional advanced materials and material processing [12–14], biotechnology applications [15], polymer science [16], extraction, chromatography, and electrophoresis [17], lubricants [18] and heat transfer fluids [19–23], among others.

Precise determination of thermophysical properties of ILs is needed to select those with the most suitable properties for the different applications. Accurate values of liquid density are required in the design of equipment such as condensers, reboilers, liquid/liquid two phase mixer–settler units, calculation of tower heights, material and energy balances involving liquids as well as the measurements of phase equilibrium, heat capacity and viscosity with several techniques. With respect to heat transfer, the sensible heat and phase change storage depend on the density of the fluid [24]. Furthermore, in the lubrication area, compressibility is one of the properties that should be considered when a fluid is selected for an hydraulic application. A low compressibility translates into fast

response time, high pressure transmission velocity, and low power loss. In hydraulic systems that operate at high pressure, oils with low compressibility are required to transmit power efficiently. Nevertheless, a certain amount of compressibility can be convenient because it dampens pressure surges caused by switching and thus provides for a smoother operation [25,26]. Usually, the potential for energy loss and heat production of a lubricant decreases with its compressibility. Materials with high compressibility *i.e.* low bulk modulus act as damping fluids [27]. Moreover, *pVT* values are fundamental data for developing models involving equations of state, which are the main tool used for thermophysical properties prediction.

In this work, we have carried out density measurements over a broad range of pressure and temperature of two ILs, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Pyrr][NTf_2]$) and 1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)-trifluorophosphate ($[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$). From these experimental results, we have determined their compressibility, as well as their thermal expansion coefficient. Our present results for density trends complement those found previously by several researchers [28–49]. Few works were published on the pressure influence on thermal expansion coefficients [41,43,50–52] of ILs. In the case of isothermal compressibility, we are also aware of very few previous studies [53,54].

One of the important aspects of ILs is their tuneability, which allows them to be designed and tailor made with the proper combination of anion and cation to fulfil the specifications of certain processes and applications. Therefore, we have also analysed our experimental values and the literature data concerning density

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and compressibility looking for sequences in terms of the type and side lengths of the cation and the anion.

2. Materials and methods

The IL samples were kindly provided by Merck KGaA, the specified mole fraction purity for both [C$_4$C$_1$Pyrr][NTf$_2$] and[C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$] is higher than 0.98. Besides, the manufacturer gives the mole-fraction purities by alkalimetry after ionic exchange and electrophoresis as indicated in table 1. Prior to density measurements, samples were kept under vacuum and mechanical agitation for at least 48 h in order to eliminate water and other volatile compounds. Table 1 shows the water content of IL samples determined by the Karl Fischer method using a Mettler Toledo DL32 coulometric titrator, before and after the density measurements.

In order to avoid contact between the ILs and the atmosphere, they were transferred to the densimeter through a Hamilton valve, HV Standard PTFE, connected to a glass syringe. Density measurements were performed up to 120 MPa and between temperatures from (278.15 and 398.15) K in an automated vibrating tube densimeter Anton Paar HPM. This densimeter consists of two different units, the measurement cell, named DMA HPM, and the electronic processing unit, named mPDS 2000V3. The temperature Pt100 probe was calibrated with an uncertainty of 0.02 K whereas the pressure transducer with an uncertainty of 0.02 MPa. Calibration of the densimeter was performed according to the method described by Lagourette et al. [55] and modified by Comuñas et al. [56]. Milli-Q water was employed as the reference fluid within the temperature range from (278.15 to 348.15) K and pressures up to 120 MPa and also at T = (373.15 and 398.15) K for pressures higher than 0.1 MPa. Additionally, n-decane was used as the reference fluid at T = (373.15 and 398.15) K at 0.1 MPa. More details of the equipment have been previously reported [54,57,58].

Because of the high viscosity of both ILs (98.7 and 148 mPa · s at T = 293.15 K for [C$_4$C$_1$Pyrr][NTf$_2$] and [C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$], respectively), a correction factor for the DMA HPM model has been considered. This factor accounts for the effect of the sample viscosity on the density measurements of the mechanical oscillator densimeters, and is given by the following equation [57,59]:

$$\frac{\rho_{HPM} - \rho}{\rho_{HPM}} = [0.4482\sqrt{\eta/\text{mPa} \cdot \text{s}} - 0.1627] \cdot 10^{-4}, \tag{1}$$

where ρ_{HPM} represents the density value obtained from the densimeter calibration and the measured periods, ρ is the "corrected" density value due to the effect of viscosity, and η is the dynamic viscosity of the sample. This equation is valid for viscosities lower than 289 mPa · s. For viscosities higher than 289 mPa · s, the relative correction factor, i.e. $\Delta\rho/\rho$, becomes constant, taking the value of $7.5 \cdot 10^{-4}$. For this purpose, we have used viscosity values of [C$_4$C$_1$Pyrr][NTf$_2$] and [C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$] over the broad temperature and pressure ranges, measured for both ILs with a falling body viscometer in our laboratory [60,61] and also for [C$_4$C$_1$Pyrr][NTf$_2$] by Harris et al. [62].

TABLE 1
Purity and water content (mass fraction) in IL samples prior and after the density measurements.

Ionic liquid	Mole-fraction purity	Water content$_{IN}$	Water content$_{OUT}$
[C$_4$C$_1$Pyrr][NTf$_2$]	0.999[a]	57.19 · 10^{-6}	233.5 · 10^{-6}
[C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$]	>0.990[b]	30.66 · 10^{-6}	97.85 · 10^{-6}

[a] Alkalimetry after ionic exchange.
[b] Electrophoresis.

The expanded ($k = 2$) uncertainty of the density measurements with this technique was rigorously calculated by Segovia et al. [57] finding that it is $0.7 \cdot 10^{-3}$ g · cm^{-3} for temperatures below T = 373.15 K, $5 \cdot 10^{-3}$ g · cm^{-3} at T = (373.15 and 398.15) K and p = 0.1 MPa, and $3 \cdot 10^{-3}$ g · cm^{-3} in other cases, i.e. at T ⩾ 373.15 K and p > 0.1 MPa. For the ILs studied, these uncertainties correspond around to 0.05%, 0.4% and 0.2%, respectively.

3. Results and discussion

3.1. Experimental results

Direct experimental density values are reported in tables S1 and S2 of the supporting information, whereas those obtained after applying the viscosity correction are presented in tables 2 and 3 for the two ILs studied in this work. Mean relative deviations between both density values, i.e. with and without viscosity correction, are 0.03% and 0.04% for [C$_4$C$_1$Pyrr][NTf$_2$] and [C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$], respectively. Furthermore, in figure 1, density values of the ILs are plotted against pressure at T = (278.15 and 398.15) K. Density values of [C$_4$C$_1$Pyrr][NTf$_2$] are around 17% lower than those of [C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$] at the same temperature and pressure conditions.

The following modified Tammann–Tait equation was employed to correlate experimental density values with temperature and pressure:

$$\rho(T/\text{K}, p/\text{MPa}) = \frac{\rho(T/\text{K}, 0.1\,\text{MPa})}{1 - C \cdot \ln\left(\frac{B(T/\text{K}) + p/\text{MPa}}{B(T/\text{K}) + 0.1\,\text{MPa}}\right)}, \tag{2}$$

where $\rho(T/\text{K}, 0.1\,\text{MPa})$ is the density as a function of temperature at a reference pressure of 0.1 MPa, following this polynomial expression:

$$\rho(T/\text{K}, 0.1\,\text{MPa}) = \sum_{i=0}^{m} A_i (T/\text{K})^i. \tag{3}$$

The parameters A_i were determined with the experimental ρ values at atmospheric pressure, their number being determined by using an F-test with a 0.05 of significance level for both ILs data series.

C is a parameter independent of temperature and pressure and $B(T)$ is a parameter depending on temperature as a polynomial function:

$$B(T/\text{K}) = \sum_{j=0}^{n} B_j (T/\text{K})^j. \tag{4}$$

The parameters B_j and C were determined with the experimental ρ values at pressures higher than 0.1 MPa. All parameters obtained for the Tammann–Tait correlation are presented in table 4, along with standard deviations, σ, for $\rho(T/\text{K}, 0.1\,\text{MPa})$ and σ^* for $\rho(T/\text{K}, p/\text{MPa})$. As can be observed, standard deviations, σ^*, of $1 \cdot 10^{-4}$ and $3 \cdot 10^{-4}$ g · cm^{-3}, obtained respectively for [C$_4$C$_1$Pyrr][NTf$_2$] and [C$_1$OC$_2$C$_1$Pyrr][(C$_2$F$_5$)$_3$PF$_3$], are lower than the density uncertainty.

In figure 2, corrected density values of [C$_4$C$_1$Pyrr][NTf$_2$] are compared with literature values at atmospheric pressure and different temperatures. The Absolute Average Deviations, AADs%, with data from Jacquemin et al. [63], Gaciño et al. [37], Pereiro et al. [64] and Kolbeck et al. [38] as well as from Harris et al. [62] for three samples are within the combined estimated expanded uncertainties, whereas the values of AAD% with Deng et al. [65] and with Shamsipur et al. [66] are slightly higher. Moreover, values of AAD% from densities of Katsuta et al. [67], Zarrougui et al. [68] and Gardas et al. [69] are considerably higher than the estimated combined uncertainty. In figure 3, we have plotted the relative density deviations with literature data [63,69] for [C$_4$C$_1$Pyrr][NTf$_2$]