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Thermodynamic Properties at Saturation Derived from Experimental Two-Phase Isochoric Heat Capacity of 1-Hexyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide

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Abstract

New measurements are reported for the isochoric heat capacity of the ionic liquid substance 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C6mim][NTf2]). These measurements extend the ranges of our earlier study [N.G. Polikhronidi *et al.*, *Phys. Chem. Liq.* **52**, 657 (2014)] by 5 % of the compressed liquid density and by 75 kelvins. An adiabatic calorimeter was used to measure one-phase (C_{V1}) liquid and two-phase (C_{V2}) liquid + vapor isochoric heat capacities, densities (ρ_S), and phase-transition temperatures (T_S) of the ionic liquid (IL) substance. The combined expanded uncertainty of the density ρ and isochoric heat capacity C_V measurements at the 95 % confidence level with a coverage factor of $k = 2$ is estimated to be 0.15 % and 3 %, respectively. Measurements are concentrated in the immediate vicinity of the liquid + vapor phase transition curve, in order to closely observe phase transitions. The present measurements and those of our earlier study are analyzed together, and are presented in terms of thermodynamic properties (T_S , ρ_S , C_{V1} and C_{V2}) evaluated at saturation and in terms of key derived thermodynamic properties C_p , C_S , W'_S , K'_{TS} , $(\partial P/\partial T)'_V$, and $(\partial V/\partial T)'_P$ on the liquid + vapor phase transition curve. A thermodynamic relation by Yang and Yang is used to confirm the internal consistency of measured two-phase heat capacities C_{V2} , which are observed to fall perfectly on a line as a function of specific volume at a constant temperature. The observed linear behavior is exploited to evaluate contributions to the quantity $C_{V2} = f(V, T)$ from chemical

potential $C_{V\mu} = -T \frac{d^2 \mu}{dT^2}$ and from vapor pressure $C_{VP} = VT \frac{d^2 P_S}{dT^2}$. The physical nature and specific details of the temperature and specific volume dependence of the two-phase isochoric heat capacity and some features of the other derived thermodynamic properties of IL at liquid saturation curve are considered in detail.

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Keywords

Coexistence curve; Ionic liquid; Isochoric heat capacity; Phase transition; Saturated density

1 Introduction

1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (short name [C6mim][NTf2]) has been deemed an IUPAC reference substance [1], which was selected as an aid to experimenters who want to validate their techniques and calibrations. The density and other thermodynamic properties (heat capacity, C_p , and speed of sound, W) of [C6mim][NTf2] were measured in a round-robin study using high purity samples from the same batch with a nominal purity of >99.5 mole % [1,2]. All of the reported thermodynamic properties data for [C6mim][NTf2] were compiled, critically evaluated, and provided recommended values with uncertainties by Chirico et al. [1]. They developed reference correlations for the density (ρ), heat capacity (C_p), and speed of sound (W) of [C6mim][NTf2] at atmospheric pressure in the temperature range from (258 to 373) K, from (190 to 370) K, and from (283 to 334) K, respectively. A Tait-type reference equation of state was developed in the temperature range from (298 to 423) K and at pressures from (0.1 to 40) MPa. Zaitsau et al. [3] used a Knudsen effusion method to measure the vapor pressure of [C6mim][NTf2] in the temperature range from (446 to 494) K. The uncertainty of the vapor pressure measurements is not well established due to very low pressures (between 0.007 and 0.17 Pa) in the measured temperature range. Zaitsau et al. fitted their measured vapor pressure data with a simple equation,

$$\ln P_s = 28.29 - 14840/T, \quad (1)$$

where P_s is in Pa and T in K. Eq. 1 is useful as a smoothing equation for their measurements. We would advise that the simple form of Eq. 1 is a rather poor compromise that was necessitated by the large relative uncertainties of the experimental pressures. Furthermore, it would be ill advised to try to either extrapolate Eq. 1 beyond the range of the original measurements or employ calculated derivatives based on this vapor pressure equation to evaluate other thermodynamic quantities. Rocha et al. [4] used the same technique with a different sample and apparatus to measure the vapor pressure of the IL in the temperature range from (465 to 489) K. Reasonable agreement (within 20 %) was observed between the two vapor pressure data sets, with data by Rocha et al. [4] systematically lower than data of Zaitsau et al. [3]. For the [C6mim][NTf2] round-robin study [2], two labs performed adiabatic measurements of isobaric heat capacity (C_p). An evaluation of these experimental data [1] showed that the two labs agreed very closely. The round-robin study did not include isochoric heat capacity C_v measurements. The reports from the IUPAC project [1,2] (2009) on [C6mim][NTf2] provide detailed review previous studies on thermodynamic properties. However, after 2009, a number of papers related to the density and isobaric heat capacity measurements of [C6mim][NTf2] have been published [5–27]. Bochmann and Hefler [5] reported C_p data for [C6mim][NTf2] over the temperature range from (323 to 573) K along the isobar of 10 MPa using a modified commercial Tian-

Calvet calorimeter. Adiabatic calorimeter method has been used by Blokhin et al. [8] and Shimizu et al. [9] to measure C_p [C6mim]NTf2, while the authors of the works [7,10–12] used DSC technique. As was mentioned in previous study by Bochmann and Hefler [5] large discrepancy, up to 7 % between the reported C_p data measured with DSC and adiabatic calorimeter, was found for [C6mim]NTf2 (see Fig. 1). Zaitsau et al. [14] used quartz crystal microbalance method to determine enthalpy of vaporization (139.1 kJ/mole) for [C6mim][NTf2] at reference temperature of 298.15 K. Figures 1 and 2 demonstrate the comparison reported isobaric heat capacity and density data for [C6mim][NTf2]. These figures also include the present results for saturated density and saturated two-phase isochoric heat capacity data. As can be noted, large scatter up to 7 % for heat capacity and 0.35 % for density are shown. A detailed consistency analysis of the various reported data sources and the present measurements are given below in sections 3.2 and 4.

In our previous work [27] we have measured two- and one-phase C_V for [C6mim][NTf2] over the temperature range from (330 to 480) K and pressures up to 20 MPa for 9 liquid isochores from (1217.6 to 1278.8) kg·m⁻³. The present work is the continuation of our previous study of the C_V for [C6mim][NTf2] to extend the temperature and density ranges. The main objective of the present work is to provide reliable experimental one- and two-phase C_V data for [C6mim][NTf2] at low temperatures (to 297 K) and high densities (up to 1344.14 kg·m⁻³) including saturation curve. The present results extend the temperature and density ranges in which heat capacity and saturated density data for [C6mim][NTf2] are available. For example, the saturation temperature range studied in the present work now extends 75 K below the previous study [27]. Another objective of the present study is to provide new interpretation of the present and previous two-phase C_V measurements for IL in order to explain thermodynamic bases of the experimentally observed low vapor-pressure for IL and consistency between calorimetric (C_V) and vapor-pressure measurements. Thus, in the present study we provide a new interpretation our previous [27] measured C_V data together with the present results to explain physical bases of the unusual low vapor pressure of the IL and their impact on two-phase C_V behavior, *i.e.*, temperature and specific volume dependence of the two-phase C_V and some features of the other derived thermodynamic properties of IL at liquid saturation curve. Furthermore, we propose a method of separation and extraction of the distinct C_{V2} contributions, chemical potential ($C_{V\mu}$) and vapor-pressure (C_{Vp}) terms from the measured total two-phase (C_{V2}) isochoric heat capacity of IL by using the Yang-Yang relation. The measurements of the one- (C_{V1}) and two-phase (C_{V2}) isochoric heat capacity of [C6mim][NTf2] were made in the immediate vicinity of liquid-vapor phase transition temperatures for two liquid filling densities of (1323.92 and 1344.14) kg·m⁻³ using a precise adiabatic technique previously described in our publications [27,28].

It is well-known that C_p data are widely used in process engineering calculations, while, C_V data are used to gain a better understanding of theory and thermodynamic property models, *i.e.*, scientific applications. Isochoric heat capacity is closely related with other important thermodynamic properties and is an extremely sensitive indicator of the occurrence of a phase transition in the system. For example, C_V measurements can be used to accurately determine the locus of the phase transition temperatures $T_S(\rho)$. A sharp discontinuity of the measured C_V occurs at the liquid-vapor phase transition temperature $T_S(\rho)$ for each filling density (ρ) (see, for example, [27,28]). In the present work we routinely use the existence of

a sharp discontinuity as the measurement criterion to obtain the liquid-vapor saturation curve $T_S(\rho)$ of a substance during continues heating the system at constant density. We propose to use one- and two-phase isochoric heat capacity data, saturated temperatures, and saturated densities ($C'_{V1}, C'_{V2}, \rho_S, T_S$) for [C6mim][NTf2] to accurately calculate other thermodynamically important properties along the liquid-gas phase transition curve. Heretofore, there have been no reports of measured saturated liquid density (ρ_S) or isochoric heat capacity (C_V). With the exception of vapor pressure at $T > 445$ K, no other thermodynamic properties for [C6mim][NTf2] at saturation have been reported previously. Due to the low vapor pressure of the IL, their properties on the saturation curve have some peculiar features. Using the measured data we will derive properties of [C6mim][NTf2] at saturation such as $C_p, C_S, W, K_T, H_{\text{vap}}, (\partial P/\partial T)'_{\text{v}}$, and $(\partial V/\partial T)'_{\text{p}}$.

2 Experimental Procedures

Since the method (experimental details, the physical basis and theory of the method, procedures, uncertainty assessment) and apparatus have been described in our earlier publications (see, for example [27,28]), only essential information will be briefly given here. Isochoric heat-capacity $C_V (V, T)$ measurements were performed with a high-temperature, high-pressure, and nearly constant-volume adiabatic calorimeter. The adiabatic system detects extremely small temperature differences (10^{-6} K to 10^{-5} K) between the inner and outer vessels. The combined expanded ($k = 2$) uncertainty for the heat capacity, with allowance for the propagation of uncertainty related to the departure from true isochoric conditions of the heating process, was (2 to 3) % for liquid-phase measurements. Repeatability of the measured values of C_V was shown to be (0.5 to 1.0) %. To precisely determine the phase-boundary parameters, T_S and ρ'_S , we used a combination of the quasi-static thermogram technique (readings of PRT, T - τ plot at isochoric heating of the sample) and barogram technique (readings of the pressure transducer, P - τ plot). Details of both techniques have been described in [27,28]. The thermo- and barograms provided records of the changes in temperature T , changes in pressure P , and the finite-difference derivative $(\partial P/\partial T)'_{\text{v}} = \lim_{\Delta T \rightarrow 0} (\Delta P/\Delta T)_{\text{v}}$, as a function of elapsed time τ . Data for both measured T - τ and P - τ were fitted to the linear equations $T = c + d\tau$ and $P = a + b\tau$, then the temperature derivative of pressure could be estimated as $(\partial P/\partial T)'_{\text{v}} = (b/d)$. The measurements were made during slow heating of the calorimeter at nearly equilibrium conditions, hence we refer to quasi-static techniques. The rate of the temperature changes was less than $5 \times 10^{-4} \text{ K} \cdot \text{s}^{-1}$ (far from the phase transition point) and $1.7 \times 10^{-4} \text{ K} \cdot \text{s}^{-1}$ (near the phase transition point).

The IL sample [C6mim][NTf2] (CAS # 382150-50-7, $\text{C}_{12}\text{H}_{19}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$) used in this work was supplied by IoLiTec (Germany)¹. The supplier furnished its purity assay (NMR) > 99 %, water (KF) < 70 ppm with the substance. The purity of our sample was slightly worse

¹Commercial equipment, instruments, or materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the products identified are necessarily the best available for the purpose.

than that for the IUPAC reference sample [1,2], which had a reported purity of (NMR) > 99.5 % and water concentration $w(\text{H}_2\text{O}) = 10^{-5}$.

3 Results and Discussion

3.1 Two-Phase Isochoric Heat Capacity Measurements

Measurements of the two-phase isochoric heat capacities, C_{V2} , for [C6mim][NTf2] were performed along 2 liquid isochores (1323.92 and 1344.14) $\text{kg}\cdot\text{m}^{-3}$ as a function of temperature in the range from (279.45 to 374.08) K. For each filling density, measurements were concentrated in the immediate vicinity of the phase transition temperature to precisely determine the phase boundary properties (T_S , ρ_S , C'_{V1} , C'_{V2}) on the liquid + vapor equilibrium curve. Table 1 presents the experimental one- and two-phase C_V along the two measured liquid isochores. The phase-transition temperature (T_S), saturation liquid density (ρ_S), and saturation liquid isochoric heat capacity (one- C'_{V1} and two-phase C'_{V2}) values for [C6mim][NTf2] for the measured isochores together with our previous data [27] are presented in Table 2. Previous one-phase C'_{V1} data were slightly (within their experimental uncertainty) were corrected after their analysis together with new measurements in the present work. Table 2 contains also, derived from two-phase C_V data, new values of the second temperature derivatives of vapor-pressure and chemical potential after slightly corrections previous C_V measurements [27]. Due to the sensitivity of the vapor-pressure and chemical potential temperature derivatives to slight (even within their experimental uncertainty) changes in C'_{V2} , we observed considerable changes in (d^2P_S/dT^2) and $(d^2\mu/dT^2)$. Figure 3 depicts, the measured temperature dependence of the measured C_V along the two liquid isochores in the one- and two-phase regions near the phase transition temperature. It is clear from Fig. 3 that, for each measured liquid isochore, the two-phase C'_{V2} drops discontinuously at the phase-transition temperatures (T_S), to a value corresponding to that of the one-phase liquid (C'_{V1}). As a new observation for any ionic liquid substance, it is clear that both one- and two-phase C_V increase linearly with temperature, except one-phase C_V in the immediate vicinity of the phase transition temperature. This behavior was expected, since it is similar to observations for other heavy organic molecules at compressed-liquid state conditions. Our earlier studies [27,28] made us aware that linear behavior should be observed for internally consistent two-phase C_V as a function of specific volume V . Thus, we took advantage of the linearity with respect to temperature to interpolate isochoric two-phase C_V to integral values of temperature. For scientific applications, there is a very important specific volume behavior of the measured two-phase C_V (see below sec. 3.3). For example, $C_{V2} - V$ dependence provides other very useful scientific information for temperature behavior of important thermodynamic quantities, namely the second temperature derivatives of vapor pressure and chemical potential. It also allows us to calculate all of the derived thermodynamic properties of IL along the saturation curve (see sec. 4). Figure 4 depicts two-phase C_V isotherms as a function of specific volume V , which are linear as expected. This figure included also our previous reported two-phase C_V data [27]. It is clear from Fig. 4 that, not only are the two-phase ($C_{V2} - V$) isotherms linear, but that the slope of every isotherm is a very small positive value. Each isotherm starts at the

saturated liquid specific volume, $V_s' = 1/\rho_s'$, and slowly increases with V as it tends toward the saturated vapor specific volume, $V_s'' = 1/\rho_s''$ which is not practical to depict in Fig. 4 for two reasons: (1) this volume would be a minimum of ten orders of magnitude larger than the liquid volumes (for example, for ideal gas specific volume of the IL at 298.15 K and $P_g = 0.468 \times 10^{-9}$ Pa, $V_s'' = 1.18 \times 10^{15} \text{ cm}^3 \cdot \text{g}^{-1}$); the present results would appear in the extreme high right corner of such a graph; and, (2) this volume has never been measured due to pressures that are $\ll 1$ Pa. Thus, in this work we were limited to measurements of C_V for IL [C6mim][NTf2] for filling densities in the compressed-liquid range. In order to estimate the values of (d^2P_g/dT^2) and $(d^2\mu/dT^2)$ measurements on two reference isochores in the two-phase region are sufficient because the $C_{V2} - V$ dependence is a straight line, which will be discussed in terms of the Yang – Yang relation, Eq. 7. This relation leads to a simple and accurate approach to determine the slope, *i.e.*, (d^2P_g/dT^2) , and intercept $(d^2\mu/dT^2)$ of the $C_{V2} - V$ straight lines. In other words, a series of measurements of C_{V2} as a function of temperature along two isochores in the two-phase regions is enough information.

All the measurements reported in this work were made on a single filling of the calorimeter. Between isochores, a small amount of substance was withdrawn and weighed with a calibrated mass balance. For each of the two filling densities in this work, the sample was heated to 374 K on an isochoric path, while some isochores were cycled up to three times to detect possible decomposition or possible leakage at the high-pressure end of the isochore where pressure could be as high as 100 MPa. In this work, the measured values of C_V were internally consistent as shown in Fig. 4, which gives us considerable confidence that neither decomposition nor leakage was present. In view of these indications from the experiments and a typical sensitivity of 0.1 mol % for a proton NMR analysis, we elected to not send a sample for NMR analysis after the measurements were completed. For two ordinary hydrocarbons (*e.g.* *n*-pentane and *n*-hexane), the two-phase $C_{V2} - V$ dependence shown in Fig. 5 is illustrative. While all isotherms are linear, as expected, the slopes of the $C_{V2} - V$ isotherms are much larger than this work for the IL, and in addition, these slopes increase at a faster rate with a temperature rise. Though not experimentally accessible, gas-liquid critical point scaling theory informs us that the slope should grow to infinity at the critical-point temperature. Unlike ordinary hydrocarbons, for the IL $C_{V2} - V$ slopes are almost zero (see sec. 3.3), *i.e.*, two-phase isochoric heat capacity of an IL almost independent of the specific volume.

The temperature dependence of the measured two-phase (C_{V2}') and one-phase (C_{V1}') liquid heat capacities along the saturation curve for two measured isochores together with previous reported data [27] is shown in Fig. 6 (left). The isochoric heat capacity difference ($\Delta C_V' = C_{V2}' - C_{V1}'$) is showed in Fig. 6 (right). Figure 6 (left) also shows the ideal gas heat capacity of an IL [C6mim][NTf2] reported by Paulechka and Kabo [29]. As one can note from Fig. 6 (right), the measured isochoric heat capacity difference $\Delta C_V'$ is a linear function of temperature and thus could be represented by a simple function capable of extrapolation to both lower and higher temperatures. The magnitude of the isochoric heat capacity differences is relatively small in comparison with normal liquids [28]; for this work it ranges from (0.032 to 0.166) $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. This means that the effect of the vapor phase on the two-

phase C'_{v2} is small, due to the very low vapor pressure and density of the IL [C6mim][NTf2] in the vapor phase.

The present measured one- (C'_{v1}) and two-phase C'_{v2} saturated isochoric heat capacities together with previous measurements [27] were fitted to simple quadratic temperature functions,

$$C'_{v1} = b_0 + b_1 T + b_2 T^2, \quad (2)$$

and

$$C'_{v2} = c_0 + c_1 T + c_2 T^2, \quad (3)$$

where $b_0 = 1.5968 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$; $b_1 = -2.4086 \times 10^{-3} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-2}$; $b_2 = 5.2191 \times 10^{-6} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-3}$; $c_0 = 1.3969 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$; $c_1 = -1.8167 \times 10^{-3} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-2}$; $c_2 = 5.5799 \times 10^{-6} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-3}$. Since two-phase C_{v2} is a linear function of specific volume V (see also below very well-known Yang-Yang relation, Eq. 7, for two-phase C_{v2}), the values of isochoric heat capacity at any T and V in the two-phase region can be calculated from the following equation:

$$C_{v2} = C'_{v2}(T) + \left(\frac{\partial C_v}{\partial V} \right)_T [V - V'_s(T)], \quad (4)$$

where the derivative $\left(\frac{\partial C_v}{\partial V} \right)_T$ in the two-phase region (slope of the two-phase $C_{v2} - V$ isotherms) is related to the second temperature derivative of the vapor pressure as in the relation,

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{d^2 P_s}{dT^2} \right). \quad (5)$$

The present at saturation appear systematically lower than all previously reported data at 101 kPa (see Fig. 1), except Crosthwaite et al. [12] which appears to be the lowest of all. Acceptable agreement within 3.4 % (close to the experimental uncertainty of the present data) was found between the present data and the values measured by Hughes et al. [21]. A discrepancy of less than 3 % also was observed between our results and the data reported by Blokhin et al. [8]. Good agreement of 2.4 % was found between the present data and the data reported by Bochmann and Hefter [5] at temperatures. Also, our previous reported in Ref. [27] data at high temperatures are consistent with other reported data (see Fig. 1), except the data by Bochmann and Hefter [5], which was measured isobarically at $p = 10 \text{ MPa}$. For example, the discrepancy between our previous report in Ref. [27] and the data by

Diedrichs and Gmehling [7] is less than 1 % (good agreement also was found between the present saturated densities and densities at 101 kPa from the same lab, Kato and Gmehling [16], see above). In the temperature range from (399 to 450) K our previous data [27] are in good agreement (AAD=1.53 %) with the data by Bochmann and Hefter [5], although at higher temperatures (above 450 K), the discrepancy grows, reaching 7.5 %. However, as clearly demonstrated in Fig. 1, the temperature trend all of the previous reported data (high temperature behavior of for the IL) are consistent with our previous results [27]. Moreover, the data reported by Bochmann and Hefter [5] at high temperatures (above 535 K) are effected by decomposition, which introduces an important consideration. We observed that the decomposed sample data are consistent with their data with an undecomposed sample, i.e., there's no significant difference between the data for decomposed and stable (undecomposed) IL samples. Looking to the future, we feel that additional measurements which include the high temperature range above 450 K are called for to help decide which data are the most reliable.

3.2 Saturated Liquid Density (ρ_g') and Phase Transition Temperature (T_S) Measurements

As we mentioned above, isochoric heat capacity exhibits a discontinuity at the intersection of the liquid-gas phase-transition curve (see Fig. 3). We have determined each phase transition temperature (T_S) for each filling density from the observed discontinuity in $C_V - T$ curves and confirmed the phase transition temperature with its $P - T$ isochore break point. The measured phase-transition temperature for each liquid isochore is presented in Table 2 together with previous measurements [27] and shown in Fig. 2 in a projection of $T_S - \rho_S$ data. This figure also depicts the values of density as a function of temperature at atmospheric pressure $\rho(T)$ calculated from reference correlation [1] at atmospheric pressure and other reported density data [6,13,15–25,27] at atmospheric pressure published after IUPAC project reports [1,2] (after 2009). Table 3 presents the deviations (absolute average deviation, AAD) between the present saturated density data and reported densities at atmospheric pressure (second column). This table also contains the deviations between the correlation by Tariq et al. [6] and various data sources including the present results (first column). The IUPAC recommended reference correlation for the density at 101 kPa is agree with the present saturated density data within 0.18 %. As one can see from Table 3, the present saturated density data for the IL are deviate from the measurements by González et al. [15] within 0.22 %. Good agreement within 0.07 % to 0.10 % was observed between the present and the reported density data by Kato and Gmehling [16], Azevedo et al. [17], Jacquemin et al. [22], Kandil and Marsh [23], and Ahosseini et al. [24]. Acceptable agreement within 0.14 %, 0.15 %, 0.17 %, and 0.17 % was found between the present and the data of Iguchi et al. [25], Mohammad et al. [18], Widegren and Magee [20], and Safarov et al. [13], respectively. The relative large discrepancy within 0.30 %, 0.27 %, and 0.22 % is observed between the data reported by Esperança et al. [19], Tariq et al. [6], and Gonzalez et al. [15] and the present saturated density data, respectively. Our previous saturated density measurements [27] at high temperatures deviate from the Tariq et al. [6] and Safarov et al. [13] reported data within 0.35 %. The deviations within 0.34 % was also observed between our previous studies [27] and the data reported recently by Iguchi et al. [25]. The large discrepancy maybe attributed due to purity effect or contact with remaining air in the

calorimeter after evacuation. Other possible reason is at high temperature the difference between densities at saturation and 101 kPa is increasing, therefore, the comparison saturated liquid density and the density at 101 kPa is thermodynamically incorrect, although the differences between them is small. The deviation plots between the density correlation at 101 kPa by Tariq et al. [6] and the present measurements and other reported data are shown in Fig. 7. As this figure shows, in general the agreement between the most reliable reported data is acceptable. Table 3 (first column) presents AAD between the Tariq's et al. [6] correlation and reported data. As can be note, the deviations between the reported datasets and the correlation [6] are within 0.14 % to 0.30 %. The present saturated densities agree with the correlation [6] within 0.27 %. Thus, deviation of the present saturated density data from correlation [6] are lying within the same deviation range as all other reported data. This is confirming the accuracy and consistency of the present saturated density data with other reported data.

The phase transition temperature for each constant liquid-density (isochore) experiment was very clearly exhibited on its thermogram and barogram as break points of the slopes [27]. The discontinuity of the temperature behavior of $C_V - T$ isochores for the IL has also been experimentally observed in measured $\gamma_V - T$, where, $\gamma_V = (P/T)_V$, and $P - T$ data as break points at the saturation curve (see Fig. 8 and Table 4). As Fig. 8 demonstrates for two measured isochores, $\gamma_V - T$ data show sharp break points at the same temperatures as the isochoric heat capacity jumps (see Fig. 3). This is additional confirmation of the reliability of the reported saturated density and temperature data for the IL. As one can see from Fig. 2, ρ'_S decreases with temperature, and is slightly nonlinear. The present measured values of saturated-liquid specific volumes, $V'_S = 1/\rho'_S$, together with our previous reported data [27] were fitted to a simple quadratic temperature function, as in the form,

$$V'_S = V_0 + V_1 T + V_2 T^2, \quad (6)$$

where the values of the fitting parameters are $V_0 = 0.61282 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$; $V_1 = 0.341192 \times 10^{-6} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$; and $V_2 = 0.190627 \times 10^{-9} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{K}^{-2}$. This equation together with measured one-phase C'_{V1} and two-phase C'_{V2} will be used (see below, sec. 4) to calculate the derived thermodynamic properties of an IL at saturation.

3.3 Two-Phase Isochoric Heat Capacities and Second Temperature Derivatives of Vapor-Pressure ($d^2 P_S/dT^2$) and Chemical Potential ($d^2 \mu/dT^2$)

In order to understand the physical nature of the effects of temperature and volume on the two-phase isochoric heat capacity, as well as related thermodynamic properties, the chemical potential ($C_{V\mu}$) and vapor-pressure (C_{VP}) contributions were separated from the measured total two-phase isochoric heat capacity data. These separate contributions ($C_{V\mu}$ and C_{VP}) were extracted from the measured total two-phase isochoric heat capacity of the IL by using the well-known theoretically based Yang-Yang relation for two-phase C_{V2} (see below, Eq. 7).

It is well known that vapor pressure for an IL is very small. According to measurements by Zaitsau et al. [3] and Rocha et al. [4] for [C6mim][NTf2] in the temperature range from (446 to 494) K, the values of vapor pressure are in the range of (0.007 to 0.170) Pa. Therefore, it comes as no surprise that their temperature derivatives (especially the second temperature derivative are also too small to directly measure in vapor-pressure experiments or accurately calculate from available vapor–pressure correlation by direct differentiation (Eq. 1, for example, [3]). However, two-phase isochoric heat capacity measurements allow us to directly calculate the values of second temperature derivatives (d^2P_S/dT^2) and ($d^2\mu/dT^2$) using the theoretically based Yang-Yang relation (see below, Eq. 7). For the gas + liquid coexistence region, the Yang and Yang [30] relation for two-phase isochoric heat capacity is given by,

$$C_{V2} = -T \frac{d^2\mu}{dT^2} + VT \frac{d^2P_S}{dT^2}, \quad (7)$$

or, in terms of the contributions from chemical potential and vapor pressure, we have the sum,

$$C_{V2} = C_{V\mu} + C_{VP}, \quad (8)$$

where C_{V2} is the total measured two-phase isochoric heat capacity; V is the specific volume;

$C_{VP} = VT \frac{d^2P_S}{dT^2}$ and $C_{V\mu} = -T \frac{d^2\mu}{dT^2}$ (where $d^2\mu/dT^2 < 0$) are the vapor-pressure and chemical potential contributions to two-phase heat capacity, respectively. It follows from Eq. 7 that the experimentally observed two-phase isochoric heat capacity in Eq. 7 consists of two contributions, namely, the vapor-pressure (C_{VP}) and chemical potential ($C_{V\mu}$) terms. An extremely useful quantity that formally describes the relative contribution of the chemical potential ($C_{V\mu}$) to the measured two-phase C_{V2} is the Yang-Yang parameter, defined as

$R_\mu \equiv \frac{C_{V\mu}}{C_{VP} + C_{V\mu}}$. In this way, R_μ characterizes the contribution of the chemical potential to the total experimentally observed two-phase heat capacity C_{V2} . Originally devised by Fisher and co-workers [31–33], the Yang-Yang anomaly parameter is an estimate of the contribution of (d^2P_S/dT^2) and ($d^2\mu/dT^2$) to the divergence of two-phase C_{V2} near the critical point. This parameter also can be successfully used to estimate the contributions of vapor-pressure (C_{VP}) and chemical potential ($C_{V\mu}$) to the total measured two-phase isochoric heat capacity for IL.

According to the Yang-Yang relation Eq. 7, two-phase isochoric heat capacity must be a linear function of specific volume V at a fixed temperature (see Figs. 4 and 5). The slope of a $C_{V2} - V$ isotherm is equal to $T(d^2P_S/dT^2)$, while the intercept for $V=0$ is exactly $-T(d^2\mu/dT^2)$. The relation Eq. 7 has been experimentally confirmed for pure fluids in our earlier work (see, for example, [27,28] as illustrated in Fig. 5 for *n*-pentane and *n*-hexane [34]). It follows from Eq. 7 that saturated two-phase liquid (C'_{V2}) and vapor (C''_{V2}) heat

capacities are directly related to the second temperature derivatives (d^2P_S/dT^2) and ($d^2\mu/dT^2$) as in the relations,

$$\frac{d^2P_S}{dT^2} = \frac{C''_{v2} - C'_{v2}}{T(V'' - V')} \quad \text{and} \quad \frac{d^2\mu}{dT^2} = \frac{V''C'_{v2} - V'C''_{v2}}{T(V' - V'')}, \quad (9)$$

where V'' and V' are the vapor and liquid specific volumes at saturation, respectively, corresponding to a given fixed temperature T (isotherm). Usually Eq. 9 is applied for pure fluids to calculate the values of temperature derivatives (d^2P_S/dT^2) and ($d^2\mu/dT^2$) using measured values of saturated properties ($T_S, V', C'_{v2}, V'', C''_{v2}$) [27,28,34]. For ordinary fluids the properties on the saturated liquid (T_S, V', C'_{v2}) and vapor (T_S, V'', C''_{v2}) curves are either well-known or can be readily obtained experimentally. Therefore, using Eq. 9 both derivatives can be readily calculated from measured ($T_S, V', C'_{v2}, V'', C''_{v2}$) data. If saturated properties are not experimentally known, the relation (7) can be directly used to calculate the values of (d^2P_S/dT^2) and ($d^2\mu/dT^2$) by fitting measured two-phase C_{v2} as a function of V in the two-phase region. In the present case for our IL, direct measurements of both two-phase vapor heat capacity C''_{v2} and vapor specific volume V'' at saturation were not practical, due to the fact that the vapor is far too dilute at all practical temperatures below the thermal decomposition temperature threshold. In the present work, we directly applied Eq. 7 to the present and previously reported [27] two-phase sochoric heat capacities for various isotherms. The derived values of (d^2P_S/dT^2) and ($d^2\mu/dT^2$) as a function of temperature are given in Table 2 and are depicted in Figs. 9 and 10 together with the values calculated from a previously published vapor-pressure Eq. 1 [3] and [4]. As mentioned earlier, as expected, the values of (d^2P_S/dT^2) calculated from Eq. 1 are systematically wrong. While these calculated derivatives display the same qualitative profile in Fig. 9, they differ from our derivatives derived from experiments by orders of magnitude. We report that the derived values of (d^2P_S/dT^2) and ($d^2\mu/dT^2$) are very sensitive to small changes in our C_{v2} measurements. This finding follows from the relations Eq. 9 where (d^2P_S/dT^2) and ($d^2\mu/dT^2$) are functions of the four measured quantities ($T_S, V', C'_{v2}, V'', C''_{v2}$). Even rather small changes of C'_{v2} and C''_{v2} or (V' and V''), will cause considerable change to values of (d^2P_S/dT^2) and ($d^2\mu/dT^2$). This would explain why we observed large relative differences between the present and previous [27] reported (d^2P_S/dT^2) and ($d^2\mu/dT^2$) data, while our two-phase C_{v2} data were corrected just slightly (within their experimental uncertainty). Values of the Yang-Yang parameter R_μ were calculated from the Yang-Yang relation Eq. 7 by using the extracted C_{vp} and $C_{v\mu}$ from the present measured two-phase C_{v2} for the IL, and are presented in Fig. 11 as a function of temperature. As shown in Fig. 11 over a range of intermediate temperatures (350 K to 430 K), R_μ values range from 0.995 to 0.980. This means that values of C_{v2} at intermediate temperatures (< 430 K) are dominated by the chemical potential contribution,

$$C_{v\mu} = -T \frac{d^2\mu}{dT^2}, \text{ i.e., the contribution of vapor pressure is quite small. At high temperatures } (> 430 \text{ K}), \text{ the contribution of the vapor pressure } C_{vp} = VT \frac{d^2P_S}{dT^2} \text{ to the measured two-phase}$$

C_{V2} increases sharply from 0.02 to 0.2 at our largest measured temperature, while the contribution of $C_{V\mu}$ falls sharply to 0.86.

It is well known that the vapor pressure of an IL substance is quite small [3] at temperatures at least up to their threshold of thermal decomposition. The second temperature derivatives are very small as well. For example, when calculated from Eq. 1 [3], values of (d^2P_S/dT^2) in the same temperature range are within $< 6 \times 10^{-4} \text{ Pa} \cdot \text{K}^{-2}$. It follows from Eq. 9 that small values of (d^2P_S/dT^2) for the IL means that the heat capacity difference $(C''_{V2} - C'_{V2})$ must be small because $C''_{V2} \approx C'_{V2}$ (or $C''_{V2} - C'_{V2} \approx 0$, two-phase C_{V2} is almost independent of V , see Fig. 4) and $(V'' - V')$ is large because the vapor specific volume (V'') at saturation $V'' \gg V'$ than the saturated liquid volume (V'). Thus, for an IL (especially at low temperatures) the Eq. 9 can be simplified as

$$\frac{d^2P_S}{dT^2} = \frac{C''_{V2} - C'_{V2}}{T(V'' - V')} \approx \frac{C''_{V2} - C'_{V2}}{TV''}. \quad (10)$$

From the present calorimetric measurements, it is apparent why the vapor pressure and (d^2P_S/dT^2) of IL are quite small. Thus, two different experiments (calorimetric and effusion) have independently confirmed anomalously small values of the quantity (d^2P_S/dT^2) . Since $V''C'_{V2} \gg V'C''_{V2}$, because $C''_{V2} \approx C'_{V2}$ and $V'' \gg V'$, the second temperature derivative of the chemical potential can be obtained with a greatly simplified relation,

$$\frac{d^2\mu}{dT^2} = \frac{V''C'_{V2} - V'C''_{V2}}{T(V' - V'')} \approx -\frac{C'_{V2}}{T}. \quad (11)$$

Thus, we have shown that the quantity $(d^2\mu/dT^2)$ is completely defined by the saturated two-phase liquid heat capacity at saturation C'_{V2} .

The values of (d^2P_S/dT^2) derived from the present two-phase C_{V2} measurement were compared with the values calculated from vapor pressure Eq. 1 by Zaitsau et al. [3] and Rocha et al. [4] (see Fig. 9). Equation 1 has a single temperature term and was fitted with experimental measurements of vapor pressure over a short range of temperature. No one would have expected such a short equation to calculate useful values of the second derivative. Thus, we were not surprised that agreement was merely qualitative and was limited to an order of magnitude and the sign of the value of the second derivative. For example, at a temperature of 457.31 K, the value of (d^2P_S/dT^2) derived from the C_{V2} measurement is $2.635 \times 10^{-4} \text{ Pa} \cdot \text{K}^{-2}$, while the value of (d^2P_S/dT^2) calculated with Eq. 1 is $0.736 \times 10^{-4} \text{ Pa} \cdot \text{K}^{-2}$. The small absolute value of (d^2P_S/dT^2) is due to the observation that two-phase C_{V2} of the IL along the $T = 457.31 \text{ K}$ isotherm is almost independent of specific volume, *i.e.*, the slope of $C_{V2} - V$ lines is quite small for the experimental data in this work. The present calorimetric measurements clearly show that $C_{V2} - V$ isotherms are linear with a very small slope that increases slowly with rising temperature. For isotherms (below 430

K) $C_{V2} - V$ the observed dependence is almost flat and the vapor phase is almost an ideal gas. From the physical point of view, this means that the effect of the vapor phase on the total observed heat capacity of the two-phase IL is negligibly small, *i.e.*, when we isochorically heat the IL, most of the energy is used to increase the internal energy of the liquid phase, or in other words, almost no energy is spent to evaporate liquid to the vapor phase.

4 Derived Thermodynamic Properties of IL [C6mim][NTf2] at the Saturation Curve

As was mentioned above, due to small vapor pressures of the IL, their thermodynamic properties at saturation exhibit certain features that considerably simplify calculation. We used well known general differential equations of thermodynamics [27] to calculate thermodynamic properties and one-phase partial temperature derivatives at saturation from the measured saturated calorimetric properties ($T_S, \rho'_S, C'_{V2}, C'_{V1}$) and vapor-pressure data. Since for IL (dP_S/dT) is small, the calculated values of isobaric heat capacity at saturation (C_P) and saturated liquid heat capacity (C'_S) are equal to two-phase liquid isochoric heat capacity (C'_{V2}) at saturation, that is $C_P \approx C'_{V2} \approx C'_S$. The maximum absolute differences between the calculated C_P and measured C'_{V2} are $< 2.7 \times 10^{-9} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, while the maximum absolute differences between the calculated C_S and measured C'_{V2} are $< 1.35 \times 10^{-9} \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. The general assumption ($C_P \approx C'_{V2} \approx C'_S$), which applies at very low vapor pressure conditions, was confirmed in this work by comparison of calculated C_P values at $P = 101 \text{ kPa}$ from a reference correlation [1] and the present C'_{V2} measurements (see Figs. 1 and 6 (left)).

Speed of sound of the saturated liquid IL [C6mim][NTf2] was calculated from the present measured saturated-liquid specific volume V_S , its temperature derivative, (dV_S/dT), and one- and two-phase isochoric heat capacities ($\Delta C'_V = C'_{V2} - C'_{V1}$) by using the relation,

$$W_S = V_S \left(\frac{dV_S}{dT} \right)^{-1} \sqrt{\frac{C'_{V2}}{C'_{V1}} \left(\frac{\Delta C'_V}{T} \right)}. \quad (12)$$

Values of speed of sound at saturation that were calculated with Eq. 12 together with the values calculated from IUPAC reference correlation [1] at $P = 101 \text{ kPa}$ are presented in Table 5. As is often the case for derived thermodynamic values, agreement with experimental data by Widegren and Magee [20] is not satisfactory. In this case the calculation of W_S depends on a knowledge of five quantities, where each quantity has an uncertainty. Perhaps it is not surprising that deviations between the measured [20] speed of sound data and derived from the heat capacity measurements are within 15 % to 30 %. Because of uncertainties that are propagated to calculated W_S values, we trust the experimental W_S measurements over the calculations. The values of one-phase isothermal

compressibility at saturation, K'_{TS} , calculated from the present isochoric heat capacity differences $\Delta C'_V$ and V_S , and (dV_S/dT) are presented in Table 5; because of the underlying calculations with (dV_S/dT) , we cannot put much faith in K'_{TS} values calculated in this way. The values of the partial temperature derivative of pressure at saturation in the one-phase region, $(\partial P/\partial T)_{V'}^{sat.}$, derived from the present measured isochoric heat capacity jumps $\Delta C'_V$ and (dV_S/dT) are presented in Table 5 and depicted in Fig. 12 together with the values directly measured in the present work. Since the values of the vapour pressure derivative (dP_S/dT) are very small, the V values of $(\partial P/\partial T)_{V'}^{sat.}$ are completely determined by the values of isochoric heat capacity differences $\Delta C'_V$ and (dV_S/dT) derived in the present work (see Eqs. 2, 3, and 6).

$$\left(\frac{\partial P}{\partial T}\right)_{V'}^{sat.} = \frac{1}{T} \left(\frac{dV_S}{dT}\right)^{-1} \Delta C'_V. \quad (13)$$

As Fig. 12 demonstrates, the agreement between independent calorimetric (heat capacity) and direct P - T measurements is good. This is additional confirmation of thermodynamic consistency of the simultaneous calorimetric and thermal measurements.

The values of the partial temperature derivative of specific volume at saturation in the one-phase region, $(\partial V/\partial T)_P^{sat.}$, calculated from the present data, $\Delta C'_V$ and (dV_S/dT) , and vapour-pressure Eq. 1 [3] are almost the same, *i.e.*,

$$\left(\frac{\partial V}{\partial T}\right)_P^{sat.} = \left(\frac{dV_S}{dT}\right) \quad (14)$$

the maximum difference on the order of $10^{-11} \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{K}^{-1}$. The calculated values of derived thermodynamic properties of [C6mim][NTf2] using the present calorimetric measurements C'_{V2} , C'_{V1} , $\Delta C'_V$, V_S , dV_S/dT are presented in Table 5 as a function of temperature.

5 Conclusions

One- (C'_{V1}) and two-phase (C'_{V2}) isochoric heat capacities and saturated densities (ρ_S) and temperatures (T_S) of the ionic liquid ([C6mim][NTf2]) in the temperature range from (297 to 374) K are reported in this work for two liquid isochores (1323.92 and 1344.14 $\text{kg} \cdot \text{m}^{-3}$). We experimentally observed that two-phase isochoric heat capacity of the [C6mim][NTf2] is a very weak function of volume (nearly independent of volume, especially at low temperatures below 430 K) which means extremely small (within $0.01 \times 10^{-4} \text{ Pa} \cdot \text{K}^{-2}$ to $6.5 \times 10^{-4} \text{ Pa} \cdot \text{K}^{-2}$) values of the second temperature derivative of the vapor pressure, $(d^2 P_S/dT^2)$. The present measured one- and two-phase saturated liquid heat capacities (C'_{V1} , C'_{V2}) and saturated liquid densities (ρ'_S , T_S) together with our previous reported data [27] were used to calculate other derived thermodynamic properties C_p ,

$C'_s, \Delta H'_s, \Delta S'_s, W'_s, K'_{TS}, (\partial P/\partial T)_V^{\text{sat}}$, and $(\partial V/\partial T)_P^{\text{sat}}$ of [C6mim][NTf2] at saturation.

The second temperature derivatives of the vapor pressure, (d^2P/dT^2) , and chemical potential, $(d^2\mu/dT^2)$, were calculated directly from the measured two-phase isochoric heat capacity data using the theoretically based Yang-Yang relation. For the IL the values of the second temperature derivative of chemical potential can be estimated using the two-phase

liquid heat capacity at saturation as $\frac{d^2\mu}{dT^2} = -\frac{C'_{v2}}{T}$. For [C6mim][NTf2] $C'_s \approx C'_{ps} \approx C'_{v2}$, and the speed of sound at saturation can be calculated directly from calorimetric experiment,

$W_s = V_s \left(\frac{dV_s}{dT} \right)^{-1} \sqrt{\frac{C_{v2}}{C_{v1}} \left(\frac{\Delta C_v}{T} \right)}$, without using vapor-pressure data. The contribution vapor-pressure data to the derived thermodynamic data along the saturated liquid curve can be neglected. The distinct contributions of the chemical potential and vapor pressure parts of the measured two-phase isochoric heat capacity have been estimated using Yang-Yang relation. Temperature behavior of measured two-phase C_{v2} at low temperature (up to about

430 K) completely defined by chemical contribution (98 %), $C_{v\mu} = -T \frac{d^2\mu}{dT^2}$, while at high temperature (above 430 K), the contribution of a vapor-pressure term rapidly increases from 2 % to 20 % (at temperatures around 500 K).

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Fig. 1.

Measured two-phase liquid C'_{V2} (C'_P at saturation, one-phase) of $[C_6mim][NTf_2]$ at saturation as a function of temperature together with isobaric heat capacity, C_P , data at atmospheric pressure reported by other authors. ■, our previous measurements [27] (C'_{V2}); ◆, this work (C'_{V2}); ◇, Bochmann and Hefter [5]; △, Diedrichs and Gmehling [7]; ○, Blokhin et al. [8]; □, Shimizu et al. [9]; ●, Archer [10]; ▲, Ge et al. [11]; ▼, Crosthwaite et al. [12]; ×, Hughes et al. [21]. Dashed line is calculated from reference correlation by Chirico et al. [1] (extrapolation to higher temperatures, out of validity of the correlation); (---), Safarov et al. [13]. Solid line is calculated from correlation by Bochmann and Hefter [5]

Fig. 2.

Measured saturated liquid densities of $[\text{C}_6\text{mim}][\text{NTf}_2]$ from the present calorimetric (C_V) experiments together with reported data. ■, Tariq et al. [6]; ○, our previous study [27]; △, Safarov et al. [13]; □, González et al. [15]; ◇, Kato and Gmehling [16]; ▲, Azevedo et al. [17]; ▼, Muhammad et al. [18]; ▽, Esperança et al. [19]; ◆, Widegren and Magee [20]; +, Jacquemin et al. [22]; *, Kandil and Marsh [23]; ⊗, Ahosseini et al. [24]; ⊠, Iguchi et al. [25]; ●, this work. Solid line is the density of the IL at atmospheric pressure calculated from the IUPAC [1] reference correlation. Dashed line is calculated from Eq. (6). Dotted-dashed line is the extrapolation of the reference correlation [1] to high temperatures

Fig. 3.
Detailed view of temperature behavior of the measured one- and two-phase isochoric heat capacities of $[\text{C}_6 \text{ mim}][\text{NTf}_2]$ near the phase-transition points for two liquid isochores

Fig. 4.

Experimental two-phase isochoric heat capacities of [C₆mim][NTf₂] as a function of specific volume for various selected isotherms together with two-phase isochoric heat capacities C'_{V2} along the phase-transition curve together with our previous data from [27]: ▼, 350.36 K; □, 399.35 K; ■, 414.60 K; △, 422.30 K; ▲, 429.38 K; ○, 436.51 K; ×, 443.46 K; ◆, 457.31 K. Solid lines are interpolated data (smoothed lines); Dashed line is the coexistence curve calculated from Eqs. (2) and (6); Dotted lines would extend to the vapor branch of the coexistence curve

Fig. 5.

Measured two-phase isochoric heat capacities of n -pentane and n -hexane as a function of specific volume along the various isotherms. ●-Amirkhanov et al. [34]; ○- two-phase liquid and vapor C_{V2} at the saturation curve

Fig. 6.

Measured one- and two-phase liquid (C'_{v1} , C'_{v2} , left) isochoric heat capacities of $[\text{C}_6\text{mim}][\text{NTf}_2]$ as a function of temperature along the L-V coexistence curve together with V isochoric heat capacity differences ($\Delta C'_v = C'_{v2} - C'_{v1}$, right) at the phase-transition curve. The solid line is the isobaric heat capacity of $[\text{C}_6\text{mim}][\text{NTf}_2]$ at atmospheric pressure calculated from IUPAC reference correlation by Chirico et al. [1]. Dashed lines are calculated from correlation Eqs. (2) and (3). Dashed-dotted line is ideal gas isochoric heat capacity from [29]. Circles are present data and squares are previously reported data [27]

Fig. 7.

Percentage deviations, $\delta\rho_s = 100 \left(\frac{\rho_s^{\text{cal}} - \rho_s^{\text{exp}}}{\rho_s^{\text{exp}}} \right)$ of the present and reported experimental densities of $[\text{C}_6\text{mim}][\text{NTf}_2]$ from the values calculated from the correlation by Tariq et al. [6]. $\times$, this work; $\bullet$, Safarov et al. [13]; $\blacklozenge$, Widegren and Magee [20]; ∇ , Esperança et al. [19]; $\blacktriangledown$, Muhammad et al. [18]; $+$, Jacquemin et al. [22]; $*$, Kandil and Marsh [23]; $\otimes$, Ahosseini et al. [24]; $\boxtimes$, Iguchi et al. [25]; $\square$, Kato and Gmehling [16]; $\circ$, González et al. [15]; $\triangle$, IUPAC reference correlation [1]. Dashed line is the deviation between the correlations Tariq et al. [6] and IUPAC [1]; Solid line is the deviation between the correlations Tariq et al. [6] and Azevedo et al. [17]

Fig. 8.
Measured thermal pressure coefficients of [C₆mim][NTf₂] along two isochores in the immediate vicinity of the phase-transition temperatures

Fig. 9.

Second temperature derivative of vapor pressure (d^2P_S/dT^2) as a function of temperature derived from the present two-phase isochoric heat capacity measurements (symbols) for $[C_6mim][NTf_2]$ together with the values calculated from vapor-pressure equation by Zaitsau et al. [3] (dashed curve) and Rocha et al. [4] (dotted curve). Solid line is the smoothed curve

Fig. 10.

Second temperature derivative of chemical potential ($d^2\mu/dT^2$) as a function of temperature derived from the present two-phase isochoric heat capacity measurements (symbols) for $[\text{C}_6\text{mim}][\text{NTf}_2]$. The solid line is smoothed curve.

Fig. 11. Contribution (R_{μ} , Yang-Yang parameter) of chemical potential ($C_{V\mu}$) to the measured total two-phase isochoric heat capacity C_{V2} of $[\text{C}_6\text{mim}][\text{NTf}_2]$

Fig. 12.

One-phase thermal pressure coefficient, $\gamma_v = (\partial P / \partial T)_v^{\text{sat}}$ at saturation for $[\text{C}_6\text{mim}][\text{NTf}_2]$: directly measured (●) and derived (○) from the present two-phase measurements at saturation C_{V2} and one-phase C_{V1} measurements at saturation

Table 1 One- and two-phase isochoric heat capacities* of IL ([C₆mim][NTf₂])

<i>T</i> (K)	<i>C_V</i> (kJ·kg ⁻¹ ·K ⁻¹)	<i>T</i> (K)	<i>C_V</i> (kJ·kg ⁻¹ ·K ⁻¹)
$\rho = 1344.14 \text{ kg}\cdot\text{m}^{-3}$		$\rho = 1323.92 \text{ kg}\cdot\text{m}^{-3}$	
297.45	1.340	301.64	1.356
297.76	1.359	301.75	1.361
297.89	1.351	301.88	1.369
298.02	1.338	302.01	1.356
298.15	1.333	302.13	1.371
298.28	1.355	302.26	1.354
298.41	1.345	333.63	1.418
298.53	1.341	333.82	1.417
298.66	1.349	333.94	1.401
288.87	1.346	334.06	1.412
288.72	1.339	334.18	1.406
289.04	1.325	334.30	1.414
289.17	1.335	334.42	1.423
289.30	1.352	334.54	1.415
289.44	1.320	334.66	1.402
289.57	1.333	334.79	1.411
289.70	1.341	334.91	1.408
289.83	1.345	339.73	1.428
304.30	1.360	339.83	1.424
304.69	1.348	339.95	1.419
304.82	1.356	340.03	1.438
304.95	1.369	340.15	1.421
305.08	1.351	340.27	1.432
305.20	1.365	340.39	1.435
305.33	1.358	340.51	1.427
305.46	1.371	344.34	1.434
305.59	1.362	344.46	1.443
314.15	1.385	344.58	1.436
314.57	1.375	344.70	1.441
314.69	1.358	344.82	1.429
314.82	1.379	344.93	1.449
314.94	1.367	345.05	1.447
315.07	1.369	345.17	1.442
315.20	1.382	345.29	1.427
315.32	1.374	345.41	1.439
315.45	1.361	348.64	1.442
320.89	1.386	348.76	1.439

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T (K)	C_V (kJ·kg ⁻¹ ·K ⁻¹)	T (K)	C_V (kJ·kg ⁻¹ ·K ⁻¹)
$\rho = 1344.14 \text{ kg·m}^{-3}$		$\rho = 1323.92 \text{ kg·m}^{-3}$	
321.17	1.392	348.88	1.449
321.30	1.374	348.99	1.446
321.42	1.388	349.11	1.452
321.55	1.371	349.23	1.450
321.67	1.379	349.35	1.441
321.79	1.377	349.47	1.447
321.92	1.384	349.58	1.438
322.04	1.391	349.70	1.443
322.16	1.388	349.65	1.449
322.29	1.382	349.82	1.438
322.41	1.394	349.94	1.443
323.89	1.395	350.05	1.441
324.15	1.387	350.17	1.446
324.28	1.398	350.29	1.448
324.40	1.403	<u>350.36^c</u>	<u>1.447^a</u>
324.52	1.406	350.36 ^c	1.397 ^b
324.65	1.389	350.41	1.395
324.77	1.392	350.53	1.393
324.89	1.381	350.64	1.391
325.02	1.388	350.76	1.398
325.14	1.397	350.88	1.396
325.24	1.391	350.99	1.388
<u>325.26^c</u>	<u>1.394^a</u>	351.11	1.390
325.26 ^c	1.362 ^b	351.23	1.393
325.39	1.360	351.35	1.386
325.51	1.361	351.46	1.388
325.63	1.360	351.58	1.391
325.75	1.363	351.70	1.387
325.88	1.361	351.82	1.389
326.00	1.359	351.93	1.385
326.13	1.356	352.03	1.389
326.26	1.360	360.03	1.400
328.58	1.363	360.19	1.395
328.70	1.360	360.30	1.404
328.82	1.358	360.42	1.392
328.94	1.355	360.53	1.397
329.07	1.357	360.65	1.391
329.19	1.362	360.76	1.393
329.31	1.363	360.88	1.388
329.43	1.353	360.99	1.389

T (K)	C_V (kJ·kg ⁻¹ ·K ⁻¹)	T (K)	C_V (kJ·kg ⁻¹ ·K ⁻¹)
$\rho = 1344.14 \text{ kg·m}^{-3}$		$\rho = 1323.92 \text{ kg·m}^{-3}$	
333.09	1.368	361.11	1.392
333.21	1.355	361.22	1.387
333.33	1.362	361.34	1.402
333.45	1.372	365.26	1.395
333.57	1.358	365.35	1.407
333.70	1.365	365.47	1.402
333.82	1.371	365.58	1.398
333.94	1.363	365.69	1.414
341.28	1.375	365.81	1.391
341.40	1.365	365.92	1.406
341.52	1.380	366.04	1.402
341.64	1.370	366.15	1.409
341.76	1.386	366.27	1.394
341.88	1.376	366.38	1.408
342.00	1.374	372.87	1.421
342.12	1.383	372.96	1.418
348.64	1.384	373.07	1.412
348.76	1.381	373.18	1.415
348.88	1.390	373.29	1.423
348.99	1.386	373.41	1.406
349.11	1.383	373.52	1.419
349.23	1.394	373.63	1.408
349.35	1.380	373.74	1.411
349.47	1.392	373.86	1.426
349.58	1.385	373.97	1.423
		374.08	1.428

* Standard uncertainties u are: $u(T)=15 \text{ mK}$; $u(C_V)=3 \%$; $u(\rho)=0.12 \%$;

^aTwo-phase saturated C_V ;

^bOne-phase saturated C_V ;

^cPhase transition temperature.

Table 2

Measured one- (C'_{V1}) and two-phase (C'_{V2}) saturated liquid isochoric heat capacities, saturated liquid densities (ρ'_S), isochoric heat capacity jumps ($\Delta C'_V$) and derived values of the second temperature derivative of vapor pressure and chemical potential* for [C₆mim][NTf₂]

$T(K)$	$\rho'_S (kg \cdot m^{-3})$	$C'_{V2} (kJ \cdot kg^{-1} \cdot K^{-1})$	$C'_{V1} (kJ \cdot kg^{-1} \cdot K^{-1})$	$\Delta C'_V (kJ \cdot kg^{-1} \cdot K^{-1})$	$\left(\frac{d^2 P_s}{dT^2}\right) \times 10^4 (Pa \cdot K^{-2})$	$\left(\frac{d^2 \mu}{dT^2}\right) \times 10^3 (kJ \cdot kg^{-1} \cdot K^{-2})$
325.26	1344.14	1.394	1.362	0.032	0.010	-4.200
350.36	1323.92	1.447	1.397	0.050	0.020	-4.141
399.91 ^a	1279.75	1.570	1.476	0.094	0.500	-3.930
414.60 ^a	1270.65	1.603	1.496	0.107	0.738	-3.876
422.30 ^a	1265.02	1.624	1.508	0.116	0.910	-3.850
429.38 ^a	1259.13	1.644	1.523	0.121	1.110	-3.834
436.51 ^a	1253.60	1.664	1.536	0.128	1.310	-3.817
443.46 ^a	1248.13	1.684	1.551	0.133	1.630	-3.804
457.31 ^a	1236.55	1.733	1.587	0.146	2.635	-3.796
470.13 ^a	1227.45	1.775	1.616	0.159	4.500	-3.780
479.69 ^a	1217.58	1.814	1.648	0.166	6.520	-3.780

* Standard uncertainties u are: $u(T)=15$ mK; $u(CV)=3$ %; $u(\rho)=0.12$ %; $u\left(\frac{d^2 P_s}{dT^2}\right)=5$ %; $u\left(\frac{d^2 \mu}{dT^2}\right)$

^aOur previous measurements [27].

Table 3

Percentage Absolute Average Deviation (AAD) between reported densities of [C6mim][NTf2] at atmospheric pressure and the present measurements at saturation

References	AAD ^a (%)	AAD ^b (%)
[1]	0.14	0.18
[6]	-	0.27
[13]	0.18	0.17
[15]	0.21	0.22
[16]	0.30	0.08
[17]	0.26	0.09
[18]	0.14	0.15
[19]	0.16	0.30
[20]	0.24	0.17
[22]	0.25	0.07
[23]	0.21	0.10
[24]	0.29	0.07
[25]	0.12	0.14
[27]	0.35	-
this work	0.27	-

^a AAD between the values calculated from correlation by Tariq et al. [6] and reported data;

^b AAD between the present saturated density data and the values reported by other authors.

Table 4

Directly measured one-phase thermal-pressure coefficient, $\gamma_v = (\partial P / \partial T)_v^{\text{sat}}$, at saturation^{*} of IL

ρ_s , $\text{kg} \cdot \text{m}^{-3}$	T_s , K	$(\partial P / \partial T)_v^{\text{sat}}$, $\text{MPa} \cdot \text{K}^{-1}$
1344.14	325.26	0.626
1323.92	350.36	0.596
1279.75 ^a	399.91	0.534
1270.65 ^a	414.60	0.523
1265.02 ^a	422.30	0.515
1259.13 ^a	429.38	0.504
1253.60 ^a	436.51	0.485
1248.13 ^a	443.46	0.488
1236.55 ^a	457.31	0.461
1227.45 ^a	470.13	0.451
1217.58 ^a	479.69	0.447

^{*} Standard uncertainties u are: $u(\rho) = 0.12\%$; $u(T) = 15 \text{ mK}$; $u(\partial P / \partial T)_v^{\text{sat}} = 0.5\%$;

^a Our previous measurements [27].

Table 5

Derived, from the present two-phase isochoric heat capacity measurements, values of thermodynamic properties* of [C₆mim][NTf₂] at saturation, $\Delta H'_s = H'_s(T) - H'_s(T_0)$; $\Delta S'_s = S'_s(T) - S'_s(T_0)$; and $T_0 = 298.15$ K

T (K)	$\Delta H'_s$ (kJ · kg ⁻¹)	$\Delta S'_s$ (kJ · kg ⁻¹ · K ⁻¹)	$\left(\frac{\partial P}{\partial T}\right)^{\text{sat}}_V$ (MPa · K ⁻¹)	$\left(\frac{\partial V}{\partial T}\right)^{\text{sat}}_P \times 10^{-3}$ (m ³ · kg ⁻¹ · K ⁻¹)	$K'_{\text{TS}} \times 10^9$ (Pa ⁻¹)	W'_s (m · s ⁻¹)
325.26	34.633	0.111	0.641	0.4652	0.9754	905.42
350.36	67.797	0.209	0.607	0.4748	1.0352	885.67
399.91	137.08	0.394	0.542	0.4937	1.1656	848.18
414.60	158.75	0.447	0.522	0.4993	1.2159	833.09
422.30	170.34	0.475	0.514	0.5022	1.2361	827.98
429.38	181.15	0.500	0.503	0.5049	1.2644	820.20
436.51	192.17	0.526	0.501	0.5076	1.2703	820.28
443.46	203.06	0.551	0.486	0.5103	1.3101	808.88
457.31	225.21	0.600	0.475	0.5155	1.3419	802.67
470.13	246.25	0.645	0.466	0.5204	1.3710	796.88
479.69	262.30	0.679	0.457	0.5241	1.3949	792.87

* Standard uncertainties u are: $u(V'_s) = 0.12\%$; $u(K'_T) = 30\%$; $u(W'_s) = 30\%$; $u\left(\frac{\partial P}{\partial T}\right)^{\text{sat}}_V = 0.15\%$; $u\left(\frac{\partial V}{\partial T}\right)^{\text{sat}}_P = 3\%$, depending on T and P .