Thermodynamic Properties of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

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(p,ρ,T) data of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTf$_2$] at T = (283.15 to 373.15) K and pressures up to p = 100 MPa are reported with an estimated experimental relative combined standard uncertainty of $\Delta\rho/\rho = \pm$ (0.01 to 0.08) % in density. The measurements were carried out with a newly constructed Anton Paar DMA HPM vibration-tube densimeter. The system was calibrated using double-distilled water, methanol, toluene and aqueous NaCl solutions. An empiric equation of state for fitting of the (p,ρ,T) data of [EMIM][NTf$_2$] has been developed as a function of pressure and temperature. This equation was used for the calculation of the thermal properties of IL, such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient, and internal pressure.

1. Introduction

An ionic liquid (ILs) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C, or even room temperature. ILs are excellent solvents for a broad range of polar organic compounds, and they show partial miscibility with aromatic hydrocarbons. As is well-known the ILs have been suggested as potentially "green" replacements for conventional organic solvents since they are nonflammable, are thermally stable, are recyclable, and have negligible vapor pressure.

The main application of ILs is momentarily located in the following segments: in chemical processing and fine chemicals as solvents for organic, organometallic syntheses, and homogeneous and heterogeneous catalysis; in electrochemistry and electrolytes; in polymer and biopolymer processing; in metal processing; and in engineering and functional fluids and separation processes. They are claimed to be useful as heat transfer fluids in solar heating and absorption refrigerating systems.[1−3] Their applications are successful also in fuel, in solar cells, as lubricants, and in biological reactions media. Beside these, ILs also apply for the stationary phase for chromatography, as matrices for mass spectrometry, supports for the immobilization of enzymes, in separation technologies, as liquid crystals, as templates for the synthesis of mesoporous, nanomaterials and ordered films, and as materials for embalming and tissue preservation.[4]

While scientific and technological interest in the properties of room-temperature ILs and their mixture properties with other fluids are rapidly increasing.[5−8] Thermodynamic properties of ILs, their mixtures, and nonaqueous mixtures containing ILs were reviewed recently by Heintz.[9]

This work is a continuation of our investigations in the field of (p,ρ,T) properties of ionic liquids.[10−15] Included are the (p,ρ,T) properties of [EMIM][NTf$_2$] at T = (283.15 to 373.15) K and at pressures up to p = 100 MPa. The (p,ρ,T) properties were measured using a vibration tube densimeter (method description comes later).

Analysis of the literature[16−29] showed the necessity of careful (p,ρ,T) measurement of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide:

The first research work dedicated to the density of [EMIM][NTf$_2$] was carried out by Bonhôte and their research group in Switzerland[16] in 1996. The density, melting point, viscosity, conductivity, refractive index, electrochemical window, thermal stability, and miscibility with water and organic solvents of [EMIM][NTf$_2$] were determined. Only one density result at T = 295.15 K was reported.

Noda et al.,[17] in 2001, carried-out the density measurement of [EMIM][NTf$_2$] using a density/specific gravity meter DA-100 at T = (293.15 and 313.15) K. The IL was dehydrated under high vacuum.

Krummen et al.,[18] in 2002, measured the density of [EMIM][NTf$_2$] at T = (293.15 to 353.15) K using a Anton Paar DMA 4500 vibrating tube densimeter with the 10^{-4} g·cm^{-3} uncertainty.

Fredlake et al.,[19] in 2004, measured the density of [EMIM][NTf$_2$] with a 1 mL pycnometer at T = (296.15 to 333.65) K and at ambient pressure.

Tokuda et al.,[20] in 2005, measured the density of [EMIM][NTf$_2$] at T = (288.15 and 313.15) K using a thermoregulated density/specific gravity meter DA-100. The linear dependence of density vs temperature was developed and fitting parameters of this dependence were presented.

Canongia Lopes et al.,[21] in 2005, investigated the excess molar volumes [EMIM][NTf$_2$] at (298 and 333) K. Karl Fischer titrations revealed very low levels of water (below mass fraction of 7×10^{-5}) for all treated ILs. Density measurements were performed in an Anton Paar DMA 5000 vibrating-tube den-

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simeter with temperature stability better than 0.005 K over periods of more than 10 min. Typically, density precision was 0.001 %.

Jacquemin et al.,[22] in 2006, measured the density of [EMIM][NTf$_2$] at T = (292.79 to 391.29) K using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode. The precision of the density measurement is of the order 10^{-4} g·cm^{-3}, the results are expected to be accurate to 10^{-3} g·cm^{-3}.

Tokuda et al.,[23] in 2006, measured the density of [EMIM][NTf$_2$] at T = (288.15 and 313.15) K using a thermoregulated density/specific gravity meter DA-100 (Kyoto Electronics Manufacturing Co., Ltd.).

Gardas et al.,[24] in 2007, measured the density of [EMIM][NTf$_2$] at T = (293.15 to 393.15) K and pressures up to 30 MPa using an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 512P measuring cell. This is the first (p,ρ,T) measurements of [EMIM][NTf$_2$]. IL was synthesized in laboratory conditions.

Jacquemin et al.[25] in 2007 investigated the densities of [EMIM][NTf$_2$] as a function of temperature from T = (293 to 415) K and over an extended pressure range from p = (0.1 to 40) MPa using a vibrating tube densimeter (Anton Paar, DMA 512). IL was supplied by the group of Wasserscheid (University of Erlangen-Nürnberg, Germany) with a minimum stated purity of 0.99 in mole fraction. The uncertainty of the density measurement was 10^{-4} g·cm^{-3}.

Wandschneider et al.,[26] in 2008, measured the densities of [EMIM][NTf$_2$] at T = (278.15 to 328.15) K and at ambient pressure using a vibrating tube densimeter (Anton Paar DMA 512 P). The uncertainty of the density data was estimated to be 1×10^{-4} g·cm^{-3}.

Jacquemin et al.,[27] in 2008, used two methods of measuring the density of [EMIM][NTf$_2$] at T = (293.15 to 363.15) K and at 0.1 MPa, both based upon the vibrating-tube densitometer. A U-shaped vibrating-tube densitometer (Anton Paar, DMA 512, in France), operated in the static mode, was used at atmospheric pressure. An analogous apparatus (Anton Paar, DMA 4500 operating in a static mode in Belfast) was also used to measure the densities at atmospheric pressure. The repeatability of the density measurements was 10^{-4} g·cm^{-3}, and the results have an uncertainty to 10^{-3} g·cm^{-3}, a value determined by comparing the two data sets obtained in the two laboratories using the same sample of [EMIM][NTf$_2$].

Fröba et al.,[28] in 2008, studied the density of [EMIM][NTf$_2$] using a vibrating tube densimeter (Anton Paar, DMA 5000) at temperatures T = (273.15 to 363.15) K and at ambient pressure. The IL was synthesized under laboratory conditions. The purity of sample was higher than 99 %. The uncertainties of density measurements have an expanded to be less than ± 0.02 %.

Tariq et al.,[29] in 2008, measured the density of [EMIM][NTf$_2$] at T = (293 K to 333) K using an Anton Paar DMA 5000 vibrating tube densimeter, operating at atmospheric pressure and in the temperature range T = (293 K to 333) K. The repeatability of the density measurements was better than 0.04 kg·m^{-3} and the expanded uncertainty was estimated to be ± 0.3 kg·m^{-3}.

This literature analysis reveals that there are only two published works[24,25] which have (p,ρ,T) results of [EMIM][NTf$_2$]. The comparison of these two literature results showed large uncertainties, especially at high pressures (until $\Delta\rho/\rho$ = ± 0.4 %). Therefore it was necessary to carry out more experimental (p,ρ,T) measurements of [EMIM][NTf$_2$] in a wide range of temperatures and pressures, including temperatures below ambient temperature.

We measured (p,ρ,T) properties of [EMIM][NTf$_2$] at T = (283.15 to 373.15) K and at pressures p = (0.101 to 100) MPa using a high pressure–high temperature vibrating tube densimeter. Densities of [EMIM][NTf$_2$] at ambient pressure and at temperatures T = (283.15 to 363.15) K were also measured using Anton Paar DMA 5000 vibrating tube densimeter.

2. Experimental Section

The (p,ρ,T) measurements were carried out using a new modernized high pressure–high temperature Anton Paar DMA HPM vibrating tube densimeter.[30−32] Density measurements with a vibrating tube are based on the dependence of the period of oscillation of a unilaterally fixed U-tube (Hastelloy C-276) on its mass. This mass consists of the U-tube material and the mass of the fluid filled into the U-tube.

The temperature in the measuring cell was controlled using a thermostat (F32-ME Julabo, Germany) with an error of ± 10 mK and was measured using the (ITS-90) Pt100 thermometer (Type 2141) with an experimental error of ± 15 mK. Pressure was measured by pressure transmitter P-10 (WIKA Alexander Wiegand GmbH & Co., Germany) with an relative uncertainty of 0.1 % of the measured value.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was purchased from Ionic Liquids Technologies GmbH, Germany (Product Code IL-0023, Purity ≥ 99.0 %). It was purified by applying a low-pressure vacuum of (1 to 10) Pa at temperature T = 398.15 K during 48 h using the magnet stirring. This removed the water and other volatile impurities. The water concentration of dried IL was determined through Karl Fisher titration and they were less than mass fraction $3 \cdot 10^{-4}$.

The sample in the oscillating tube is part of a complex system. As well as the force of inertia shear forces occur on the wall, influencing the resonant frequency of the oscillator. If samples of higher viscosities are measured one notices that the displayed density is too high. Up to a certain level, this error is a function of viscosity.[33,34] The behavior can be explained by considering a segment of the oscillator in motion. Investigating a "slice" of sample one finds that both translational and rotational movements take place. The force required to keep the slice rotating is introduced by shear forces on the wall. As the viscosity increases, an increasing part will rotate until the whole slice rotates like a solid body. The momentum of inertia of the rotated section when added to the force of inertia of the movement of translation, simulates a higher mass with respect to volume, and so a higher density. A correction can easily be performed if the form of the error curve and the sample viscosity are known.[33,34]

In the present work the viscosity correction $(\rho_{\mathrm{HPM}} - \rho)/\rho_{\mathrm{HPM}}$[35] on the densities measurements was evaluated

$$\frac{\rho_{\mathrm{HPM}} - \rho}{\rho_{\mathrm{HPM}}} = [0.4482\sqrt{\eta} - 0.1627]\cdot 10^{-4} \qquad (1)$$

For evaluation of eq 1, we need $(\rho_{\mathrm{HPM}} - \rho)/\rho_{\mathrm{HPM}}$ as a function of viscosity η which must be known in the same temperature and pressure range where densities are determined. For the determination of the dependence of this correction term on temperature and pressure viscosity values of [EMIM][NTf$_2$] from literature[28,36] and a little bit extrapolation to T = (283.15 and 373.15) K were used.

The mPDS2000 V3 control unit displays the vibration period to seven digits. According to the specifications of Anton Paar and calibration procedures the observed repeatability of the density measurements at temperatures T = (283.15 to 373.15)

Table 1. Experimental Values of Pressure, p, Density, ρ, Temperature, T, Calculated Values of Isothermal Compressibility, k_T, Isobaric Thermal Expansibility, α_p, Difference in Isobaric and Isochoric Heat Capacities, $c_p - c_v$, Thermal Pressure Coefficient, γ, and Internal Pressure, p_{int}, of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

p	ρ	T	$k_T \cdot 10^6$	$\alpha_p \cdot 10^6$	$c_p - c_v$	γ	p_{int}	p	ρ	T	$k_T \cdot 10^6$	$\alpha_p \cdot 10^6$	$c_p - c_v$	γ	p_{int}
MPa	$kg \cdot m^{-3}$	K	MPa^{-1}	K^{-1}	$J \cdot kg^{-1} \cdot K^{-1}$	$MPa \cdot K^{-1}$	MPa	MPa	$kg \cdot m^{-3}$	K	MPa^{-1}	K^{-1}	$J \cdot kg^{-1} \cdot K^{-1}$	$MPa \cdot K^{-1}$	MPa
1.750	1533.90	283.19	470.7	638.9	160.1	1.3573	382.6	49.994	1538.48	313.15	416.9	588.4	169.0	1.4113	392.0
5.136	1536.34	283.19	462.8	632.8	159.5	1.3671	382.0	60.124	1544.89	313.15	399.8	576.9	168.8	1.4431	391.8
10.046	1539.78	283.20	452.0	624.2	158.5	1.3810	381.0	69.993	1550.88	313.15	384.5	566.6	168.6	1.4737	391.5
20.030	1546.57	283.21	431.5	607.8	156.8	1.4085	378.9	80.342	1556.93	313.16	369.8	556.6	168.5	1.5053	391.1
29.957	1553.14	283.20	412.8	592.5	155.1	1.4353	376.5	89.994	1562.32	313.16	357.2	548.1	168.5	1.5342	390.5
40.033	1559.47	283.20	395.7	578.2	153.4	1.4613	373.8	100.087	1567.72	313.17	345.2	539.8	168.6	1.5639	389.7
49.993	1565.54	283.19	380.0	564.9	151.9	1.4863	370.9	2.359	1485.34	333.17	560.7	661.1	174.8	1.1790	390.4
60.272	1571.51	283.19	365.4	552.1	150.3	1.5110	367.6	5.331	1487.73	333.17	551.4	655.4	174.5	1.1887	390.7
69.996	1577.00	283.19	352.5	540.7	148.9	1.5338	364.3	9.791	1491.26	333.19	537.8	647.1	174.0	1.2032	391.1
80.287	1582.65	283.19	339.8	529.2	147.5	1.5572	360.7	18.829	1498.27	333.19	512.2	631.5	173.1	1.2329	392.0
89.994	1587.84	283.19	328.7	518.9	146.1	1.5788	357.1	30.001	1506.61	333.18	483.7	614.2	172.5	1.2698	393.1
100.034	1593.02	283.21	317.9	508.8	144.8	1.6004	353.2	40.159	1513.90	333.17	460.3	600.1	172.1	1.3036	394.1
1.027	1524.24	293.17	488.3	648.7	165.7	1.3283	388.4	49.997	1520.69	333.16	439.8	587.7	172.1	1.3363	395.2
4.981	1527.10	293.17	478.8	641.8	165.1	1.3403	388.0	60.111	1527.39	333.15	420.6	576.2	172.2	1.3699	396.3
10.202	1530.80	293.15	466.8	633.0	164.4	1.3560	387.3	69.997	1533.66	333.14	403.5	566.0	172.4	1.4026	397.3
20.787	1538.14	293.16	444.1	616.2	162.9	1.3874	385.9	80.064	1539.77	333.13	387.7	556.6	172.9	1.4356	398.2
29.994	1544.31	293.17	426.1	602.6	161.8	1.4143	384.6	89.994	1545.53	333.13	373.5	548.2	173.4	1.4678	399.0
39.872	1550.73	293.19	408.2	588.9	160.6	1.4426	383.1	99.911	1551.00	333.14	360.5	540.5	174.1	1.4995	399.6
49.993	1557.07	293.17	391.5	575.9	159.5	1.4710	381.2	2.168	1465.71	353.18	604.4	664.2	175.8	1.0988	385.9
59.685	1562.92	293.16	376.8	564.3	158.5	1.4975	379.3	5.223	1468.32	353.18	593.1	657.3	175.2	1.1083	386.2
69.993	1568.91	293.16	362.5	552.7	157.5	1.5250	377.1	9.673	1472.06	353.19	577.3	647.8	174.4	1.1221	386.7
79.912	1574.47	293.17	349.7	542.3	156.6	1.5508	374.7	20.093	1480.58	353.19	543.1	627.3	172.9	1.1551	387.9
89.934	1579.84	293.15	337.9	532.5	155.7	1.5760	372.1	29.997	1488.37	353.19	514.0	610.1	171.9	1.1870	389.3
99.755	1584.89	293.14	327.2	523.5	154.9	1.5999	369.2	39.951	1495.89	353.19	487.7	594.8	171.3	1.2196	390.8
1.156	1519.10	298.14	498.1	652.9	168.0	1.3108	389.6	49.979	1503.15	353.19	463.8	581.0	171.0	1.2527	392.4
5.194	1522.08	298.17	487.9	645.7	167.4	1.3234	389.4	60.184	1510.23	353.19	441.8	568.5	171.0	1.2866	394.2
10.066	1525.62	298.19	476.2	637.5	166.8	1.3386	389.1	69.993	1516.73	353.18	422.8	557.8	171.4	1.3193	396.0
19.701	1532.45	298.12	454.7	622.2	165.6	1.3682	388.2	80.056	1523.09	353.18	405.0	548.0	171.9	1.3528	397.7
29.779	1539.35	298.12	434.1	607.2	164.5	1.3988	387.2	90.001	1529.06	353.18	389.2	539.3	172.6	1.3857	399.4
39.926	1546.05	298.13	415.2	593.3	163.5	1.4291	386.1	99.944	1534.73	353.19	374.8	531.6	173.5	1.4183	401.0
49.997	1552.45	298.15	398.0	580.5	162.6	1.4586	384.9	0.724	1445.01	373.12	663.2	676.6	178.2	1.0202	379.9
59.613	1558.32	298.20	382.9	569.1	161.9	1.4862	383.6	4.935	1448.84	373.14	644.3	664.9	176.7	1.0320	380.1
69.997	1564.42	298.19	368.1	557.8	161.1	1.5152	381.8	10.147	1453.42	373.17	622.5	651.4	175.0	1.0465	380.4
79.938	1570.00	298.19	355.1	547.7	160.4	1.5422	379.9	19.879	1461.85	373.18	584.6	628.4	172.4	1.0748	381.2
90.001	1575.41	298.18	343.1	538.2	159.8	1.5688	377.8	30.001	1470.33	373.16	549.4	607.3	170.4	1.1054	382.5
99.950	1580.52	298.18	332.1	529.5	159.2	1.5942	375.4	39.858	1478.08	373.16	519.4	589.6	169.0	1.1352	383.8
1.963	1504.67	313.16	523.9	658.7	172.4	1.2573	391.8	49.997	1485.67	373.16	491.9	573.7	168.1	1.1664	385.2
5.147	1507.08	313.17	515.2	653.0	172.0	1.2675	391.8	60.448	1493.21	373.14	466.3	559.2	167.6	1.1993	387.1
10.156	1510.84	313.15	502.1	644.5	171.5	1.2838	391.9	69.979	1499.69	373.14	445.5	547.7	167.5	1.2294	388.7
19.902	1517.96	313.16	478.2	629.0	170.7	1.3152	392.0	79.868	1506.16	373.14	425.8	536.9	167.7	1.2610	390.7
29.996	1525.09	313.15	455.8	614.2	170.0	1.3476	392.0	89.963	1512.49	373.14	407.5	527.2	168.3	1.2937	392.8
39.897	1531.84	313.15	435.7	600.9	169.4	1.3793	392.0	99.920	1518.52	373.14	391.0	518.6	169.0	1.3264	395.0

Table 2. Experimental Density Values of [EMIM][NTf_2] at p = 0.101 MPa

T	ρ
K	$kg \cdot m^{-3}$
283.15	1533.48
293.15	1523.37
298.15	1518.34
313.15	1503.33
333.15	1483.53
353.15	1463.97
363.15	1454.28

K and pressures up to $p = 100$ MPa is within $\Delta\rho = \pm$ (0.1 to 0.3) $kg \cdot m^{-3}$ or $\Delta\rho/\rho = \pm$ (0.01 to 0.03) %. But the described uncertainty of the viscosity measurements in the literature and the application of those results to the temperature and pressure intervals of our work increase the possible uncertainty of the density measurements of the present work. From the other point of view the effect of the right side of eq 1 is small and the uncertainty increase in the density correction is not very high. Thus the uncertainty of the density measurements can be predicted to be between $\Delta\rho/\rho = \pm$ (0.01 to 0.08) %.

The density measurements at ambient pressure also were carried out using the Anton Paar DMA 5000 densimeter with an uncertainty of ±0.01 K. The overall uncertainty of the experimental density measurements at ambient pressure was better than $\pm 2 \times 10^{-5}$ $g \cdot cm^{-3}$.

3. Results and Discussion

(p,ρ,T) data of [EMIM][NTf_2] were measured at T = (283.15 to 373.15) K and pressures up to p = 100 MPa, and an equation of state fitted to the (p,ρ,T) data of the [EMIM][NTf_2] is reported. The temperature and pressure steps in the experiments are typically T = (5 to 20) K and p = (5 to 10) MPa, respectively. The obtained values are presented in Tables 1 and 2 and are compared with the available literature results, and these comparison are in good agreement. The measured densities as a function of pressure and temperature were fitted to the equation of state (1) from ref 37

$$p/\text{MPa} = A(\rho/\text{g}\cdot\text{cm}^{-3})^2 + B(\rho/\text{g}\cdot\text{cm}^{-3})^8 + C(\rho/\text{g}\cdot\text{cm}^{-3})^{12} \quad (2)$$

where the coefficients of eq 2 $A(T)$, $B(T)$, and $C(T)$ are functions of temperature.

$$A(T) = \sum_{i=1}^{3} a_i T^i, \quad B(T) = \sum_{i=0}^{2} b_i T^i, \quad C(T) = \sum_{i=0}^{2} c_i T^i \tag{3}$$

The coefficients a_i, b_i, and c_i of eq 3 are given in Table 3. Equations 2 and 3 describe the experimental results of density of [EMIM][NTf$_2$] within $\pm \Delta\rho/\rho = \pm 0.011$ %, corresponding to $\Delta\rho = \pm 0.19$ kg m^{-3} standard with a maximal deviation of $\Delta\rho = \pm 0.43$ kg m^{-3}.

Figures 1 and 2 show the plots of pressure p of [EMIM][NTf$_2$] vs density ρ and deviations of experimental density ρ of [EMIM][NTf$_2$] from the calculated density ρ by eqs 2 and 3 vs pressure p.

The isothermal compressibility k_T of [EMIM][NTf$_2$] is a measure for the relative volume change of a fluid as a response to a pressure change at constant temperature

$$k_{\mathrm{T}} = (1/\rho)(\partial p/\partial \rho)_{\mathrm{T}}^{-1} \tag{4}$$

and can be calculated from the experimental (p,ρ,T) results of [EMIM][NTf$_2$] using eqs 2 and 3

$$k_{\mathrm{T}} = 1/[2A(T)\rho^2 + 8B(T)\rho^8 + 12C(T)\rho^{12}] \tag{5}$$

The calculated values of the isothermal compressibility k_{T} are given in Table 1 and are shown in Figure 3 vs pressure p.

Another thermal property that can be calculated from eqs 2 and 3 is the isobaric thermal expansibility α_{p} that is the tendency of matter to change in volume in response to a change in temperature at constant pressure

$$\alpha_{\mathrm{p}} = (1/\rho)(\partial p/\partial T)_{\rho}(\partial p/\partial \rho)_{\mathrm{T}}^{-1} \tag{6}$$

and can be calculated from the experimental (p,ρ,T) results using eqs 2 and 3

$$\alpha_{\mathrm{p}} = [A'(T) + B'(T)\rho^6 + C'(T)\rho^{10}]/[2A(T) + 8B(T)\rho^6 + 12C(T)\rho^{10}] \tag{7}$$

where A', B', and C' are the derivatives of the A, B, and C

$$A'(T) = \sum_{i=1}^{3} i a_i T^{i-1}, \quad B'(T) = \sum_{i=1}^{2} i b_i T^{i-1}, \quad C'(T) = \sum_{i=1}^{2} i c_i T^{i-1} \tag{8}$$

The results of calculations of the isobaric thermal expansibility α_{p} are given in Table 1.

Measuring the heat capacity at constant volume can be prohibitively difficult for liquids. Instead it is easier to measure the heat capacity at constant pressure and solving for the heat capacity at constant volume using mathematical relationships derived from basic thermodynamic laws

$$c_{\mathrm{p}} = c_{\mathrm{v}} + T\frac{(\partial p/\partial T)_{\rho}^{2}}{\rho^2(\partial p/\partial \rho)_{\mathrm{T}}} \tag{9}$$

Table 3. Values of the Coefficients a_i, b_i, and c_i in eqs 2 and 3

a_i	b_i	c_i
$a_1 = -1.23826752$	$b_0 = -44.936067$	$c_0 = 6.44671308$
$a_2 = 2.885292 \cdot 10^{-3}$	$b_1 = 0.336768446$	$c_1 = -0.040829737$
$a_3 = -9.205253244 \cdot 10^{-7}$	$b_2 = -5.077887 \cdot 10^{-4}$	$c_2 = 6.62619034 \cdot 10^{-5}$

where c_{p} and c_{v} are the heat capacities at constant pressure and volume, respectively. Using eqs 4 and 6, we can find the following relationship for $c_{\mathrm{p}} - c_{\mathrm{v}}$:

$$c_{\mathrm{p}} - c_{\mathrm{v}} = \frac{\alpha_{\mathrm{p}}^{2} T}{\rho k_{\mathrm{T}}} \tag{10}$$

The calculated values of the differences in specific heat capacities $c_{\mathrm{p}} - c_{\mathrm{v}}$ of the [EMIM][NTf$_2$] are given in Table 1.

The thermal pressure coefficient γ is calculated as the ratio of the isobaric thermal expansibility α_{p} to the isothermal compressibility k_{T} at the same state parameters T and p

$$\gamma = \frac{\alpha_{\mathrm{p}}}{k_{\mathrm{T}}} \tag{11}$$

The calculated values of thermal pressure coefficient γ of the [EMIM][NTf$_2$] are given in Table 1.

Internal pressure p_{int} is a measure of how the internal energy of a system changes when it expands or contracts at constant temperature. It has the same dimensions as pressure. It is defined as a partial derivative of internal energy with respect to volume at constant temperature and related to thermal pressure coefficient γ. Internal pressure defined by the following relationship:

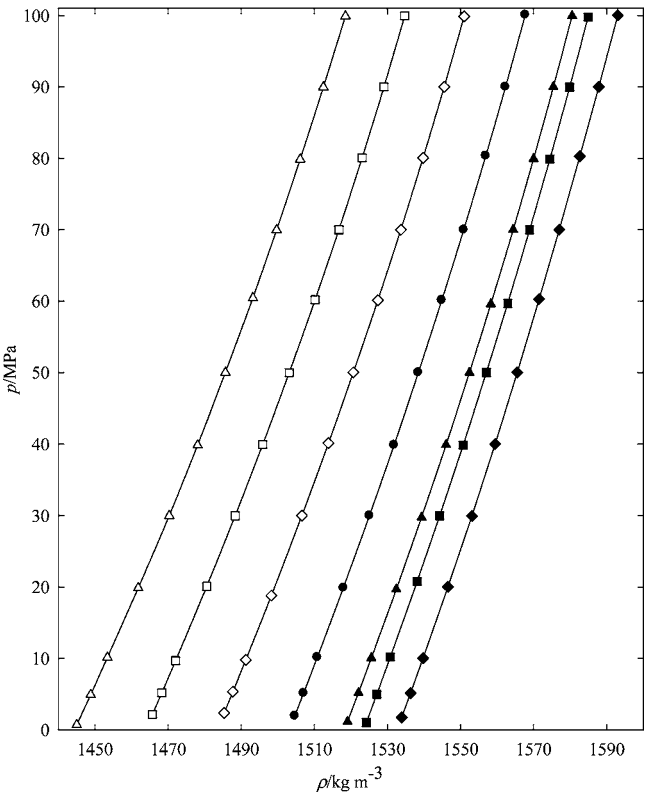

Figure 1. Plot of pressure p of [EMIM][NTf$_2$] vs density ρ: ◆, 283.20 K; ■, 293.16 K; ▲, 298.16 K; ●, 313.16 K; ◇, 333.16 K; □, 353.19 K; △, 373.15 K; — calculated by eqs 2−3.

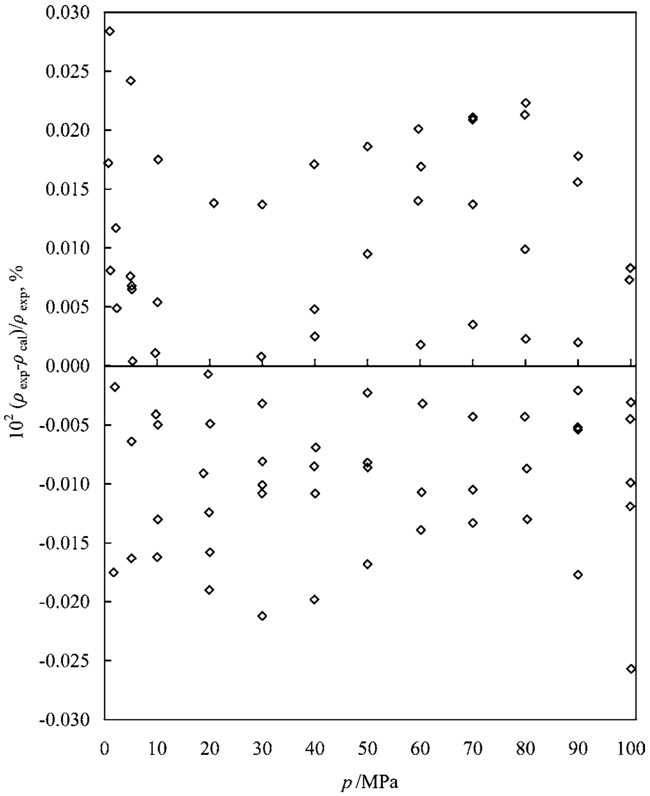

Figure 2. Plot of deviations of experimental density $\rho_{exp.}$ of [EMIM][NTf$_2$] from the calculated by eqs 2−3 density ρ_{cal} vs pressure p at T = (283.15 to 373.15) K.

$$p_{int} \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\gamma - p = \frac{T\alpha_p}{k_T} - p \tag{12}$$

The calculated p_{int}/MPa values of [EMIM][NTf$_2$] are given in Table 1.

The comparison of the measured (p,ρ,T) values of [EMIM][NTf$_2$] with the available literature results[16−29] is shown in the Figures 4 and 5. Within these comparisons the percent (PD) and average relative deviations (APD) between the literature values and our experimental density values are calculated as

$$\mathrm{PD} = \frac{\rho_{lit} - \rho_{exp}}{\rho_{lit}} \tag{13}$$

$$\mathrm{APD} = \frac{1}{n}\sum\left|\frac{\rho_{lit} - \rho_{exp}}{\rho_{lit}}\right| \tag{14}$$

where ρ_{lit} is the density of IL reported in the literature, ρ_{exp} is the experimental density measured in this work, and n is the number of compared points.

One density value has been published by Bonhôte et al.[16] at T = 295.15 K and ambient pressure. This value has $\Delta\rho/\rho$ = −0.089 % deviation with our interpolated value and is smaller than our value.

The five experimental results of Noda et al.[17] have $\Delta\rho/\rho$ = ± 0.062 % deviation with our values and they are smaller than our values. The deviation of both results increases with increasing temperature.

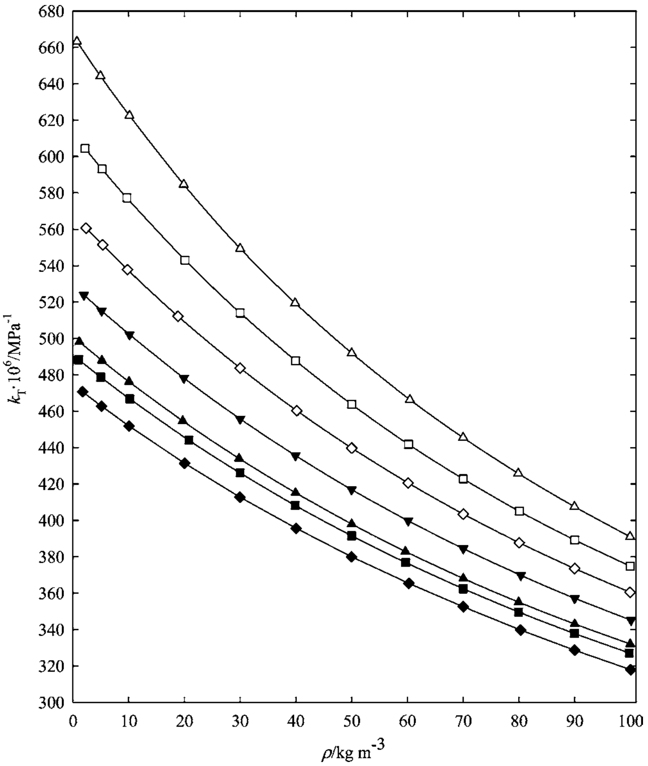

Figure 3. Plot of isothermal compressibility $k_T \cdot 10^6$/MPa^{-1} of [EMIM][NTf$_2$] vs pressure p: ◆, 283.20 K; ■, 293.16 K; ▲, 298.16 K; ▼, 313.16 K; ◇, 333.16 K; □, 353.19 K; △, 373.15 K.

Krummen et al.[18] presented 13 measured values of density at ambient pressure and various temperatures. The comparison of these values with our results shows the $\Delta\rho/\rho$ = ± 0.043 % average deviation, and it is higher than our measured values.

The five density results of [EMIM][NTf$_2$] by Fredlake et al.[19] were compared with the presented density results in our work. The comparison shows the $\Delta\rho/\rho$ = ± 0.194 % average deviation, and the values of ref 19 are higher than our values.

The six experimental density values of Tokida et al.[20] and their other six results[23] at ambient pressure show $\Delta\rho/\rho$ = ± 0.231 % and $\Delta\rho/\rho$ = ± 0.065 % average deviations with our experimental values, respectively. These literature values mainly are higher than our results, and they increase with the increasing temperature.

The nine density results of Jacquemin et al.[22] have a $\Delta\rho/\rho$ = ± 0.048 % average deviation with our experimental values and are smaller than our values.

There are two literature works (Gardas et al.[24] and Jacquemin et al.[25]) with (p,ρ,T) values of [EMIM][NTf$_2$]:

- The 96 results of Gardas et al.[24] have a $\Delta\rho/\rho$ = ± 0.084 % average deviation with our experimental values. The deviations of these density results between T = (293.15 and 313.15) K are higher than our results but between T = (323.15 and 393.15) K are smaller than our results.
- The 36 density results of Jacquemin et al.[25] have a $\Delta\rho/\rho$ = ± 0.306 % average deviation with our experimental values, and they are smaller than our results.

From a comparison of six density results of Wandschneider et al.[26] with our results we observe a $\Delta\rho/\rho$ = ± 0.025 % deviation. The density values are the higher than our results.

Nineteen density results of Jacquemin et al.[27] were compared with our results. The average deviation of these values was $\Delta\rho/\rho$ = ± 0.022 %. The density values are mostly smaller than our results.

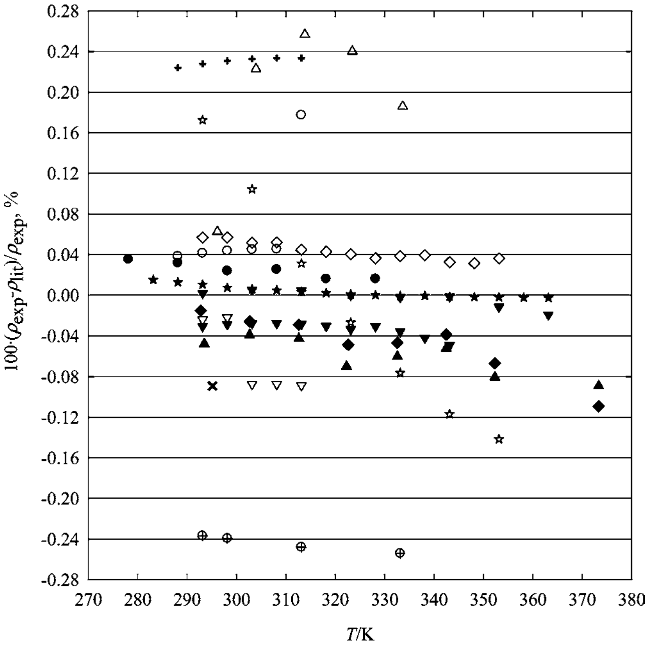

Figure 4. Plot of deviation of experimental ρ_{exp} and literature ρ_{cal} densities of [EMIM][NTf$_2$] at $p = 0.101$ MPa vs temperature: ×, ref 16; ▽, ref 17; ◇, ref 18; △, ref 19; +, ref 20; ◆, ref 22; ○, ref 23; ☆, ref 24; ▲, ref 25; ●, ref 26; ▼, ref 27; ★, ref 28; ⊕, ref 29.

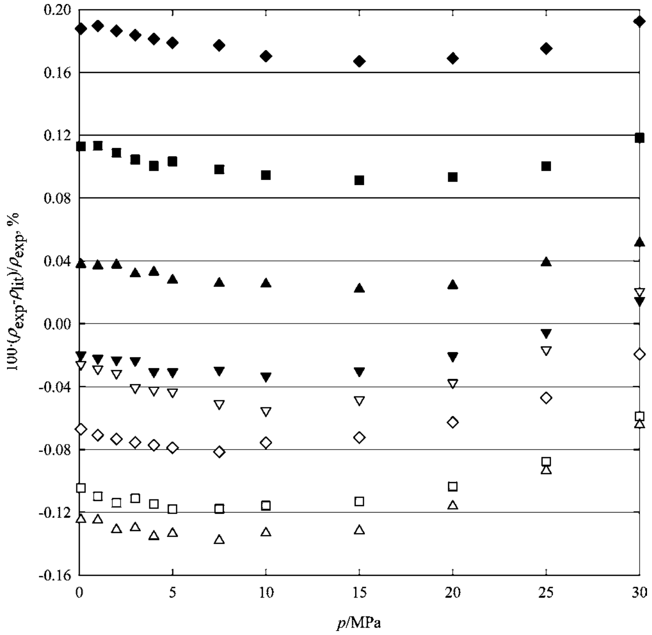

Figure 5. Plot of deviation of the experimental (p,ρ,T) results of [EMIM][NTf$_2$] from literature values of ref 24 vs pressure: ◆, $T = 293.15$ K; ■, $T = 313.15$ K; ▼, $T = 323.15$ K, ◇, $T = 333.15$ K; □, $T = 343.15$ K; △, $T = 353.15$ K; ▽, $T = 393.15$ K.

Seventeen density results from 19 measured density values of Fröba et al.[28] were compared with our results. The first two density points at $T = 273.17$ K and $T = 278.17$ K were outside of our temperature interval. The average deviation of these 17 values was $\Delta\rho/\rho = \pm\ 0.004$ %. The deviation of all 17 points in these literature work from our results is very small (max. deviation in the $T = 283.15$ K is $\Delta\rho/\rho = +0.015$ %). The density values of ref 28 are mostly higher than our results.

Four experimental density results of [EMIM][NTf$_2$] measured by Tariq et al.[29] deviate on average with $\Delta\rho/\rho = \pm\ 0.245$ % from our experimental values. The maximum uncertainty of results in ref 29 is $\Delta\rho/\rho = -0.254$ % at $T = 333.15$ K. All density results of ref 16 are smaller than our results.

4. Conclusion

The main objective of the presented work is the density measurements of [EMIM][NTf$_2$] high state parameters. This study presents the (p,ρ,T) measurements of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTf$_2$] at $T = (283.15$ to $373.15)$ K and pressures up to $p = 100$ MPa. The constructed empirical equation of state can be used to calculate various thermal and caloric parameters.

All density values from literature have been compared with our results and show good agreement.

Appendix

List of Symbols

p	Absolute pressure
T	Absolute temperature
k_T	Isothermal compressibility
c_p	Isobaric heat capacity
c_v	Isochoric heat capacity
p_{int}	Internal pressure
U	Internal energy
V	Volume
PD	Percent deviations
APD	Average relative deviations

Greek Letters

ρ	Density
η	Viscosity
α_p	Isobaric thermal expansibility
γ	Thermal pressure coefficient

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