Thermal properties of 1-butyl-3-methylimidazolium dicyanamide at high pressures and temperatures

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Abstract: Thermophysical properties of 1-butyl-3-methylimidazolium dicyanamide [BMIM][DCA] $\{(p, \rho, T)$ data at T = (283.15 to 393.15) K, pressures up to p =100 MPa, and viscosity at T = (283.15 to 373.15) K and p = 0.101 MPa$\}$ are reported with an estimated experimental relative combined standard uncertainty of $\Delta\rho/\rho$ = ±(0.01 to 0.08) % in density and $\Delta\eta/\eta$ = ±0.35 % in dynamic viscosity. The measurements were carried out with a recently constructed Anton-Paar DMA HPM vibration-tube densimeter and a fully automated SVM 3000 Anton-Paar rotational Stabinger viscometer. The vibration-tube densimeter 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 [BMIM][DCA] has been developed as a function of pressure and temperature. This equation was used for the calculation of thermomechanical properties of the IL, such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient and internal pressure. Viscosity measurements were fitted to the polynomial equation.

Keywords: Density, viscosity, vibration tube densimeter, equation of state, isothermal compressibility.

Introduction

An ionic liquid (ILs) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting points are 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, thermal stable, recyclable and have negligible vapor pressure. But, the same time the green character of ILs is not true for all the possible ionic liquids, recent studies are rising important issues about the toxicity, biodegradability and other relevant aspects of these fluids.

The main application of ILs is located in the following segments at present: in chemical processing and fine chemicals as solvents for organic, organometallic syntheses, homogeneous and heterogeneous catalysis; in electrochemistry and electrolytes; in polymer and biopolymer processing; in metal processing; 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 (Wu et al., 2001;

Valkenburg et al., 2005; Kim et al., 2003). Their applications are successful also in fuel, solar cells, as lubricants and biological reactions media. Beside these, ILs are also applicable for the stationary phase in chromatography, matrices in mass spectrometry, supporting immobilization of enzymes, in separation technologies, liquid crystals, templates in the synthesis of mesoporous, nano-materials and ordered films, materials for embalming and tissue preservation (Dupont, 2004).

Scientific and technological interest in the properties of room-temperature ILs is rapidly increasing (Rogers and Seddon, 2003; Wasserscheid and Welton, 2003; Deetlefs and Seddon, 2006; MacFarlane and Seddon, 2007). Thermodynamic properties of ILs, their mixtures, and non-aqueous mixtures containing ILs were reviewed recently by Heintz (2005) and Aparicio (Aparicio et al., 2010).

This work is a continuation of our investigations in the field of (p, ρ, T) properties of ionic liquids (Tekin et al., 2007; Abdulagatov et al., 2008 and 2009; Safarov and Hassel, 2010; Safarov et al., 2011). Included are the (p, ρ, T) properties of [BMIM][DCA] at T = (283.15 to 393.15) K, at pressures up to p = 100 MPa, and viscosity measurements at T = (278.15 to 373.15) K, at pressures p = 0.101 MPa. The (p, ρ, T) properties were measured using a

vibration tube densimeter and viscosity in a fully automated SVM 3000 Anton-Paar rotational Stabinger viscometer (method description follows).

Literature analysis (Fredlake et al., 2004, Stoppa et al., 2009; Sánchez et al., 2009; Carvalho et al., 2010; Zech et al., 2010; Nieto de Castro et al., 2010) showed the need for careful measurements of thermophysical properties of 1-butyl-3-methylimidazolium dicyanamide:

The first research work dedicated to the density of [BMIM][DCA] was carried out by Fredlake et al., in 2004. They used 1 mL pycnometers for the measurements at T = (296.15 to 333.65) K and ambient pressure. The IL was synthesized at laboratory conditions. The IL was dried with stirring at 70 °C for 48 h under a vacuum of approximately 0.01 Pa. The water content determined by Karl Fisher titration was 5150 ppm. Calibration experiments indicated the accuracy of the measurements to be within 0.4 %.

Stoppa et al., in 2009, carried out the density measurement of [BMIM][DCA] at T = 298.15 ± 0.02 K. The vibrating tube densimeter (Anton Paar DMA 60, DMA 601HT) used during the experiments was calibrated with degassed water and purified nitrogen at atmospheric pressure. The IL was dried at a high-vacuum line ($p < 10^{-8}$ bar) for 7 days at ≈ 40 °C prior to use. Water mass fractions were always <50 ppm. The precision of the measurements was ±0.001 kg·m⁻³. Taking into account the sources of error (calibration, measurement, purity of materials), the uncertainty of ρ was estimated to be within ±0.05 kg·m⁻³.

Sánchez et al., in 2009, investigated the density and viscosity of [BMIM][DCA] at atmospheric pressure using a densimeter (Anton Paar DMA 5000), which was calibrated with high purity water standard provided by Anton Paar. Kinetic viscosities of the ionic liquids were measured at atmospheric pressure using Ubbelohde-type viscometers purchased from Schott. Given the large range of viscosity and temperatures measured, three capillaries were used. The IL was supplied from Merck (grade purum ≥0.97 and water content ≤2000 ppm). The uncertainty in the density measurement was estimated to be ±0.1 kg·m⁻³ and in the absolute viscosity η to be ±1 %.

Carvalho et al., in 2010, measured the density and viscosity of [BMIM][DCA] at T = (278.15 to 363.15) K using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The IL was acquired at IoLiTec with mass fraction purities higher than 99 %. Thus, to reduce to negligible values both water and volatile compounds, vacuum (0.1 Pa), stirring, and moderate temperature (353 K) for a period of at least 48 h were applied prior to the measurements. The final water content of the IL was determined with a Mettler Toledo DL32 Karl Fischer coulometer (using the Hydranal − Coulomat E from Riedel-de Haën as analyte), indicating a water mass fraction of 16 ppm for [BMIM][DCA]. The relative uncertainty of the dynamic viscosity is ±0.35 % and the absolute uncertainty of the density is ±0.5 kg·m⁻³.

Zech et al., in 2010, measured the density of ρ of the [BMIM][DCA] over the temperature range (278.15 to 338.15) K using a vibrating-tube densimeter (Anton Paar DMA 60). The instrument was calibrated at each measurement temperature with purified dry nitrogen and degassed Millipore water using precise density values from the literature. The uncertainty in ρ was estimated to be <0.05 kg·m⁻³. The IL was synthesized at the laboratory conditions and dried under high vacuum ($p < 10^{-8}$ bar) at 40 °C for 1 week. The water mass fraction of <80 ppm (as determined by coulometric Karl Fischer titration using a Mitsubishi Moisturemeter MCI CA-02) was obtained.

Nieto de Castro et al., in 2010, investigated the density of [BMIM][DCA] at ambient pressure and at T = (293.15 to 363.15) K using a vibrating tube densimeter DMA 5000 with uncertainties better than ±0.005 kg·m⁻³. The ionic liquid was synthesized at the organic chemistry laboratories of the Centro de Química-Física Molecular (IST, UTL).

Nieto de Castro et al. in 2010 investigated also the density of this IL at high pressures. This is only one publication with (p, ρ, T) properties of [BMIM][DCA]. The (p, ρ, T) data were obtained using a high-pressure Anton Paar DMA HP cell up to 60 MPa and at T = (293.15 to 393.15) K. In this paper, the infinite dilution diffusion coefficients, using the Taylor dispersion method, heat capacity, using DSC equipment and surface tension, using the Wilhelmy plate method also were analysed.

The ambient pressure density results of [BMIM][DCA] in literature do not have a wide temperature interval and also some literature results do not have high quality. The (p,ρ, T) measurements of [BMIM][DCA] in (Nieto de Castro et al., 2010) were carried out using the old version of Anton-Paar instrument (DMA 60) at pressures up to 60 MPa. Authors of (Nieto de Castro et al., 2010) used the Tait equation for the every isotherm separately without interpolation of not measured isotherms.

Therefore, it was necessary to carry out experimental (p, ρ, T) measurements of [BMIM][DCA] in a wide range of temperatures and pressures, including temperatures below ambient temperature.

We measured the (p, ρ, T) properties of [BMIM][DCA] at T = (283.15 to 393.15) K and at pressures p = (0.101 to 100) MPa using a last model of high pressure − high temperature vibrating tube den-

simeter DMA HPM from Anton-Paar. Densities and dynamic viscosities of [BMIM][DCA] at ambient pressure, at temperatures T = (283.15 to 363.15) K were measured using Anton-Paar DMA 4500 vibrating tube densimeter, and SVM 3000 Stabinger Viscometer, respectively.

Experimental

The (p, ρ, T) measurements were carried out using a new modernized high pressure − high temperature Anton-Paar DMA HPM vibrating tube densimeter (Safarov et al. 2009; Guliyev et al., 2009; Nabiyev et al., 2009). 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, where located the U-tube, 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 a relative uncertainty of 0.1 % of the measured value.

The density measurements at ambient pressure were carried out using the Anton-Paar DMA 4500 densimeter with an uncertainty of ±0.01 K. The DMA 4500 density meter combines the wellknown Anton Paar U-tube measuring principle with the patented reference oscillator and a high-precision Platinum thermometer. The overall uncertainty of the experimental density measurements at ambient pressure was better than $\pm 1 \cdot 10^{-4}\,\mathrm{g \cdot cm^{-3}}$.

The dynamic viscosity of [BMIM][DCA] were measured using an automated SVM 3000 Anton Paar rotational Stabinger viscometer with a cylinder geometry (http://www.anton-paar.com). The viscometer is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob which rotates more slowly. A rotating magnet in the SVM 3000 produces an eddy current field with an exact speed-dependent brake torque. The eddy current torque is measured with extremely high resolution. Combined with the integrated thermoelectric thermostatting, this ensures unparalleled precision. The very small measuring cell contains a tube which rotates at a constant speed. This tube is filled with the sample. Floating in the sample is a measuring rotor with a built-in magnet. Shortly after the start of the measurement the rotor reaches a stable speed. This is determined by the equilibrium between the effect of the eddy current brake and the shear forces at work in the sample. The dynamic viscosity is calculated from the rotor speed (http://www.anton-paar.com).

1-butyl-3-methylimidazolium dicyanamide was purchased from Ionic Liquids Technologies GmbH, Germany (Product Code IL-0010-HP, 448245-52-1, Purity ≥ 98.0 %). 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. The force of inertia shear forces occurs 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 (Fitzgerald, 1992; Stabinger, 1994). 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 (Stabinger, 1994). 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 (Fitzgerald, 1992; Stabinger, 1994).

The viscosity correction $(\rho_{HPM} - \rho)/\rho_{HPM}$ (Segovia et al. 2009) in the density measurements can be calculated if the high pressure and high temperature viscosity values of [BMIM][DCA] are available. There are some ambient pressure viscosity values of [BMIM][DCA] in literatures (Sánchez et al., 2009; Carvalho et al., 2010), but no high pressure results. In this case, presented high pressures density values in this work are without viscosity corrections.

The mPDS2000V3 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 393.15) K and pressures up to p = 100 MPa is within $\Delta \rho$ = ±(0.1 to 0.3) kg·m^{-3} or $\Delta \rho / \rho$ = ±(0.01 to 0.03) %. But the described viscosity correction problems increase the possible uncertainty of the density measurements of the present work. Thus the uncertainty of the density measurements can be predicted to be between $\Delta \rho / \rho$ = ±(0.01 to 0.08) %.

Results and discussion

(p, ρ, T) data and viscosity of [BMIM][DCA] were measured at $T = (283.15$ to $393.15)$ K and pressures up to $p = 100$ MPa and an equation fitted to the (p, ρ, T) and viscosity data of [BMIM][DCA] are reported. The temperature and pressure steps in the density experiments are typically $T = (5$ to $20)$ K and $p = (5$ to $10)$ MPa, in the viscosity experiments is $T = (5$ to $10)$ K, respectively. The obtained values presented in the Tables 1—3, were compared with the available literature results and this comparison showed the good agreement.

The measured densities as a function of pressure and temperature were fitted to the equation of state (1) from ref. (Safarov, 2003):

$$p/\text{MPa} = A(\rho \cdot 10^{-3}/\text{kg} \cdot \text{m}^{-3})^2 + B(\rho \cdot 10^{-3}/\text{kg} \cdot \text{m}^{-3})^8 + C(\rho \cdot 10^{-3}/\text{kg} \cdot \text{m}^{-3})^{12} \quad (1)$$

where the coefficients of eq.1 A, B and C are functions of temperature.

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

The coefficients a_i, b_i and c_i of the eq. 2 are given in Table 4 together with the standard uncertainties of fitting in Table 5. The eqs.1 and 2 describe the experimental results of density of [BMIM][DCA] within $\Delta\rho/\rho = \pm 0.011$ % percent, corresponding to

Tab. 1. Experimental values of pressure p in MPa, density ρ in kg·m⁻³, temperature T in K, calculated values of isothermal compressibility $\kappa_T \cdot 10^6$ in MPa⁻¹, isobaric thermal expansibility $\alpha_p \cdot 10^6$ in K⁻¹, difference in isobaric and isochoric heat capacities $c_p - c_v$ in J·kg⁻¹·K⁻¹, thermal pressure coefficient γ in MPa⁻¹·K⁻¹ and internal pressure p_{int} in MPa of *1-butyl-3-methylimidazolium dicyanamide*.

p	ρ	T	κ_T	α_p	$c_p - c_v$	γ	p_{int}
1.903	1070.34	283.13	355.2	570.7	242.5	1.6066	453.0
5.035	1071.47	283.13	351.5	566.9	241.6	1.6130	451.7
9.948	1073.14	283.15	346.0	561.4	240.4	1.6225	449.5
19.678	1076.54	283.16	335.3	550.4	237.7	1.6417	445.2
29.997	1080.15	283.16	324.3	539.0	234.8	1.6617	440.5
39.590	1083.43	283.16	314.8	528.7	232.1	1.6796	436.0
49.993	1086.97	283.15	304.9	517.8	229.1	1.6986	431.0
59.387	1090.08	283.15	296.5	508.4	226.5	1.7150	426.2
69.993	1093.52	283.15	287.5	498.2	223.5	1.7328	420.6
79.913	1096.66	283.15	279.6	488.9	220.7	1.7486	415.2
89.996	1099.79	283.15	272.0	479.8	217.9	1.7640	409.5
99.916	1102.80	283.15	264.9	471.2	215.2	1.7785	403.7
2.517	1064.22	293.14	367.4	582.9	254.7	1.5863	462.5
5.250	1065.11	293.17	364.4	580.1	254.2	1.5919	461.4
9.841	1066.90	293.15	358.4	574.6	253.1	1.6030	460.1
20.030	1070.58	293.16	346.5	563.5	250.9	1.6260	456.7
29.999	1074.16	293.16	335.4	552.9	248.7	1.6483	453.2
39.813	1077.59	293.17	325.2	543.0	246.7	1.6697	449.7
49.994	1081.16	293.16	315.0	532.9	244.4	1.6918	446.0
60.157	1084.60	293.16	305.5	523.3	242.3	1.7129	442.0
69.979	1087.84	293.16	296.9	514.5	240.2	1.7328	438.0
79.759	1090.95	293.17	288.9	506.1	238.3	1.7518	433.8
89.993	1094.22	293.16	280.8	497.5	236.1	1.7715	429.3
98.971	1096.99	293.16	274.2	490.3	234.3	1.7881	425.2
1.527	1060.80	298.11	374.6	588.6	259.9	1.5713	466.9
5.031	1062.04	298.13	370.3	584.8	259.3	1.5794	465.8
10.127	1063.87	298.15	364.1	579.3	258.4	1.5912	464.3
19.639	1067.41	298.15	352.5	569.0	256.5	1.6142	461.6
29.996	1071.19	298.15	340.6	558.2	254.6	1.6387	458.6
39.572	1074.53	298.17	330.5	548.8	252.9	1.6605	455.6
49.997	1078.23	298.16	319.8	538.7	251.0	1.6846	452.3
59.652	1081.53	298.16	310.6	529.9	249.3	1.7062	449.1
69.991	1085.04	298.15	301.2	520.8	247.4	1.7290	445.5
79.524	1088.14	298.15	293.2	512.8	245.8	1.7492	442.0
89.998	1091.48	298.15	284.8	504.4	244.0	1.7710	438.0
98.948	1094.29	298.14	278.0	497.4	242.5	1.7892	434.5
2.493	1051.44	313.18	392.2	598.1	271.7	1.5252	475.2
5.188	1052.51	313.18	388.3	595.1	271.4	1.5325	474.8
10.081	1054.72	313.12	380.6	589.0	270.6	1.5476	474.5
19.819	1058.33	313.16	368.2	579.0	269.5	1.5727	472.7
29.997	1062.26	313.15	355.4	568.7	268.3	1.6003	471.1

Tab. 1. — continue.

p	ρ	T	κ_T	α_p	$c_p - c_v$	γ	p_{int}
39.539	1065.87	313.14	344.1	559.4	267.2	1.6260	469.6
49.994	1069.66	313.14	332.7	550.0	266.2	1.6534	467.7
59.618	1073.16	313.12	322.6	541.6	265.3	1.6789	466.1
69.997	1076.60	313.15	313.0	533.5	264.5	1.7045	463.8
79.808	1079.89	313.15	304.2	526.0	263.8	1.7291	461.7
89.997	1083.18	313.15	295.7	518.7	263.0	1.7540	459.3
99.676	1086.18	313.16	288.2	512.2	262.4	1.7770	456.8
2.011	1038.78	333.15	416.4	604.5	281.5	1.4518	481.7
5.116	1040.05	333.16	411.5	600.9	281.1	1.4605	481.5
10.059	1042.19	333.15	403.4	595.0	280.6	1.4752	481.4
20.000	1046.30	333.15	388.3	584.1	279.7	1.5041	481.1
29.946	1050.29	333.15	374.4	574.0	279.1	1.5329	480.7
39.776	1054.14	333.15	361.6	564.6	278.6	1.5614	480.4
49.997	1058.02	333.15	349.2	555.6	278.3	1.5908	480.0
59.702	1061.55	333.16	338.4	547.7	278.2	1.6183	479.5
69.996	1065.28	333.15	327.5	539.7	278.2	1.6480	479.0
80.151	1068.77	333.15	317.7	532.5	278.3	1.6764	478.4
89.997	1072.04	333.15	308.8	526.0	278.5	1.7037	477.6
99.101	1074.95	333.15	301.1	520.5	278.8	1.7284	476.7
0.949	1025.65	353.14	444.8	610.2	288.3	1.3719	483.5
5.134	1027.45	353.16	437.1	604.8	287.6	1.3834	483.4
10.221	1029.75	353.15	427.7	598.0	286.8	1.3984	483.6
19.804	1034.08	353.12	410.5	585.9	285.6	1.4273	484.2
29.980	1038.29	353.14	394.6	574.8	284.7	1.4565	484.4
40.069	1042.44	353.14	379.7	564.4	284.2	1.4864	484.8
49.997	1046.32	353.15	366.4	555.2	283.9	1.5153	485.1
59.903	1050.01	353.17	354.3	546.9	283.9	1.5437	485.3
69.997	1053.77	353.16	342.4	538.8	284.2	1.5736	485.7
79.923	1057.28	353.16	331.8	531.7	284.6	1.6024	486.0
89.993	1060.74	353.15	321.8	525.0	285.2	1.6317	486.2
98.489	1063.51	353.15	314.0	519.9	285.9	1.6558	486.3
1.946	1013.51	373.13	473.5	616.5	295.5	1.3019	483.8
5.239	1015.03	373.14	466.4	611.3	294.5	1.3106	483.8
10.245	1017.43	373.13	455.5	603.3	293.0	1.3245	484.0
19.993	1021.77	373.16	436.4	589.5	290.8	1.3507	484.0
29.958	1026.24	373.15	417.9	576.3	288.9	1.3789	484.6
39.714	1030.51	373.13	401.1	564.5	287.6	1.4072	485.3
49.996	1034.66	373.15	385.6	553.6	286.7	1.4359	485.8
60.024	1038.58	373.16	371.6	544.0	286.2	1.4642	486.4
69.994	1042.37	373.16	358.6	535.3	286.1	1.4927	487.0
79.655	1045.86	373.16	347.2	527.7	286.2	1.5200	487.6
89.993	1049.49	373.15	335.8	520.3	286.7	1.5496	488.2
98.898	1052.41	373.15	326.9	514.6	287.2	1.5742	488.5
1.948	1001.13	393.17	509.9	631.6	307.2	1.2386	485.0
5.173	1002.84	393.15	501.0	624.7	305.3	1.2468	485.0
10.149	1005.27	393.16	488.6	615.1	302.8	1.2589	484.8
20.000	1010.07	393.15	465.2	597.2	298.4	1.2838	484.7
29.994	1014.72	393.15	443.8	581.1	294.8	1.3094	484.8
39.930	1019.12	393.16	424.7	567.0	292.0	1.3350	485.0
49.988	1023.47	393.15	406.8	553.9	289.8	1.3618	485.4
59.675	1027.49	393.14	391.0	542.7	288.2	1.3879	486.0
69.996	1031.47	393.15	376.1	532.2	287.1	1.4151	486.4
79.829	1035.12	393.15	363.1	523.3	286.5	1.4413	486.8
89.994	1038.68	393.15	350.9	515.1	286.2	1.4680	487.2
99.002	1041.71	393.14	340.9	508.5	286.3	1.4917	487.5

$\Delta\rho = \pm 0.14$ kg m^{-3} standard, $\Delta\rho = \pm 0.14$ kg m^{-3} root-mean-square and $\Delta\rho = \pm 0.36$ kg m^{-3} maximum absolute deviation.

Figures 1 and 2 show the plots of pressure p of [BMIM][DCA] *vs* density ρ together with high pressure values of ref. (Nieto de Castro et al., 2010) and deviations of experimental density ρ of [BMIM][DCA] from the calculated density ρ by eqs. 1 and 2 *vs* pressure p.

Various thermal and caloric properties were calculated from the eq.1 using the related thermodynamic derivations (Safarov et al., 2010, 2011)

Tab. 2. Experimental density ρ, kg·m^{-3} values of [BMIM][DCA] at $p = 0.101$ MPa and various temperatures T, K.

T	ρ
283.16	1069.3
293.16	1062.8
298.13	1059.7
303.14	1056.5
313.16	1050.2
323.14	1043.9
333.16	1037.8
343.14	1031.6

Tab. 3. Experimental dynamic viscosity η, mPa·s values of [BMIM][DCA] at $p = 0.101$ MPa.

T, K	η, mPa·s	T, K	η, mPa·s
278.15	73.4	323.15	13.1
283.14	56.5	323.15	13.3
283.15	58.2	328.15	11.5
288.14	44.6	333.15	10.2
293.15	36.7	333.15	10.3
293.15	35.8	338.15	9.1
298.15	29.3	343.15	8.2
298.15	29.9	343.15	8.2
303.15	24.3	348.15	7.4
303.15	24.8	353.15	6.7
308.14	20.6	358.15	6.1
313.15	17.5	363.15	5.6
313.15	17.7	368.15	5.2
318.15	15.2	373.15	4.8

and the results of calculations are shown in Table 1 together with experimental (p, ρ, T) data and shown in Figure 3.

The viscosity results were fitted to the empirical equation:

$$\ln \eta(T) = A + \frac{B}{T - 43.15} + \frac{C}{(T - 43.15)^2} \qquad (3)$$

where: A, B and C are the empiric coefficients of eq. 4 as follow:

$$A = 1.7844278097, \ B = -1696.41115$$
$$\text{and } C = 537098.341913 \qquad (4)$$

The eqn. 3 describe the experimental viscosity results of [BMIM][DCA] within $\Delta\eta/\eta = \pm 0.72$ % percent deviation.

The comparison of the measured (p, ρ, T) values of [BMIM][DCA] with the available literature results at ambient pressure are shown in the Figure 4.

The sixth density values of Fredlake et al. were compared with our measured density results at $p = 0.101$ MPa. These values have $\Delta\rho/\rho = \pm 0.27$ % deviation with our interpolated value at the experimental temperature of ref. (Fredlake et al., 2004).

One density value has been published by (Stoppa et al., 2009) at $T = 298.15$ K and ambient pressure. This value has $\Delta\rho/\rho = 0.052$ % deviation with our measured value and is smaller than our value.

Tab. 4. Values of the coefficients a_i, b_i and c_i in eqs. 1 and 2.

a_i	b_i	c_i
$a_1 = -3.18457727$	$b_0 = -1107.55946926$	$c_0 = 687.58461$
$a_2 = 0.64800231 \cdot 10^{-2}$	$b_1 = 8.22671$	$c_1 = -4.291863633$
$a_3 = -0.9802423 \cdot 10^{-6}$	$b_2 = -0.011886$	$c_2 = 0.659824 \cdot 10^{-2}$

Tab. 5. The standard, root-mean-square, absolute and average deviations of fitting by eqs.1 and 2.

Standard Deviation[a], $\Delta\rho$, kg·m^{-3}	Root-Mean-Square deviation[b], $\Delta\rho$, kg·m^{-3}	Absolute Deviation[b], $\Delta\rho$, kg·m^{-3}	Maximum Absolute Deviation[b], $\Delta\rho$, kg·m^{-3}	Average percent deviation[c], $\Delta\rho/\rho$ %
0.14	0.14	0.11	0.36	0.011

[a]Standard deviation: $\text{STD} = \sqrt{\dfrac{\sum(\rho_{\exp} - \rho_{cal})^2}{n(n-1)}}$,

[b]Root-Mean-Square deviation: $\text{RMS} = \sqrt{\dfrac{\sum(\rho_{\exp} - \rho_{cal})^2}{n}}$,

[c]Absolute deviation: $\text{ABD} = \dfrac{1}{n}\sum|\rho_{cal} - \rho_{\exp}|$,

[c]Average percent deviation: $\text{APD} = \dfrac{100}{n}\sum\left|\dfrac{\rho_{\exp} - \rho_{cal}}{\rho_{\exp}}\right|$,

where: $\rho_{\exp}$ is the experimental density; ρ_{cal} is the density obtained by fitting of EOS; n is number of experimental points.
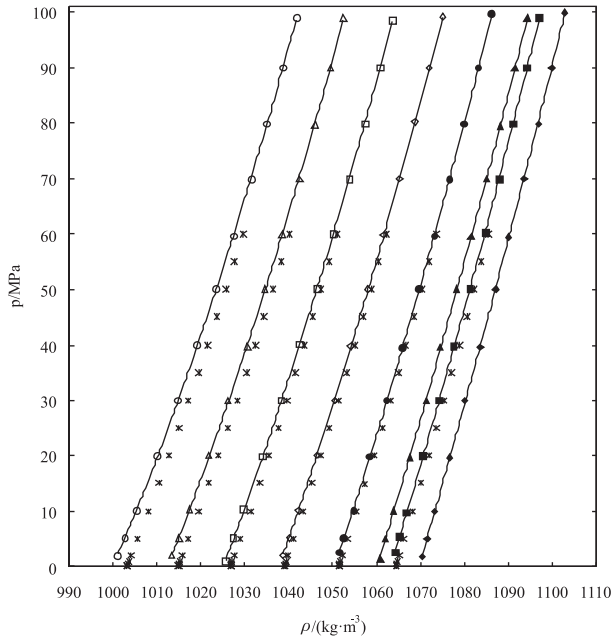
**Fig. 1.** Plot of pressure p of [BMIM][DCA] vs density ρ: $\blacklozenge$, 283.15 K; $\blacksquare$, 293.16 K; $\blacktriangle$, 298.15 K; $\bullet$, 313.15 K; $\diamondsuit$, 333.15 K; $\square$, 353.15 K; $\triangle$, 373.15 K; $\bigcirc$, 393.15 K; __ calculated by eqs.1 and 2; *, (Nieto de Castro et al., 2010).
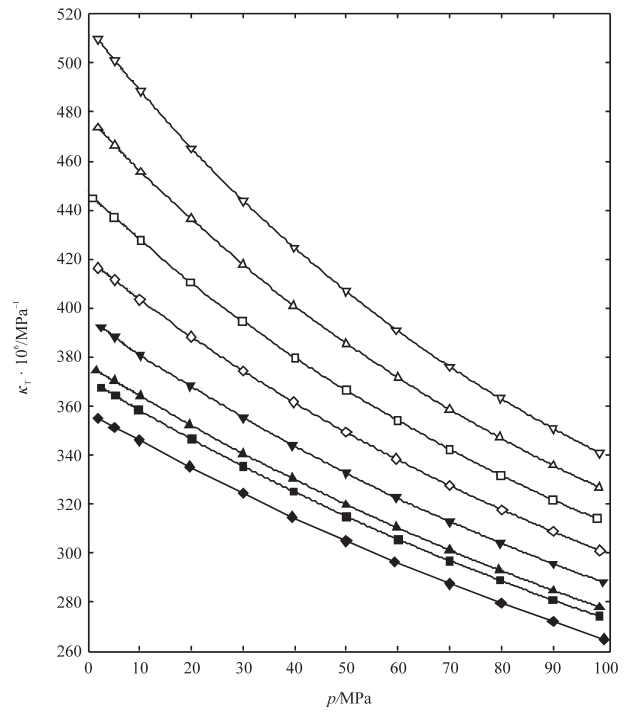
Fig. 3. Plot of isothermal compressibility $\kappa_T \cdot 10^6/\text{MPa}^{-1}$ of [BMIM][DCA] vs pressure p: $\blacklozenge$, 283.15 K; $\blacksquare$, 293.16 K; $\blacktriangle$, 298.15 K; $\blacktriangledown$, 313.15 K; $\diamondsuit$, 333.15 K; $\square$, 353.15 K; $\triangle$, 373.15 K; $\triangledown$, 393.15 K.
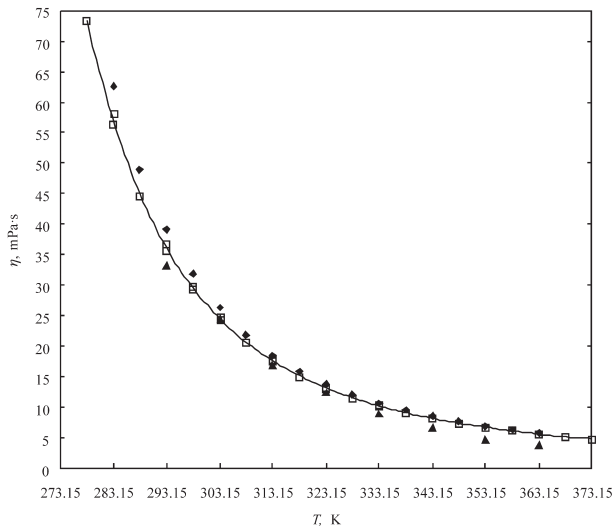
Fig. 2. Plot of deviations of experimental density $\rho_{\text{exp.}}$ of [BMIM][DCA] from the calculated values of density $\rho_{\text{cal.}}$ vs pressure p by eqs.1 and 2: $\blacklozenge$, 283.15 K; $\blacksquare$, 293.15 K; $\blacktriangle$, 298.15 K; $\blacktriangledown$, 313.15 K; $\diamondsuit$, 333.15 K; $\square$, 353.15 K; $\triangle$, 373.15 K; $\triangledown$, 393.15 K.
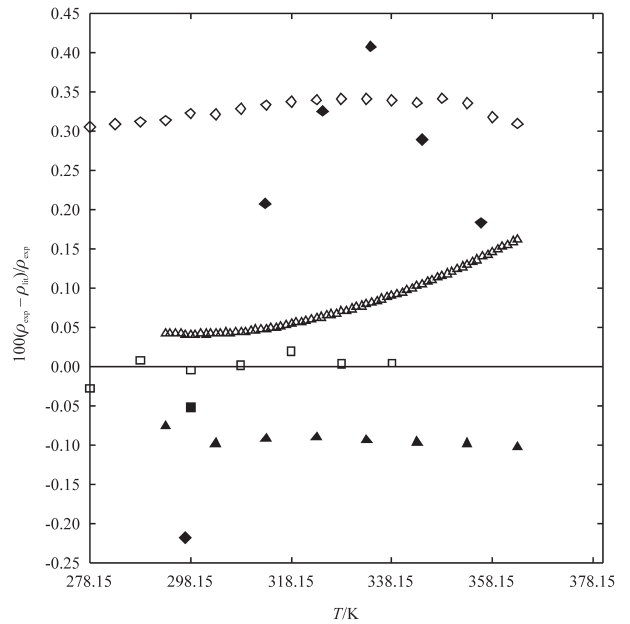

Fig. 4. Plot of deviation of experimental ρ_{exp} and literature ρ_{lit} densities of [BMIM][DCA] at $p = 0.101$ MPa vs temperature: $\blacklozenge$, (Fredlake et al., 2004); $\blacksquare$, (Stoppa et al., 2009); $\blacktriangle$, (Sánchez et al., 2009); $\diamondsuit$, (Carvalho et al., 2010); $\square$, (Zech, et al., 2010); $\triangle$, (Nieto de Castro et al., 2010).

The 16 experimental density and viscosity results of (Sánchez et al., 2009) have $\Delta\rho/\rho = \pm 0.072$ % and $\Delta\eta/\eta = \pm 14,7$ % average deviation with our values. The density values are systematically smaller than our values. The deviation of the density results in both measured parameter increase with increasing temperature. The viscosity values are smaller than our results.

Carvalho et al., in 2010, presented 36 measured density and viscosity values of [BMIM][DCA] at ambient pressure and $T = (278.15$ to $363.15)$ K. The comparison of these values with our measured results shown in density $\Delta\rho/\rho = \pm 0.33$ % and in viscosity $\Delta\eta/\eta = \pm 5.04$ % average deviation. The density and viscosity results are higher than our values.

Nieto de Castro et al., in 2010, presented 71 density results of [BMIM][DCA] at ambient pressure, $T = (293.15$ to $363.15)$ K and 170 density results in high pressures. The comparison of these values with our measured results shown in density $\Delta\rho/\rho = 0.081$ % at ambient pressure and $\Delta\rho/\rho = 0.128$ % at high pressures. The density results of (Nieto de Castro et al., 2010) are systematically higher than our values.

The measured viscosity values together with literature values (Sánchez et al., 2009; Carvalho et al., 2010) are shown in Figure 5.
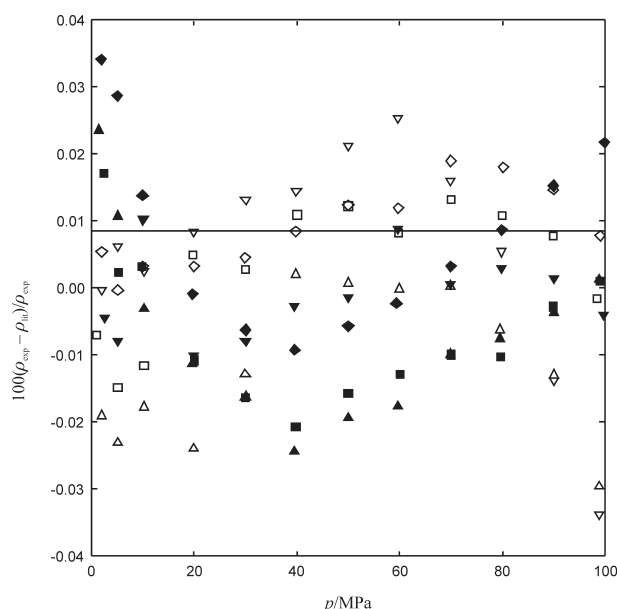
Fig. 5. Plot of viscosity η of [BMIM][DCA] *vs* temperature T together with literature results: □, our results; ▲, (Sánchez et al., 2009); ◆, (Carvalho et al., 2010); __ calculated by eq. 3.

Conclusion

The (p, ρ, T) properties of [BMIM][DCA] at wide range of temperature and pressures were measured using a new model of high pressure − high temperature vibrating tube densimeter. The viscosity of this IL also experimentally analysed using the SVM 3000 Stabinger viscometer. The thermomechanical properties, κ_T, α_p, γ, p_{int} and the difference in isobaric and isochoric heat capacities $c_p - c_v$ were calculated using the empirical equation of state in the temperature and pressure ranges. The isothermal compressibility κ_T and thermal expansibility α_p increase with temperature at constant pressure, and decrease with increasing pressure for all the isotherms, as expected.

The literature values of density and viscosity have been compared with our results and good agreements were obtained.

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