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Pressure−Density−Temperature ($p-\rho-T$) Surface of [C_6mim][NTf_2][‖]

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In the framework of the IUPAC Project entitled “Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems”, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [C_6mim][NTf_2], was selected as the standard ionic liquid on which to perform round-robin measurements on a series of selected properties. In this work, the pressure, density, temperature (p, ρ, T) surface was determined in the temperature range (293 to 338) K and up to a nominal pressure of 65 MPa. The isothermal compressibility and isobaric expansion coefficients were calculated from the (p, ρ, T) data.

Introduction

In the case of ionic liquids, the development of predictive, classical equations of state for the fluid state is impaired by the absence of (hypothetical) critical point data. In this context, the direct, experimental determination of the density of selected ionic liquids as a function of temperature and pressure turns out to be both an urgent and important issue.

In recent years, ionic liquids of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [$C_n$mim][NTf_2], family have become popular due to their combined high thermal stability[1] and relatively low viscosity.[2,3] The member of this family with six carbon atoms in the alkyl side chain, [C_6mim][NTf_2], has gained enhanced importance as it was selected by the coordinators of the IUPAC Project 2002-005-1-100 entitled “Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems” to be used as a model, standard ionic liquid. In this work, the temperature and pressure dependence of the density of [C_6mim][NTf_2] was determined up to a nominal pressure of 65 MPa, in the temperature range (293 to 338) K.

Experimental Section

Materials. The 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6mim][NTf_2], ionic liquid used in this project came from a batch synthesized by Dr. Mark Muldoon in Professor Joan Brennecke’s laboratories at the University of Notre Dame, where it underwent several purification stages. The 50 cm^3 batch labeled as “Tube #8” came from the material being used for the entire IUPAC Project 2002-005-1-100 (http://www.iupac.org/projects/2002/2002-005-1-100.html) and is known to be of high purity: the sample was colorless to the eye, contained less than $10 \cdot 10^{-6}$ mass fraction of halide, measured by an ion-selective electrode, and contained less than $20 \cdot 10^{-6}$ mass fraction of water, analyzed by coulometric Karl Fischer titration. Additionally, ^{1}H NMR and ^{19}F NMR spectra performed by Dr. Muldoon showed the ionic liquid purity to be greater than 99.5 % (excluding water contamination and other peaks known to originate from the NMR solvent). During the manipulation of the sample, it was expected that the ionic liquid would increase its water content; however, subsequent Karl Fischer analyses have never revealed mass fractions of water after the measurements greater than $200 \cdot 10^{-6}$. It must be stressed that the original sample, contained in a sealed flask, was opened in a glovebox under inert atmosphere and a septum adapted to its neck. The insertion of the ionic liquid into the densimeter cell was performed using a gastight syringe. The high-pressure vibrating-tube densimeter is, by its nature, a gastight apparatus, which means that until the completion of the density measurements the sample was never in contact with air (and moisture). After the measurements, the cell must be necessarily opened to the atmosphere, and it is during the removal of the ionic liquid from the densimeter that its water content is increased.

After the present set of volumetric determinations, the ionic liquid was recycled by moderate warming (up to 120 °C) in a vacuum line (0.1 Pa) and reused in further experiments, including its mixture with other substances.[4] After those experiments, the ionic liquid was again recycled and its purity checked by further analyses (NMR and Karl Fischer titration), which showed purity levels similar to those of the samples obtained after the experiments described in this work, with water mass fractions in the $(100 \text{ to } 200) \cdot 10^{-6}$ range. Tests comparing the density of the recycled ILs (an average value of 1371 $kg \cdot m^{-3}$ at 298 K and 0.1 MPa) with that of the original sample (1372.4 $kg \cdot m^{-3}$ under the same conditions) revealed that the latter showed lower densities (around −0.10 % relative deviation). This is consistent with the results obtained by Magee and co-workers[2] that measured in the scope of the same IUPAC project the influence of water content in the density of the [C_6mim][NTf_2] samples.

Method. Densities were measured using a commercial Anton Paar DMA 512P vibrating-tube densimeter in the temperature range $293 < T/K < 338$ and pressure range $0.1 < p/MPa < 65$. The density data repeatability is estimated to be less than $\pm 0.3 \ kg \cdot m^{-3}$.[5–7] The uncertainty associated with the measurements, which also depends on previous calibrations of the apparatus with standard fluids over the whole range of pressures

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Table 1. p, ρ, T Data for [C_6mim][NTf_2] over the 293 < T/K < 338 and 1 < p/MPa < 65 Temperature and Pressure Ranges

T = 293.15 K		T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
0.10	1377.3	0.10	1372.3	0.10	1367.9	0.10	1363.1	0.10	1358.8
2.50	1379.0	2.50	1374.1	10.01	1375.3	2.50	1365.0	2.50	1360.7
10.01	1384.4	10.01	1379.6	20.02	1382.4	10.01	1370.8	10.01	1366.6
20.01	1391.1	20.01	1386.6	30.03	1389.1	20.04	1378.0	20.03	1373.9
30.01	1397.7	30.01	1393.2	40.01	1395.5	30.01	1384.8	30.01	1380.8
40.04	1403.9	40.01	1399.4	50.01	1401.5	40.01	1391.2	40.01	1387.4
50.01	1409.8	50.01	1405.4	59.89	1407.2	50.01	1397.3	50.00	1393.5
59.97	1415.5	59.98	1411.1	65.02	1410.0	60.00	1403.0	60.01	1399.3
65.02	1418.2	65.02	1413.9	55.02	1404.4	65.01	1405.9	65.02	1402.0
55.02	1412.6	55.01	1408.2	45.02	1398.5	55.02	1400.2	55.03	1396.4
45.05	1406.8	45.02	1402.4	35.02	1392.3	45.05	1394.3	45.02	1390.4
34.99	1400.8	34.99	1396.3	25.05	1385.9	35.04	1388.1	34.99	1384.1
25.05	1394.5	25.02	1389.9	15.02	1378.9	25.02	1381.4	25.02	1377.4
15.02	1387.8	15.02	1383.1	15.02	1379.0	15.02	1374.4	15.02	1370.3
5.03	1380.8	5.02	1376.0	5.02	1371.7	5.03	1367.0	5.03	1362.7
0.10	1377.3	0.10	1372.4	0.10	1367.9	0.10	1363.2	0.10	1358.8

T = 318.15 K		T = 323.15 K		T = 328.15 K		T = 333.15 K		T = 338.15 K	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
0.10	1354.2	0.10	1350.2	0.10	1345.7	0.10	1341.0	0.10	1336.2
2.50	1356.2	2.50	1352.3	2.50	1347.8	2.50	1343.2	2.50	1338.4
10.01	1362.3	10.01	1358.4	10.02	1354.2	10.01	1349.7	10.04	1345.1
20.01	1369.8	20.01	1366.1	20.01	1362.0	20.01	1357.7	20.01	1353.4
30.01	1376.9	30.01	1373.3	30.01	1369.3	30.00	1365.2	30.01	1361.0
40.01	1383.5	40.01	1380.0	40.01	1376.1	40.01	1372.1	40.01	1368.1
50.01	1389.7	50.03	1386.3	49.99	1382.5	50.01	1378.6	49.99	1374.6
59.98	1395.4	59.96	1392.2	59.97	1388.4	59.98	1384.5	59.97	1380.6
65.00	1398.3	65.00	1395.0	65.02	1391.2	65.02	1387.3	65.02	1383.4
55.03	1392.6	55.02	1389.3	55.02	1385.5	55.02	1381.6	55.02	1377.7
45.05	1386.6	45.05	1383.3	45.02	1379.4	45.08	1375.4	45.02	1371.4
35.01	1380.2	35.02	1376.8	34.99	1372.8	35.02	1368.7	35.02	1364.6
25.02	1373.4	25.02	1369.8	25.05	1365.7	25.01	1361.5	25.02	1357.3
15.05	1366.1	15.02	1362.4	15.02	1358.2	15.02	1353.7	15.03	1349.4
10.01	1362.3	5.04	1354.5	5.02	1350.0	5.02	1345.4	5.03	1340.8
5.02	1358.3	0.10	1350.3	0.10	1345.7	0.10	1341.0	15.02	1349.4
		2.52	1352.4					5.02	1340.7
		10.01	1358.5						

and temperatures[7] and also on the influence of the sample viscosity on those calibrations, is estimated to be ± 1.5 kg·m^{-3}.

The density was determined along different isotherms (separated by nominal pressure intervals of 5 MPa) both in ascending and descending pressure modes. The density data from the DMA 512P densimeter were corrected for the effect of viscosity on density determinations using a vibrating tube, according to the empirical equation[8]

$$(\rho - \rho_{\text{raw}})/\rho_{\text{raw}} = (0.5 - 0.45(\eta/\text{mPa}\cdot\text{s})^{0.5})\cdot 10^{-4} \quad (1)$$

where ρ and ρ_{raw} are the corrected and measured raw densities, respectively, and η is the viscosity of the sample. The viscosity data necessary to perform the corrections were taken from the work of Marsh and co-workers.[3] Missing data at high pressure and low temperature were obtained by linear extrapolations in pressure at constant temperature. The largest correction was done at 293 K and 65 MPa and corresponds to a decrease in the measured density value from 1419.0 kg·m^{-3} to 1418.2 kg·m^{-3} (a correction of −0.05 %). All density data reported in this work were corrected for the viscosity effect.

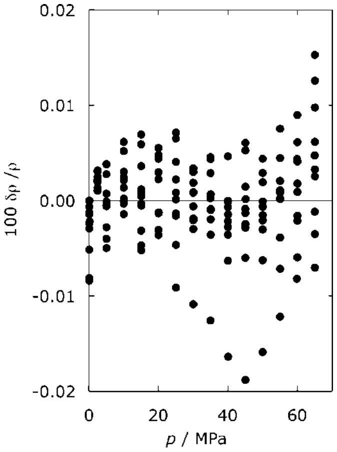

Figure 1. Fractional deviations ($\delta\rho/\rho = (\rho - \rho_{\text{calcd}})/\rho$) of the experimental density results, ρ, from densities calculated using eq 2, ρ_{calcd}.

Results

The density of [C_6mim][NTf_2] is given as a function of pressure and temperature in Table 1. Molar volumes can be calculated using the molar mass of 447.426 g·mol^{-1}. Figure 1 represents graphically the results, along with their relative deviations from a temperature-dependent Tait equation fitted to all data points

$$1/\rho = 1/\rho_0 + (A_0 + A_1T + A_2T^2)\ln[(B_0 + B_1T + B_2T^2 + p)/(B_0 + B_1T + B_2T^2 + 0.1)] \quad (2)$$

where ρ is the density and p is the pressure. ρ_0 is the density at the reference pressure of 0.1 MPa. The A_i and B_i coefficients are given in Table 2. Figure 1b shows that eq 2 is able to fit to the experimental results to better than 0.02 % over the studied temperature and pressure ranges.

The isothermal compressibility and thermal expansion coefficients, κ_T and α_p, respectively, were also calculated and are shown in Figure 2. The isothermal compressibilities at a given

Table 2. Parameters of the Global Tait Equation (Equation *2*) Used to Fit All the *pVT* Data[a]

A_0 ($\mathrm{m^3 \cdot kg^{-1}}$)	A_1 ($\mathrm{m^3 \cdot kg^{-1} \cdot K^{-1}}$)	A_2 ($\mathrm{m^3 \cdot kg^{-1} \cdot K^{-2}}$)	B_0 MPa	B_1 ($\mathrm{MPa \cdot K^{-1}}$)	B_2 ($\mathrm{MPa \cdot K^{-2}}$)
$-6.173 \cdot 10^{-4}$	$3.3063 \cdot 10^{-6}$	$-4.7748 \cdot 10^{-9}$	$2.2091 \cdot 10^{3}$	$-1.1872 \cdot 10^{+1}$	$1.6535 \cdot 10^{-2}$

[a] The standard deviation of the fit is $100 \cdot \sigma(\rho)/\rho = \pm\, 0.018$.

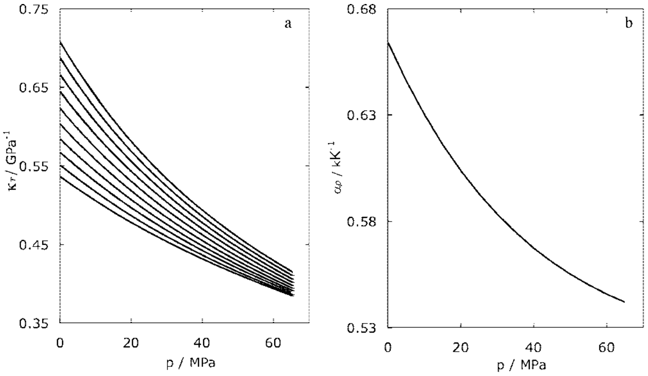

Figure 2. (a) Isothermal compressibility, κ_T, from 293.15 K (lower curve) to 338.15 K (upper curve) at 5 K intervals and (b) thermal expansion coefficient, α_p, of [C$_6$mim][NTf$_2$], valid in the studied temperature range.

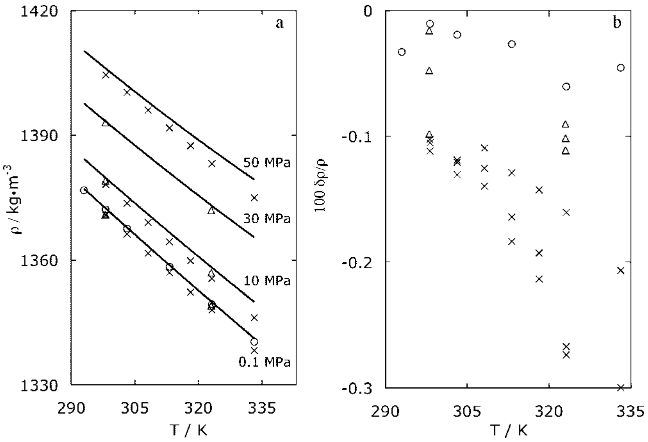

Figure 3. Comparison between $p-\rho-T$ data for [C$_6$mim][NTf$_2$] at four selected isobars: ●, ref 2; △, ref 3; ×, ref 6; solid lines, this work (eq 2). (a) Density as a function of temperature and pressure. (b) Relative deviations from eq 2.

temperature were obtained directly by differentiation of the Tait equation

$$\kappa_T = -\rho(A_0 + A_1 T + A_2 T^2)/(B_0 + B_1 T + B_2 T^2 + p) \quad (3)$$

The thermal expansion coefficients, α_p, were calculated considering that, in the studied temperature range, the logarithm of the density at constant pressure is approximately a linear function of the temperature. This means that α_p is constant for a given isobar, and its value can be obtained from the slope of the corresponding fitting line.

Discussion

The data obtained in this work were compared in Figures 3a and 3b with previous p, ρ, T results also obtained in our laboratory with a different [C$_6$mim][NTf$_2$] sample.[6] Although the water mass fraction of the samples used in that earlier work was initially below $75 \cdot 10^{-6}$, the density values reported in that work are ca. (0.15 to 0.30) % lower than those reported in the current study. Such discrepancy can be attributed to the higher water content of the samples used in the earlier work or simply to the different synthesis/purification routes employed in that case. This highlights the rationale behind the present IUPAC project, i.e., the importance of round-robin experiments using a common-source sample and the definition of a standard substance in the area of ionic liquids.

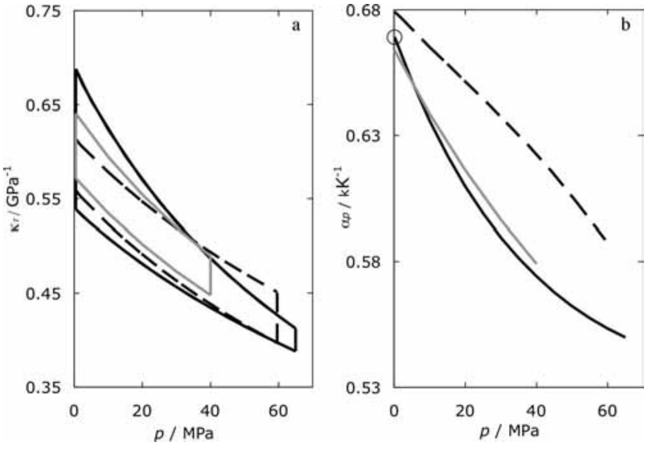

Figure 4. (a) Range of the isothermal compressibility of [C$_6$mim][NTf$_2$] between two isotherms at 298 K (lower curved lines) and 323 K (upper curved lines) calculated from different sources. Area delimited by the black lines, this work; by gray lines, ref 3; by dashed lines, ref 6. (b) Thermal expansion coefficient as a function of pressure calculated from different sources. Black line, this work; ○, ref 2 (atmospheric pressure results); light gray line, ref 3; dark gray line, ref 6.

Figures 3a and 3b also show density data measured using other samples from the IUPAC project material.[2,3] The atmospheric pressure results reported in ref 2 differ from 0.01 % (lower temperatures) to around 0.06 % (higher temperatures). The p, ρ, T data reported in ref 3 exhibit relative deviations in the (0.02 to 0.12) % range (also larger at higher temperatures). The density data are all in agreement within the stated expanded uncertainties of the different measurements (0.14 % in ref 2 and 0.2 % in ref 3).

The thermodynamic properties κ_T and α_p calculated with data from the present work and the results from refs 2, 3, and 6 are compared in Figure 4. Although the relative deviations between the two sets in terms of κ_T and α_p are 1 order of magnitude higher than the corresponding relative deviations in terms of density, one has to bear in mind that the former quantities are first-derivative properties of the latter.

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