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High-temperature and high-pressure (*p*, *ρ*, *T*) measurements and derived thermodynamic properties of 1-octyl-3-methylimidazolium hexafluorophosphate

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Abstract: Densities of ionic liquid (IL) 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF$_6$] at high temperatures and high pressures were measured. The measurements were made along 10 isotherms over a temperature range $T = 278.15$ to 413.15 K, at pressures up to 140 MPa by means of an Anton Paar DMA HPM vibration tube densimeter (VTD). The combined expanded relative uncertainties of the density, pressure and temperature measurements at the 95 % confidence level with a coverage factor of $k = 2$ are estimated to be 0.03 to 0.08 % (depending on temperature and pressure ranges), 0.1 %, and 0.015 K, respectively. We have critically assessed all of the reported high-pressure densities for [OMIM][PF$_6$], together with the presented results, in order to carefully select primary data for development of a reference wide-ranging equation of state. Values of ρ–T isobars curvatures, $(\partial^2\rho/\partial T^2)_n$, were estimated using the present high-pressure ρ-T measurements and they were pretty low (0.78×10^{-7} to $1.50\cdot\times10^{-7}$ m^3 kg^{-1} K^{-1}), indicating that the heat capacity of [OMIM][PF$_6$] very weakly depends on pressure, since $(\partial C_\mathrm{P}/\partial P)_T \approx$ $\approx (\partial^2\rho/\partial T^2)_n$. Density data were fitted to the modified Tammann–Tait equation and the multiparametric polynomial-type equation of state (EOS) for the IL was developed using the measured high-pressure and high-temperature (*p*, *ρ*, *T*) data. This EOS, together with our previous measured heat capacity data at atmospheric pressure, was used to calculate high-pressure and high-temperature derived thermodynamic properties, such as isothermal compressibility,

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isentropic compressibility, isobaric thermal expansion coefficient, heat capacities, *etc*.

Keywords: density; high-pressure; high-temperature; ionic liquid, equation of state.

INTRODUCTION

During our continuous experimental studying of the thermodynamic (density, heat capacity, vapour pressure), acoustic (speed of sound), and transport (viscosity) properties of ILs and their mixtures with alcohols, we reported the thermophysical properties of several ILs. We have examined [EMIM][EtSO$_4$], [EMIM][MeSO$_3$], [BMIM][NTf$_2$], [BMIM][FAP], and [HMIM][NTf$_2$][1–9] and binary mixtures containing ILs: ethanol+[BMIM][BF$_4$], methanol+[BMIM][BF$_4$], methanol+[BMIM][PF$_6$] and methanol+[BMIM][OcSO$_4$],[10–14] at high temperatures and pressures. The experimental density data of [OMIM][PF$_6$] sample at ambient pressure have been reported in our previous publication,[15] where we provided comprehensive evaluation of all reported densities and other thermodynamic properties (heat capacity, speed of sound and viscosity) for [OMIM][PF$_6$] in the wide temperature range from 278.15 to 413.15 K. In this study, the high-pressure density data, (p, ρ, T) properties, for [OMIM][PF$_6$] were measured over a temperature range from 278.15 to 413.15 K and at pressures up to 140 MPa. The measured (p, ρ, T) data were used to develop an accurate multiparametric polynomial equation of state and calculate various thermodynamic properties of OMIM][PF$_6$], such as adiabatic coefficient of bulk compressibility, isothermal coefficient of bulk compressibility, thermal expansion coefficient, thermal pressure coefficient, internal pressure, enthalpy difference, entropy difference, isochoric heat capacity, isobaric heat capacity, and speed of sound. The present results complement the previous high-pressure (p, ρ, T) measurements for [OMIM][PF$_6$] and they represent good contribution to the field, *i.e.*, the expanding of the available data base for [OMIM][PF$_6$] (Supplementary material to this paper, Table S-I). The literature survey revealed that very restricted high-pressure and high-temperature (p, ρ, T) data were reported for [OMIM][PF$_6$]. Namely, only six data sources[16–21] for the high-pressure density of [OMIM][PF$_6$] were found in the literature (Table S-I), and one of them, Harris *et al.*,[21] reported the data calculated using densities measured at atmospheric pressure. Density measurements for [OMIM][PF$_6$] at temperatures below T = 293.15 K are given for the first time in this work. The literature search was based on the SciFinder and TRC/NIST archive.[22] The mentioned papers are listed in Table S-I together with the method employed, uncertainty of the measurements, purity of the samples, and the temperature and pressure ranges. The quoted uncertainties of the reported density data at high pressures are within $\Delta\rho/\rho$ of ±0.05 to ±1.3 %. The reported experimental data sets cover temperature range from 293.15 to 473.15 K and pressures up to p = 204 MPa and were measured using various methods such as bellows dilatometer,[16] ultrahigh-pressure density apparatus,[17] glass piezometer[18] and VTD (DMA 512P).[19] The reported high-pressure (p, ρ, T) data for [OMIM][PF$_6$][16–21] were correlated using the Tait-type EOS.

EXPERIMENTAL

Material

The IL sample 1-octyl-3-methylimidazolium hexafluorophosphate, [OMIM][PF$_6$], (Chemical formula: $C_{12}H_{23}N_2F_6P$; product number IL-0020-HP-0100; CAS: 304680-36-2) used in this work was supplied by Iolitech GmbH, Germany. The supplier reported its purity assay (NMR) > 0.99 mass fraction. Before use, the IL sample was degassed under vacuum and dried at about 423.15 K for a minimum period of 48 h. Water content was determined using Karl Fischer titration and found to be less than 227 ppm.

High-pressure density measurements

Density of [OMIM][PF$_6$] as a function of temperature and pressure was measured using a modernized high-pressure and high-temperature Anton Paar DMA HPM vibration tube densimeter (VTD).[9,23-24] The apparatus and the experimental method (the physical basis and theory of the method, procedures, uncertainty assessment) were successfully employed and described in details previously[3,6,9,10,13,23-26] for measurements of the densities of ILs, ILs containing binary mixtures, ocean and geothermal waters at high temperatures and high pressures, so only a brief review will be given here. The temperature in the measuring cell, where the U-tube is located, was controlled using a thermostat (F32-ME Julabo, Germany) within 0.01 K and was measured with the (ITS-90) Pt100 thermometer (Type 2141), with an expanded absolute uncertainty of 0.015 K. Pressure was measured using transmitters P-30 (max. pressure 2.5 and 25 bar), P-10 (max. pressure 1000 bar), all with an expanded relative uncertainty of 0.1 %, and HP-1 (max. pressure 1600 bar) with an expanded relative uncertainty of 0.5 %. The mPDS2000V3 control unit measures the vibration period with an accuracy of $\Delta\tau =$ $= \pm 0.001$ μs. According to the specifications of Anton Paar and calibration procedures performed in our laboratory,[23] the observed repeatability of the density measurements at temperatures from 273.15 to 413.15 K and pressures up to p = 140 MPa is within $\Delta\rho$ of ±0.1 to ±0.3 kg m^{-3}. The measuring system of the DMA HPM VTD was calibrated using various standard fluids (double-distilled water, NaCl (aq), methanol, ethanol, toluene, acetone, *etc.*) with the well-known density data (REFPROP, NIST Standard Reference Database 23).[27] During the oscillation of the measuring U-tube in DMA HPM device, the effect of damping of the oscillation has been noticed. Since density is a function of viscosity (see also the literature[28-30]), it has been concluded that the density values of more viscous samples, measured using the described method, are higher than their actual densities. Therefore, all measured density data should be corrected for the effect of viscosity on density determination with a VTD instruments[30,31] using the equation:

$$\rho_{\text{cor}} = \rho_{\text{unc}}\left[1-\left(0.4482\sqrt{\eta}-0.1627\right)\times 10^{-4}\right] \tag{1}$$

where ρ_{cor} is the "corrected", ρ_{unc} is the "uncorrected" densities, and η / mPa s is the dynamic viscosity of the sample, so, the correction can easily be estimated if the sample's viscosity is known.[30,31] All Anton Paar VTD instruments which are used to measure the density at atmospheric pressure (DSA 5000 M, SVM 3000 and DMA 5000M) automatically correct the effect of viscosity on the measured values of density. In order to apply Eq. (1) to the present density measurements at high pressures using DMA HPM densimeter, the viscosities η of the [OMIM][PF_6] at the same experimental temperatures and pressures are required. We have reported dynamic viscosity, η, of [OMIM][PF_6] measured at atmospheric pressure over the experimental temperature range from 270.15 to 414.15 K using an Anton Paar SVM 3000 Stabinger viscometer (accuracy of viscosity measurements according the manufacturer's instructions is ±0.35 %) and Anton Paar rheometer MCR 302.[8] High-pressure viscosity data, needed to estimate the high-pressure corrections to the measured densities of [OMIM][PF_6], were taken from Tomida *et al.*[18] and Harris *et al.*[21] In the present experimental temperature and pressure ranges the relative percentage deviations between the "corrected" densities and the "uncorrected" values, calculated from Eq. (1) vary from 0.01 % at high temperatures (at 413.15 K) to 1.01 % (at low temperature 275.15 K and high pressure 140 MPa). It is apparent that increasing the pressure and lowering the temperature leads to the increase in the viscosity and, therefore, to higher corrections of the measured densities.

The uncertainties of temperature and pressure measurements, as well as the density correction due to damping effect, were taken into account and the estimated expanded relative uncertainty of the experimental density data reported here is within $\Delta\rho/\rho$ of 0.03 to 0.08 % (depending on pressure and temperature), at a 95 % confidence level, a coverage factor $k = 2$.

In order to verify the reliability of the measured densities for [OMIM][PF_6] and correctness of the calibration procedure of the high-pressure and high-temperature DMA HPM VTD, the densities of the same IL sample at atmospheric pressure were measured using various Anton Paar densimeters: DMA 5000, DMA 4500, SVM 3000 and DSA 5000M[15] with the uncertainties of $\Delta\rho$ of $\pm 5\times10^{-3}$ to ±0.3 kg m^{-3} and compared with the DMA HPM VTD results in the temperature range from 273.15 to 413.15 K. The detailed evaluation of densities at atmospheric pressure and comparison with the data reported in literature were provided in our recent publication.[15] Deviations between the reported data for [OMIM][PF_6][15] and the densities measured by means of DMA HPM VTD at atmospheric pressure are: average absolute percentage deviation, *AAD* = 0.06 % and maximum absolute percentage deviation *MD* = 0.23 %. The discrepancy between the present density measurements at atmospheric pressure and the most reliable reported data[16,17,19-21] is within 0.01 to 0.05 %, which confirms the accuracy of the high-pressure (p, ρ, T) measurements for [OMIM][PF_6] using DMA HPM desimeter.

RESULTS AND DISCUSSIONS

High pressure density data

Measurements of the (p, ρ, T) data for [OMIM][PF_6] were made along 10 isotherms between 278.15 and 413.15 K as a function of pressure in the range 0.101 to 140 MPa, which is presented in Table I. The expected behaviour can be noticed, the density increases when pressure goes up and decreases with the increase in temperature (Fig. S-1 of the Supplementary material to this paper).

Density correlation

Multiparametric polynomial-type EOS. For practical use and to facilitate calculation of the derived properties (caloric properties, for example) the multiparametric equation of state (EOS)[32] for [OMIM][PF_6] was developed on the bases of present high-pressure and high-temperature (p, ρ, T) data:

$$p(\rho, T) / \text{MPa} = A(T)/(\rho / \text{g cm}^{-3})^k + B(T)\,(\rho / \text{g cm}^{-3})^m + C(T)\,(\rho / \text{g cm}^{-3})^n \quad (2)$$

where the coefficients $A(T)$, $B(T)$ and $C(T)$ are temperature dependent fitting parameters.

TABLE I. Experimental values of (p, ρ, T) data of [OMIM][PF$_6$] at various temperatures, T, and pressures, p

T^{a}	p^{b}	ρ^{c}	T^{a}	p^{b}	ρ^{c}	T^{a}	p^{b}	ρ^{c}	T^{a}	p^{b}	ρ^{c}
K	MPa	kg m^{-3}	K	MPa	kg m^{-3}	K	MPa	kg m^{-3}	K	MPa	kg m^{-3}
278.15	0.101	1252.2	293.14	70.00	1274.7	333.15	0.101	1209.9	373.15	69.99	1223.7
278.15	1.00	1252.7	293.15	79.79	1279.0	333.11	1.42	1210.8	373.15	80.23	1228.9
278.15	5.02	1254.7	293.15	90.00	1283.4	333.12	5.41	1213.4	373.15	90.00	1233.8
278.15	10.00	1257.1	293.15	100.00	1287.5	333.14	9.97	1216.2	373.15	98.77	1238.0
278.15	19.95	1262.0	293.15	109.99	1291.6	333.14	20.87	1222.7	373.16	109.81	1243.1
278.15	29.96	1266.7	293.15	119.99	1295.5	333.15	30.00	1228.0	373.17	120.39	1247.8
278.15	39.96	1271.4	293.15	130.00	1299.3	333.15	40.64	1233.7	373.16	129.81	1251.8
278.15	49.93	1275.9	293.15	140.00	1303.0	333.15	50.00	1238.8	373.16	139.39	1255.8
278.15	59.96	1280.4	298.15	0.101	1236.5	333.15	59.97	1244.0	393.15	0.101	1165.2
278.15	70.01	1284.8	298.15	1.01	1237.0	333.15	70.00	1248.8	393.17	0.89	1165.8
278.15	79.96	1289.0	298.15	5.02	1239.2	333.15	80.06	1253.6	393.15	5.07	1169.1
278.15	89.93	1293.1	298.15	10.01	1241.8	333.15	89.99	1258.2	393.15	10.50	1173.3
278.15	99.96	1297.2	298.16	19.92	1247.1	333.15	98.04	1261.8	393.15	20.29	1180.4
278.15	109.95	1301.1	298.15	30.00	1252.3	333.15	109.80	1266.9	393.14	30.00	1187.1
278.15	119.99	1305.0	298.15	40.00	1257.3	333.15	116.02	1269.5	393.14	40.38	1193.8
278.15	129.95	1308.7	298.13	50.01	1262.1	333.15	129.80	1275.1	393.14	50.00	1199.7
278.15	139.96	1312.3	298.15	59.92	1266.8	333.15	139.95	1279.2	393.15	59.92	1205.5
283.15	0.101	1248.0	298.15	69.93	1271.4	353.15	0.101	1195.2	393.14	70.00	1211.2
283.15	1.02	1248.5	298.14	79.94	1275.9	353.18	1.36	1196.0	393.14	80.18	1216.6
283.15	5.02	1250.6	298.15	89.92	1280.2	353.15	5.21	1198.5	393.14	90.00	1221.7
283.15	10.02	1253.2	298.15	99.92	1284.4	353.16	10.56	1202.0	393.14	98.91	1226.1
283.15	19.93	1258.3	298.12	109.93	1288.5	353.18	20.39	1208.1	393.14	109.82	1231.3
283.15	29.93	1263.2	298.15	119.96	1292.4	353.17	30.00	1214.0	393.14	121.15	1236.5
283.15	39.95	1267.9	298.15	129.95	1296.2	353.17	40.36	1220.1	393.14	129.82	1240.3
283.15	49.95	1272.6	298.15	139.92	1299.8	353.16	50.00	1225.5	393.15	139.72	1244.6
283.15	59.99	1277.1	313.15	0.101	1224.9	353.15	60.20	1231.1	413.15	0.101	1151.6
283.15	70.00	1281.5	313.12	1.84	1226.0	353.15	70.00	1236.3	413.18	1.36	1152.6
283.15	79.92	1285.8	313.14	5.53	1228.1	353.15	79.90	1241.3	413.17	4.97	1155.6
283.15	89.92	1290.0	313.15	10.20	1230.8	353.15	90.00	1246.2	413.16	10.19	1159.7
283.15	99.96	1294.1	313.18	21.17	1236.9	353.15	98.97	1250.4	413.16	20.33	1167.3
283.15	109.93	1298.0	313.17	30.00	1241.7	353.15	109.85	1255.2	413.15	29.99	1174.2
283.15	119.95	1301.9	313.16	40.57	1247.3	353.16	118.12	1258.8	413.15	40.07	1180.9
283.15	129.99	1305.7	313.16	50.00	1252.1	353.15	129.86	1263.5	413.15	50.00	1187.2
283.15	139.95	1309.3	313.17	59.86	1257.0	353.15	139.99	1267.4	413.15	60.07	1193.3
293.15	0.101	1240.2	313.16	69.99	1261.6	373.15	0.101	1180.0	413.15	69.99	1199.0
293.17	1.39	1240.9	313.16	80.40	1266.4	373.17	1.61	1181.1	413.15	79.82	1204.4
293.16	4.76	1242.7	313.15	90.00	1270.6	373.16	5.27	1183.8	413.15	90.00	1209.8
293.15	8.25	1244.6	313.15	95.95	1273.2	373.16	10.43	1187.5	413.15	98.65	1214.2
293.14	19.75	1250.8	313.15	109.81	1279.1	373.15	20.22	1194.2	413.15	109.80	1219.6
293.14	30.20	1256.1	313.16	119.27	1283.0	373.15	30.00	1200.6	413.13	119.81	1224.3
293.14	39.69	1260.8	313.16	129.81	1287.0	373.15	40.63	1207.2	413.14	129.80	1228.9

TABLE I. Continued

T^{a} K	p^{b} MPa	ρ^{c} kg m^{-3}	T^{a} K	p^{b} MPa	ρ^{c} kg m^{-3}	T^{a} K	p^{b} MPa	ρ^{c} kg m^{-3}	T^{a} K	p^{b} MPa	ρ^{c} kg m^{-3}
293.14	50.00	1265.7	313.16	139.45	1290.5	373.15	50.00	1212.7	413.15	139.56	1233.2
293.13	58.94	1269.6				373.15	60.38	1218.5			

$^{a}U(T)$ = 0.015 K; $^{b}U_{r}(p)$ 0.1–0.5 %; $^{c}U_{r}(\rho)$ 0.03-0.08 %

$$A(T)=\sum_{i=1}^{4}a_iT^i\ ,\ B(T)=\sum_{i=0}^{3}b_iT^i\ ,\ C(T)=\sum_{i=0}^{3}c_iT^i \tag{3}$$

This EOS was successfully used for accurate representation of the experimental high-pressure and high-temperature (p, ρ, T) data for various pure liquids, binary mixtures and sea water in the liquid phase.[23–26,33–35] The theoretical bases of the EOS, Eq. (2), was developed by Putilov[36] using Gabriel,[37] Me,[38] and Grüneisen[39] intermolecular potential function. Unfortunately, theory cannot predict the values of exponents k, m and n, these values can be estimated only using the fitting procedure on the bases of direct experimental high-pressure (p, ρ, T) data.[40–42] The derived optimal values of k, m and n for [OMIM][PF$_6$] are 2, 8, and 12, respectively,[43] similar to most studied liquids.[23,33–35] The coefficients a_i, b_i and c_i were determined by the least-squares method and are given in Table II. The standard deviation of values calculated using Eq. (2), ρ_{cal}, from experimental densities, ρ_{exp}, was σ = 0.3 kg m^{-3}, *AAD* = 0.005 %, *MD* = 0.02 % and average percentage deviation, *Bias* = 0.0. The plot of pressure of [OMIM][PF$_6$] *versus* density are shown in Fig. 1.

TABLE II. Values of fitting parameters a_i, b_i, c_i of the Eq. (3) for [OMIM][PF$_6$]

	a_i		b_i		c_i	Parameter
a_1	–4.27944	b_0	–9.79224×10^{2}	c_0	2.90243×10^{2}	*AAD* = 0.005 %
a_2	0.012825	b_1	10.52682	c_1	–2.860582	σ = 0.1 kg m^{-3}
a_3	0.59225×10^{-5}	b_2	–0.033937	c_2	0.90228×10^{-2}	*MD* = 0.02 %
a_4	–0.34158×10^{-7}	b_3	0.35151×10^{-4}	c_3	–0.91062×10^{-5}	*Bias* = 0.0 %

$$AAD=\frac{100}{n}\sum_{i=1}^{n}\left|\frac{\rho_{\rm exp}-\rho_{\rm cal}}{\rho_{\rm exp}}\right|;\ Bias=\frac{100}{n}\sum_{i=1}^{n}\frac{\rho_{\rm exp}-\rho_{\rm cal}}{\rho_{\rm exp}};$$

$$\sigma=\sqrt{\frac{\sum_{i=1}^{n}\left(\rho_{\rm exp}-\rho_{\rm cal}\right)^2}{n(n-1)}}\ ;\ MD=\max\left(100\left|\frac{\rho_{\rm exp}-\rho_{\rm cal}}{\rho_{\rm exp}}\right|\right),i=1,n$$

We have critically assessed all of the reported[16–21] and the present high-pressure density data for [OMIM][PF$_6$] for their agreement and consistence. All

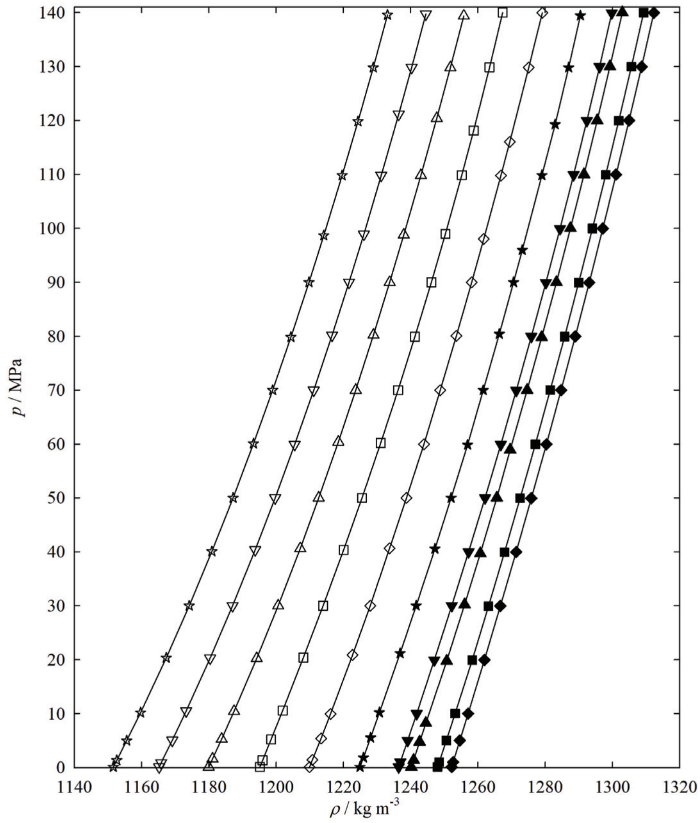

Fig. 1. Plot of pressure *p* of [OMIM][PF$_6$] *versus* density *ρ*: ◆ – 278.16 K; ■ – 283.15 K; ▲ – 293.15 K; ▼ – 298.15 K; ★ – 313.16 K; ◇ – 333.14 K; □ – 353.16 K; △ – 373.16 K; ▽ – 393.15 K; ☆ – 413.15 K; Solid lines represent values calculated using Eq. (2).

previously reported Tait-type EOS[16–21] were fitted to authors' own experimental data only. Therefore, these EOS are based on the restricted data and cover very limited temperature and pressure ranges. In most cases the direct comparison of the present results and other reported data is somewhat inconvenient, because of the experimental temperature differences between the various data sources. The best way to compare such data is using the correlation or EOS. For this purposes the present high-pressure density data and other reported data[16–21] (Table S-I of the Supplementary material) were compared with the values calculated from wide-ranged Tait-type EOS by Taguchi *et al.*[16] The direct comparison of the present high-pressure results for [OMIM][PF$_6$] and the values calculated from EOS by Taguchi *et al.*[16] showed that the values of calculated densities are systematically lower than the experimental results by *AAD* = 0.09 %. The results of the detailed quantitative comparisons, the deviation statistics for the present and each reported data source, are given in Table III.

TABLE III. Deviation statistics between the present and densities reported in the literature

First author	Temperature range K	Pressure range MPa	*AAD* %	*Bias* %	σ kg m^{-3}	*MD* %
Taguchi[16]	312.80–472.30	0.1–200	0.02	–0.01	0.03	0.10
Gu[17]	298.20–323.20	0.1–200	1.01	–1.01	0.19	1.44
Gardas[19]	293.15–393.15	0.1–10	0.08	0.06	0.09	0.25
Tomida[20]	295.10–335.20	0.1–20	0.07	–0.04	0.02	0.15
Harris[21]	273.15–353.15	0.1–176	0.08	0.08	0.05	0.24
This work	278.15–413.15	0.1–140	0.09	0.09	0.04	0.18

Modified Tammann–Tait equation. The measured density values were fitted to the modified Tammann–Tait equation:

$$\rho(T,p)=\frac{\rho^{\text{ref}}(T)}{1-C\ln\left(\dfrac{B(T)+p}{B(T)+p^{\text{ref}}}\right)} \tag{4}$$

where *C* is temperature independent parameter while parameter *B*(*T*) depends on temperature as follows:

$$B(T)=\sum_{i=0}^{2}b_iT^i \tag{5}$$

ρ^{ref} denotes density at reference pressure, p^{ref}, and it can be calculated from the polynom:

$$\rho^{\text{ref}}(T)\;=\sum_{i=0}^{2}a_iT^i \tag{6}$$

In Eqs. (4)–(6) a_i, b_i and *C* are adjustable parameters and they were optimized using standard deviation as the objective function. First, the parameter a_i was obtained by fitting density data at p^{ref} (0.1 MPa), and, further, parameters b_i and *C* were gained from the correlation of the entire density data set by Eq. (4). Parameters of the modified Tammann–Tait equation, as well as deviations criteria between the measured and the calculated densities are presented in Table IV. The average absolute percentage deviation, *AAD*, of 0.014 % between the measured and the calculated densities confirmed the accuracy of the chosen correlation method.

Fig. S-1 of the Supplementary material depicts the temperature dependences measured densities of [OMIM][PF$_6$], along the four selected isobars of 10, 50, 100, 140 MPa. As it can be seen, the ρ–T dependence for various isobars is almost linear, *i.e.*, it shows very small curvature, $(\partial^2\rho/\partial T^2)_p$ (slopes of the isobars hardly change). This means that the pressure influence on the heat capacity, $(\partial c_p/\partial p)_T$, is also weak (almost independent on pressure, see, for example, experimental results by Gardas *et al.*[19]). We estimated the values of the isobar's curvature, $(\partial^2\rho/\partial T^2)_p$, using the present high-pressure the ρ–T measurements, and it was shown that the values of $(\partial^2\rho/\partial T^2)_p$ for [OMIM][PF$_6$] at pressures between 0.101 and 140 MPa changed from 0.46×10^{-3} to 0.52×10^{-3} kg m^{-3} K^{-2}. Thus, the average value of the derivative $(\partial c_p/\partial p)_T$ in the pressure range from 0.101 to 140 MPa is about 0.78×10^{-7} to 1.50×10^{-7} m^3 kg^{-1} K^{-1}.

TABLE IV. The parameters of the modified Tammann–Tait equation

a_0 = 1495.020 kg m^{-3}	AAD = 0.014%
a_1 = –0.96034 kg m^{-3} K^{-1}	MD = 0.048 %
a_2 = 0.312464·10^{-3} kg m^{-3} K^{-2}	$Bias$ = –0.004 %
b_0 = 582.365 MPa	σ = 0.23 kg m^{-3}
b_1 = –1.86907 MPa K^{-1}	
b_2 = 0.00183746 MPa K^{-2}	
C = 0.0878587	

The agreement of the experimentally determined densities and the values calculated using the multiparametric polynomial EOS and the modified Tammann–Tait equation is presented in Fig. S-2 of the Supplementary material, while the deviations between the high-pressure data reported in literature[16–21] and the values calculated from multiparametric polynomial EOS, Eq. (2), are depicted in Fig. 2.

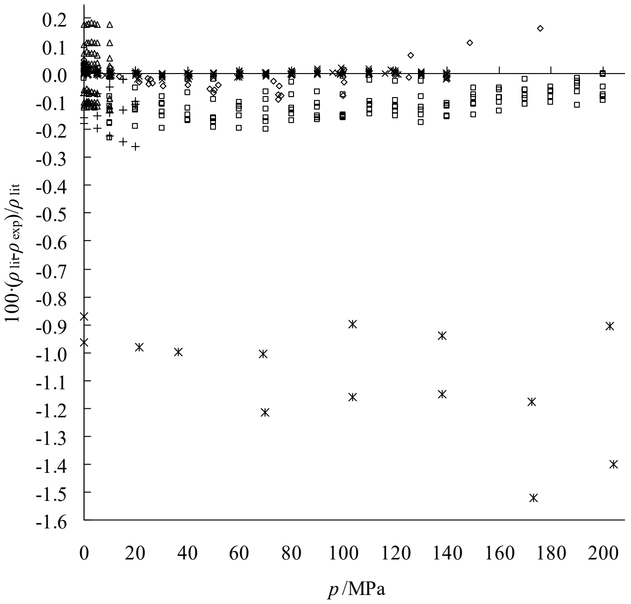

Fig. 2. Percentage deviations of the values calculated using multiparametric polynomial-type EOS (Eq. (2)) for [OMIM][PF$_6$] from literature high-pressure densities: (□) Taguchi *et al.*,[16] (✱) Gu *et al.*,[17] (△) Gardas *et al.*,[19] (+) Tomida *et al.*,[20] (◇) Harris *et al.*,[21] (×) presented results.

The percentage average absolute deviations between the values calculated using Eq. (2) and the reported data sources are: 0.09,[19] 0.13,[16] 0.15,[20] 0.05,[21] 1.12 %.[17] As one can see, the agreement is within the experimental uncertainties, except the data reported by Gu and Brennecke.[17] As Fig. 2 shows, the density data reported by Gu *et al.*[17] systematically deviate from all other reported data by about 1.0 %. In most cases the deviations between the various data sources are systematical (Table III) *AAD* and *Bias* are very close, although within their experimental uncertainties. The reason for the systematic deviations could be the difference in water contents or an incorrect calibration of the instrument, *i.e.*, incurrect reference data (or reference fluid) used for the calibration.

Derived volumetric properties

The modelling of high pressure densitiese, using Eqs. (2) and (4), enabled the calculation of derived volumetric properties. The multiparametric polynomial-type EOS (Eq. (2)) was used to calculate various thermodynamic properties, such as isothermal compressibility, thermal expansion coefficient, thermal pressure coefficient, internal pressure, isochoric heat capacity, isobaric heat capacity, speed of sound, isentropic exponent of [OMIM][PF_6] over the experimental temperature range 278.15 to 413.15 K and at pressures 0.101 to 140 MPa using well-known thermodynamic relations[44] (Supplementary material, Table S-II). Our previous heat capacity measurements at atmospheric pressure [15] have been used as a reference data to calculate the high -pressure heat capacities using equation of state, Eq. (2). The present heat capacity data calculated from EOS Eq. (2) for [OMIM][PF_6] are in excellent agreement (deviations within 0.1 %) with the values reported by Gardas *et al.*[19] Unfortunately, there are no reported direct experimental thermodynamic data for [OMIM][PF_6] to compare with the present results and validate the accuracy and reliability of the developed EOS, Eq. (2).

The optimized parameters of the modified Tammann–Tait equation were, also, used for calculation of the derived volumetric properties isothermal compressibility and isobaric thermal expansivity (Eqs. (7) and (8)) and the obtained results are presented in Fig. 3.

The isothermal compressibility, κ_T, of the examined ionic liquid shows the behaviour characteristic for this property, meaning it decreases with temperature drop at constant pressure and decreases along isotherms when pressure goes up. The influence of pressure on density is higher at higher temperatures and a bit more noticeable at lower pressures close to atmospheric. On the other hand, the behaviour of the isobaric thermal expansivity, α_p, is not really typical for this property, but it is quite common for ionic liquids.[45,46] It goes down along isotherms when the pressure increases and rises with the temperature drop at constant pressure.

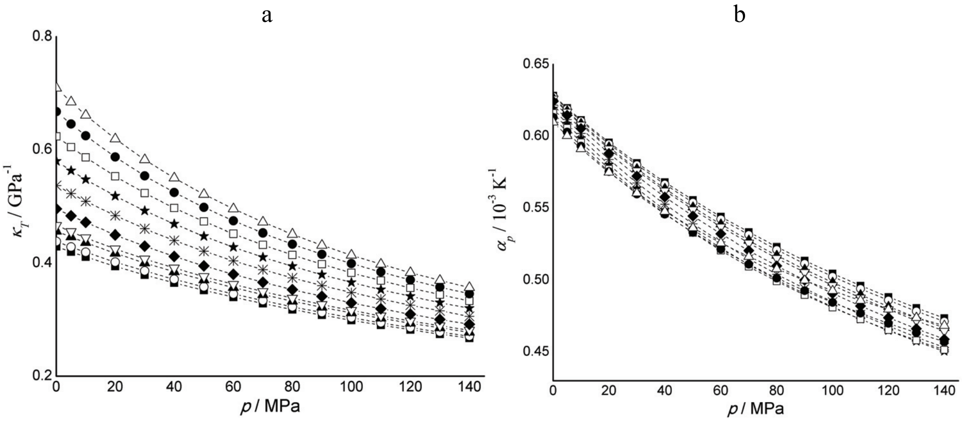

Fig. 3. a) The isothermal compressibilities and b) the isobaric thermal expansivity of [OMIM][PF$_6$] at: (■) 278.15 K, (○) 283.15 K, (▲) 293.15 K, (▽) 298.15 K, (◆) 313.15 K, (✳) 333.15 K, (★) 353.15 K, (□) 373.15 K, (●) 393.15 K and (△) 413.15 K. Lines are guides for eyes.

CONCLUSIONS

A total of 170 high-pressure and high-temperature data are reported for (p, ρ, T) of [OMIM][PF$_6$] in the liquid phase over the temperature range from 278.15 to 413.15 K at pressures up to 140 MPa. The experimental data reported here have an expanded uncertainty at a 95 % confidence level within $\Delta\rho/\rho$ of ±0.03 to ±0.08 %. The present high-pressure ρ/T data were used to estimate the real curvature, $(\partial^2\rho/\partial T^2)_p$ of the experimental isobars. We found that the slopes of the isobars hardly change. For various isobars between 0.101 and 140 MPa, the values of $(\partial^2\rho/\partial T^2)\text{P}_p$ are changing from 0.00046 to 0.00052 kg m^{-3} K^{-2}. This means that the pressure dependence of the heat capacity, $(\partial c_p/\partial p)_T$, is also small (almost independent on pressure), *i.e.*, the heat capacity of [OMIM][PF$_6$] c_p very poorly depends on pressure. The average value of derivative $(\partial c_p/\partial p)_T$ in the pressure range from 0.101 to 140 MPa is about 0.78×10^{-7} to 1.50×10^{-7} m^3 kg^{-1} K^{-1}.

The experimentally determined density values were fitted to the modified Tammann–Tait equation and the obtained parameters were used for the calculation of isothermal compressibility and isobaric thermal expansivity. While κ_T showed characteristic changes as a response to temperature and pressure changes, the behaviour of α_p wasn't typical for this property, but the similar dependence on temperature and pressure has been noticed for other ionic liquids.

Based on the present measurements, the multiparametric polynomial type EOS was developed for the (p, ρ, T) surface of liquid [OMIM][PF$_6$]. The developed EOS represents the present density measurements in the whole experimental range with an *AAD* of 0.005 % (standard deviation of 0.01 %). The derived EOS was used to calculate various thermodynamic properties of [OMIM][PF$_6$], in the experimental pressure and temperature ranges, such as adiabatic coefficient of bulk compressibility, isothermal coefficient of bulk compressibility, thermal expansion coefficient, thermal pressure coefficient, internal pressure, enthalpy difference, entropy difference, isochoric heat capacity, isobaric heat capacity, and speed of sound.

SUPPLEMENTARY MATERIAL

The derived thermodynamic properties of [OMIM][PF$_6$] in the experimental pressure and temperature ranges are available electronically on the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

(p, ρ, T) МЕРЕЊА И ИЗВЕДЕНА ТЕРМОДИНАМИЧКА СВОЈСТВА 1-ОКТИЛ-3-МЕТИЛИМИДАЗОЛИЈУМ-ХЕКСАФЛУОРОФОСФАТА НА ВИСОКИМ ТЕМПЕРАТУРАМА И ПРИТИСЦИМА

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У раду је приказано експериментално одређивање густине јонске течности 1-октил-3-метилимидазолијум-хексафлуорофосфата [OMIM][PF6] на високим температурама и високим притисцима. Мерења су извршена на 10 изотерми у температурном опсегу T = 278,15 до 413,15 K при притисцима до 140 MPa, коришћењем Anton Paar DMA HPM густиномера са вибрирајућом цеви. Заједно са резултатима приказаним у овом раду узете су у обзир и литературне густине за [OMIM][PF$_6$] на високим притисцима, да би се одабрали примарни подаци за развој референтне једначине стања која би имала широку примену. Вредности ρ–T изобара процењене су помоћу представљених мерења на високим притисцима и прилично су ниске (0,78×10^{-7}–1,50×10^{-7} m^3·kg^{-1}·K^{-1}), што указује на то да топлотни капацитет [OMIM][PF$_6$] веома мало зависи од притиска, пошто је $(\partial c_p/\partial P_T) \approx (\partial^2\rho/\partial T^2)_p$. Подаци о густини су обрађени модификованом Таман–Тејтовом једначином, а за ову јонску течност је развијена и мултипараметарска једначина стања применом (p, ρ, T) података измерених на високим притисцима и температурама. Ова једначина стања, заједно са раније измереним вредностима топлотног капацитета на атмосферском притиску, коришћена је за израчунавање изведених термодинамичких својстава на високим притисцима и температурама, као што су изотермска стишљивост, изентропска стишљивост, коефицијент изобарског топлотног ширења, топлотни капацитети, итд.

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