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Full Length Article

High-temperature and high-pressure density measurements and other derived thermodynamic properties of 1-butyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate

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ABSTRACT

Density of ionic liquid (IL) 1-butyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate (short name BMIM][FAP]) at high temperatures and high pressures were measured. The measurements have been made at pressures up to 140 MPa for 10 isotherms between (273 and 413) K using an Anton Paar DMA HPM vibration tube densimeter (VTD). The measuring system was calibrated using various standard fluids (double- distilled water, aqueous NaCl solutions, methanol, ethanol, toluene and acetone) with well-known density data (Internationally accepted NIST standard data). The combined expanded uncertainty of the density (ρ), pressure (*P*), and temperature (*T*) measurements at the 95% confidence level with a coverage factor of $k = 2$ is estimated to be (0.01–0.08) % depending on temperature and pressure ranges, 0.1%, and 15 mK, respectively. We have critically assessed all of the reported density data at atmospheric pressure together with the present results for their internal consistence to carefully select primary data to fit reference correlation, $\rho_0(T)$. This correlation $\rho_0(T)$ together with the present high-pressure density measurements (ρ, *P*, *T*) were used to develop two-parametric (*c* and *B*) and theoretically based Tait- type equation of state. The theoretical interpretation and physical meaning of the Tait's parameters (*c* and *B*) and their temperature behavior was discussed.

1. Introduction

The ionic liquids (ILs) based on the anion tris (pentafluoroethyl) trifluorophosphate (FAP anion) and series of cations of the family of 1-alkyl-3-methylimidazolium are new type of air- and water-stable ILs [1–4]. This type of ILs can be used as an efficient liquid absorbers for gaseous solutes [2]. This new class of the ILs was developed by Merck (Germany) as a replacement for ILs containing $[PF_6]$ anion. The present work is the continuation of our previous studies of the volumetric and calorimetric properties of pure ILs ($[EMIM][EtSO_4]$, [C6mim][NTf2], [C4mim][NTf2], 1-ethyl-3-methylimidazolium methanesulfonate) [5–11] and IL containing binary mixtures (Ethanol + $[BMIM][BF_4]$, Methanol + $[BMIM][BF_4]$, Methanol + $[BMIM][PF_6]$, methanol + $[BMIM^+][OcSO_4^-]$) [12–16] at high temperatures and high pressures. The main objective of the present work is to provide reliable experimental density data for BMIM][FAP] at high temperatures (from 273 to 413) K and high pressures (up to 140 MPa). The present results are considerably expanding of the temperature and pressure ranges in which density data for BMIM][FAP] are available (see below Table 1). For example, in the present work we first time reported new high-accuracy density data for BMIM][FAP] under high pressures (up to 140 MPa). The temperature range studied in the present work for the density of BMIM][FAP] at atmospheric pressure also were expanded to high temperatures (to 413 K). A literature survey revealed that very restricted number of measurements reported for the density of BMIM][FAP] under pressure and at high temperature. Only four data sources [1–4] for the density of BMIM][FAP] were found in the literature. Only one of them Almantariotis et al. [2] reported the measured density data at high pressures (up to 25 MPa). Table 1 summarizes experimental measurements of the density [1–4] of BMIM][FAP] reported in the literature. The literature search was based on the author's own literature search. No data were found in the TRC/NIST archive [17]. In Table 1 the first author is given together with the year of publication, 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 atmospheric pressure are

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Table 1
Summary of reported density data of 1-Butyl-3-methylimidazolium tris (pentafluoroethyl)trifluorophosphate [BMIM][FAP].[a]

First author	Reference	Year	Method	Properties	Temperature T (K)	Pressure P(MPa)	Uncertainty	Purity (kg m^{-3})	Source (mass%)
Součkova	[1]	2012	HW	ρ,T,σ	279 to 354	0.101	$3 \times 10^{-4}\rho$	99.0	Merck
Almantariotis	[2]	2012	VTD	ρ,T,η	293 to 353	up to 25	$\pm 1 \times 10^{-1}$	99.5	Merck
Vraneš	[3]	2014	VTD	ρ,T	293 to 323	0.101	2×10^{-2}	99.0	Merck
Liu[b]	[4]	2010	VTD	ρ,T,η	298	0.101	2×10^{-2}	99.67	Merck
Safarov	[79]	2017	VTD	ρ,T,η,C_P,c	262 to 414	0.101	0.08%	99.0	Merck
Safarov	this work	2017	VTD	ρ,T,P	273 to 413	up to 140	0.01–0.08%	99.0	Merck

P, pressure; ρ, density; η, viscosity; σ, surface tension; C_P, heat capacity; c, speed of sound; HW-hydrostatic weighing.
[a] T temperature.
[b] Predicted value.

within (0.0001–0.035) %. The reported data sets cover temperature range from (279–354) K and pressures up to 25 MPa. The reported data were measured using hydrostatic weighing [1,3] and VTD [2,4] techniques. Previous high-pressure density measurements (up to 25 MPa) Almantariotis et al. [2] were performed using U-shape VTD (Anton Paar, model DMA 512) operating in a static mode with typical uncertainty for this method of 10^{-4} g cm^{-3}. These measurements for BMIM][FAP] were made along the seven isotherms between (293 and 353) K at pressures to 25 MPa. The authors used the ILs sample from Merck with purity of 99.5 mass%. The measured densities at atmospheric pressure were fitted to linear function of temperature

$$\rho_0(T) = 1955.4\text{-}1.114T. \quad (1)$$

The high-pressure densities as a function of pressure were correlated using the Tait EOS with constant value of Tait-parameter $c = 0.06922$and quadratic function of temperature for B-parameter. The measurements of density of the ILs BMIM][FAP] by Součkova et al. [1] were made using hydrostatic weighing method over the temperature range from (279–354) K at atmospheric pressure with an uncertainty within 0.035%. The measured data were correlated with the temperature function of

$$\rho_0(T) = \frac{2076.3}{1\text{-}0.0009254T}. \quad (2)$$

These data are agreed with the densities reported by Almantariotis et al. [2] within 0.095%. The data by Součkova et al. [1] are systematically higher than by Almantariotis et al. [2]. Vranes et al. [3] also employed the same hydrostatic weighing technique to measure the density of BMIM][FAP] in the temperature range between (293 and 323) K with the unusual high uncertainty of 5%, although the accuracy of the method has been verified with the use organic fluids with very well-known densities. Liu et al. [4] reported predicted value of the density of IL BMIM][FAP] at standard state (298.15 K and 0.101 MPa) 1629.62 kg m^{-3}, which is deviate from the reported data [1–3] and the present result within (0.15–0.25) % (see below). All reported experimental density data together with present data for BMIM][FAP] at atmospheric pressure are depicted in Fig. 1. This figure also included the values of density calculated from various correlations.

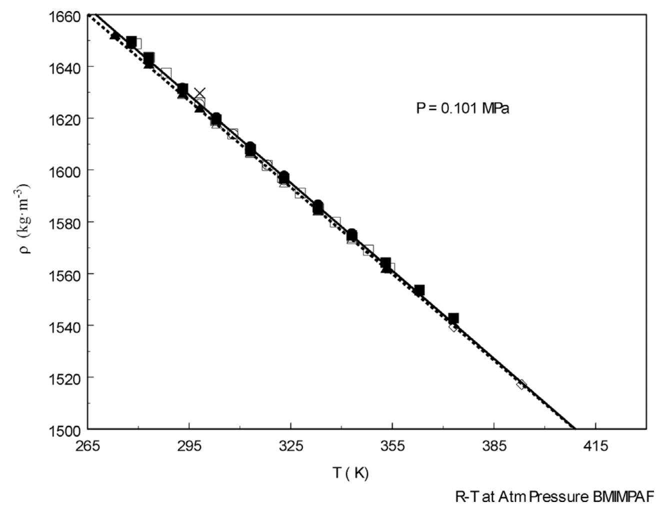

Fig. 1. Measured densities of the IL [BMIM][FAP] at atmospheric pressure as a function of temperature together with reported data. ●, (DSA 5000 M) [79]; ○, Vraneš et al. [3]; □, Součkova et al. [1]; △, Almantariotis et al. [2]; ■, (SVM 3000) [79]; ◊, this work (DMA HPM); ▲, (DMA-500M) [79]; ×, Liu et al. [4] Solid line is calcultaed from the present correlation Eq. (4). Dased line is calculated from correlation by Almantariotis et al. [2], Eq. (1).

Table 2
Ionic liquid sample 1-Butyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate (Chemical formula $C_{14}H_{15}F_{18}N_2P$) description studied in this work.

Sample	M (g mol^{-1})	CAS#	Source	Purity (mass%)	H_2O content
[BMIM] [FAP]	584.23	917762 – 91-5	Merck Co. LLC	> 99.0 (NMR)	120 ppm

2. Experimental

2.1. Materials

The IL sample 1-butyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate [BMIM][FAP] (Chemical formula $C_{14}H_{15}F_{18}N_2P$; CAS # 917762-91-5, product number 4.91232.0100, $M_{IL} = 584.2315$ g mol^{-1}) used in this work was supplied by Merck Co. LLC (Germany). The supplier furnished its purity assay (NMR) > 99 mass%. Before use, the IL sample was degassed under vacuum and dried at about 423 K for a minimum time period of 48 h. Water contents were determined using Karl Fischer titration (a Metrohm 831 KF Coulometer in Canberra and a KEM MKC-510 in Sendai) and found to be less than 120 ppm. Table 2 lists the commercial sources, purities, water content, and analysis method of the samples used.

2.2. Density measurements

Density of the ILs [BMIM][FAP] as a function of temperature and pressure were measured using a modernized high-pressure and high-temperature Anton Paar DMA HPM vibration tube densimeter [11,18,19]. The method and experimental apparatus was successfully employed previously for measurements of the density of ILs ([EMIM][$MeSO_3$]), ocean and geothermal water [11,18,19] at high temperatures and high pressures. The method (experimental details, the physical basis and theory of the method, procedures, uncertainty assessment) and apparatus have been described in our previous publications [18,19]. 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 10 mK and was measured with the (ITS-90) Pt100 thermometer (Type 2141) with an