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Effect of temperature on thermal (density), caloric (heat capacity), acoustic (speed of sound) and transport (viscosity) properties of 1-octyl-3-methylimidazolium hexafluorophosphate at atmospheric pressure

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ABSTRACT

Density$\rho(T)$, heat capacity$C_P(T)$, speed of sound$c(T)$, and viscosity,$\eta(T)$, were measured for the ionic liquid (IL) 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF_6] at atmospheric pressure as a function of temperature from (278.15 to 413.15) K for the density (ρ), from (253.15 to 413.15) K for the heat capacity (C_P), from (278.15 to 343.15) K for the speed of sound (c), and from (269.96 to 413.82) K for the viscosity (η), using various type of commercial instruments. The combined expanded uncertainty of the viscosity, heat capacity, speed of sound, density, and temperature measurements at the 68% confidence level with a coverage factor of $k = 2$ is estimated to be 0.5% (for SVM 3000 Stabinger viscometer) and 1.5% (for Rheometer MCR 302), 1.5%, ±0.5 $m \cdot s^{-1}$, 0.23% (including the purity and calibration effects), and 15 mK, respectively. These new experimental data were used to develop wide range correlations for the viscosity based on theoretically confirmed Arrhenius-Andrade and Vogel-Tamman-Fulcher (VTF) models. The value of the glass temperature (T_g) for the IL was estimated using the VTF parameters derived from the present viscosity measurements. Measured values of density, heat capacity, and speed of sound were used to calculate other important thermodynamic properties, κ_S,κ_T, α_P, γ_V, ΔH, C_V, $\left(\frac{\partial H}{\partial P}\right)_T$, and $\left(\frac{\partial U}{\partial V}\right)_T$.

1. Introduction

As part of a continuing study [1–15] of the effect of temperature and pressure on the thermophysical properties of ILs, the density, heat capacity, speed of sound, and viscosity measurements have been made for [OMIM][PF_6], using various Anton Paar commercial instruments DMA 5000, DSA 5000M, Rheometer MCR 302, SVM 3000 Stabinger viscometer, and DSC Q2000 from TA Instruments, over a wide temperature and pressure ranges. The instruments were successfully used in our previous publications for accurate measurements of the density, heat capacity, speed of sound, and viscosity of pure ILs [1–11] and their mixtures with alcohols [12–16] at temperatures from (273.15 to 413.15) K and at pressures up to 140 MPa. In this work the same instruments to measure of the density, heat capacity, speed of sound, and viscosity measurements of [OMIM][PF_6] at temperatures from (253.15 to 414.15) K and atmospheric pressure have been used.

Accurate thermodynamic and transport properties of ionic liquids (ILs) are very important for various industrial applications due to their unique physical and chemical characteristics, for example, negligible vapor pressure, low volatility ("green" solvent), chemical stability, high conductivity, ability to dissolve organic and inorganic solutes and gases, *etc.* [17–22]. For example, reliable thermophysical properties data of ILs such as density, heat capacity, speed of sound, viscosity, and thermal conductivity, are essential for process design and product development [21–24]. The proper design and development of chemical reaction and separation processes in the chemical industry are based on accurate knowledge of the thermophysical properties of ILs. ILs are very useful as heat-transfer fluids in solar heating and absorption refrigerating systems [18–20].

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The main aim of the present work is to experimental study of the temperature effect on the density, heat capacity, speed of sound, and viscosity of ILs [OMIM][PF_6]at atmospheric pressure. The present study is considerably expanding of the temperature range in which these properties for [OMIM][PF_6]are available. In the present work, we first time reported new heat capacity data for [OMIM][PF_6] in the temperature range above 353.15 K and viscosity data above 363.15 K (up to 413.82 K) and below 273.15 K. Also, in the present study we have first time reported a new speed sound data at temperatures below 293.15 K. The high-pressure (up to 140 MPa) and high-temperature (from 278.15 K to 413.15 K) density (*PVT* properties) data for this IL will be reported in our other publication [25]. In addition, we used measured data to develop wide ranged correlations for density, heat capacity, speed of sound, and viscosity. Based on the measured properties density, heat capacity, and speed of sound we have calculated very useful derived thermodynamic property data such as κ_S, κ_T, α_P, γ_V, ΔH, C_P, C_V, $(\frac{\partial H}{\partial P})_T$, and $(\frac{\partial U}{\partial V})_T$.

1.1. Review of the reported density, heat capacity, speed of sound, and viscosity data for IL ([OMIM][PF_6]) at atmospheric pressure

Table 1 summarizes the measurements of the density [26–50], speed of sound [31,37–39,41–44], and viscosity [26,29–32,37,48,51] of [OMIM][PF_6] at atmospheric pressure reported in the literature. The literature search was based on the TRC/NIST archive (TDE search result) and own search results. A literature survey revealed that one heat capacity C_P data source reported by Serra [91] is available in the literature for [OMIM][PF_6] at atmospheric pressure. The heat capacity measurements were made using Setaram μDSCIIIa with scanning rate of step (0.3 and 0.5) $K\cdot min^{-1}$ for the continuous method. The measurements were made over a temperature range from (253 to 355) K. Uncertainty of C_p measurements is 1%. The measured C_p were represented by a quadratic fit. In difference of heat capacity the density of [OMIM][PF_6] is studied extensively, although very scattered data are available in the literature (see below). In total 28 density data sources are listed in the NIST SOURCE Data Archive. 25 selected density data sources [26–50] are listed in Table 1 representing about 137 density measurements at atmospheric pressure. Only 8 data sources for the speed of sound [31,37–39,41–44] and viscosity [26,29–32,37,48,51] of [OMIM][PF_6]were found in the literature (see Table 1)representing 55 speed of sound and 74 viscosity measurements. Most sources reported very limited data. For example, sources [45–50] reported only single data point at standard condition (at 298.15 K). Three data points were reported in the works [40,43,44]. All reported density data are covering the temperature range from (273.15 to 393.15) K, while speed of sound and viscosity data are cover very restricted temperature ranges from (278.15 to 343.15) K and from (283.15 to 363.15) K, respectively. As can be note from Table 1, most of the reported density data [26,27,30,31,33–44,50] were measured using commercial Anton Paar instruments DMA 5000, DMA 4500A, DMA-60, DMA-48, and SVM 3000 (VTD, vibrating tube densimeter method) at atmospheric pressure. The typical uncertainty of the reported density data is within (0.02% to 0.5%). Only two sources are reported densities of [OMIM][PF_6] which were measured using pycnometric method [28,32] with an uncertainty of (0.18–0.20)%. Measurements of the reported speed of sound data were also performed using Anton Paar Instruments (DSA 5000 and DSA-48) with an uncertainty of (0.5 to 1.0) $m\cdot s^{-1}$. Majority reported viscosity data were measured using various techniques, for example, a falling-body [26], rolling ball [32], capillary flow [31], and Cone & Plate Viscometer [52] techniques. The uncertainty for most reported viscosity data is within (0.35 to 1.6)%. Three data sources for the viscosity [32,48,51,52] are reported a few (only 1 to 4) data points. The purity of the ILs sample used by the author for the all reported data is within (0.95 to 0.99) mass fraction, while the water content is within from (18 to 300) 10^{-6}. Most ILs samples studied previously by various authors were synthesized by the authors. As will be shown below (see Section 3), large scatter and inconsistence, up to 1.2%, 2.6%, and 17% between the various reported density, speed of sound, and viscosity data, respectively, were found for [OMIM][PF_6], although the author's claimed uncertainties of the measured data are considerable lower (see Table 1) than their scatter.

Thus, the main goal of the present study was to expand the existing database to lower and higher temperatures and provide new accurate experimental density, heat capacity, speed of sound and viscosity data for [OMIM][PF_6] in the wide temperature range at atmospheric pressure using a different Anton Paar Instruments (DMA 5000, DSA 5000M, Rheometer MCR 302, SVM 3000 Stabinger viscometer) and DSC Q2000 from TA Instruments [53]. The present work is considerably expanding the temperature range (up to 414 K) in which density, heat capacity, speed of sound, and viscosity data for [OMIM][PF_6] are available. In addition, we have developed new wide ranging correlations for the measured properties of [OMIM][PF_6]. All available reported density, heat capacity, speed of sound, and viscosity data for [OMIM][PF_6] together with the present measurements were comprehensive evaluated and critically analysed for their accuracy, reliability and thermodynamic consistence. The results can be used to select preliminary data for develop of the wide ranging reference correlations. In the present work we reported accurate 37 density, 34 heat capacity, 7 speed of sound, and 406 viscosity data points for [OMIM][PF_6] over the wide temperature range from (253.15 to 413.82) K at atmospheric pressure.

2. Experimental

2.1. Material

The IL sample 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF_6] (CAS: 304680-36-2, Chemical formula $C_{12}H_{23}N_2F_6P$, product number IL-0020-HP-0100, M_{IL}= 340.2922 $g\cdot mol^{-1}$) used in this work was supplied by Iolitech GmbH, Germany. The supplier furnished its purity assay > 0.99 wt fraction. Before use, the IL sample was degassed under vacuum and dried at about 423.15 K for a minimum time period of 48 h. Water contents were determined before and after measurements using Karl Fischer titration (a Metrohm 831 KF Coulometer in Canberra and a KEM MKC-510 in Sendai) and found to be less than 227 ppm. Table 2 lists the commercial sources, purities, water content, and analysis method of the samples used.

2.2. Density measurements

Different Anton Paar vibrating tube densimeters SVM 3000, DMA 5000 and DSA 5000 M were used for the density measurements of [OMIM][PF_6] at atmospheric pressure as a function of temperature with an uncertainty of ±0.3 $kg\cdot m^{-3}$(or less than 0.03%, without consideration of the purity and calibration effects). The purity of the sample and other factors (calibration, for example) must be considered in the estimates of uncertainty. As was discussed in detail [92] the relative standard uncertainty for density measurement of a sample with mass fraction purity 0.99 was estimated to be 0.1%.This recommendation was used to estimate the effect of purity and calibration on the final uncertainty of the present density measurements. In total the combined expanded uncertainty in density measurements is 0.23%. The DSA 5000M was calibrated using the detailed procedure described earlier [3],