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Liquid density of oxygenated additives to bio-fuels: 1-Hexanol at pressures up to 140 MPa and from 293.15 K to 403.15 K

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ABSTRACT

This work reports new density data (180 points) of 1-hexanol at twelve different temperatures between 293.15 and 403.15 K (every 10 K), and fifteen different pressures from 0.1 to 140 MPa (every 10 MPa). An Anton Paar vibrating tube densimeter, calibrated with an uncertainty of ±0.5 kg m^{-3} was used to perform these measurements. The experimental density data were fitted with the Tait-like equation with low standard deviations. In addition, the isobaric thermal expansivity and the isothermal compressibility were derived from the Tait-like equation.

1. Introduction

Second generation bio-fuels are being developed because the manufacturing of first generation bio-fuels has shown considerable limitations, indeed some undesirable effects for example on food supplies and the biodiversity. Second generation bio-fuels are usually derived from lignocellulosic crops. In so doing it is possible to prevent these problems and at the same time meet a larger need of fuel in a sustainable and affordable way, and with greater environmental benefits.

Microbial systems have been extensively explored and successfully used for the biosynthesis of some bio-fuels, most notably ethanol [1,2]. Higher-chain alcohols, however, offer several advantages compared with ethanol, such as higher energy density and lower water solubility.

The work of Zhang et al. [3] focuses on the biosynthesis of a number of higher-chain alcohols (>C5), such as 1-hexanol, and provides a new paradigm in the area of bio-fuel synthesis because it describes the vast potential of evolving a metabolic pathway from the ground up and is certainly the first important step toward the application of longer-chain alcohols as bio-fuels. Furthermore, these long-chain alcohols produced could also provide new alternatives as renewable chemical agents in several other applications.

From the thermo-physical point of view, accurate PVT properties of pure alkanols are required to develop and test equations of state, because the test and development of equations of state to calculate densities at high pressure is very important in the chemical industry (Zuñiga-Moreno et al. [4,5]). For the optimized design of several industrial processes, reliable experimental data are needed. Among others, volumetric properties such as density and its derived properties are important thermodynamic properties which characterize chemical compounds. These quantities provide important information on the behavior of pure liquids useful for the understanding of the molecular interactions.

This paper reports the volumetric properties measurements of pure 1-hexanol such as density and its derived properties in the temperature range from 293.15 to 403.15 K at pressure up to 140 MPa.

The density values for 1-hexanol obtained in the present work (180 experimental data) will be compared with previous literature data, which are rather scarce. To our knowledge, liquid densities for 1-hexanol under high pressure have been measured successively by Bridgman [6] (23 data points from 273.15 K to 368.15 K up to 700 MPa), Gylmanov et al. [7] (121 data points from 290.1 K to 623.5 K up to 58.8 MPa), Matsuo and Makita [8] (11 data points from 298.15 K to 348.15 K at 0.1 MPa and 39 other data points from 298.15 K to 348.15 K up to 40.02 MPa), Shakhverdiev et al. [9] (96 data points from 298.15 K to 573.15 K up to 58.6 MPa), Garg et al. [10] (60 data points from 323.15 K to 373.15 K up to 10 MPa), Audonnet and Padua [11] (40 data points from 303.15 K to 423.15 K

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Nomenclature

List of symbols

AAD	absolute average deviation
a_i	coefficients of isobaric thermal expansivity correlation
A_i, B_i, C	coefficients of density correlation
Bias	average deviation
calc	calculated
exp	experimental
lit	literature
MD	maximum deviation
N	number of experimental data points which are in our p, T ranges
p	pressure
p_0	reference pressure
RMSD	root mean square deviation
T	temperature

Greek letters

σ	standard deviation
α_p	isobaric thermal expansivity
ρ	density
ρ_0	density at a reference pressure p_0
K_T	isothermal compressibility

up to 50.27 MPa), Troncoso et al. [12] (72 data points from 278.15 K to 313.15 K up to 40 MPa), Zuñiga-Moreno et al. [13] (150 data points from 313.14 K to 362.8 K up to 25.048 MPa), Valencia et al. [14] (72 data points from 283.15 K to 323.15 K up to 60 MPa) and Dávila et al. [15] (126 data points from 278.15 K to 358.15 K up to 60 MPa). Except for the data of Bridgman [6] which is the oldest reference, all other measurements, including the most recente ones, were carried out under a pressure lower than 60 MPa.

It is also worth to mention that in 1993 and 1994, Cibulka and Zikova [16,17] made a critical evaluation of experimental data for liquid density of some 1-alkanols, which they completed in 1997 for higher 1-alkanols (Cibulka et al., [18]). For 1-hexanol, the temperature and pressure ranges of validity of their correlation are 290.10–490.20 K and 0.2–58.8 MPa [17]. They noticed a huge difference with [6]. In addition, as the values obtained by extrapolating (at higher pressure, or higher/lower temperature) any correlation may be uncertain, it is useful to make additional experimental measurements in order to increase the temperature or pressure ranges and get a new correlation.

Moreover, the study of this compound presents obvious industrial interest in engineering applications and it also presents fundamental aspects as 1-hexanol is a very associative compound. We can expect that these experimental data will be valuable in testing various theoretical models taking into account the polar and associating effects between molecules.

2. Experimental

2.1. Materials

1-Hexanol ($C_6H_{14}O$, molar mass 102.177 g mol^{-1}, CAS. 111-27-3) was obtained from Sigma–Aldrich with purity of 99.9 mol%. This chemical was subject to no further purification and directly injected into the high pressure cell as soon as the bottle was open.

2.2. Measurement technique. Experimental procedure

An Anton-Paar DMA HPM high-pressure vibrating-tube densimeter was used to measure the density ρ as a function of pressure p (up to 140 MPa) and temperature T (between 293.15 and 403.15 K). The experimental setup was similar to the one described in a previous paper [19]. The calibration of the densimeter was performed according to the new procedure described by Comuñas et al. [20] which is modification of the procedure previously adopted by Lagourette et al. [21].

(a) At $0.1 \le p \le 140$ MPa and $293.15 \le T \le 363.15$ K. The densimeter calibration over these temperature and pressure intervals was performed by using the procedure previously proposed by Lagourette et al. [21]. The density values of water were taken from the equation of state (EoS) reported by Wagner and Pruss [22]. The uncertainty in density of this EoS is 0.0001% at 0.1 MPa in the liquid phase, 0.001% at other liquid states at pressures up to 10 MPa and temperatures up to 423 K, and 0.003% under pressures in the interval 10–100 MPa and temperature up to 423 K. The uncertainty is of the order of 0.02% at 1000 MPa.

(b) At $p = 0.1$ MPa and $T \ge 373.15$ K. The limitation of this procedure [21] appears when the measurements are performed at 0.1 MPa and at temperatures higher or equal to the boiling point of water (373.15 K). This is the case in the present work because part of this study is done up to temperatures above 373.15 K. So, in this work decane has been selected as reference substance at the conditions $p = 0.1$ MPa and $T \ge 373.15$ K, because its density is well known at atmospheric pressure over wide temperature intervals [23].

(c) At $p > 0.1$ MPa and $T \ge 373.15$ K. One can think that in the interval 0–1 MPa, the volume of the cell does not significantly change with pressure changes. Following the new procedure proposed in [20] the reference pressure for water density is 1 MPa instead of 0.1 MPa. It is necessary to know the oscillation period of the evacuated cell (over the entire temperature interval), the period of the cell filled with water and the density of water (for $p > 0.1$ MPa and for $T \ge 373.15$ K). Over the above T, p intervals, only one reference fluid is needed (water) together with the period of the evacuated cell.

After the densimeter was filled with the sample to be studied as described in Ref. [19] the sample was warmed up to the desired temperature and brought under the pressure of interest and measured when thermal and mechanical equilibrium were reached. The temperature of the high-pressure vibrating-tube cell of the densimeter was controlled by an external circulating temperature-controlled fluid and was measured inside the high-pressure cell. With an AOIP PHP602 thermometer with an uncertainty of ±0.05 K above 353.15 K, and with an Anton-Paar CKT100 with an uncertainty of ±0.01 K between 293.15 and 353.15 K. Above atmospheric pressure, the pressure was measured with a digital pressure transmitter (Presens Precise Gold Plus) with an uncertainty of ±0.015 MPa (1/10000 of the full scale).

Taking into account the accuracy of the temperature, the pressure, the period of oscillation measurement for water, the vacuum and the studied systems, and the water density accuracy, the overall experimental uncertainty in the reported density values is estimated to be ±0.5 kg m^{-3} (i.e. around 0.05% for density close to water density). This uncertainty is similar to the one reported in several studies [19,20,24–28]. However, for measurements under atmospheric pressure at $T = 373.15$, 383.15, 393.15 and 403.15 K we used decane as reference fluid. The uncertainty of the decane density data reported in [23] (of the order of 0.0001 g cm^{-3}) is greater than that of water and consequently for the 4 data points at 373.15 K,