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(p, V^E, T) Measurements of mixtures (DBE + alcohol) at temperatures from (293.15 to 353.15) K and at pressures up to 140 MPa

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ABSTRACT

This work reports new experimental density data (960 points) for 1-propanol and for binary mixtures of dibutyl ether + 1-propanol, +2-propanol and +1-hexanol over the full composition range (5 compositions; 0.15 ≤ dibutyl ether mole fraction x ≤ 0.85), between 293.15 and 353.15 K (every 20 K), and for 15 pressures from 0.1 MPa up 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 a Tait-like equation with low standard deviations. Excess volumes have been calculated from the experimental data and fitted by the Redlich–Kister equation. In addition, the isobaric thermal expansivity and the isothermal compressibility have been derived from the Tait-like equation.

1. Introduction

Increasing global concern due to greenhouse gas emissions has generated much interest in the environmental friendly alternative bio-fuels. Bio-fuels for internal combustion engines as oxygenated compounds are also becoming important because of diminishing petroleum reserves and increasing air pollution [1].

The oxygenated compounds used worldwide like simple alcohols and ethers, are used here as gasoline additives to reduce pollutants from vehicle exhaust gases. Proponents of these oxygenates claim several advantages: they are octane enhancers, they have significant anti-knock properties important for unleaded fuels, they can be produced from renewable agricultural and raw materials instead of fossil sources, and they reduce carbon monoxide pollution from vehicle exhaust [2–4].

In this sense, there has been an increasing interest in the thermodynamic behavior of liquid mixtures of alcohols with ethers. From a thermodynamic point of view, experimental property studies of binary mixtures can provide valuable information about the fluid behavior under various temperature and pressure conditions. One of these properties is the density or specific molar volume, which is an important property required in a wide range of engineering disciplines as well as in the determination of different fluid properties. This work continues the research on binary mixtures of alcohols and ethers of our group. In previous works [5–7], we have studied high pressure and high temperature density of dibutyl ether (DBE), 1-hexanol and 2-propanol as pure compounds, while Refs. [8,9] refer to 1-butanol and its mixture with DBE, respectively. With the aim of studying the intermolecular interactions during the mixing process, this work presents the experimental densities of the systems DBE + 1-propanol, or +2-propanol or +1-hexanol at pressures from 0.1 MPa up to 140 MPa and temperatures between 293.15 and 353.15 K over the full composition range. We report densities, excess molar volumes, isobaric thermal expansion coefficient and the isothermal compressibility coefficient for the binary mixtures dibutyl ether + alcohol at elevated pressures.

2. Experimental

2.1. Materials

All the chemicals used here were purchased from Sigma–Aldrich and were of the highest purity available, chromatography quality reagents. The purity of all reagents was checked by gas chromatography, and its values are presented in Table 1. These chemicals were subject to no further purification and directly injected into the high pressure cell as soon as the bottles were open.

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Table 1
Purity and related data of chemicals.

Compound	Formula	Molar mass/ $g\,mol^{-1}$	Stated purity[a]/ mol%	CAS number
DBE	$C_8H_{18}O$	130.228	>99.3	142-96-1
1-Propanol	C_3H_8O	60.095	>99.9[b]	71-23-8
2-Propanol	C_3H_8O	60.095	>99.9[b]	67-63-0
1-Hexanol	$C_6H_{14}O$	102.177	>99.9[b]	111-27-3

[a] Determined by gas chromatography (GC).
[b] The water content was checked to be less than 0.01%.

2.2. Measurement technique

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 353.15 K). Details of the equipment and its operation have been described previously [5–10]. The densimeter was calibrated with water and vacuum using the procedure described by Lagourette et al. [11].

The estimated uncertainty of the measured temperature was ±0.01 K between 293.15 and 353.15 K (Anton Paar MKT50 thermometer).

The estimated uncertainty of the measured pressure was ±0.015 MPa (Presens Precise Gold Plus pressure transmitter) and the estimated uncertainty of the determined density was $\pm 0.5\,kg\,m^{-3}$ (i.e., around 0.05% for density close to water density). This uncertainty is similar to that reported in several studies [5–10,12–15].

The binary xDBE + $(1-x)$ alcohol mixtures (x is the DBE mole fraction) were prepared immediately before use by weighing at atmospheric pressure using a high-precision Sartorius balance with an uncertainty of ±0.001 g. For each mixture, a sample of 50 g was prepared, which, taking into account the uncertainty of the balance, resulted in an uncertainty in the mole fraction of less than 6×10^{-5}.

3. Results and discussion

3.1. Density

The measured densities of 1-propanol and of binary mixtures of dibutyl ether + 1-propanol, 1-hexanol and 2-propanol (5 DBE molar ratio composition x: 0.15, 0.325, 0.5, 0.675, 0.85) are reported in Tables 2 and 3, respectively, along the 4 isotherms between 293.15 and 353.15 K and at pressures up to 140 MPa (15 isobars). The density of pure DBE, 1-hexanol and 2-propanol has been already determined and reported in [5–7].

For the purpose of comparing the experimental density values with those obtained with the correlations considered in this work, we have used the Absolute Average Deviation (AAD), the Maximum Deviation (MD), the Average Deviation (Bias), the standard deviation (σ) and the Root Mean Square Deviation (RMSD), which are defined as follows:

$$\mathrm{AAD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}}}{\rho_i^{\mathrm{exp}}}\right| \tag{1}$$

$$\mathrm{MD} = \mathrm{Max}\left(100\left|\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}}}{\rho_i^{\mathrm{exp}}}\right|\right) \tag{2}$$

$$\mathrm{Bias} = \frac{100}{N}\sum_{i=1}^{N}\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}}}{\rho_i^{\mathrm{exp}}} \tag{3}$$

Table 2
Experimental densities, ρ ($g\,cm^{-3}$) for 1-propanol at various temperatures T and pressures p.[a]

p/MPa	T/K			
	293.15	313.15	333.15	353.15
ρ/g cm^{-3}				
0.1	0.8038	0.7871	0.7699	0.7520
10	0.8113	0.7955	0.7800	0.7625
20	0.8181	0.8030	0.7883	0.7718
30	0.8244	0.8100	0.7957	0.7802
40	0.8300	0.8164	0.8025	0.7879
50	0.8356	0.8223	0.8090	0.7950
60	0.8410	0.8279	0.8150	0.8014
70	0.8459	0.8332	0.8206	0.8077
80	0.8507	0.8383	0.8262	0.8134
90	0.8552	0.8430	0.8312	0.8187
100	0.8596	0.8479	0.8363	0.8238
110	0.8637	0.8523	0.8409	0.8288
120	0.8678	0.8566	0.8453	0.8335
130	0.8716	0.8607	0.8496	0.8379
140	0.8753	0.8646	0.8536	0.8421

[a] The estimated uncertainty of the measured temperature is 0.01 K. The estimated uncertainty of the measured pressure is 0.015 MPa. The estimated relative uncertainty of the determined density $\rho/g\,cm^{-3}$ is ±0.05%. Coverage factor $k = 2$ has been used for the estimated uncertainties.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}})^2}{N-m}} \tag{4}$$

$$\mathrm{RMSD} = \sqrt{\frac{\sum_{i=1}^{N}(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}})^2}{N}} \tag{5}$$

where N is the number of experimental data ($N = 60$ for each composition) and m the number of parameters (we will see below that with our correlation $m = 8$).

3.2. Tait representation

In order to correlate correctly our values over our entire temperature and pressure ranges, and consequently to get a correct evaluation of the derived properties, we use the following Tait-like equation, which has been used in previous works [5–10,12–14,16–18]:

$$\rho(T,p) = \frac{\rho_0(T)}{1 - C\ \ln\left(\frac{B(T)+p}{B(T)+0.1\ \mathrm{MPa}}\right)} \tag{6}$$

where

$$\rho_0(T) = A_0 + A_1T + A_2T^2 + A_3T^3 \tag{7}$$

$$B(T) = B_0 + B_1T + B_2T^2 \tag{8}$$

Mention here that the A_i, B_i and C parameters values were determined by correlating simultaneously for each composition (60 values) the experimental density values versus pressure and temperature. The Tait-correlation parameters with the ADD, MD, Bias, standard deviation, σ, and RMSD, obtained with this correlation for 1-propanol and for each mole fraction for each mixture of DBE + alcohol are given in Tables 4 and 5, respectively.

Notice that the AAD and the standard deviations are lower than the experimental uncertainty; consequently these Eqs. (6)–(8) make it possible to interpolate the density at any T, p conditions.