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Density and speed of sound measurements of 1- and 2-butanol☆

Stephanie L. Outcalt *, Arno Laesecke, Tara J. Fortin

Thermophysical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305-3337, USA

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ABSTRACT

The density and speed of sound of 1- and 2-butanol have been measured with two instruments; both instruments used vibrating-tube sensors for measuring density. At ambient pressure (83 kPa), density and speed of sound were measured from 278.15 K to 343.15 K. Adiabatic compressibilities were derived from these density and speed of sound data. Compressed liquid density measurements were carried out in a second instrument over a range from 270 K to 470 K with pressures from 0.5 MPa to 50 MPa. The measured density data were correlated with a modified Tait equation within their experimental uncertainty, and this correlation provides a baseline for extensive comparisons with literature data. Differences between the measured macroscopic properties of the two butanol isomers are related to differences on the molecular level. These were characterized by quantum mechanical calculations using the second-order Møller–Plesset model with the polarization basis set 6-311+G**.

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1. Introduction

This contribution is part of a series of measurements, the goal of which is to systematically characterize the thermophysical properties of fuels and their constituents over wide ranges of temperature and pressure. While previous reports have communicated measurement results for jet fuels [1], rocket fuels [2], and their constituents methyl- and propylcyclohexane [3] and hexadecane [4], two butanol isomers (1- and 2-butanol) have been characterized in this work.

There are four isomers of the aliphatic alcohol with the molecular formula C_4H_9OH. One of the two isomers with a primary hydroxyl group is 1-butanol or *n*-butanol (CAS no. 71-36-3). The only isomer with a secondary alcohol group at an internal carbon atom is 2-butanol (CAS no. 78-92-2), also known as sec-butanol, 2-butyl alcohol, or 1-methyl-1-propanol. The other isomer with a primary hydroxyl group is 2-methyl-1-propanol, and the isomer with a tertiary hydroxyl group is 1,1-dimethyl-ethanol or 2-methyl-2-propanol.

Interest in butanols as a second-generation biofuel has increased in recent years because they have many advantages over other potential alternative fuel candidates such as ethanol. At 85% by volume with gasoline, butanols can be used in cars designed for gasoline without requiring any retrofit to the engine (unlike 85% ethanol, E85) [5]. They have a higher energy content for a given volume than ethanol, and almost as much as gasoline. Butanols can also be used as a blended additive to gasoline to reduce carbon monoxide emissions [6], and are less susceptible to separation in the presence of water than ethanol/gasoline blends, therefore allowing use of the industry's existing distribution infrastructure without requiring modifications to blending facilities, storage tanks or retail station pumps [5].

Despite the advantages butanols may provide as an alternative fuel, there are still significant gaps in the thermophysical properties data, particularly for 2-butanol. Also, there is a fair amount of scatter in the data for both 1- and 2-butanol. The measurements reported here were undertaken to provide data where none exist, and to help resolve some of the differences between published data sets.

Results of density and speed of sound measurements for 1- and 2-butanol are reported in this work. Adiabatic compressibilities have been derived from the ambient pressure density and speed of sound data and are also included. Compressed liquid density data have been extrapolated to saturation pressure and combined with ambient pressure density data for correlation with a Rackett equation. Additionally, the compressed liquid density data have been correlated with a modified Tait equation and compared to existing literature data.

2. Molecular characterization

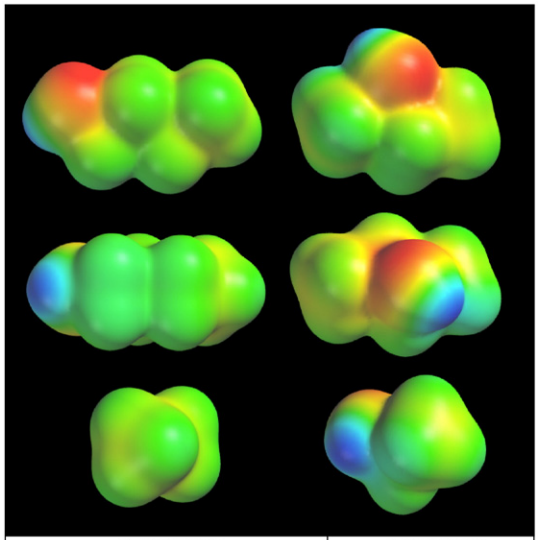
A major goal of our research is to provide accurate macroscopic thermophysical properties data and to relate them to the molecular

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* Corresponding author. Tel.: +1 303 497 5786; fax: +1 303 497 5224.
E-mail address: Outcalt@Boulder.NIST.Gov (S.L. Outcalt).

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size, shape, and charge distribution of the measured compounds. The isomers 1- and 2-butanol were chosen for the measurements reported in this work to elucidate how the change of the hydroxyl group from a primary to a secondary position on the molecular level is reflected in the densities and speeds of sound of the two compounds over a wide range of temperature and pressure. Measurements over wide temperature ranges provide particularly detailed insight into the effects of electrostatic attractions between polar molecules such as alcohols that associate with each other and form hydrogen bonds. On the molecular level, our approach includes the computational characterization of the test compounds by *ab initio* calculations of their equilibrium geometries and charge distributions in the Møller–Plesset theory level MP2 with 6-311+G** basis sets [7]. The two molecules are compared in Fig. 1 in three views of their electron density isosurface at 0.002 electrons a.u.$^{-3}$ (where 1 a.u. = 5.292 nm, the Bohr radius of hydrogen). The electrostatic potential is color-mapped onto the electron density isosurface indicating the charge distribution in the molecules [8]. The three views of the molecules, two frontal and one along the longitudinal axes, reveal differences in shape and polarity between the two isomers. They give an appreciation of the possible ordering of the molecules in condensed phases and the associated void volumes. While the calculated molecular volumes agree very well, the molecular surface area of 2-butanol is 2.4% smaller than that of 1-butanol. Visualizations of the molecular charge distributions as in Fig. 1 facilitate the understanding of structural effects due to electrostatic attractions and repulsions, which are prominent in polar molecules such as 1- and 2-butanol. At 1.7 debye, the calculated dipole moment of 2-butanol agrees with the same value reported in the compilation of Poling, Prausnitz, and O'Connell [9]. In contrast, at 1.74 debye, the calculated dipole moment of 1-butanol is 2.4% lower than the reported value of 1.8 debye [9]. The work reported here illustrates how these characteristics on the molecular level are reflected in the measured macroscopic properties density and speed of sound.



1-butanol	2-butanol
Molecular surface area 124.50 Å^2	121.45 Å^2
Molecular volume 102.54 Å^3	102.29 Å^3
Dipole moment 1.74 debye (1.8 [9])	1.7 debye (1.7 [9])

Fig. 1. Comparison of molecular size, shape, and charge distribution of 1- and 2-butanol. The electrostatic potential is color-mapped onto an electron density isosurface at the level of 0.002 electrons a.u.$^{-3}$ (with 1 a.u. = 5.292 nm being the Bohr radius of hydrogen). This surface represents approximately 99% of a molecule. The color scale ranges from red (negative charge) to blue (positive charge). Each molecule is shown in two frontal views (top row and center row) and along the longitudinal axis (bottom row) to illustrate size and shape differences. Molecular data in the table are based on equilibrium geometry calculations at the MP2 theory level with 6-311+G** basis sets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Experimental

The 1- and 2-butanol samples measured in this work were obtained from Sigma-Aldrich Chemicals[1] both with a stated minimum purity of 99.5%. Because of their hygroscopicity, activated molecular sieves type 5A, grade 521, with an effective pore size of 5 Å were added to each of the sample bottles to keep the butanols dry of contamination from ambient humidity. Karl Fischer analysis performed on each of the samples prior to measurements determined the water content to be just at the detection limit of approximately 20 ppm. Measurements at ambient pressure were conducted on the samples with no additional analysis or purification.

Prior to measurements of compressed liquid density, samples were transferred to stainless steel cylinders and degassed as described in Outcalt and McLinden [10]. The sample of 2-butanol used to charge the system for the compressed liquid density measurements was analyzed in our laboratory with a gas chromatographic method and found to be within manufacturer specifications. An analysis was also performed on the 2-butanol collected at the outlet of the instrument to determine whether thermal breakdown or any type of contamination took place during the measurements. No significant differences between fresh and used samples were detected.

A DSA 5000 analyzer from Anton Paar Company was used to measure density and speed of sound at ambient pressure. Details of the instrument and experimental procedures have been reported in Laesecke et al. [3]; thus, only a brief description is given here. The instrument contains a sound speed cell and a vibrating quartz tube densimeter in series. Temperature is measured with an integrated Pt-100 thermometer with an estimated uncertainty of 0.01 K. The instrument was adjusted with air and deionized water at 293.15, 313.15, and 333.15 K. In addition, the instrument performance is checked before and after measurements to ensure that the density and speed of sound of water at 293.15 K are reproduced within 100 ppm. For the 1- and 2-butanol measurements, temperature scans were programmed from 343.15 K to 278.15 K in 5 K increments. Fresh samples of test liquid were injected for each temperature scan instead of performing repetitive measurements on the same sample. At least four temperature scans were performed for both fluids. The relative standard deviation (reproducibility) of these repeated sound speed measurements was no greater than 0.07% and no more than 0.001% for density. Based on repeated measurements of the speed of sound of water, we conservatively estimate the uncertainty of our sound speed measurements to be 0.3% ($k = 2.3$). To more accurately estimate the uncertainty of the ambient pressure density measurements, densities of NIST SRM 211d (toluene) were measured over the temperature range of the instrument and compared to the correlation of McLinden and Splett [11]. Based on these comparisons, we conservatively estimate the uncertainty of our ambient pressure density measurements to be 0.04% ($k=2.3$).

Densities of the compressed liquids were measured with the automated densimeter of Outcalt and McLinden, details of which have been described in a previous publication [10]. The core of the apparatus is a commercial vibrating-tube densimeter (DMA-HPM from Anton Paar Company) which is housed in a custom designed

[1] In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

thermostat to maximize temperature stability and control. The apparatus includes several other physical improvements, and procedures such as regular calibration of temperature and pressure measurement devices are implemented to minimize the uncertainty in the measurements beyond that of the commercial instrument operated in a stand-alone mode. The temperature range of the instrument is 270 K to 470 K with pressures up to 50 MPa. In this work, both of the samples were measured along eleven isotherms at pressures from 0.5 MPa to 50 MPa. The instrument was calibrated with propane and toluene over the entire temperature and pressure range. The overall uncertainty ($k=2$) in density is 0.64 kg m^{-3} to 0.81 kg m^{-3}, corresponding to a relative uncertainty in density of 0.09% to 0.14%.

4. Results

Table 1 lists values of density, speed of sound, and derived adiabatic compressibilities for 1-and 2-butanol from 278.15 K to 343.15 K at a pressure of 83 kPa. Speed of sound and adiabatic compressibility results are also illustrated in Figs. 2 and 3, respectively. Adiabatic compressibilities were calculated from the measured densities and speeds of sound via the thermodynamic relation

$$\kappa_s = -(\partial V/\partial p)_s / V = 1/(\rho w^2), \quad (1)$$

where V denotes volume, p is pressure, ρ is the density, and w the speed of sound. The subscript s indicates that the derivative is taken "at constant entropy." Figs. 2 and 3 illustrate that even over a fairly small temperature range and at ambient pressure, the differences in the molecular characteristics of the butanol isomers studied in this

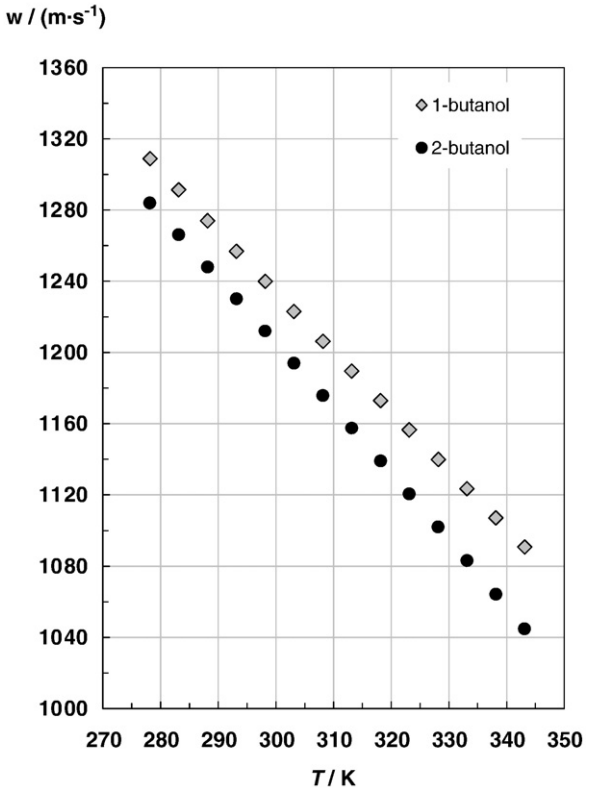


Fig. 2. Measured speed of sound of 1- and 2- butanol at ambient pressure as a function of temperature.

Table 1
Density, speed of sound, and adiabatic compressibility of 1- and 2-butanol measured in the density and sound speed analyzer. The ambient pressure during the measurements was approximately 0.083 MPa.

Temperature T K	Density ρ kg m^{-3}	Speed of sound w m s^{-1}	Adiab. compressibility κ_s TPa^{-1}
1-butanol			
278.15	820.9	1308.8	711.2
283.15	817.1	1291.3	733.9
288.15	813.3	1274.0	757.5
293.15	809.5	1256.8	782.0
298.15	805.7	1239.8	807.5
303.15	801.9	1222.9	833.9
308.15	798.0	1206.2	861.3
313.15	794.1	1189.6	890.0
318.15	790.1	1173.0	919.8
323.15	786.1	1156.5	951.1
328.15	782.1	1140.0	983.9
333.15	778.0	1123.5	1018.3
338.15	773.8	1107.0	1054.5
343.15	769.6	1090.6	1092.4
2-butanol			
278.15	818.3	1284.0	741.3
283.15	814.4	1266.0	766.1
288.15	810.4	1248.0	792.2
293.15	806.3	1230.1	819.6
298.15	802.2	1212.1	848.5
303.15	798.0	1194.0	879.0
308.15	793.7	1175.8	911.3
313.15	789.3	1157.6	945.5
318.15	784.8	1139.2	981.9
323.15	780.2	1120.6	1020.6
328.15	775.5	1102.0	1061.8
333.15	770.7	1083.2	1105.9
338.15	765.8	1064.2	1153.1
343.15	760.7	1044.8	1204.2

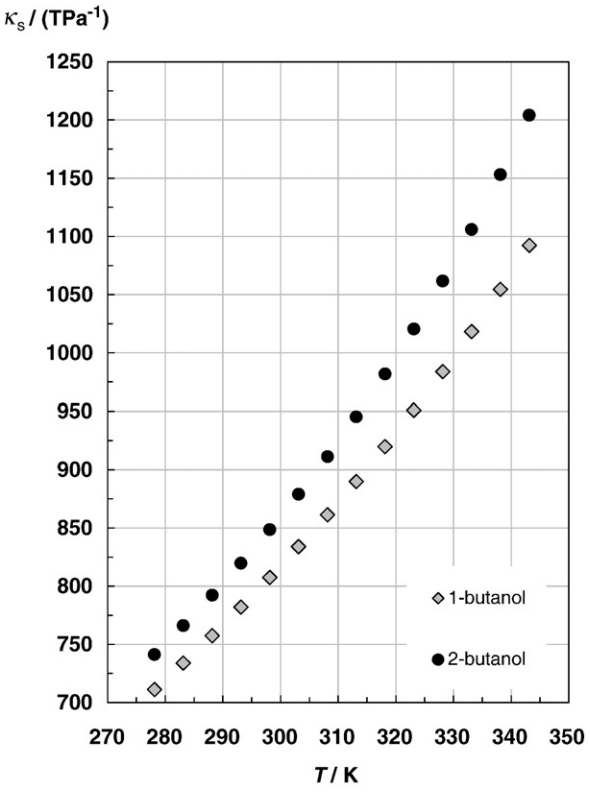


Fig. 3. Derived adiabatic compressibilities of 1- and 2-butanol as a function of temperature.

work are manifested in significant differences in speed of sound and adiabatic compressibility.

Tables 2 and 3 list measured density values for compressed liquid 1- and 2-butanol over the temperature range 270 K to 470 K and pressure range 0.5 MPa to 50 MPa. Also listed are density values extrapolated to the saturation pressure (as given by the American Institute for Chemical Engineers (AIChE) Design Institute for Physical Properties (DIPPR) correlation [12]) for each temperature. These saturated liquid densities were obtained by fitting a second-order polynomial to the isothermal data at pressures less than or equal to 10 MPa and extrapolating to saturation pressure. This extrapolation was performed to examine the consistency of the compressed liquid data with the measurement results at ambient pressure from the density and sound speed analyzer. Figs. 4 and 5 depict measured compressed liquid and ambient pressure densities as a function of temperature for 1- and 2-butanol, respectively.

5. Correlation of data and discussion

The speed of sound data measured at atmospheric pressure were correlated as a function of temperature with the second-order polynomial

$$w = A_1 + A_2 T + A_2 T^2, \tag{2}$$

where w is the speed of sound in units of m s^{-1}, and T is the absolute temperature in Kelvin. Coefficients for the correlation parameters for 1- and 2-butanol are listed in Table 4. The speed of sound data of both the 1- and 2-butanol are fit with an average absolute deviation (AAD) of 0.01%. A search of the ThermoData Engine database (TDE) [13] for available atmospheric pressure speed of sound data for 1-butanol resulted in 67 sources [14–80] with a total of 135 points. Fig. 6 shows deviations of data found in those sources from a baseline of our polynomial correlation. Because of the large number of sources, the data sets were not identified individually. A similar search for 2-butanol atmospheric pressure speed of sound data resulted in 24 sources [25,44,48,49,53,57,59,61,69,72,74,80–91] with a total of 71 points. Their deviations are shown in Fig. 7. All but three points of the 2-butanol literature data agree with our correlation within our stated experimental uncertainty of ±0.3%.

Density measurements at ambient pressure and values extrapolated to saturation pressure from measured compressed liquid data were correlated with the Rackett equation to check the repeatability of the instruments and the consistency of our data up to the normal boiling point (as given in DIPPR [12]) of 390.6 K for 1-butanol and 372.1 K for 2-butanol. The Rackett equation is written as

$$\rho = \beta_1 \cdot \beta_2^{-\left(1 + \left(1 - T/\beta_3\right)^{\beta_4}\right)}. \tag{3}$$

While the equation was developed to represent saturated liquid densities (and our data are not truly saturated liquid densities) it adequately serves as a baseline to compare our data sets to one

Table 2
Compressed liquid densities of 1-butanol. Values extrapolated to saturation pressure as given in [12] are indicated in *italics*.

270 K		290 K		310 K		330 K		350 K		370 K	
Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}
50.03	856.0	49.98	842.9	50.00	830.0	49.99	816.9	50.01	803.6	50.00	789.7
45.01	853.5	44.99	840.2	45.01	827.1	45.00	813.9	45.00	800.3	45.00	786.1
40.01	850.9	40.00	837.5	40.00	824.2	40.00	810.8	40.01	796.9	40.00	782.5
35.01	848.3	35.00	834.7	35.02	821.2	35.00	807.5	35.00	793.4	35.00	778.6
30.01	845.5	30.01	831.8	30.00	818.1	30.00	804.2	30.00	789.7	30.01	774.7
25.00	842.8	25.00	828.8	24.99	814.9	25.01	800.7	25.00	785.9	25.00	770.5
20.00	839.9	20.00	825.7	20.02	811.5	20.00	797.1	20.00	782.0	20.00	766.1
15.00	837.0	14.99	822.6	15.00	808.1	15.00	793.3	15.00	777.8	14.99	761.4
10.01	833.9	10.00	819.3	10.00	804.5	10.01	789.3	10.00	773.4	10.00	756.5
5.00	830.8	5.00	815.9	5.00	800.7	4.99	785.2	5.00	768.8	5.00	751.3
4.00	830.2	3.99	815.1	3.99	800.0	4.00	784.3	4.00	767.8	4.00	750.2
3.00	829.5	2.99	814.4	3.01	799.2	3.00	783.4	3.00	766.8	3.00	749.0
2.01	828.9	2.00	813.7	2.00	798.4	2.00	782.6	2.00	765.8	2.00	747.9
1.01	828.2	1.00	813.0	1.00	797.6	1.00	781.7	1.00	764.8	1.00	746.7
0.50	827.9	0.50	812.6	0.51	797.2	0.50	781.2	0.50	764.3	0.50	746.1
9.05×10^{-5}	*827.5*	*4.90×10^{-4}*	*812.3*	*2.03×10^{-3}*	*796.8*	*6.77×10^{-3}*	*780.8*	*1.89×10^{-2}*	*763.8*	*4.59×10^{-2}*	*745.6*

390 K		410 K		430 K		450 K		470 K	
Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}
50.01	775.2	50.01	760.0	50.00	744.0	50.00	727.8	49.99	711.2
44.99	771.3	44.99	755.7	45.00	739.4	45.00	722.8	45.01	705.6
39.99	767.3	39.99	751.3	39.99	734.6	40.00	717.4	40.00	699.7
34.99	763.1	35.00	746.7	35.01	729.5	35.01	711.7	35.00	693.3
30.00	758.7	29.99	741.8	30.01	724.0	30.01	705.6	30.00	686.4
25.01	754.1	25.00	736.7	25.00	718.2	25.01	699.0	25.01	678.9
19.99	749.2	20.01	731.2	20.01	711.9	20.00	691.8	19.99	670.6
15.00	744.0	15.00	725.2	15.00	705.1	15.00	683.8	15.00	661.3
10.00	738.4	10.01	718.8	9.99	697.6	10.00	674.9	10.00	650.6
5.00	732.3	5.00	711.7	5.00	689.2	5.00	664.7	5.00	637.9
4.00	731.1	4.00	710.2	4.00	687.4	4.00	662.5	4.00	635.0
3.00	729.7	3.00	708.7	3.00	685.5	3.00	660.2	2.99	632.0
2.00	728.4	1.99	707.1	2.00	683.6	2.00	657.7	2.00	628.8
0.99	727.1	0.99	705.5	1.00	681.6	1.00	655.2	0.99	625.4
0.50	726.4	0.50	704.6	0.51	680.6	*0.571*	*654.1*	*0.898*	*625.1*
9.85×10^{-2}	*725.8*	*0.191*	*704.1*	*0.342*	*680.3*				

Table 3
Compressed liquid densities of 2-butanol. Values extrapolated to saturation pressure as given in [12] are indicated in *italics.*

270 K		290 K		310 K		330 K		350 K		370 K	
Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}
50.00	853.0	49.97	840.4	50.04	827.6	50.01	813.0	50.02	797.5	50.01	781.1
45.01	850.5	45.00	837.7	45.01	824.6	45.01	809.8	45.01	794.0	45.01	777.3
40.01	848.0	40.01	834.9	40.01	821.6	40.00	806.5	40.01	790.4	40.01	773.3
35.01	845.3	35.01	832.1	35.01	818.6	35.01	803.1	35.02	786.7	35.01	769.1
30.02	842.6	30.00	829.1	30.01	815.4	30.01	799.6	30.00	782.8	30.01	764.7
25.01	839.8	25.00	826.1	25.00	812.0	25.01	795.9	25.01	778.6	24.99	760.1
20.01	836.9	20.01	822.9	20.01	808.6	20.00	792.1	20.01	774.3	20.01	755.2
15.01	833.9	15.01	819.7	15.02	804.9	15.00	788.0	15.01	769.7	15.01	749.9
10.01	830.8	10.00	816.3	10.00	801.1	10.01	783.7	10.00	764.8	10.01	744.3
5.01	827.6	5.00	812.7	5.00	797.1	5.00	779.2	5.01	759.6	5.01	738.2
4.00	826.9	4.01	812.0	4.00	796.3	4.00	778.3	4.00	758.5	4.01	736.9
3.00	826.3	3.00	811.2	3.01	795.5	3.01	777.3	3.01	757.4	3.01	735.6
2.01	825.6	2.01	810.5	2.01	794.6	2.01	776.3	2.01	756.3	2.01	734.2
1.01	824.9	1.00	809.7	1.00	793.8	1.01	775.3	1.00	755.1	1.00	732.9
0.51	824.6	0.50	809.3	0.50	793.3	0.51	774.8	0.50	754.5	0.50	732.2
2.63×10^{-4}	*824.2*	*1.32×10^{-3}*	*808.9*	*5.03×10^{-3}*	*792.9*	*1.55×10^{-2}*	*774.4*	*4.04×10^{-2}*	*754.0*	*9.10×10^{-2}*	*731.6*

390 K		410 K		430 K		450 K		470 K	
Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}	Pressure p MPa	Density ρ kg m^{-3}
50.00	764.1	50.02	746.6	50.00	728.7	50.02	710.5	50.03	692.7
45.01	759.8	45.01	741.9	45.01	723.6	45.00	704.8	45.01	686.3
40.01	755.4	40.01	737.0	40.01	718.1	40.02	698.7	40.02	679.6
35.01	750.8	35.02	731.8	35.01	712.3	35.00	692.1	35.00	672.1
30.02	745.9	30.02	726.3	30.01	706.0	30.02	685.0	30.01	664.1
25.02	740.6	25.02	720.3	25.00	699.2	25.01	677.2	25.01	655.1
20.01	735.0	20.02	713.9	20.00	691.7	20.01	668.6	20.02	645.1
15.01	729.0	15.01	706.9	15.01	683.5	15.00	658.8	15.01	633.4
10.01	722.4	10.00	699.1	10.01	674.2	10.01	647.5	10.01	619.4
5.00	715.2	5.01	690.4	5.01	663.5	5.00	634.0	5.01	601.7
4.00	713.7	4.01	688.5	4.01	661.1	4.02	630.9	4.01	597.4
3.01	712.1	3.01	686.6	3.01	658.6	3.50	629.3	3.52	595.1
2.00	710.5	2.01	684.6	2.00	656.0	3.00	627.6	3.00	592.7
1.01	708.9	1.00	682.5	1.00	653.4	2.51	625.9	2.51	590.2
0.51	708.0	0.51	681.4	0.50	652.0	2.00	624.1	2.00	587.6
0.183	*707.5*	*0.334*	*681.1*	*0.565*	*652.2*	1.51	622.3	1.51	584.9
						1.008	620.4	*1.36*	*584.2*
						0.898	*620.1*		

another as well as to literature data, particularly at low reduced temperatures. It is common practice when the Rackett equation is used, to constrain β_3 to the critical temperature of the fluid for which the correlation is being performed. We constrained the β_3 values to the critical temperatures in the DIPPR database [12], namely, for 1-butanol and 2-butanol, 563.1 K and 535.9 K, respectively. The correlation parameters for the Rackett equations are listed in Table 5. In Figs. 8 and 9 our Rackett correlations for 1-and 2-butanol, respectively, serve as the baseline to compare our ambient pressure and extrapolated density values, as well as the DIPPR correlation of densities, and the TDE [13] correlation of saturated liquid densities. The DIPPR correlation includes densities measured at one atmosphere for temperatures below the normal boiling point, and densities at saturation pressure for temperatures above the normal boiling point.

There is an abundance of ambient pressure and saturated liquid density data in the literature for both 1-and 2-butanol, and the scatter in the data is substantial. For the purpose of comparison, the DIPPR and TDE database correlations are considered to represent the majority of the available literature data. It can be seen in both Figs. 8 and 9 that the TDE correlation agrees well with our data, but that the DIPPR correlation (also a Rackett equation) does not. In fact, it can be argued that the DIPPR correlation does not agree well with the data used in its very formulation. Although not shown here, the deviations of that data

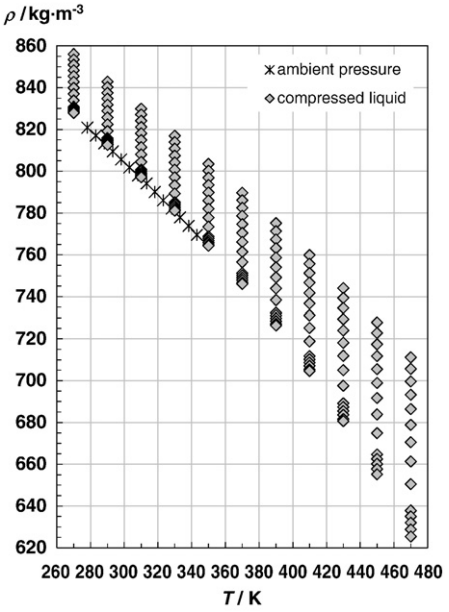


Fig. 4. Measured compressed liquid and ambient pressure densities of 1-butanol as a function of temperature.

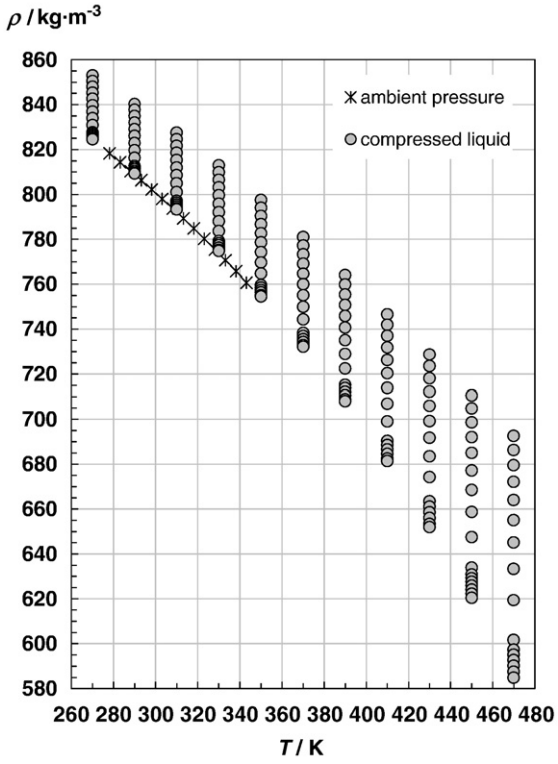


Fig. 5. Measured compressed liquid and ambient pressure densities of 2-butanol as a function of temperature.

Table 4
Parameters of the sound speed correlation (Eq. (2)), for 1- and 2-butanol at an ambient pressure of 83 kPa.

Parameter	Value	Std. dev.
1-butanol		
A_1	2408.8	12.5
A_2/K	−4.447	0.080
A_3/K^2	0.00177	0.00013
2-butanol		
A_1	2099.8	13.3
A_2/K	−2.337	0.086
A_3/K^2	−0.00215	0.00014

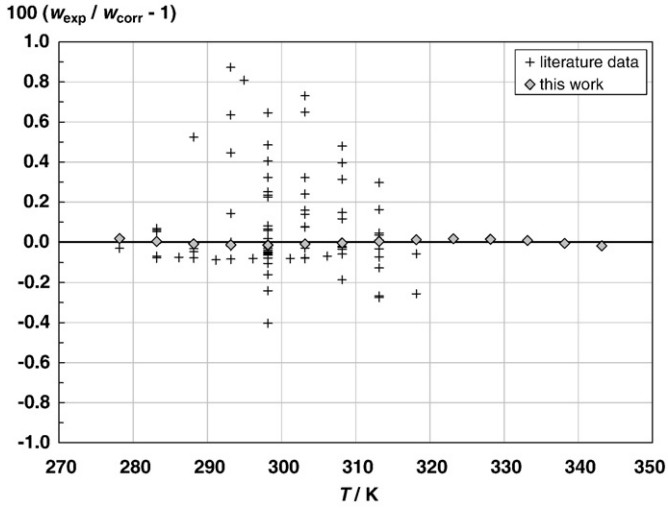


Fig. 6. Comparison of the speed of sound data of 1-butanol reported in this work and in the literature at ambient pressure relative to the correlation, Eq. (2).

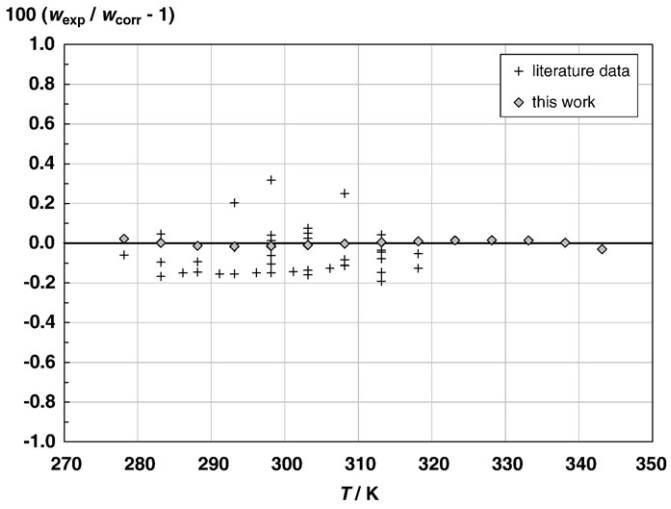


Fig. 7. Comparison of the speed of sound data of 2-butanol reported in this work and in the literature at ambient pressure relative to the correlation, Eq. (2).

Table 5
Parameters of the Racket correlations (Eq. (3)) for 1- and 2-butanol.

Parameter	Value
1-butanol	
β_1/kg m^{-3}	9.92×10^{-2}
β_2	1.01×10^{-2}
β_3/K	563.1 (constrained)
β_4	5.66×10^{-2}
2-butanol	
β_1/kg m^{-3}	1.08×10^{-3}
β_2	1.05×10^{-3}
β_3/K	535.9 (constrained)
β_4	3.80×10^{-2}

from the DIPPR correlation are similar in sign and magnitude to the deviations observed with our data. Thus, our data generally agree with the literature data referenced in the DIPPR database but not with its representative Rackett correlation. This is an indication that the Rackett

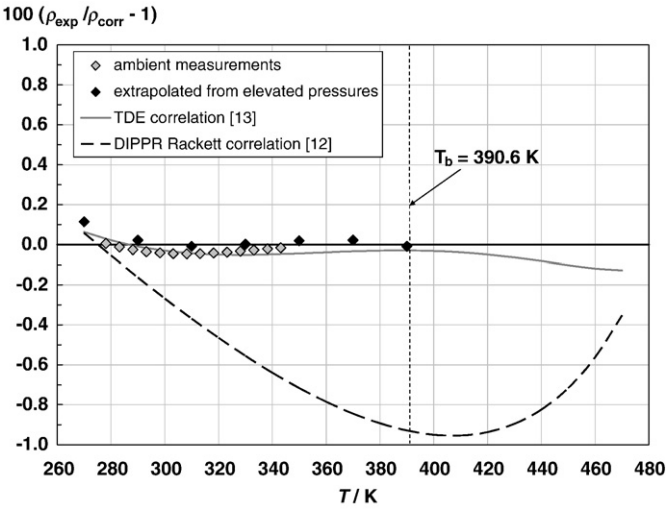


Fig. 8. Comparison of ambient pressure and extrapolated 1-butanol density data reported in this work with saturated liquid density correlations in the literature relative to the correlation, Eq. (3).

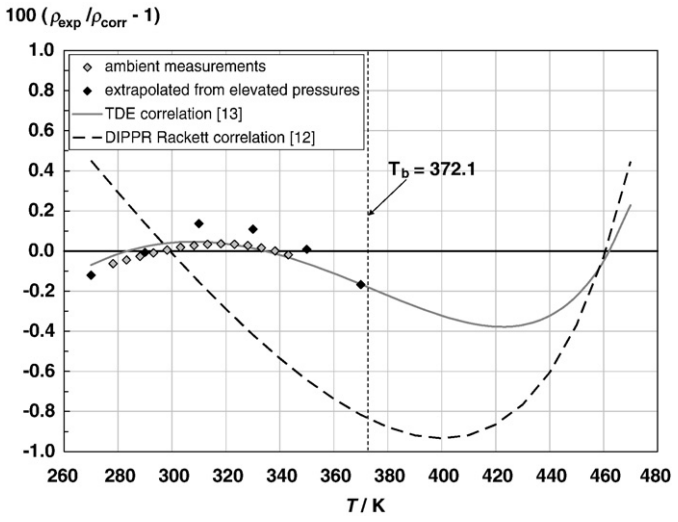


Fig. 9. Comparison of ambient pressure and extrapolated 2-butanol density data reported in this work with saturated liquid density correlations in the literature relative to the correlation, Eq. (3).

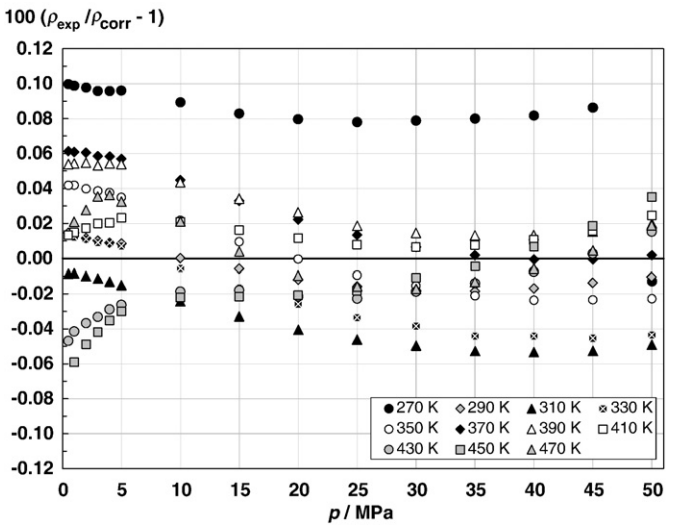


Fig. 10. Deviations of measured compressed liquid densities of 1-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of pressure.

equation may not be the best choice for correlating alcohol densities, particularly at high reduced temperatures. This later point is corroborated in the recent work of Lai et al. [92].

The reported compressed liquid density results were correlated with a Tait equation similar to that of Dymond and Malhotra [93]. The equation used to fit the compressed liquid density data is

$$\rho(T,p) = \frac{\rho_{\mathrm{ref}}(T,p_{\mathrm{ref}})}{1-C\ln\left(\frac{p+B(T)}{p_{\mathrm{ref}}+B(T)}\right)}, \tag{4}$$

Table 6
Parameters of the polynomial correlation (Eq. (5)), for the saturated liquid densities that have been derived from extrapolating the isothermal compressed liquid densities of 1- and 2-butanol to saturation pressure from 270 K to 470 K.

Parameter	Value
1-butanol	
D_1	448.77183
D_2	1298.77857
D_3	−1511.08340
D_4	583.77972
D_5	406.58208
2-butanol	
D_1	431.90443
D_2	1508.90032
D_3	−2575.93025
D_4	3361.54274
D_5	−2193.28711

Table 7
Parameters of the Tait correlation (Eqs. (4) and (6)) for the density of 1- and 2- butanol.

Parameter	Value	Std. dev.
1-butanol		
C	8.4917×10^{-2}	0.0096×10^{-2}
E_1	305.38	0.49
E_2	−250.50	0.53
E_3	47.38	0.16
2-butanol		
C	8.3979×10^{-2}	0.0039×10^{-2}
E_1	382.27	0.25
E_2	−367.87	0.27
E_3	87.243	0.080

where p_{ref} is the vapor pressure according to the DIPPR correlation, and $\rho_{\mathrm{ref}}(T)$ is derived from a fourth order polynomial fit of the isothermal compressed liquid density data that were extrapolated to the vapor pressure as given in Tables 2 and 3. The correlation equation for the extrapolated saturated liquid densities is

$$\rho_{\mathrm{sat}} = D_1 + D_2\tau + D_3\tau^2 + D_4\tau^3 + D_5\tau^4, \tag{5}$$

where $\tau = 1 - T/T_c$ and the parameters are listed in Table 6. The temperature dependence of the Tait parameters $B(T)$ was expressed by the quadratic polynomial,

$$B(T) = E_1 + E_2T_r + E_3T_r^2 \tag{6}$$

where T_r is the absolute temperature T divided by 273.15 K. Parameters for the Tait correlations are given in Table 7. The correlations represent our 1- and 2-butanol data with AADs of 0.029% and 0.019%, respectively. Deviations of our measured compressed liquid densities from our Tait correlations for 1- and 2-butanol are shown in Figs. 10 and 11. These figures illustrate that the Tait equations for 1- and 2-butanol fit our data within the overall

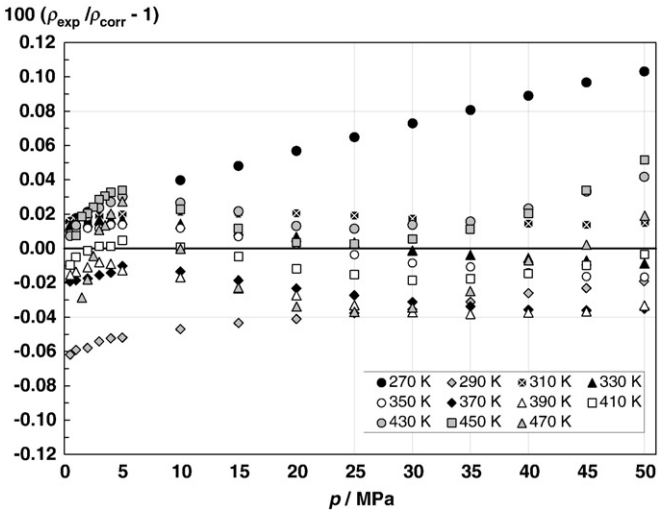


Fig. 11. Deviations of measured compressed liquid densities of 2-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of pressure.

combined uncertainty of 0.12%. and 0.14%, respectively. A search of the literature for compressed liquid density data resulted in 11 sources for 1-butanol [94–104] and three for 2-butanol [99,104,105]. Figs. 12a,b, 13a, and b show deviations of literature values of compressed liquid density data from our Tait equations as a function of pressure and temperature for 1- and 2-butanol, respectively. Again, there is a fair amount of scatter in the literature data and in general, our data lie in the middle of that scatter. No 2-butanol compressed liquid density data were found in the literature at temperatures above 362 K.

Data reported here show significant differences between the densities and speeds of sound between 1- and 2-butanol. These

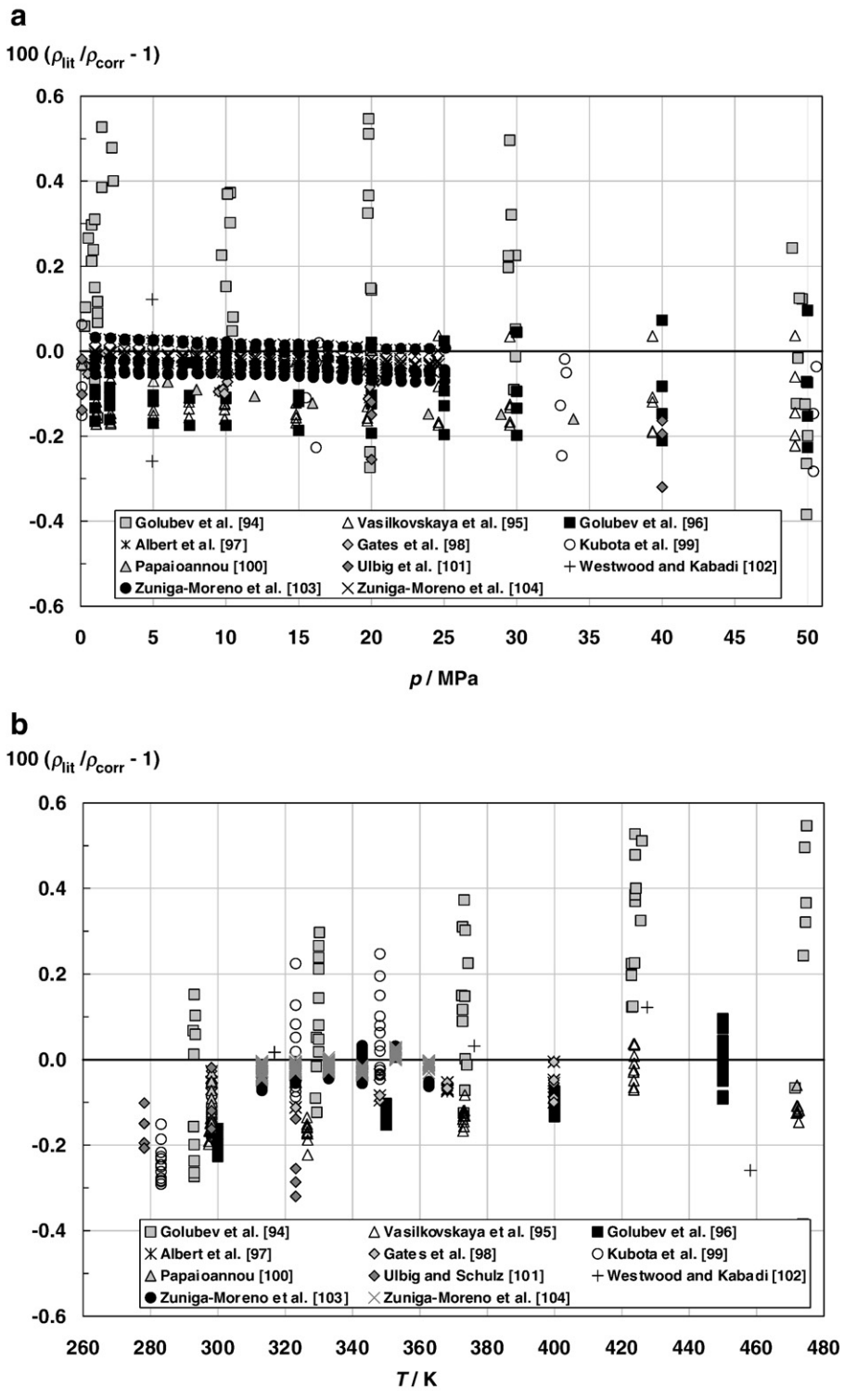


Fig. 12. a. Deviations of literature data for the density of compressed liquid 1-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of pressure. b. Deviations of literature data for the density of compressed liquid 1-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of temperature.

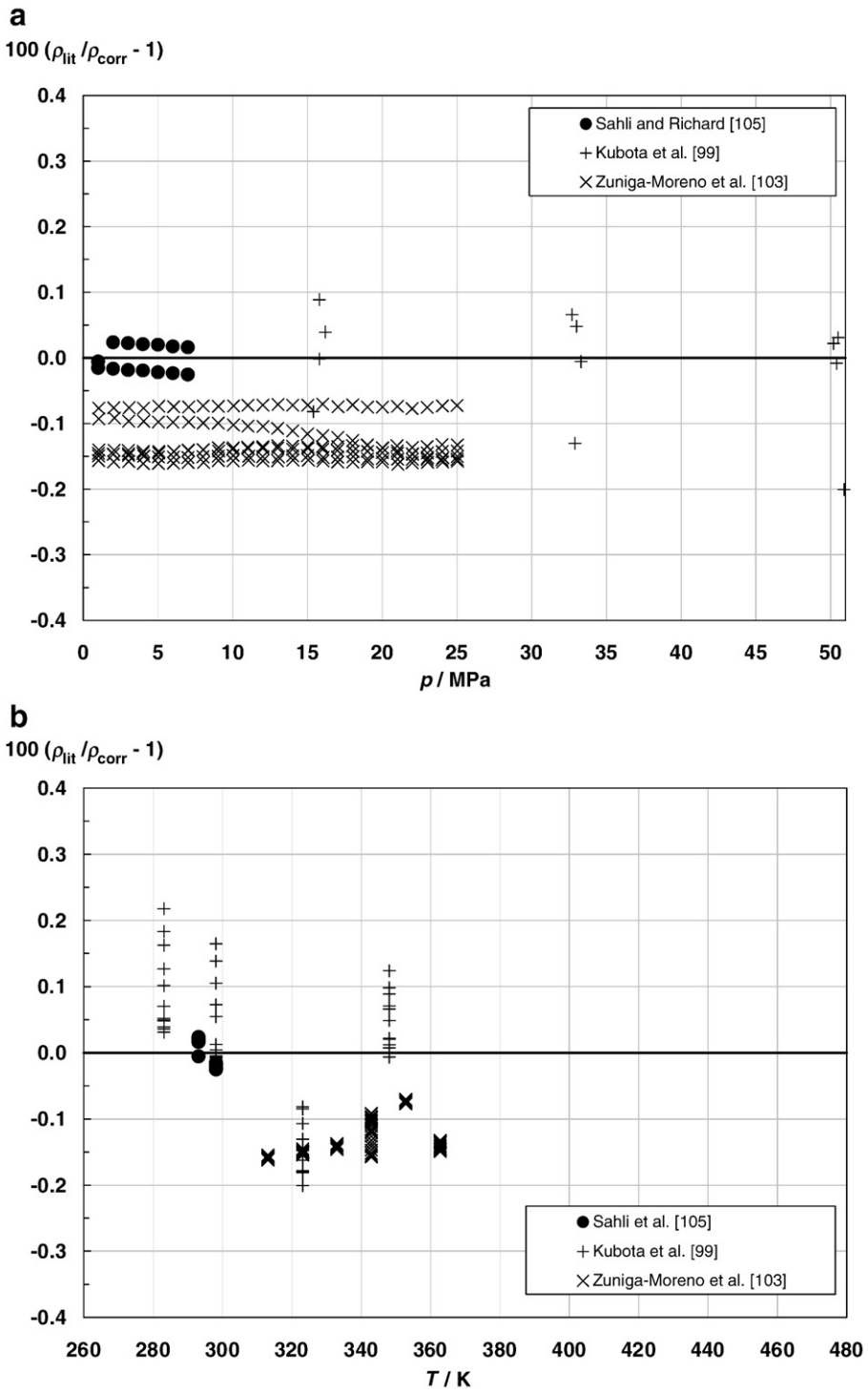


Fig. 13. a. Deviations of literature data for the density of compressed liquid 2-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of pressure. b. Deviations of literature data for the density of compressed liquid 2-butanol from the Tait correlation (Eqs. (4)–(6)) as a function of temperature.

differences are indicative of the differences in the molecular shape and charge distribution of the isomers. At the lowest measured temperature of 270 K the higher density of 1-butanol is consistent with the difference in shape from 2-butanol. Fig. 1 shows that 1-butanol molecules can be packed with less void volume than 2-butanol molecules. The temperature dependence of the density difference between the two isomers indicates differences in polar attractions. The density of 2-butanol decreases faster with temperature than that of 1-butanol as a result of lower attractive forces in the secondary alcohol due to the different shape and charge distribution compared to the primary alcohol.

Literature surveys of the speed of sound and density data of 1- and 2-butanol showed significant scatter as well as gaps, particularly for 2-butanol. The speed of sound data reported here extend the range of available data from 318 K to 343 K for both 1- and 2-butanol. Compressed liquid density data for 2-butanol reported here extend the range of available data from 363 K to 470 K. Differences in sample purity likely contribute to the scatter seen in the literature data;

butanols are hygroscopic and it is therefore difficult to keep samples free of water, and very pure (better than 99.5%) samples of 1-and 2-butanol are not readily commercially available or are prohibitively expensive. Our measurements are consistent with previously published data, generally falling in the middle of the scatter, and thus identifying data that are clear outliers.

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