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SHORT ARTICLE

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Acoustic and Thermodynamic Properties of 2-Ethyl-1-hexanol by Means of High-Pressure Speed of Sound Measurements at Temperatures from (293 to 318) K and Pressures up to 101 MPa

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S *Supporting Information*

ABSTRACT: The speed of sound in 2-ethyl-1-hexanol has been measured in the temperature range from (293.15 to 318.15) K at pressures up to 101 MPa by the pulse-echo-overlap method. The density has been measured in the temperature range from (278.15 to 363.15) K under atmospheric pressure with a vibrating tube densimeter. These experimental results are then used to calculate the densities, isobaric and isochoric heat capacities, isobaric coefficients of thermal expansion, and isentropic and isothermal compressibilities, as well as the internal pressure and ratio of heat capacities as a function of temperature and pressure. The effects of pressure and temperature on these properties are discussed. Densities are correlated with a Tait equation.

INTRODUCTION

Although the acoustic method has found acceptance as a relatively simple and accurate tool of determining thermodynamic properties of compressed liquids, the experimental data of the thermodynamic properties at elevated pressures, which are of particular importance in the study of the liquid state, are still rather scarce. Furthermore, the data are scattered in various journals, and some original papers (often not in English) are available with difficulty. An overview of speed of sound measurements under elevated pressures is given by Oakley et al.[1] but contains publications until 1997/98 only.

This work is a part of a continuing temperature—pressure study of associated hydroxyl liquids (that are one of the key substances in the chemical industry) by means of the acoustic method. Previously, among others, the results for some 1-alkanols[2] and alkanediols[3−5] have been reported. The present work is devoted to the study of the effects of pressure and temperature on the speed of sound in 2-ethyl-1-hexanol (branched primary alkanol, CAS No. 104-76-7) to provide experimental data for the calculation of the density, isobaric and isochoric heat capacities, isobaric coefficient of thermal expansion, and isentropic and isothermal compressibilities, as well as the internal pressure and ratio of heat capacities as a function of pressure and temperature. As an integral part of this study, the densities at atmospheric pressure and temperatures ranging from (278.15 to 363.15) K are measured.

Because of the low cost, very low solubility in water, good solubility in a wide variety of organic liquids, and a wide temperature range of the liquid phase, that is, high boiling (457.49 K)[6] and low freezing temperature (glass transition at 197 K),[6] 2-ethyl-1-hexanol is a good solvent for industrial applications. This fatty alcohol is also widely used as plasticizer and in the production of esters that have a variety of uses. At the same time it is also important to mention that 2-ethyl-1-hexanol is an organic compound that is detected in indoor air (primarily emitted from poly(vinyl chloride) (PVC) building materials)[7] at relatively high concentrations (above 400 $\mu g \cdot m^{-3}$) and is a significant pollutant in indoor air (sick building syndrome).[7] 2-Ethyl-1-hexanol is also detected in outdoor air (biodiesel vapors).[8] It irritates the skin, eyes, and respiratory track.

To the best of our knowledge, the speeds of sound under elevated pressures for 2-ethyl-1-hexanol have not been reported yet in the available literature, nor have we found the data on the compressed-liquid density or related quantities. In turn, the polythermal data on the densities and speeds of sound at atmospheric pressure reported in the literature are very limited.

EXPERIMENTAL SECTION

Materials. 2-Ethyl-1-hexanol (mass fraction > 0.996) from Fluka was used in this study without further purification. The water content declared by the supplier was $< 1 \cdot 10^{-3}$. The water content determined in our lab by the Karl Fischer method was $2.6 \cdot 10^{-4}$. The refractive index n_D ($T = 298.15$ K) measured with an Abbe refractometer RL3 (uncertainty ± 0.0004) was 1.4292. The agreement with the literature data (1.4290) reported by Riddick et al.[6] is satisfactory. In this study, just before all of the measurements, the samples were degassed by means of an ultrasonic cleaner.

Methods and Apparatus. The speeds of sound at a frequency of 2 MHz were measured under atmospheric and elevated pressures using two measuring sets with measuring vessels of the same acoustic path and construction (a single transmitting-receiving ceramic transducer and an acoustic mirror). The sets operate on the principle of the pulse-echo-overlap method that has been applied by us for many years.[9] A detailed description of the high-pressure measuring set and those under atmospheric pressure can be found elsewhere.[10,11] Briefly, the instruments

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Table 1. Experimental Speeds of Sound (u) in 2-Ethyl-1-hexanol at Various Temperatures (T) and Pressures (p)

P/MPa	T/K	u/m·s^{-1}	T/K	u/m·s^{-1}	T/K	u/m·s^{-1}
0.101	293.15	1336.28	298.15	1318.44	303.15	1300.61
15.20	292.89	1418.51	298.19	1400.23	303.15	1383.53
30.39	292.89	1487.16	298.19	1470.11	303.15	1454.42
45.59	292.89	1549.63	298.19	1533.20	303.15	1518.40
60.79	292.89	1607.23	298.19	1591.51	303.15	1577.48
75.99	292.89	1660.42	298.19	1645.44	303.15	1631.84
91.18	292.89	1710.47	298.19	1695.97	303.15	1682.67
101.32	292.89	1741.98	298.19	1728.00	303.15	1715.06
0.101	308.15	1282.77	313.15	1264.94	318.15	1247.10
15.20	308.13	1367.15	313.10	1351.15	318.26	1334.79
30.39	308.13	1438.87	313.10	1423.98	318.26	1408.75
45.59	308.13	1503.82	313.10	1489.57	318.26	1475.22
60.79	308.13	1563.46	313.10	1549.74	318.26	1535.88
75.99	308.13	1618.57	313.10	1605.47	318.26	1592.22
91.18	308.13	1669.75	313.10	1657.18	318.26	1644.45
101.32	308.13	1702.55	313.10	1689.92	318.26	1677.39

were calibrated with redistilled and degassed (by boiling) water. Its electrolytic conductivity was $1 \cdot 10^{-4}\ \Omega^{-1} \cdot \text{m}^{-1}$. The standard values of the speed of sound in water at atmospheric pressure were taken from the polynomial proposed by Marczak[12] and, at elevated pressures, from the Kell and Whalley polynomial.[13] The pressure was measured by means of Hottinger Baldwin System P3MD with an uncertainty better than ± 0.15 %. The temperature (ITS-90) was measured using an Ertco Hart 850 platinum resistance thermometer (NIST certified) with an uncertainty of ± 0.05 K. During the measurements, a stability of ± 0.01 K was maintained. The repeatability of the measured speeds of sound was better than ± 0.02 % at atmospheric pressure and ± 0.04 % under elevated pressures. The uncertainty was estimated to be better than $\pm\ 0.5\ \text{m} \cdot \text{s}^{-1}$ and $\pm\ 1\ \text{m} \cdot \text{s}^{-1}$, respectively.

The densities at atmospheric pressure were measured by means of a vibrating-tube densimeter DMA 5000 (Anton Paar) with an uncertainty better than $\pm\ 5 \cdot 10^{-2}\ \text{kg} \cdot \text{m}^{-3}$ and repeatability better than $\pm\ 5 \cdot 10^{-3}\ \text{kg} \cdot \text{m}^{-3}$. The calibration was made by the use of air and redistilled, freshly degassed (by boiling) water with the above-mentioned electrolytic conductivity. More experimental details can be found in our previous papers.[2−4]

■ MEASUREMENT RESULTS

Speeds of Sound. The experimental values of speed of sound in 2-ethyl-1-hexanol are collected in Table 1. A comparison of the speed of sound at atmospheric pressure, u_0, with the literature values is shown in Figure 1. Unexpectedly, the literature data on the speed of sound of 2-ethyl-1-hexanol at atmospheric pressure (both isothermal and polythermal) are very limited. As seen from Figure 1, the agreement between our results and the values extracted from the paper of Marks[14] (temperature dependence reported in the form of a linear equation) is rather unsatisfactory (an average absolute deviation (AAD = $(100/n) \cdot \Sigma_{i=1}^{n} |(u_{0,\text{lit}} - u_{0,\text{exptl}})/u_{0,\text{exptl}}|_i$) was found to be 0.32 %). At the same time the agreement between our results and those reported by Zotov et al.[15] is very satisfactory (AAD is 0.06 %). It should be noted here that the mentioned authors reported the speed of sound data on saturation line up to 633 K. Generally, a comparison of the speeds of sound reported in this work with the literature values results in an AAD of 0.23 %. In our opinion, the differences are related most probably to the purity of the 2-ethyl-1-hexanol as well as maybe to the measuring method. We would like to point out that the value of Awwad and Pethrick[18] shows an extreme deviation of −0.66 % at T = 298.15 K and seems unreliable.

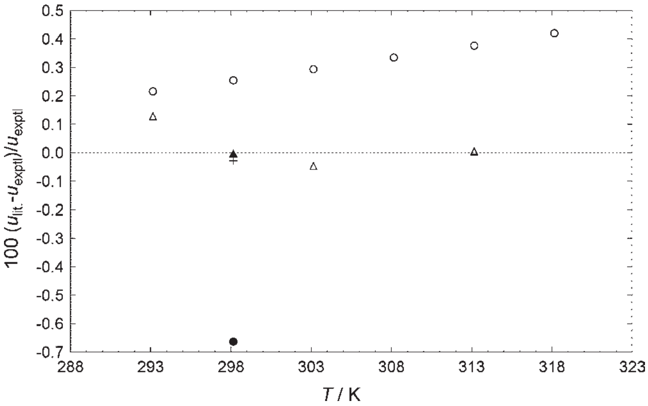

Figure 1. Comparison of speed of sound for 2-ethyl-1-hexanol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (u_{\text{lit.}} - u_{\text{exptl.}})/u_{\text{exptl}}$ between values of this work and literature values of: ○, Marks;[14] △, Zotov et al.;[15] +, Zorębski et al.;[16] ▲, Zorębski and Kulig;[17] and ●, Awwad and Pethrick.[18]

Table 2. Experimental Densities (ρ_0) at Atmospheric Pressure and Various Temperatures (T) for 2-Ethyl-1-hexanol

T/K	ρ_0/kg·m^{-3}	T/K	ρ_0/kg·m^{-3}
278.15	843.49	323.15	810.33
283.15	839.89	328.15	806.52
288.15	836.26	333.15	802.68
293.15	832.62	338.14	798.80
298.14	828.96	343.15	794.87
303.15	825.28	348.15	790.91
308.15	821.58	353.15	786.89
313.14	817.86	358.15	782.83
318.15	814.11	363.15	778.72

The speeds of sound values u_0 under atmospheric pressure have been approximated by the following polynomial:

$$u_0 = \sum_{j=0}^{n} b_j \cdot T^j \qquad (1)$$

The coefficients b_j, determined by the unweighted least-squares method (to reduce the number of nonzero coefficients, the stepwise rejection procedure was used), are reported in Table 3. Because the mean deviation ($\delta = (\Sigma_{i=1}^{n}(u_{0,\text{calc}} - u_{0,\text{exptl}})_i^2/(n - m))^{1/2}$ where n is the number of the experimental points and m is the number of the fitted coefficients) as well as the residual deviations of the fit are small, the speeds estimated from the regression function are equal to the raw data within the limits of the measurement repeatability.

As expected, for a given pressure, the speed of sound in the liquid under test is decreasing almost linearly with increasing temperature, while at constant temperature the speed of sound increases evidently nonlinearly with increasing pressure (not shown graphically). Moreover, with increasing pressure its effect

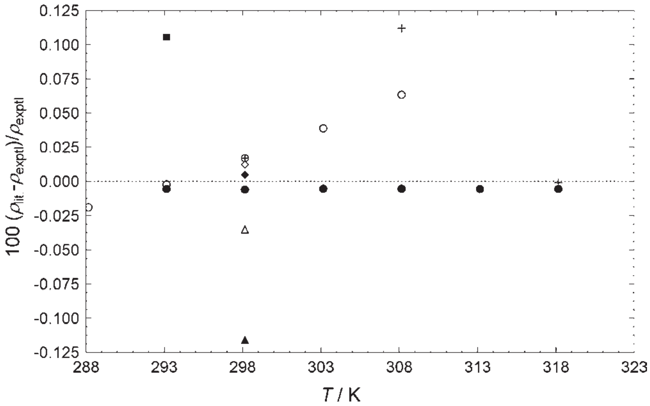

Figure 2. Comparison of density for 2-ethyl-1-hexanol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (\rho_{\text{lit.}} - \rho_{\text{exptl}})/\rho_{\text{exptl}}$ between values of this work and literature values of: ◆, Riddick et al.;[6] ○, Marks;[14] ●, Zotov et al.;[15] ■, Zorębski et al.;[16] △, Zorębski and Kulig;[17] ◇, Awwad and Pethrick;[18] +, Solimo;[19] and ▲, Behrens and Kaatze.[20]

Table 3. Coefficients b_j of the Polynomials (1) and (2) for the Speed of Sound u_0 (within the Temperature Range from (293.15 to 318.15) K) and Density ρ_0 (within the Temperature Range from (278.15 to 363.15) K) at Atmospheric Pressure Together with Mean Deviations (δ) for 2-Ethyl-1-hexanol

	b_0	b_1	b_2	b_3	δ
u_0/m·s^{-1}	2381.970	−3.56709			0.003[a]
ρ_0/kg·m^{-3}	1108.169	−1.45536	$-2.79918 \cdot 10^{-3}$	$-3.5514 \cdot 10^{-6}$	0.01[b]

[a] $\delta(u_0)$/m·s^{-1}. [b] $\delta(\rho_0)$/kg·m^{-3}.

on the speed of sound becomes smaller. The results are very similar to those reported previously for the alkanols studied[2] and in agreement with the usual observations for the liquids (the positive pressure coefficients $(\partial u/\partial p)_T$ and negative temperature coefficients $(\partial u/\partial T)_p$). The form of the equation used for smoothing out the u, p, and T values is given in the next section.

Densities at Atmospheric Pressure. Table 2 lists the experimental densities ρ_0 measured at atmospheric pressure in the temperature range from (278.15 to 363.15) K. The values of ρ_0 were approximated by the polynomial

$$\rho_0 = \sum_{j=0}^{n} b_j \cdot T^j \qquad (2)$$

where b_j are coefficients determined as above. The corresponding values are given in Table 3. The fit is very good, and the mean deviation is of the order of measurement repeatability. A comparison with the density data reported in the literature shows, however, that the values published by various authors are rather scattered (as seen from Figure 2, the best agreement over whole temperature range show the data of Zorębski et al.[16]). Most likely, those discrepancies are caused mainly by systematic errors related to apparatus, its calibration procedure, and so forth. However, sample purity must also be taken into account, in particular the water content. A comparison of the smoothed densities of 2-ethyl-1-hexanol reported in this work with the literature values (mostly polythermal data) results in an average absolute deviation (AAD = $(100/n) \cdot \sum_{i=1}^{n} |(\rho_{0,\text{lit}} - \rho_{0,\text{exptl}})/\rho_{0,\text{exptl}}|_i$) of 0.032 %. Generally, this comparison reveals that the experimental uncertainties given in the literature sources are very often far too optimistic.

Table 4. Coefficients of eq 3 Together with the Mean Deviation (δ) for 2-Ethyl-1-hexanol

j	a_{1j}	a_{2j}	a_{3j}	δ/m·s^{-1}
0	$2.61442 \cdot 10^{-1}$	$2.49296 \cdot 10^{-4}$	$-2.22370 \cdot 10^{-8}$	0.35
1				
2	$-1.03417 \cdot 10^{-6}$	$-5.73832 \cdot 10^{-10}$		

Calculations of Material Constants at Elevated Pressures. Since details of the calculation procedure can be found elsewhere,[2,21] only a brief summary is given below.

Generally, the acoustic method is based on the speeds of sound measured as function of temperature and pressure. However, the density and isobaric heat capacity measured as functions of temperature at atmospheric pressure[22−25] (so-called reference isobars) are an integral part of this method. In the assumed absence of the sound wave absorption, the speed of sound may be regarded as a thermodynamic quantity, and the Newton−Laplace relation can be used. In the calculations, a modified numerical procedure proposed by Sun et al.,[23] based on the earlier suggestions of Davies and Gordon,[22] has been applied.

As in previous papers,[2−5,26] the speed of sound data were approximated as a function of temperature and pressure with the equation suggested by Sun et al.:[23]

$$p - p_0 = \sum_{i=1}^{m} \sum_{j=0}^{n} a_{ij} (u - u_0)^i \cdot T^j \qquad (3)$$

where u is the speed of sound at $p > 0.1$ MPa and u_0 is the speed of sound at atmospheric pressure p_0. The corresponding coefficients a_{ij} and mean deviation are given in Table 4. The calculation procedure of the thermodynamic properties under elevated pressure is based on the pressure dependencies of the density and heat capacity given by the following thermodynamic relationships:

$$\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{u^2} + \frac{T \alpha_p{}^2}{c_p} \qquad (4)$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -\frac{T}{\rho}\left[\alpha_p{}^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p\right] \qquad (5)$$

where α_p ($\alpha_p = -\rho^{-1}(\partial \rho/\partial T)_p$) is the isobaric coefficient of thermal expansion and c_p is the specific isobaric heat capacity. The above relations form a set of equations that can be integrated over the entire pressure range covered by the $u(T, p)$ function and by using suitable initial conditions in the form of $\rho(T, p_0)$ and $c_p(T, p_0)$ functions at the starting pressure p_0, that is, the reference isobars of density and specific isobaric heat capacity in the form of smoothing functions of temperature at atmospheric pressure. In the calculations, the data on the temperature dependence of the isobaric heat capacity of 2-ethyl-1-hexanol at atmospheric pressure recommended by Zábranský et al.[27] were used. In the case of density, the results obtained in this work were used (see eq 2 and Table 3).

At last, the procedure gives the isobars of density and heat capacity in the form of polynomials similar to eqs 1 and 2. Generally, however, the values of the heat capacities obtained in

Table 5. Densities (ρ) Calculated by the Use of the Acoustic Method for 2-Ethyl-1-hexanol at Various Temperatures (T) and Pressures (p)

	ρ/kg·m^{-3} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
0.101[a]	832.61	828.96	825.28	821.58	817.86	814.11
10	838.85	835.35	831.83	828.29	824.73	821.15
20	844.66	841.29	837.91	834.52	831.10	827.67
30	850.09	846.84	843.58	840.30	837.01	833.71
40	855.19	852.05	848.89	845.72	842.54	839.35
50	860.02	856.97	853.90	850.83	847.74	844.65
60	864.61	861.64	858.65	855.67	852.67	849.66
70	868.99	866.09	863.18	860.27	857.35	854.42
80	873.17	870.34	867.50	864.66	861.81	858.95
90	877.19	874.42	871.64	868.86	866.08	863.29
100	881.05	878.34	875.62	872.90	870.17	867.44

[a] Density measured directly with vibrating-tube densimeter at atmospheric pressure.

Table 6. Molar Isobaric and Isochoric Heat Capacities (C_p and C_V) Calculated by the Use of the Acoustic Method for 2-Ethyl-1-hexanol at Various Temperatures (T) and Pressures (p)

	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
	C_p/J·K^{-1}·mol^{-1}					
0.101[a]	311.94	317.47	323.04	328.64	334.27	339.93
10	310.8	316.3	321.8	327.3	332.9	338.5
20	309.8	315.2	320.7	326.2	331.8	337.3
30	308.9	314.3	319.8	325.3	330.8	336.3
40	308.1	313.5	319.0	324.4	329.9	335.4
50	307.5	312.8	318.3	323.7	329.2	334.6
60	306.9	312.2	317.6	323.0	328.5	333.9
70	306.3	311.7	317.0	322.4	327.9	333.3
80	305.8	311.1	316.5	321.9	327.3	332.7
90	305.3	310.6	316.0	321.4	326.8	332.2
100	304.9	310.2	315.5	320.9	326.3	331.7
	C_V/J·K^{-1}·mol^{-1}					
0.101	267.2	272.1	277.1	282.1	287.1	292.2
10	266.9	271.8	276.8	281.8	286.8	291.9
20	266.7	271.6	276.6	281.6	286.6	291.7
30	266.7	271.6	276.5	281.5	286.5	291.5
40	266.6	271.5	276.4	281.4	286.4	291.4
50	266.6	271.5	276.4	281.4	286.4	291.4
60	266.6	271.5	276.4	281.4	286.3	291.3
70	266.6	271.5	276.4	281.4	286.3	291.3
80	266.7	271.5	276.4	281.4	286.3	291.3
90	266.7	271.6	276.4	281.3	286.3	291.2
100	266.7	271.6	276.4	281.3	286.2	291.2

[a] Zábranský et al.[27]

this way seem to be less reliable than the values of densities.[2−5,23] An estimation of the uncertainty of ρ and C_p (in consequence related properties too) under elevated pressures, calculated by the use of acoustic method, is by no means straightforward. Recently, an interesting method, based on the so-called recursive equation method (REM), has been proposed to estimate the uncertainties associated with the calculated thermodynamic quantities of interest over a wide range of temperatures and pressures.[28,29] In this work, however, the perturbation analysis is used. Such an analysis has been reported years ago by Sun et al.[23] and very recently by Peleties et al.[30] Taking into account the uncertainty in the measured speed of sound and in the initial values of density and isobaric heat capacity at the starting (atmospheric) pressure, the respective uncertainties are estimated to be ± 0.02 % and ± 0.3 % for density and isobaric heat capacity, respectively. Obviously, these estimates entirely neglect the unknown effects related to purity of samples. Simultaneously, as reported previously,[5,31] a comparison of most results obtained by us with those obtained in other laboratories by different experimental methods can lead to the conclusion that the total uncertainties do not exceed ± 0.05 % and ± 1 % for density and heat capacity, respectively. In our opinion, however, this is a rather pessimistic estimation, and we believe that the uncertainties are better.

In the next step, the isentropic and isothermal compressibilities, κ_S and κ_T, as well as the internal pressures, P_{int}, and molar isochoric heat capacities C_V were calculated as a function of temperature and pressure from the general formulas:

$$\kappa_S = (\rho \cdot u^2)^{-1} \tag{6}$$

$$\kappa_T = \kappa_S + \alpha_p{}^2 \cdot T \cdot (\rho \cdot c_p)^{-1} \tag{7}$$

$$P_{\text{int}} = T \cdot \alpha_p \cdot \kappa_T^{-1} - p \tag{8}$$

$$C_V = C_p - \alpha_p{}^2 \cdot M \cdot T \cdot (\rho \cdot \kappa_T)^{-1} \tag{9}$$

where C_p is the molar isobaric heat capacities and M is the molecular weight. The values of $\rho(p,T)$, $\alpha_p(p,T)$, $\kappa_S(p,T)$, $\kappa_T(p,T)$, $C_p(p,T)$, and $C_V(p,T)$ are presented in Tables 5 to 8. The values of $P_{\text{int}}(p,T)$ are summarized in Table 1 of the Supporting Information (SI). Additionally, in Table 2 of the SI, the ratios of heat capacities $\gamma(p,T)$ are given.

As seen from Table 5, the densities increase monotonically with increasing pressure and decreasing temperature. A maximum change of the density with changing pressure occurs near the atmospheric pressure. In other words, with increasing pressure the changes of the density are smaller. To make the densities obtained in this work in the temperature and pressure ranges from (293.15 to 318.15) K and (0.101 to 101) MPa immediately usable for engineering purposes, the density data are also correlated with a Tait equation in form

$$\rho(T,p) = \rho_0(T,p_0)/[C \cdot \ln(p + B(T)/(p_0 + B(T)))] \tag{10}$$

where ρ_0 is the temperature-dependent density at the reference (atmospheric) pressure p_0 (here 0.101325 MPa) and $B(T) = A_1 + A_2 \cdot (T/100) + A_3 \cdot (T/100)^2$ is the temperature-dependent Tait coefficient. This equation is similar to that of Dymond and Malhotra[32] with the exception that the parameter C is treated as a temperature-independent constant. Respective coefficients are summarized in Table 9. The correlation represents our data with the mean deviation of ± 0.03 kg·m^{-3} which corresponds excellently with the estimated uncertainty in compressed liquids.

Table 7. Isentropic and Isothermal Compressibilities (κ_S and κ_T) Calculated by the Use of the Acoustic Method for 2-Ethyl-1-hexanol at Various Temperatures (T) and Pressures (p)

	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			κ_S/TPa^{-1}			
0.101[a]	672.61	693.98	716.32	739.69	764.15	789.79
10	616.7	634.7	653.4	672.8	693.0	713.9
20	571.4	586.9	602.9	619.4	636.5	654.2
30	533.8	547.3	561.3	575.7	590.5	605.7
40	501.8	513.9	526.2	538.9	551.9	565.3
50	474.2	485.0	496.0	507.4	518.9	530.8
60	450.0	459.7	469.7	479.9	490.3	500.9
70	428.5	437.4	446.4	455.7	465.1	474.6
80	409.2	417.4	425.7	434.1	442.6	451.3
90	391.9	399.4	407.0	414.7	422.5	430.4
100	376.1	383.0	390.0	397.2	404.3	411.6
			κ_T/TPa^{-1}			
0.101[a]	785.1	809.6	835.1	861.8	889.6	918.7
10	718.0	738.5	759.6	781.6	804.4	828.1
20	663.6	681.0	699.0	717.6	736.8	756.7
30	618.4	633.5	649.2	665.3	681.8	698.8
40	580.0	593.4	607.2	621.3	635.8	650.6
50	546.9	558.9	571.1	583.7	596.5	609.6
60	517.9	528.7	539.7	551.0	562.4	574.1
70	492.2	502.0	512.0	522.2	532.5	543.0
80	469.3	478.2	487.3	496.6	506.0	515.5
90	448.6	456.8	465.2	473.7	482.3	491.0
100	429.9	437.5	445.2	453.0	460.9	468.9

[a] Calculated from direct measurements of density and speed of sound at atmospheric pressure.

Table 8. Isobaric Coefficient of Thermal Expansion (α_p) Calculated by the Use of the Acoustic Method for 2-Ethyl-1-hexanol at Various Temperatures (T) and Pressures (p)

	$\alpha_p \cdot 10^4$/ K^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
0.101[a]	8.75	8.85	8.96	9.06	9.17	9.28
10	8.32	8.40	8.49	8.57	8.66	8.75
20	7.95	8.02	8.09	8.16	8.24	8.31
30	7.63	7.69	7.75	7.81	7.87	7.94
40	7.35	7.40	7.45	7.51	7.56	7.62
50	7.09	7.14	7.19	7.24	7.28	7.33
60	6.87	6.91	6.95	7.00	7.04	7.08
70	6.67	6.70	6.74	6.78	6.82	6.86
80	6.48	6.51	6.55	6.58	6.62	6.66
90	6.31	6.34	6.37	6.41	6.44	6.47
100	6.15	6.18	6.21	6.24	6.27	6.30

[a] Calculated from direct measurements of density at atmospheric pressure.

Table 9. Coefficient of the Tait Correlation (eq 10) and Its Mean Deviation δ for the Density of 2-Ethyl-1-hexanol in the Temperature and Pressure Ranges from (293.15 to 318.15) K and (0.101 to 101) MPa, Respectively

C	A_1	A_2	A_3	δ/kg·m^{-3}
0.08377	409.801	−140.562	12.8018	0.03

It should be noted that since a very good agreement between the densities of ethanol, heptane, and their binary mixtures determined by one of us from the speed of sound measurements[33] with those obtained from direct measurements has been reported by independent investigators,[34] the acoustic method used by us yields in point of fact reliable values of the density under elevated pressures.

The molar isobaric heat capacities for 2-ethyl-1-hexanol increase monotonically with increasing temperature (at constant pressure) and decrease monotonically with increasing pressure (at constant temperature). However, the effect of pressure on the heat capacity is much smaller than that of temperature (Table 6). The decrease of C_p with increasing pressure can be treated as an indicator of the increasing molecular order because C_p is related to entropy S ($C_p = T \cdot (\partial S/\partial T)_p$). Similar results have been obtained for previous investigated 1-alkanols[2,21] as well as butanediols[3] and propanediols.[4] Obtained in this work pressure−temperature dependencies of C_V are similar to those of C_p; however, the C_V is here almost pressure-independent (especially at lower temperatures, Figure 3). The ratio of heat capacities decreases very slightly with increasing temperature and decreases more evidently with increasing pressure (SI, Table 2).

In turn, the dependency of the κ_S on temperature is almost linear. The linearity of the isobars increases with increasing pressure, and at the same time, the higher the pressure the smaller is temperature dependence. On the other hand, the dependency of the κ_S on pressure has evidently nonlinear character, and the nonlinearity of the κ_S isotherms increases with increasing temperature (Figure 4). Generally, the isentropic compressibility increases with increasing temperature at constant pressure and decreases with increasing pressure at constant temperature. It is not surprising that the shapes of the isobars and isotherms of the κ_T are identical to those of the κ_S (Figure 4) since the curves are only translated by the term $T \cdot \alpha_p^{\,2} \cdot (\rho \cdot c_p)^{-1}$. This term shows weak temperature dependence (increases with increasing temperature) and considerable pressure dependence (decreases with increasing pressure). Simultaneously, both the isentropic and the isothermal compressibilities depend significantly on the pressure for pressures close to the atmospheric one, while the pressure effect on the compressibility is gradually decreasing with increasing pressure. The overall uncertainties of the reported by us compressibility values are estimated to be ± 0.15 % and ± 0.3 % for κ_S and κ_T, respectively.

The dependencies of the isobaric coefficient of thermal expansion on pressure and temperature (a graphic presentation has been omitted) are similar to those of the isentropic compressibility. Generally, the α_p (Table 8) decreases monotonically with increasing pressure and increases monotonically with increasing temperature. The estimated uncertainty of the α_p is ± 1 %.

As for the other alkanols,[2] the internal pressure (the uncertainty of P_{int} in this work is estimated to be ± 1 % at most unfavorable conditions) changes linearly with the temperature along the isobars (SI, Table 1 and Figure 5). Simultaneously, for the pressures (30 to 50) MPa the temperature coefficients of internal pressure $(\partial P_{\text{int}}/\partial T)_p$ are near zero, below 30 MPa are negative, and above 50 MPa are positive.

The pressure dependence of P_{int} for 2-ethyl-1-hexanol shows evidently a maximum along the isotherms (Figure 5). The maxima

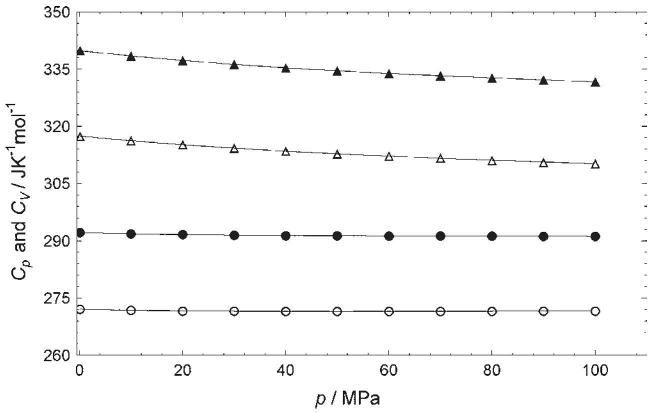

Figure 3. Isobaric and isochoric molar heat capacities, C_p and C_V, plotted against the function of pressure p for temperatures: 293.15 K; ●, C_p, and ○, C_V and 318.15 K; ▲, C_p and △, C_V.

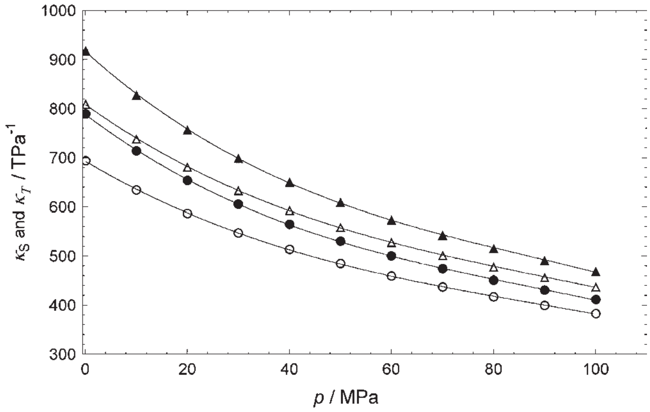

Figure 4. Isentropic and isothermal compressibilities plotted against the function of pressure p for temperatures: 293.15 K; ●, κ_S, and ○, κ_T and 318.15 K; ▲, κ_S and △, κ_T.

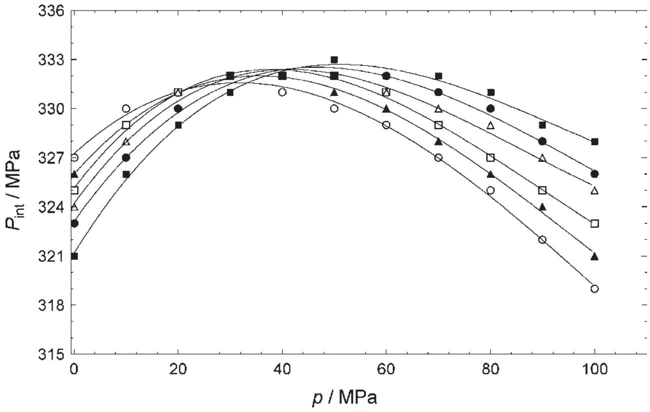

Figure 5. Internal pressure P_{int} plotted against the function of pressure p for various temperatures: ○, 293.15 K; ▲, 298.15 K; □, 303.15 K; △, 308.15 K; ●, 313.15 K; and ■, 318.15 K.

of the P_{int} isotherms for 2-ethyl-1-hexanol are shifted toward higher pressures with increasing temperature; that is, for $T = 293.15$ K the maximum lies at about 30 MPa, whereas for $T = 318.15$ K it lies in the vicinity of 50 MPa. It is important to mention that internal pressure isotherms are known to reach a maximum with increasing pressure (i.e., for some $p_{\max}$ $(\partial P_{\text{int}}/\partial p)_T = 0$) for various liquids;[35] that is, there is a general rule.

Generally, the results show that a very interesting similarity is observed between 2-ethyl-1-hexanol studied in this work and 1-octanol studied previously.[2] This similarity is not surprising because both alkanols (structural isomers) have the same molecular weight and very similar dipole moment, that is, (1.74 and 1.76) D for 2-ethyl-1-hexanol and 1-octanol, respectively,[6] and show relatively small difference between both the speeds of sound and isentropic compressibilities.

CONCLUSION

The pressure−temperature effects on the speeds of sound and related thermodynamic properties of 2-ethyl-1-hexanol are emphasized. Both fundamental material constants, that is, the isobaric coefficients of thermal expansion and isothermal compressibilities, decrease with increasing pressure and decreasing temperature. Furthermore, for pressures close to the atmospheric one, both mentioned material constants depend significantly on pressure, while with increasing pressure its effect on these material constants is gradually decreasing.

Moreover, a new temperature dependence of the densities in the temperature range from (278.15 to 363.15) K at atmospheric pressure is reported. The ambient pressure and compressed liquid densities are also correlated with a Tait equation within the uncertainty of ± 0.03 kg·m^{-3} which is well within the estimated uncertainty for the densities under elevated pressures.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Values of internal pressure P_{int} and ratio of heat capacities γ for 2-ethyl-1-hexanol in the temperature range from (293.15 to 318.15) K and at pressures up to 100 MPa. This material is available free of charge via the Internet at http://pubs.acs.org.

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