Study of the Acoustic and Thermodynamic Properties of 1,2- and 1,3-Butanediol 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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The speeds of sound in 1,2- and 1,3-butanediol have been measured in the temperature range from (293 to 318) K at pressures up to 101 MPa by the pulse−echo−overlap method. The densities of both the butanediol isomers have been measured in the temperature range from (288.15 to 363.15) K under atmospheric pressure with a vibrating tube densimeter. From the experimental results the densities, isobaric heat capacities, isobaric coefficients of thermal expansion, isentropic and isothermal compressibilities, as well as the internal pressure as function of temperature and pressure have been calculated. The effects of pressure and temperature are discussed.

Introduction

Thermodynamic properties of organic liquids are of considerable interest from both the fundamental as well as practical points of view. However, the experimental data of the thermodynamic properties at elevated pressures, which are of particular importance in the study of the liquid state, are still yet rather scarce. This refers, in particular, to associating liquids that are key substances in the chemical industry. Their structure and thermodynamics are still not properly understood.

In the last decades, the acoustic method has found wide acceptance as a satisfactory and relatively simple tool of determining thermodynamic properties of compressed liquids. The acoustic method is based on measurements of the speed of sound as functions of temperature and pressure.[1−4] Sun et al.[2] have even claimed that the accuracy attained by the acoustic method is much better than that of direct measurements.

This work is aimed at the effects of pressure and temperature on the speed of sound in two isomeric butanediols (1,2- and 1,3-butanediol) in order to provide experimental data for the calculation of several important quantities under elevated pressures, such as the density, isobaric heat capacity, isobaric coefficient of thermal expansion, isentropic and isothermal compressibilities, as well as the internal pressure. Additionally, measurements of the densities of both the isomers under test at atmospheric pressure and temperatures ranging from (288.15 to 363.15) K are an integral part of this work. To the best of our knowledge, the speeds of sound under elevated pressures for 1,2- and 1,3-butanediol have not been reported yet. Densities at atmospheric pressure reported in literature are rather scattered.

Experimental Section

Materials. 1,2- and 1,3-Butanediol (anhydrous, packaged under nitrogen in Sure/Seal bottles) used in this study were supplied by Aldrich and were used without further purification. According to the supplier, the purity of the materials on mass fraction were > 0.99 and > 0.995, respectively, while the water contents declared by the supplier were $< 1\cdot10^{-3}$ and $< 3\cdot10^{-5}$, respectively. In practice, the mass fractions of water in both the 1,2- and 1,3-butanediol determined in our laboratory by the Karl Fischer method were $3\cdot10^{-4}$ and $1\cdot10^{-4}$, respectively. The refractive indexes n_D (T = 298.15 K) measured with an Abbe refractometer RL3 (uncertainty ± 0.0002) were 1.4370 and 1.4384 for 1,2- and 1,3-butanediol, respectively. These results are in reasonable agreement with the literature data[5−7] since the average absolute deviations ($\mathrm{AAD} = (100/n)\sum_{i=1}^{n}|n_{\mathrm{D,lit}} - n_{\mathrm{D,exp}}/n_{\mathrm{D,lit}}|_i$) are of 0.035 % and 0.031 %, respectively. Each sample was degassed in an ultrasonic cleaner just before the measurements.

Methods and Apparatus. The speed of sound at a frequency of 2 MHz was measured under atmospheric and elevated pressures using two measuring sets designed and constructed in our laboratory. Two measuring vessels of the same acoustic path and construction (a single transmitting−receiving ceramic transducer and an acoustic mirror), one for the measurements under atmospheric pressure and another one for measurements under elevated pressures, have been used. Both sets operate on the principle of the pulse−echo−overlap method that has been applied in our laboratory for many years. More details of the high-pressure device and the method of the speed of sound measurements can be found in previous papers.[8,9]

The pressure was measured with a strain gauge measuring system (Hottinger Baldwin System P3MD) with an uncertainty better than 0.15 %. The temperature was measured using an Ertco Hart 850 platinum resistance thermometer (NIST certified) with an uncertainty of ± 0.05 K. All temperatures are expressed in the ITS-90. During the measurements, a stability of ± 10 mK was achieved over the whole operating range. Re-distilled water, degassed by boiling, was used as a standard for the calibration of the apparatus for the speed of sound measurements. Its electrolytic conductivity was $1\cdot10^{-4}\ \Omega^{-1}\cdot\mathrm{m}^{-1}$. The values of the speed of sound in water at atmospheric pressure were taken from the polynomial proposed by Marczak[10] and, at elevated pressures, from the Kell and Whalley polynomial.[11]

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 $\pm\ 0.5\ \mathrm{m\cdot s^{-1}}$ and $\pm\ 1\ \mathrm{m\cdot s^{-1}}$, respectively.

The densities at atmospheric pressure were measured by means of a vibrating-tube densimeter DMA 5000 (Anton Paar).

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Table 1. Speed of Sound (*u*) in 1,2- and 1,3-Butanediol 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}
1,2-Butanediol						
0.1	292.93	1466.45	298.10	1451.31	303.18	1436.45
15.20	292.88	1528.18	298.15	1513.55	303.13	1500.00
30.40	292.88	1583.21	298.15	1569.21	303.13	1556.36
45.60	292.87	1634.28	298.15	1621.06	303.13	1608.77
60.79	292.87	1681.52	298.15	1668.75	303.13	1657.14
75.99	292.87	1726.00	298.15	1713.76	303.13	1702.16
91.19	292.87	1767.98	298.15	1755.94	303.13	1745.03
101.32	292.87	1794.72	298.15	1783.03	303.13	1772.29
0.1	308.17	1421.82	313.35	1406.66	318.15	1392.60
15.20	308.13	1486.59	313.31	1472.75		
30.40	308.13	1543.51	313.30	1530.35		
45.60	308.13	1596.48	313.30	1583.69		
60.79	308.12	1645.52	313.30	1633.40		
75.99	308.13	1690.99	313.30	1679.32		
91.19	308.12	1734.25	313.30	1723.02		
101.32	308.13	1761.67	313.30	1750.42		
1,3-Butanediol						
0.1	292.92	1537.73	298.20	1523.31	303.17	1509.72
15.20	292.87	1592.09	298.15	1578.42	303.13	1565.32
30.39	292.87	1641.04	298.15	1627.99	303.13	1615.87
45.59	292.86	1686.46	298.15	1673.84	303.13	1662.19
60.79	292.87	1729.45	298.15	1717.36	303.13	1705.98
75.99	292.86	1770.09	298.15	1758.28	303.13	1747.28
91.18	292.86	1808.68	298.15	1797.29	303.13	1786.71
101.32	292.86	1833.59	298.15	1822.09	303.13	1811.64
0.1	308.16	1495.99	313.14	1482.26	318.32	1467.86
15.20	308.13	1552.43	313.11	1539.62	318.29	1526.20
30.39	308.13	1603.47	313.11	1591.21	318.29	1578.39
45.59	308.12	1650.63	313.11	1639.14	318.29	1626.98
60.79	308.13	1694.59	313.11	1683.62	318.29	1671.97
75.99	308.12	1736.67	313.11	1725.92	318.29	1714.82
91.18	308.13	1776.31	313.11	1765.94	318.29	1755.19
101.32	308.11	1801.68	313.11	1791.50	318.29	1781.07

The uncertainty was estimated to be better than ± $5 \cdot 10^{-2}$ kg·m^{-3}, whereas the repeatability was estimated to be better than ± $5 \cdot 10^{-3}$ kg·m^{-3}. The instrument was calibrated with air and re-distilled, freshly degassed (by boiling) water with the above electrolytic conductivity. This type of densimeter can be used to perform measurements in a temperature range from (273.15 to 363.15) K and has a built-in correction procedure for viscosity effects on the measured density. All the results of density measurements presented here include viscosity corrections.

Measurement Results

Speeds of Sound. The experimental speeds of sound in 1,2- and 1,3-butanediol have been measured within temperature ranges from (293 to 313) K and from (293 to 318) K, respectively, as well as at pressures up to 101 MPa. The experimental results are collected in Table 1. A comparison with literature values of the speed of sound at atmospheric pressure is shown in Table 2. The respective values at rounded up temperatures have been obtained by the following second-order polynomials using regression coefficients obtained from the temperature dependencies of the speeds of sound under atmospheric pressure:

$$u_0 = \sum_{j=0}^{2} b_j T^j \tag{1}$$

The regression coefficients b_j determined by the least-squares method (to reduce the number of nonzero coefficients, the stepwise rejection procedure was used) are reported in Table 4. Because the mean deviations (as well as residual deviations) of the fit are small, the speeds estimated from the regression functions are equal to the raw data within the limits of the measurement uncertainties.

As seen from Table 2, our results for 1,3-butanediol are in very good agreement (± 0.02 %) with those reported earlier by Zorębski.[15] On the other hand, a much worse agreement (± 0.26 %) is observed with the results of George and Sastry[6] (they declared an uncertainty of ± 1.6 m·s^{-1}). In turn, our result for 1,2-butanediol at $T = 298.15$ K is in satisfactory agreement (+ 0.06 %) with those of George and Sastry,[6] whereas the agreement with those of Hawrylak et al.[12] is rather worse (+ 0.13 %). Furthermore, at $T =$ (308.15 and 318.15) K, the agreement is distinctly worse (deviations up to + 0.26 %). Moreover, our values for 1,2-butanediol are in each case smaller (i.e., a systematic deviation is observed). Generally, a comparison of the speeds of sound reported in this work with the literature values given in Table 2 results in average absolute deviations (AAD $= (100/n)\sum_{i=1}^{n}|u_{0,\mathrm{lit}} - u_{0,\mathrm{exp}}/u_{0,\mathrm{lit}}|_i$) of 0.15 % and 0.08 % for 1,2- and 1,3-butanediol, respectively. In our opinion, the differences are related to the purity as well as to the relatively high viscosity and hygroscopicity of the diols, especially in the case of 1,3-butanediol. We would like to point out that some of the literature data, mostly old and less reliable ones (low purity and/or systematic errors) have been omitted consciously in Table 2. For example, an evidently poor agreement is observed for 1,3-butanediol with the old data of Marks[17] (reported in the form of a linear equation); here a systematic deviation is ca. − 0.3 %.

A graphic presentation of the $u(p,T)$ surfaces (i.e., fitted dependencies of the experimental speeds of sound on pressure and temperature for the diols under test) are given in Figure 1. In this figure, the experimental points are not shown for clarity. The form of the equation used for smoothing out the u, p, and T values is given in the next section. As can be seen from Figure 1, for a given pressure, the speed of sound in the liquids under test is decreasing almost linearly with increasing temperature, while the pressure dependencies at constant temperatures are evidently nonlinear. Moreover, with increasing pressure its effect on the speed of sound becomes smaller.

Densities at Atmospheric Pressure. The experimental densities ρ_0 of both the butanediols measured at atmospheric pressure in the temperature range from (288.15 to 363.15) K are listed in Table 3 together with some representative literature values. Generally, the literature survey shows, however, that the values published by various authors are rather scattered. Most likely, those discrepancies are caused mainly by the water contents (especially 1,3-butanediol absorbs water very readily during the storing or handling). A comparison of the densities of 1,2-butanediol reported this work with the literature values given in Table 3 results in an average absolute deviation (AAD $= (100/n)\sum_{i=1}^{n}|\rho_{0,\mathrm{lit}} - \rho_{0,\mathrm{exp}}/\rho_{0,\mathrm{lit}}|_i$) of 0.05 %. A similar comparison for 1,3-butanediol results in an AAD = 0.06 %. This comparison reveals that the experimental uncertainties given in the literature sources are very often considerably overestimated.

Some data showing great systematic deviations have been consciously omitted. For example, the densities reported by Sun et al.[21] are considerably greater than those reported in this work (deviations up to + 0.35 % for both the butanediol isomers) and are the greatest ones attainable in the literature. In our opinion, the values of Sun et al.[21] are not very reliable. This is caused by the low purity of the samples (most probably contaminated by water) and/or a systematic experimental error in their work (a high-pressure pycnometer was used for measurements at atmospheric pressure). Grineva and Zhurav-

Table 2. Speeds of Sound (u) in 1,2- and 1,3-Butanediol at Atmospheric Pressure (p_o) and Various Temperatures (T)

	1,2-butanediol u/m·s^{-1}		1,3-butanediol u/m·s^{-1}	
T/K	exp.	lit.	exp.	lit.
293.15	1465.80		1537.08	1537.75,[13] 1539[14]
298.15	1451.16	1452.0,[6] 1453.0[12]	1523.45	1523.14,[15] 1522.1,[6] 1524.1,[12] 1523.95[16]
303.15	1436.52		1509.77	
308.15	1421.88	1423.8,[6] 1423.6[12]	1496.02	1495.81,[15] 1492.1,[6] 1495.6 [12]
313.15	1407.24		1482.22	
318.15	1392.60	1396.2,[6] 1395.2[12]	1468.35	1468.20,[15] 1472.0,[6] 1469.0[12]

lev[19] have reached similar conclusions. However, it must be pointed out that "the estimated absolute accuracy" of density given by Sun et al.[21] is ± 0.25 % and seems to be real enough. Less reliable are also the values given by Czechowski et al.,[22] which has also been suggested by Grineva and Zhuravlev.[19] The systematic deviations up to + 0.13 % (for 1,2-butanediol) and + 0.23 % (for 1,3-butanediol) are considerable ones. Therefore, the latter values have been omitted in Table 3. Also the data for 1,3-butanediol reported by Apaev et al.[23] have been omitted. Here, systematic deviations up to + 0.2 % are present.

The densities ρ_0 of both butanediols were approximated by the second-order polynomials:

$$\rho_0 = \sum_{j=0}^{2} b_j T^j \tag{2}$$

where b_j are coefficients determined as above. The corresponding values are given in Table 4. The fit seems to be very good, and the mean deviations do not exceed the estimated repeatability. It is interesting that our results for 1,3-butanediol are co-incident with the data reported by McDuffie et al.[24] (in the form a linear equation). In the same validity range of both equations, the McDuffie et al. densities are somewhat smaller than those reported by us (i.e., systematic deviations up to − 0.03 % in the temperature range from (288.15 to 313.15) K are observed).

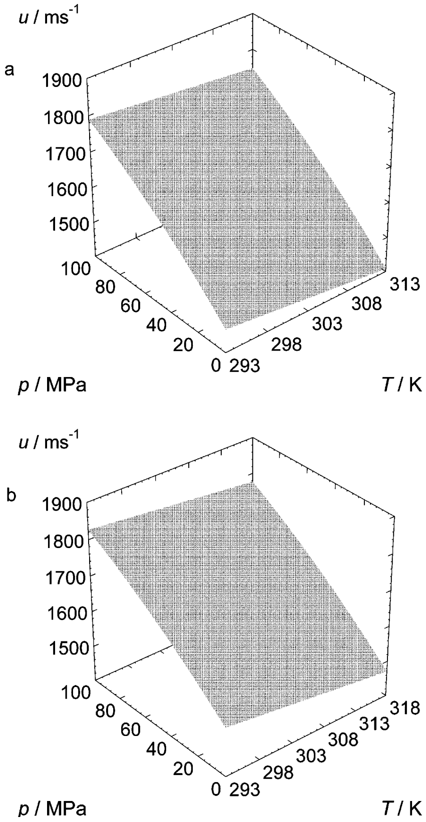

Figure 1. Speed of sound (u) as function of pressure (p) and temperature (T): (a) $u(p,T)$ smoothed surface for 1,2-butanediol; (b) $u(p,T)$ smoothed surface for 1,3-butanediol. For clarity, experimental points are not shown.

Table 3. Densities (ρ_o) at Atmospheric Pressure and Various Temperatures (T) for 1,2- and 1,3-Butanediol

	1,2-butanediol ρ/kg·m^{-3}			1,3-butanediol ρ/kg·m^{-3}	
T/K	exp.	lit.	T/K	exp.	lit.
288.15	1005.78	1005.7[18]	288.15	1006.753	
293.15	1002.119		293.155	1003.52	1003.42[19]
298.15	998.408	998.86(1)[6] 998.87[12] 998.1[18] 999.00[7]	298.15	1000.231	1000.26[15] 1000.03(4)[6] 1000.89[12] 1000.42[16] 1000.21[7]
303.155	994.659	995.31[12]	303.155	996.895	997.54[12] 996.6[19] 997.78[20]
308.155	990.872	991.42(7)[6] 991.43[12] 990.9[18]	308.15	993.524	993.83[15] 994.22(1)[6] 994.20[12]
313.155	987.048	987.63[12]	313.155	990.116	991.38[12] 989.7[19]
318.155	983.185	983.93(5)[6] 983.92[12]	318.156	986.665	987.08[15] 988.70(9)[6] 988.71[12]
323.15	979.285		323.155	983.181	982.7[19]
328.155	975.354	976.09(3)[6]	328.156	979.654	979.18(9)[6]
333.155	971.386		333.156	976.087	975.6[19]
338.156	967.378	968.11(2)[6]	338.155	972.476	971.91(4)[6]
343.15	963.333		343.15	968.825	968.3[19]
348.156	959.256		348.156	965.14	
353.15	955.143		353.15	961.411	
358.15	950.989		358.15	957.637	
363.15	946.804		363.15	953.825	

Table 4. Coefficients b_j of the Polynomials (1) and (2) for the Speed of Sound u (within the Temperature Range from (293.15 to 318.15) K) and Density ρ (within the Temperature Range from (288.15 to 363.15) K) Together with Mean Deviations (δ)

	b_o	b_1	b_2	δ
		1,2-Butanediol		
u/m·s^{-1}	2324.155	−2.92805		0.02[a]
ρ/kg·m^{-3}	1155.494	$-3.07609 \cdot 10^{-1}$	$-7.35425 \cdot 10^{-4}$	0.005[b]
		1,3-Butanediol		
u/m·s^{-1}	2228.891	−2.00132	$-1.22332 \cdot 10^{-3}$	0.03[a]
ρ/kg·m^{-3}	1125.967	$-1.81193 \cdot 10^{-1}$	$-8.04321 \cdot 10^{-4}$	0.005[b]

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

Calculations of Material Constants at Elevated Pressures

A detailed description of the algorithm was presented in previous works;[25,26] therefore, only a brief survey is given here. First of all, the densities and heat capacities at elevated pressures up to 100 MPa were calculated. To this end, a modified numerical procedure proposed by Sun et al.,[2] based on the earlier suggestions of Davies and Gordon,[1] has been applied. Generally, the procedure is based on the speeds of sound measured as functions of temperature and pressure as well as on the density and heat capacity measured as functions of temperature at atmospheric pressure.

Table 5. Coefficients of Equation 3 Together with Mean Deviations ($\delta(u)$)

j	α_{1j}	α_{2j}	α_{3j}	$\delta(u)/\mathrm{m{\cdot}s^{-1}}$
		1,2-Butanediol		
0	0.3425978	$3.086167{\cdot}10^{-4}$		0.24
1		$-2.645628{\cdot}10^{-7}$		
2	$-1.281502{\cdot}10^{-6}$			
		1,3-Butanediol		
0	0.3877077	$2.821970{\cdot}10^{-4}$		0.18
1				
2	$-1.424206{\cdot}10^{-6}$		$-8.583665{\cdot}10^{-13}$	

As in previous papers from our laboratory,[25−27] the equation suggested by Sun et al.[2] was chosen for smoothing out the speed of sound, pressure, and temperature values:

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

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} together with mean deviations are given in Table 5.

The pressure dependencies of the density and heat capacity are given by the well-known thermodynamic relationships:

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

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

where α_p is the isobaric coefficient of thermal expansion and c_p is the specific isobaric heat capacity. Simultaneously, α_p can be calculated from the relation:

$$\alpha_p = -\rho^{-1}(\partial\rho/\partial T)_p \tag{6}$$

The above relations form a complete first-order differential equation set 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 (reference isobar at atmospheric pressure). In the calculations, the temperature dependence of the isobaric heat capacity of 1,2-butanediol and 1,3-butanediol at atmospheric pressure reported by Zorębski and co-workers[28,29] was used.

Finally, the procedure gives the isobars of density and heat capacity in the form of a polynomial form similar to eqs 1 and 2. Generally, the values of the heat capacities obtained by the above method seem to be less reliable than the values of densities,[25,26] which results from the principle of the method. Taking into account the uncertainty of the measured speed of sound and analyze using the method suggested by Sun et al.,[2] the respective uncertainties are estimated to be evidently better than ± 0.3 % and ± 0.02 % for the heat capacity and density, respectively.

In turn, the isobaric coefficients of thermal expansion and isentropic and isothermal compressibilities were calculated. The latter two quantities were calculated from the formulas:

$$\kappa_S = (\rho{\cdot}u^2)^{-1} \tag{7}$$

$$\kappa_T = \kappa_S + \alpha_p{}^2{\cdot}T{\cdot}(\rho{\cdot}c_p)^{-1} \tag{8}$$

whereas eq 6 was used for the calculation of α_p.

Table 6. Densities (ρ) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	$\rho/\mathrm{kg{\cdot}m^{-3}}$ at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			1,2-Butanediol			
0.1[a]	1002.11	998.40	994.65	990.87	987.05	983.19
10	1007.19	1003.59	999.95	996.28	992.58	
20	1012.06	1008.55	1005.01	1001.44	997.84	
30	1016.69	1013.27	1009.82	1006.34	1002.83	
40	1021.11	1017.77	1014.40	1011.01	1007.58	
50	1025.35	1022.08	1018.79	1015.47	1012.12	
60	1029.43	1026.23	1023.00	1019.75	1016.47	
70	1033.36	1030.22	1027.05	1023.86	1020.65	
80	1037.15	1034.07	1030.96	1027.83	1024.68	
90	1040.82	1037.79	1034.74	1031.66	1028.56	
100	1044.38	1041.40	1038.40	1035.37	1032.33	
			1,3-Butanediol			
0.1[a]	1003.52	1000.23	996.90	993.53	990.12	986.67
10	1008.12	1004.91	1001.67	998.39	995.08	991.72
20	1012.55	1009.42	1006.26	1003.07	999.84	996.58
30	1016.79	1013.74	1010.66	1007.54	1004.39	1001.20
40	1020.88	1017.89	1014.87	1011.83	1008.75	1005.64
50	1024.81	1021.89	1018.93	1015.95	1012.94	1009.89
60	1028.61	1025.74	1022.85	1019.92	1016.97	1013.99
70	1032.29	1029.47	1026.63	1023.76	1020.87	1017.94
80	1035.85	1033.09	1030.30	1027.48	1024.64	1021.76
90	1039.30	1036.59	1033.85	1031.08	1028.29	1025.46
100	1042.66	1039.99	1037.30	1034.57	1031.83	1029.05

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

At last, the internal pressures were calculated from the formula:

$$P_{\text{int}} = T{\cdot}\alpha_p{\cdot}\kappa_T{}^{-1} - p \tag{9}$$

It is worthy of notice that in the literature the definition of the internal pressure which neglects p may be often found. At low pressures, mostly at atmospheric pressure, where $p \ll T{\cdot}\alpha_p/\kappa_T$, the second term in eq 9 can be neglected without significant error. However, it must be included at high pressures.

It must also be pointed out that the method used in this work is essentially based on the assumed negligibility of the sound wave absorption (the acoustic wave of low frequency and amplitude is used, and no dispersive effect is present); thus, the Newton−Laplace equation (eq 7) can be used. In this case, the speed of sound may be regarded as a thermodynamic quantity. All the values obtained by this method are presented in Tables 6 to 11.

As seen from Table 6, the densities of both the diols 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. For 1,2-butanediol, in contrary to the atmospheric pressure, only one data set for comparison at elevated pressures has been found in the literature. It appears that the values of density estimated by us for 1,2-butanediol are in a very good agreement with those obtained directly by Geyer et al.; [18] the comparison under elevated pressures gives an AAD = 0.024 %. At the same time, including the results at atmospheric pressure, the AAD is 0.021 %. However, as can be seen in Figure 2, the deviations show a rather systematic shift. Recently, quite independently, a very good agreement between the densities of ethanol, heptane, and their binary mixtures determined from speed of sound measurements[30] with those obtained from direct measurements has been reported too.[31] A comparison shows that the acoustic method used by us yields reliable values of the density under elevated pressures.

Table 7. Molar Isobaric Heat Capacities (C_p) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	C_p/J·K^{-1}·mol^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
1,2-Butanediol						
0.1[a]	228.2	230.9	233.6	236.3	239.0	241.6
10	227.6	230.3	232.9	235.6	238.2	
20	227.0	229.7	232.3	234.9	237.6	
30	226.4	229.1	231.7	234.3	236.9	
40	225.9	228.5	231.2	233.8	236.3	
50	225.4	228.0	230.6	233.2	235.8	
60	224.9	227.6	230.1	232.7	235.2	
70	224.5	227.1	229.7	232.2	234.7	
80	224.1	226.7	229.2	231.7	234.3	
90	223.7	226.2	228.8	231.3	233.8	
100	223.3	225.8	228.4	230.9	233.3	
1,3-Butanediol						
0.1[b]	216.6	219.7	222.8	226.0	229.3	232.5
10	215.9	219.0	222.2	225.3	228.6	231.8
20	215.4	218.4	221.6	224.7	227.9	231.1
30	214.8	217.9	221.0	224.1	227.3	230.5
40	214.3	217.4	220.5	223.6	226.7	229.9
50	213.9	216.9	219.9	223.1	226.2	229.4
60	213.4	216.4	219.5	222.6	225.7	228.8
70	213.0	216.0	219.0	222.1	225.2	228.3
80	212.5	215.5	218.6	221.6	224.7	227.8
90	212.1	215.1	218.1	221.2	224.3	227.4
100	211.7	214.7	217.7	220.7	223.8	226.9

[a] Ref 28. [b] Ref 29.

Table 8. Isentropic Compressibilities (κ_S) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	κ_S/TPa^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
1,2-Butanediol						
0.1[a]	464.44	475.62	487.19	499.18	511.59	524.46
10	437.3	447.2	457.3	467.8	478.6	
20	413.9	422.6	431.7	440.9	450.5	
30	393.4	401.3	409.4	417.7	426.3	
40	375.4	382.6	389.9	397.4	405.1	
50	359.3	365.9	372.6	379.4	386.4	
60	344.8	350.9	357.0	363.3	369.7	
70	331.7	337.3	343.0	348.8	354.7	
80	319.7	324.9	330.3	335.6	341.1	
90	308.7	313.6	318.6	323.6	328.7	
100	298.6	303.2	307.8	312.5	317.3	
1,3-Butanediol						
0.1[a]	421.78	430.77	440.08	449.72	459.71	470.08
10	400.9	408.9	417.2	425.8	434.7	443.8
20	382.4	389.7	397.2	405.0	412.9	421.1
30	366.1	372.8	379.6	386.6	393.8	401.3
40	351.5	357.6	363.9	370.3	376.9	383.6
50	338.2	343.9	349.7	355.6	361.7	367.9
60	326.1	331.4	336.8	342.3	347.9	353.6
70	315.0	320.0	325.0	330.1	335.3	340.6
80	304.8	309.4	314.1	319.8	323.7	328.6
90	295.3	299.7	304.0	308.5	313.0	317.6
100	286.5	290.6	294.7	298.8	303.1	307.4

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

Table 9. Isobaric Coefficient of Thermal Expansion (α_p) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	α_p 10^4/ K^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
1,2-Butanediol						
0.1[a]	7.37	7.47	7.57	7.67	7.78	7.89
10	7.12	7.21	7.31	7.40	7.50	
20	6.90	6.98	7.07	7.16	7.25	
30	6.70	6.78	6.86	6.94	7.03	
40	6.52	6.59	6.67	6.75	6.83	
50	6.35	6.42	6.50	6.57	6.64	
60	6.20	6.27	6.34	6.41	6.48	
70	6.05	6.12	6.19	6.26	6.32	
80	5.92	5.99	6.05	6.12	6.18	
90	5.80	5.86	5.92	5.99	6.05	
100	5.68	5.74	5.80	5.86	5.93	
1,3-Butanediol						
0.1[a]	6.52	6.62	6.72	6.83	6.93	7.03
10	6.32	6.42	6.51	6.60	6.70	6.79
20	6.14	6.23	6.31	6.40	6.49	6.58
30	5.97	6.06	6.14	6.22	6.31	6.39
40	5.82	5.90	5.98	6.06	6.14	6.22
50	5.68	5.75	5.83	5.90	5.98	6.06
60	5.55	5.62	5.69	5.76	5.84	5.91
70	5.42	5.49	5.56	5.63	5.70	5.77
80	5.31	5.37	5.44	5.51	5.58	5.65
90	5.20	5.26	5.33	5.39	5.46	5.53
100	5.10	5.16	5.22	5.29	5.35	5.42

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

Table 10. Isothermal Compressibilities (κ_T) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	κ_T/TPa^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
1,2-Butanediol						
0.1[a]	527	541	555	569	584	600
10	496	508	520	533	546	
20	469	479	490	501	513	
30	445	455	464	475	485	
40	424	433	442	451	460	
50	405	413	422	430	439	
60	389	396	404	411	419	
70	373	380	387	395	402	
80	360	366	373	379	386	
90	347	353	359	365	372	
100	335	341	347	352	358	
1,3-Butanediol						
0.1[a]	474	484	496	507	519	532
10	449	459	469	480	490	501
20	428	437	446	455	465	475
30	409	417	426	434	443	452
40	392	400	407	415	423	432
50	377	384	391	398	406	413
60	363	370	376	383	390	397
70	350	356	363	369	375	382
80	339	344	350	356	362	368
90	328	333	338	344	350	355
100	318	323	328	333	338	343

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

On the other hand, for 1,3-butanediol two older data sets have been found in the literature. In this case, however, the agreement between the values of density estimated by us and those reported by McDuffie et al.[24] (variable volume cell with bellows) as well as by Apaev et al.[23] (buoyancy method) is rather unsatisfied (see Figure 3). Generally, McDuffie et al. densities (declared uncertainty ± 0.05 %) are evidently smaller than those estimated by us (a comparison gives an AAD = 0.15 %), whereas Apaev et al. densities (declared uncertainty ± 0.1 %) are evidently greater than those estimated by us (adequate AAD = 0.21 %). It seems that the essential reason is the same as at the atmospheric pressure (i.e., sample purity). Moreover, the calibration procedure of the devices used by the mentioned authors can be also the reason of these discrepancies.

The heat capacities for both the diols increase with increasing temperature (at constant pressure) and decrease with increasing pressure (at constant temperature). However, the effect of pressure on the heat capacity is much smaller than that of temperature (Table 7). Similar results have been obtained for 1-alkanols.[25,30]

Table 11. Internal Pressure (P_{int}) for 1,2- and 1,3-Butanediol at Various Temperatures (T) and Pressures (p)

	P_{int}/MPa at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			1,2-Butanediol			
0.1[a]	410	412	414	415	417	419
10	411	414	416	418	420	
20	411	414	417	420	422	
30	411	415	418	421	424	
40	410	414	418	421	424	
50	409	413	417	421	424	
60	407	412	416	420	424	
70	405	410	414	419	423	
80	403	408	412	417	422	
90	400	405	410	415	420	
100	397	402	408	413	418	
			1,3-Butanediol			
0.1[a]	404	408	411	414	418	420
10	402	407	411	414	418	421
20	400	405	409	413	417	421
30	398	403	407	412	416	420
40	395	400	405	409	414	418
50	391	397	402	407	412	416
60	388	393	399	404	409	414
70	384	389	395	401	406	411
80	379	385	391	397	403	408
90	375	381	387	393	399	405
100	370	377	383	389	396	402

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

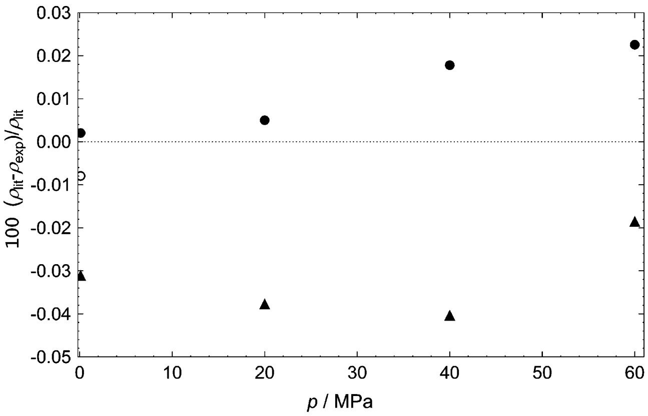

Figure 2. Comparison of densities for 1,2-butanediol as function of pressure (p) shown as the deviation$100\cdot(\rho_{\mathrm{lit}} - \rho_{\mathrm{exp}})/\rho_{\mathrm{lit}}$ between values of this work (ρ_{exp}) and literature values (ρ_{lit}) of Geyer et al.[18] at the temperatures ○, 288.15 K; ▲, 298.15 K; and ●, 308.15 K.

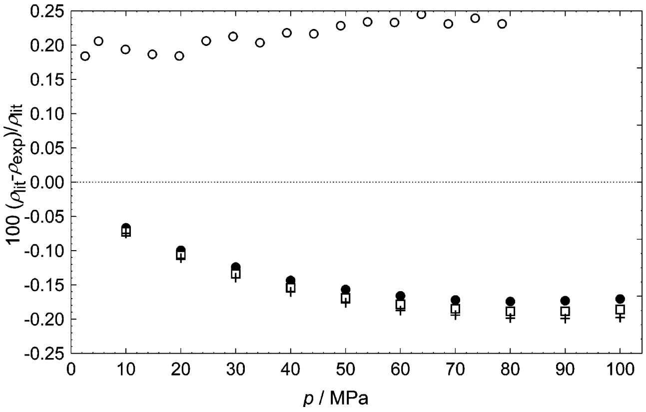

Figure 3. Comparison of densities for 1,3-butanediol as function of pressure (p) shown as the deviation$100\cdot(\rho_{\mathrm{lit}} - \rho_{\mathrm{exp}})/\rho_{\mathrm{lit}}$ between values of this work (ρ_{exp}) and literature values (ρ_{lit}) of Apaev et al.[23] at the temperature ○, 302.15 K; McDuffie et.al.[24] at the temperatures ●, 293.15 K; □, 298.15 K; and +, 303.15 K.

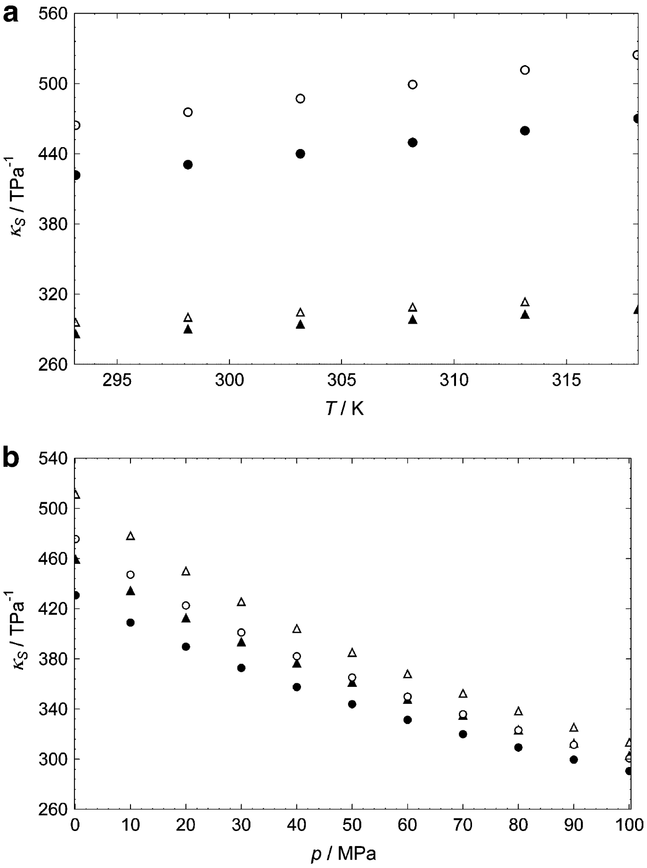

Figure 4. Isentropic compressibility (κ_S) as function: (a) temperature (T) for 1,2-butanediol at the pressures ○, 0.1 MPa; △, 100 MPa; 1,3-butanediol at the pressures ●, 0.1 MPa; ▲, 100 MPa. (b) Pressure (p) for 1,2-butanediol at the temperatures ○, 298.15 K; △, 313.15 K; 1,3-butanediol at the temperatures ●, 298.15 K; ▲, 313.15 K.

Moreover (Table 8 and Figure 4), it is observed that 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 is evidently nonlinear character and the nonlinearity of the κ_S isotherms increases with increasing temperature. Generally, the isentropic compressibility increases with increasing temperature at constant pressure and decreases with increasing pressure at constant temperature.

It appears also that the shape of the curves (both the isobars and isotherms) of the isothermal compressibility is identical to that observed and described above of the isentropic compressibility. However, the curves are translated by the term $T\cdot\alpha_p^2/\rho\cdot c_p$, which is practically almost temperature independent and whose contribution falls as the pressure increases. Simultaneously, both the isentropic and 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 compressibility values are estimated to be ± 0.15 % and ± 0.3 % for isentropic and isothermal compressibilities, respectively. Because of the similarity of the dependencies of the isentropic compressibility on pressure and temperature, a graphic presentation of the dependencies of the isobaric coefficient of thermal expansion on pressure and temperature has been omitted. Generally, the isobaric coefficient of thermal expansion decreases monotonically with increasing pressure and increase monotonically with

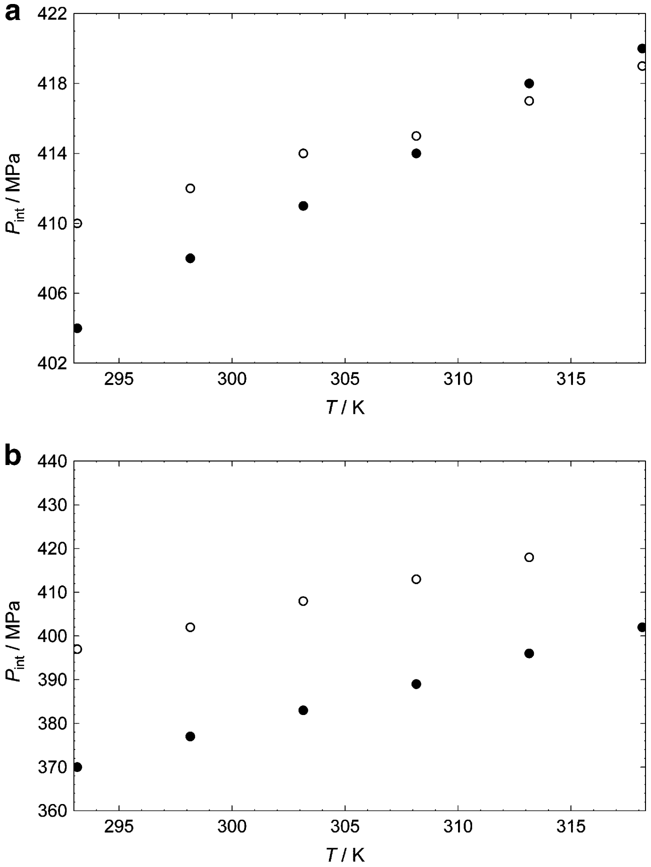

Figure 5. Internal pressure (P_{int}) as function of temperature (T) for ○, 1,2-butanediol; ●, 1,3-butanediol at the pressures: (a) $p = 0.1$ MPa; (b) $p = 100$ MPa.

increasing temperature. The estimated uncertainty of the thermal expansion coefficient is ± 1 %.

The internal pressure shows interesting pressure−temperature dependence. The internal pressure increases linearly with the temperature along the isobars (Table 11 and Figure 5). It is worth noticing that such temperature dependence of the internal pressure at constant pressure (i.e., positive temperature coefficients $(\mathrm{d}P_{int}/\mathrm{d}T)_p$) occurs also in 1,2-ethanediol[32,33] as well as in water.[33,34] Water shows, however, some peculiarities.[33,34] According to some authors,[35] the temperature dependence of internal pressure at atmospheric pressure can be used for the classification of liquids. From this point of view, liquids form two general structural groups: not hydrogen-bonded and hydrogen-bonded. Simultaneously, a positive temperature coefficient of internal pressure can be treated as a confirmation of the existence of a spatial network of H-bonds in liquids[35,36] (i.e., the larger coefficient corresponds to the greater degree of association). Moreover, some hydrogen-bonded liquids (e.g., alkanols) are characterized by an inversion of the temperature coefficient of internal pressure. In our study, the temperature coefficient of the internal pressure is slightly greater for 1,3-butanediol than for 1,2-butanediol (Figure 5). Kartsev et al.[36] assumed a minus sign for the internal pressure (in our opinion groundless); hence, the temperature coefficients of internal pressure have signs opposite to those obtained in this work.

The pressure dependence of internal pressure for the diols under test is still even more complicated (Table 11 and Figure 6). For 1,2-butanediol, the P_{int} shows evidently an extreme as the pressure rises along the isotherms. The maxima of the P_{int} isotherms for 1,2-butanediol are shifted toward higher pressures with increasing temperature (i.e., for $T = 293.15$ K the maximum lies at about 20 MPa, whereas for $T = 313.15$ K it lies in the vicinity of 50 MPa). For 1,3-butanediol, the P_{int} decreases monotonically with the exception of the $T = 318.15$ K isotherm. This facts suggest that more detailed studies are required in the near future. However, it should be noted that internal pressure isotherms are known to reach a maximum with increasing pressure.[37]

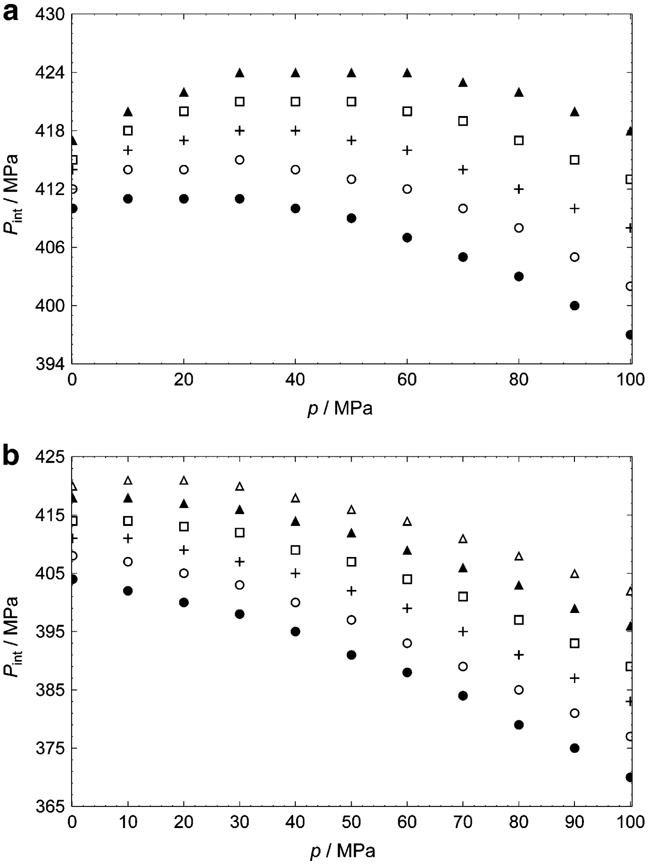

Figure 6. Internal pressure (P_{int}) as function of pressure (p) for (a) 1,2-butanediol at the temperatures ●, 293.15 K; ○, 298.15 K; +, 303.15 K; □, 308.15 K; ▲, 313.15 K. (b) 1,3-Butanediol at the temperatures ●, 293.15 K; ○, 298.15 K; +, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K.

It should be pointed out that the uncertainty of P_{int} obtained by the indirect method used in this work is estimated to be ± 1 % at most unfavorable conditions. At the same time estimations of the uncertainty of P_{int} for indirect methods of the order of both ca. ± 6 %[38] and ca. ± 0.3 %[39] can be found in the literature.

Conclusions

The pressure−temperature effects on the speeds of sound and related thermodynamic properties of 1,2- and 1,3-butanediol are emphasized. Both fundamental material constants (i.e., the isobaric coefficients of thermal expansion and isothermal compressibilities) decrease with increasing pressure and decreasing temperature. In both cases, the respective values are greater for 1,2-butanediol than for 1,3-butanediol. Furthermore, for pressures close to the atmospheric one, the isentropic and isothermal compressibilities depend significantly on pressure, while with increasing pressure its effect on the compressibilities is gradually decreasing. Moreover, a new temperature dependence of the densities of the diols under test in the temperature range from (288.15 to 363.15) K at atmospheric pressure is reported.

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