Study of the Effects of Temperature and Pressure on the Acoustic and Thermodynamic Properties of 2-Methyl-2,4-pentanediol

Edward Zorębski,* Marzena Dzida, and Magdalena Cempa

Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland

The speed of sound in 2-methyl-2,4-pentanediol has been measured in the temperature range from (293.15 to 318.15) K at pressures up to 101 MPa by the pulse-overlap method. The speed of sound at atmospheric pressure has been measured in the temperature range from (283.15 to 323.15) K by means of the same method. The density has been measured in the temperature range from (278.15 to 358.15) K under atmospheric pressure with a vibrating tube densimeter. The isobaric heat capacity has been measured in the temperature range from (284 to 358) K under atmospheric pressure with a differential scanning calorimeter. The experimental results have been used to calculate densities, isobaric heat capacities, the isobaric coefficient of thermal expansion, and isentropic and isothermal compressibilities in function of temperature and pressure; the effects of pressure and temperature have been discussed.

Introduction

This work forms part of our investigation of the thermodynamic properties of organic liquids and their binary mixtures under elevated pressures by means of the method based on the measurements of speed of sound as a function of temperature and pressure.[1–9] In the last decades, this acoustic method has found wide acceptance as a satisfactory and relatively simple method of obtaining reliable thermodynamic data of compressed liquids because the measurements of the speed of sound in liquids became more and more accurate. Moreover, the integration procedures are generally more accurate than derivation. At the same time, Daridon et al.[10] showed that excellent concordance of calculated thermodynamic properties can be obtained between results based on the acoustic method and those based on the isobaric coefficient of thermal expansion and isobaric heat capacity measurements (by the use of the correlation of Randzio et al.[11]). It must be also pointed out that to exploit this accuracy of speed of sound measurements also other approaches have been used to derive from these data related thermodynamic properties (Estrada-Alexander and Justo[12] present a short review).

The experimental data of the thermodynamic properties of compressed liquids are of considerable interest from both fundamental and practical points of view. However, these data are still rather scarce. In particular, it refers to associating liquids which are key substances in the chemical industry, while their structure and thermodynamics are still not properly understood. A very interesting liquid is 2-methyl-2,4-propanediol that is used in many different applications. The dominating use is as solvent because it dissolves easily in both water and organic solvents which makes it useful to create mixtures of fat- and water-soluble chemicals. Moreover, 2-methyl-2,4-pentanediol is used as an intermediate for many chemical syntheses, an additive in fuel, an additive in lubricant, and an additive in cosmetics. It is used for crystallization of biological macromolecules[13] as well.

This work is aimed at the effects of pressure and temperature on the speed of sound in 2-methyl-2,4-pentanediol and such

important quantities (calculated from the speeds of sound) as density, isobaric heat capacity, isobaric coefficient of thermal expansion, and isentropic and isothermal compressibility. Additionally, as an integral part of this work, the densities and isobaric heat capacities at atmospheric pressure were measured at the temperatures ranging from (278.15 to 358.15) K and (284 to 358) K, respectively. To the best of our knowledge, the speeds of sound under elevated pressures for 2-methyl-2,4-pentanediol have not been studied yet. Moreover, the densities at atmospheric pressure reported in the literature are scattered, and only one data set of isobaric heat capacities has been found.

Experimental Section

Materials. 2-Methyl-2,4-pentanediol used in this study was supplied by Aldrich and was used without further purification. According to the supplier, the purity of the materials was >0.99 on a mass fraction. At the same time, the water content declared by the supplier was $<1 \cdot 10^{-3}$. In practice, the water content determined by the Karl Fischer method was $1.9 \cdot 10^{-4}$ on the mass fraction. The refractive index n_D ($T = 298.15$ K) measured with an Abbe refractometer RL3 (uncertainty $\pm$ 0.0002) was 1.4258 for 2-methyl-2,4-pentanediol. This result is in excellent agreement with the value 1.4257 reported by Riddick et al.[14] Both here and just before all the measurements reported in this work, each sample was degassed in an ultrasonic cleaner.

Methods and Apparatus. The speed of sound was measured at atmospheric and elevated pressures using two measuring sets designed and constructed in our laboratory. In the present work, two measuring vessels have been used: one has been assigned for the measurements under atmospheric pressure at a frequency of 2.1 MHz (two transducer mode) and the second one for elevated pressures at a frequency of 2 MHz (a single transmitting−receiving ceramic transducer and an acoustic mirror). Both sets operate on the principle of the pulse-echo-overlap method that has been applied in our laboratory for many years.[15] The basic advantages and disadvantages of this relative method have been reported recently.[16] More details about the high-pressure device and the method of the speed of sound measurements can be found in previous papers.[17,18] A detailed

Table 1. Speed of Sound (u) in 2-Methyl-2,4-pentanediol 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}
0.1	288.14	1326.50	291.11	1317.09	293.14	1310.70
0.1	298.15	1295.20	298.15	1295.21	301.02	1286.35
0.1	303.15	1279.86	308.15	1264.65		
15.20	292.86	1382.21	298.15	1366.71	303.14	1351.38
30.39	292.86	1443.49	298.15	1428.84	303.13	1414.58
45.59	292.86	1499.72	298.15	1485.43	303.14	1472.10
60.79	292.86	1551.74	298.15	1538.07	303.14	1525.17
75.99	292.86	1600.92	298.15	1587.28	303.14	1575.12
91.18	292.86	1646.87	298.15	1633.95	303.14	1622.14
101.32	292.85	1675.80	298.15	1663.40	303.14	1651.78
0.1	308.18	1264.59	313.16	1249.61	318.19	1234.56
15.20	308.13	1336.94	313.10	1323.03	318.29	1308.80
30.39	308.13	1400.80	313.10	1387.64	318.29	1374.46
45.59	308.13	1459.19	313.10	1446.54	318.29	1434.25
60.79	308.13	1513.04	313.10	1501.05	318.29	1489.27
75.99	308.13	1563.06	313.10	1551.63	318.29	1539.51
91.18	308.13	1610.75	313.11	1599.58	318.29	1588.48
101.32	308.13	1640.79	313.10	1629.89	318.29	1619.25

Table 2. Speeds of Sound (u_o) in 2-Methyl-2,4-pentanediol at Atmospheric Pressure and Various Temperatures (T) in Comparison with Literature Data

	u_o/m·s^{-1}		
T/K	exptl	lit.	
288.15	1326.41	1329.4[24]	
293.15	1310.73	1314.4[24]	1311.0[23]
298.15	1295.21	1299.5[24]	1295.2[a23]
303.15	1279.85	1284.5[24]	1280.0[23]
308.15	1264.65	1269.6[24]	
313.15	1249.60	1254.6[24]	
318.15	1234.72	1239.7[24]	

[a] Interpolated value.

Table 3. Densities (ρ_0) and Molar Isobaric Heat Capacities (C_{p_0}) at Atmospheric Pressure and Various Temperatures (T) for 2-Methyl-2,4-pentanediol

T/K	ρ_o/kg·m^{-3}	T/K	C_{p_o}/J·K^{-1}·mol^{-1}
278.153	932.344	284.16	250.63
283.155	928.795	288.14	254.33
288.154	925.238	293.14	258.40
293.155	921.676	298.16	262.40
298.154	918.110	303.15	266.42
303.157	914.548	308.15	270.35
308.155	910.981	313.15	274.70
313.155	907.411	318.15	279.12
318.154	903.834	323.15	283.62
323.152	900.247	328.15	288.35
328.156	896.647	333.15	293.21
333.156	893.033	338.15	298.13
338.154	889.400	343.15	303.01
343.152	885.746	348.15	307.95
348.155	882.068	353.14	314.80
353.152	878.362	358.16	318.39
358.152	874.626		

Table 4. Coefficients b_j of the Polynomials (1), (2), and (3) for the Speed of Sound u_o (within the Temperature Range from (293.15 to 318.15) K), Density ρ_0 (within the Temperature Range from (283.15 to 363.15) K), and Molar Isobaric Heat Capacity (C_{p_0}) (within the Temperature Range from (284.15 to 358.15) K) Together with Mean Deviations (δ)

	b_o	b_1	b_2	δ
u_o/m·s^{-1}	2499.595	−4.99086	3.19076·10^{-3}	0.04[a]
ρ_0/kg·m^{-3}	1112.006	−5.88530·10^{-1}	−2.06750·10^{-4}	0.039[b]
C_{p_0}/J·K^{-1}·mol^{-1}	223.329	−54.1579	22.5427	0.10[a,c]

[a] $\delta(u_o)$/m·s^{-1}. [b] $\delta(\rho_0)$/kg·m^{-3}. [c] $\delta(C_{p0})$/J·K^{-1}·mol^{-1}.

description of the measuring set under atmospheric pressure can be found elsewhere.[15]

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, ITS-90) with an uncertainty of ± 0.05 K. During the measurements, a stability of ± 10 mK was achieved. Redistilled and degassed (by boiling) water (electrolytic conductivity 10^{-4} Ω^{-1}·m^{-1}) was used as the standard for the calibration of the apparatus for the speed of sound measurement. The values of the speed of sound at atmospheric pressure were taken from the polynomial proposed by Marczak[19] and, at elevated pressures, from the Kell and Whalley polynomial.[20]

The repeatability of the measured speeds of sound at atmospheric pressure was better than 0.01 %. At the same time, the overall uncertainty was estimated to be better than ± 0.5 m·s^{-1}. Under elevated pressures, the repeatability and uncertainty were estimated to be better than 0.04 % and ± 1 m·s^{-1}, respectively.

The densities at atmospheric pressure were measured by means of a vibrating-tube densimeter DMA 5000 (Anton Paar). An uncertainty was estimated to be better than ± 5·10^{-2} kg·m^{-3}, whereas repeatability was estimated to be better than ± 5·10^{-3} kg·m^{-3}. The apparatus was calibrated with air and redistilled, freshly degassed (by boiling) water with the above electrolytic conductivity. All measured densities include viscosity correction (this type of densimeter has built-in a correction procedure for viscosity effect on measured density).

The specific isobaric heat capacities at atmospheric pressure were measured by means of a differential scanning calorimeter Micro DSC III (Setaram; Tian-Calvet's principle). The uncertainty of the measurements was estimated to be of ± 0.5 %. Details about procedure and the calorimeter calibration have been described previously.[21,22]

Measurement Results

Speeds of Sound. The experimental speeds of sound in 2-methyl-2,4-pentanediol, measured within a temperature range from (293 to 318) K as well as under pressures up to 101 MPa, are collected in Table 1. A comparison with literature values of the speed of sound at 0.1 MPa is given in Table 2. The respective values at rounded temperatures were estimated from the regression functions, which were obtained by approximation

of the dependencies of speed of sound at atmospheric pressure u_o on temperature by the second-order polynomials

$$u_0(\text{m·s}^{-1}) = \sum_{j=0}^{2} b_j T^j \tag{1}$$

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 identical to the raw data within the limits of the measurement uncertainties.

As seen from Table 2, our results for 2-methyl-2,4-pentanediol are in very good agreement with that of one of us.[23] On the other hand, distinctly worse agreement is observed with relatively old data of Marks.[24] These results at a frequency of 0.5 MHz are reported in the form of a linear equation without experimental data. In this case, our values for 2-methyl-2,4-pentanediol are in each temperature distinctly smaller; i.e., a systematic deviation of ca. −0.3 % is observed. Generally, the
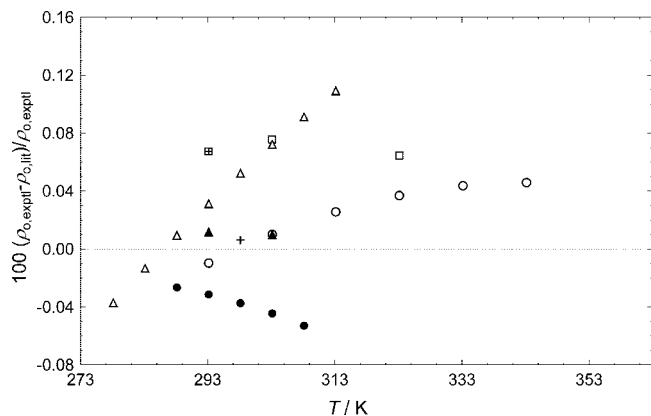
Figure 1. Comparison of densities for 2-methyl-2,4-pentanediol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (\rho_{0,\text{exptl}} - \rho_{0,\text{lit.}})/\rho_{0,\text{exptl}}$ between values of this work ($\rho_{0,\text{exptl}}$) and literature values ($\rho_{0,\text{lit.}}$) of: $\bigcirc$, Grineva et al.;[26] $\square$, Ikada;[27] $\blacktriangle$, Mellan;[28] $\triangle$, McDuffie et al.;[25] $\bullet$, Marks;[24] and $+$, Riddick et al.[14]
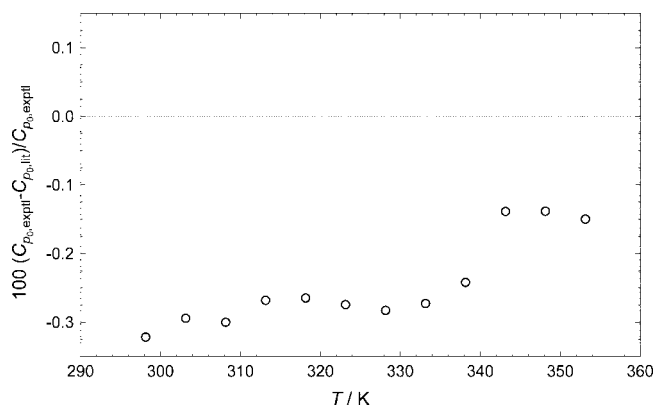

Figure 2. Comparison of isobaric heat capacities for 2-methyl-2,4-pentanediol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (C_{p_0},\text{exptl} - C_{p_0},\text{lit.})/C_{p_0},\text{exptl}$ between values of this work (C_{p_0},exptl) and literature values (C_{p_0},lit.) of $\bigcirc$, Zorębski and Gŏralski.[30]

literature data are scarce in this case. We must point out that some, mostly old and evidently less reliable literature data (low purity and/or systematic error), have been omitted consciously in Table 2.

For a given pressure, the speed of sound in the liquid under study decreases almost linearly with increasing temperature. At the same time, all isobars are almost parallel. The pressure dependencies at constant temperatures are evidently much more nonlinear. Moreover, with increasing pressure, its effect on the speed of sound decreases slightly. The form of the equation used for smoothing out the u, p, and T values is presented in the next section.

Densities at Atmospheric Pressure. The experimental densities of 2-methyl-2,4-pentanediol, measured at atmospheric pressure in the temperature range from (278.15 to 358.15) K, are listed in Table 3. A comparison for 2-methyl-2,4-pentanediol between the densities of this work and the available literature values resulted in an average absolute deviation (AAD = $(100/n)\sum_{i=1}^{n}|\rho_{0,\text{exptl}} - \rho_{0,\text{lit.}}/\rho_{0,\text{exptl}}|$) of 0.042 %. This comparison reveals that values published by various authors are rather scattered (Figure 1), and the experimental uncertainty given in literature sources is sometimes overestimated. It seems that most likely those discrepancies are caused mainly by water.

As in our two previous reports,[7,8] some data showing great systematic deviations have been omitted consciously. Generally, there are results where the authors present only equations

without experimental data, e.g., the densities reported by Waciński et al.[23] These values are considerably greater than ours (deviations up to -0.29 %) and are one of the greatest from all attainable by us in literature values. In our opinion, these values are unfortunately unreliable. It is caused most probably by a systematic experimental error (a simple, relatively small volume pycnometer was used for density measurements at atmospheric pressure). Low purity of samples (i.e., contamination by water) is excluded because, as mentioned above, speeds of sound are in very good agreement with results reported in this work. Little reliable are also the values given by Meister et al.[29] (a deviation of -0.54 % at $T = 278.15$ K is considerable). Therefore, we have omitted the above data in the comparison as well.

The densities ρ_0 of 2-methyl-2,4-pentanediol were approximated by the second-order polynomial

$$\rho_0(\text{kg} \cdot \text{m}^{-3}) = \sum_{j=0}^{2} b_j T^j \qquad (2)$$

where b_j are coefficients determined as above. Respective values are reported in Table 4. The fit is very good, and the mean deviations are within the estimated repeatability.

Heat Capacities at Amospheric Pressure. The experimental isobaric molar heat capacities C_{p_0} at atmospheric pressure are summarized in Table 3. For clarity, only the values at every 5 K are presented. All recorded data points (ca. 2800) over the temperature range studied were however used for fitting to the following equation

$$C_{p0}(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = \sum_{j=0}^{2} b_j (T/100)^j \qquad (3)$$

The values of the coefficients and mean deviation from the regression line are collected in Table 4. A comparison between the heat capacities of this work and those from the literature[30] (Figure 2) resulted in an average absolute deviation (AAD = $(100/n)\sum_{i=1}^{n}|C_{p_0},\text{exptl} - C_{p_0},\text{lit.}/C_{p_0},\text{exptl}|$) of 0.25 %. This comparison reveals that the experimental uncertainty is reliable enough. Simultaneously, the deviations show however a rather systematic shift (the values reported in this work are generally somewhat smaller).

Calculations of Material Constants at Elevated Pressures

Because details of the calculation algorithm and its application procedure have already been published,[1,3,31] only a brief overview is given below.

The acoustic method is based on the speed of sound measured as a function of temperature and pressure as well as on the density and isobaric heat capacity measured as a function of temperature at atmospheric pressure.[1,3,10,32–35] Simultaneously, 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

$$u = (K_0 \cdot \rho^{-1})^{1/2} = (\kappa_S \cdot \rho)^{-1/2} \qquad (4)$$

where K_0 is the static adiabatic compressibility modulus, i.e., in the limit $\omega(=2\pi f) \to 0$, where f is frequency. This relation indicates that the speed of sound is solely determined by the elasticity and density of the material through which it is passing. In our opinion, this condition is satisfied for the alkanediol studied in this investigation; however, the dispersive phenomena have been reported for the diol under test. According to Meister

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

j	a_{1j}	a_{2j}	a_{3j}	$\delta(u)/\text{m·s}^{-1}$
0	0.271800	$3.11796 \cdot 10^{-4}$	$-3.553 \cdot 10^{-8}$	0.27
1				
2	$-8.29496 \cdot 10^{-7}$	$-1.01422 \cdot 10^{-9}$		

et al.,[29] for frequencies up to 100 MHz, the ultrasound velocity dispersion at atmospheric pressure is absent above ca. (273 to 278) K. At the same time, considerable dispersion is present at $T = 247.15$ K, and the low-frequency limiting velocity (i.e., speed of sound) is equal to 1464 m·s^{-1}. It appears that there is a satisfactory agreement between the latter value and the value of 1461 m·s^{-1} obtained by extrapolation of our results for u_o (eq 1) to $T = 247.15$ K.

In the calculations, a modified numerical procedure proposed by Sun et al.,[32] based on the earlier suggestions of Davis and Gordon,[34] has been applied. As suitable initial conditions for the integration over the entire pressure range covered by the $u(T, p)$ function, reference densities and specific isobaric heat capacities in the form of smoothing functions $\rho(T, p_0)$ and $c_p(T, p_0)$ of temperature at the starting pressure p_0 (reference isobar at atmospheric pressure) were used. As in previous papers from our laboratory,[1,3,6–8] the equation suggested by Sun et al.[32] was chosen for smoothing out the speed of sound, pressure, and temperature values

$$p - p_0 (\text{MPa}) = \sum_{i=1}^{m} \sum_{j=0}^{n} a_{ij}(u - u_0)^i T^j \quad (5)$$

where u is the speed of sound at $p > 0.1$ MPa and u_o is the speed of sound at atmospheric pressure p_0. The corresponding coefficients a_{ij} together with mean deviations are given in Table 5.

Finally, the procedure gives the isobars of density and isobaric heat capacity in the polynomial form similar to eqs 1 and 2. Generally, the values of heat capacities obtained by the above method are seen to be less reliable than the values of densities, which results from the principle of the method. Taking into account only the uncertainty of measured speed of sound and analyses presented by Sun et al.,[32] the respective uncertainties have been estimated in our earlier papers[1,5–8] to be better than ± 0.3 % and ± 0.02 % for isobaric heat capacity and density, respectively. However, a critical survey of all results obtained in our laboratory leads to the conclusion that the AADs between our results and those measured directly by a vibrating-tube densimeter are in most cases somewhat higher. Thus, taking into account also above, we estimate finally the overall uncertainty of density under elevated pressures to be of ± 0.05 %. Consequently, the uncertainty of isobaric heat capacity under elevated pressures is estimated to be better than ± 1 %.

Using obtained $\rho(T, p)$ and $C_p(T, p)$ values, the isobaric coefficient of thermal expansion, α_p, and isentropic and isothermal compressibilities, κ_S and κ_T, were calculated. These quantities were calculated from the well-known formulas: $\alpha_p = -\rho^{-1}(\partial\rho/\partial T)_p$, $\kappa_S = (\rho \cdot u^2)^{-1}$, and $\kappa_T = \kappa_S + \alpha_p^2 \cdot T \cdot (\rho \cdot c_p)^{-1}$. The values obtained in this way are presented in Tables 6 to 10. Omitted in this report are values of internal pressures, $P_{int} = T \cdot \alpha \cdot \kappa_T^{-1} - p$, which can be easily obtained from the values given in Tables 9 and 10.

As can be expected, the density increases monotonically with an increase of pressure and decrease of temperature. And also, the maximal change of density with change of pressure occurs near the atmospheric pressure. In contrary to atmospheric pressure, we have found in the literature only one data set for

Table 6. Densities (ρ) for 2-Methyl-2,4-pentanediol at Various Temperatures (T) and Pressures (p)

	$\rho/\text{kg·m}^{-3}$ at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	921.71	918.16	914.59	911.02	907.43	903.84
10	928.02	924.61	921.19	917.76	914.32	910.88
20	933.98	930.69	927.39	924.09	920.78	917.47
30	939.57	936.39	933.20	930.01	926.82	923.62
40	944.86	941.77	938.69	935.59	932.50	929.40
50	949.88	946.88	943.88	940.88	937.87	934.86
60	954.67	951.75	948.83	945.90	942.98	940.05
70	959.24	956.40	953.55	950.70	947.84	944.99
80	963.63	960.85	958.07	955.28	952.50	949.71
90	967.84	965.13	962.41	959.68	956.96	954.23
100	971.90	969.25	966.58	963.92	961.24	958.57

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

Table 7. Molar Isobaric Heat Capacities (C_p) for 2-Methyl-2,4-pentanediol at Various Temperatures (T) and Pressures (p)

	$C_p/\text{J·K}^{-1}\text{·mol}^{-1}$ at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	258.29	262.25	266.32	270.50	274.79	279.20
10	257.7	261.7	265.7	269.9	274.2	278.5
20	257.2	261.2	265.2	269.3	273.6	278.0
30	256.8	260.7	264.7	268.9	273.1	277.5
40	256.4	260.3	264.3	268.5	272.7	277.0
50	256.1	260.0	264.0	268.1	272.3	276.6
60	255.8	259.6	263.6	267.7	271.9	276.3
70	255.5	259.3	263.3	267.4	271.6	275.9
80	255.2	259.0	263.0	267.1	271.3	275.6
90	254.9	258.7	262.7	266.8	271.0	275.3
100	254.6	258.5	262.4	266.5	270.7	275.0

[a] Calculated from the equation presented in this work.

Table 8. Isentropic Compressibilities (κ_S) for 2-Methyl-2,4-pentanediol 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
0.1[a]	631.51	649.23	667.51	686.33	705.74	725.72
10	584.6	599.9	615.6	631.7	648.3	665.2
20	545.5	558.9	572.7	586.7	601.0	615.6
30	512.4	524.4	536.5	548.9	561.5	574.3
40	483.9	494.6	505.5	516.5	527.7	539.0
50	458.9	468.6	478.4	488.3	498.3	508.4
60	436.8	445.6	454.5	463.5	472.5	481.6
70	417.1	425.1	433.2	441.4	449.6	457.8
80	399.2	406.6	414.0	421.5	429.0	436.4
90	383.1	389.9	396.7	403.5	410.4	417.2
100	368.3	374.6	380.9	387.2	393.5	399.7

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

comparison at elevated pressures. It appears that the values of density estimated by us for 2-methyl-2,4-pentanediol are not in good agreement with those obtained by McDuffie et al.[25] The comparison under elevated pressures gave an AAD = 0.21 % (including results at atmospheric pressure, the AAD is 0.20 %). As can be seen in Figure 3, the deviations show generally rather a systematic shift; i.e., McDuffie et al. densities are always evidently greater than those estimated by us. It seems that two reasons are essential: first, the sample purity, and second, measurement method (the variable volume cell with bellows has been used by McDuffie et al.). The use of ρ_0 obtained in this work instead of those of McDuffie et al. leads to a decrease of the above discrepancies. The comparison under elevated pressures gave at that time the AAD = 0.16 %. On the other

Table 9. Isobaric Coefficient of Thermal Expansion (α_p) for 2-Methyl-2,4-pentanediol at Various Temperatures (*T*) and Pressures (*p*)

p/MPa	$\alpha_p 10^4/K^{-1}$ at *T*/K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	7.70	7.75	7.81	7.86	7.91	7.97
10	7.35	7.39	7.44	7.48	7.52	7.57
20	7.04	7.08	7.11	7.15	7.19	7.23
30	6.77	6.80	6.83	6.87	6.90	6.93
40	6.53	6.56	6.58	6.61	6.64	6.67
50	6.31	6.33	6.36	6.39	6.41	6.44
60	6.11	6.14	6.16	6.18	6.21	6.23
70	5.93	5.95	5.98	6.00	6.02	6.05
80	5.76	5.79	5.81	5.83	5.86	5.88
90	5.61	5.63	5.66	5.68	5.70	5.73
100	5.47	5.49	5.51	5.54	5.56	5.58

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

**Table 10. Isothermal Compressibilities (κ_T) for 2-Methyl-2,4-pentanediol at Various Temperatures (*T*) and Pressures (*p*)**

p/MPa	κ_T/TPa^{-1} at *T*/K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	718	737	757	778	799	820
10	663	680	697	714	732	750
20	617	632	646	662	677	693
30	578	591	604	618	631	645
40	545	556	568	580	592	604
50	516	526	537	547	558	569
60	490	499	509	518	528	538
70	467	475	484	493	502	511
80	446	454	462	470	478	486
90	427	435	442	449	57	464
100	410	417	424	431	437	444

[a] Calculated from direct measurements of density and speed of sound at atmospheric pressure.
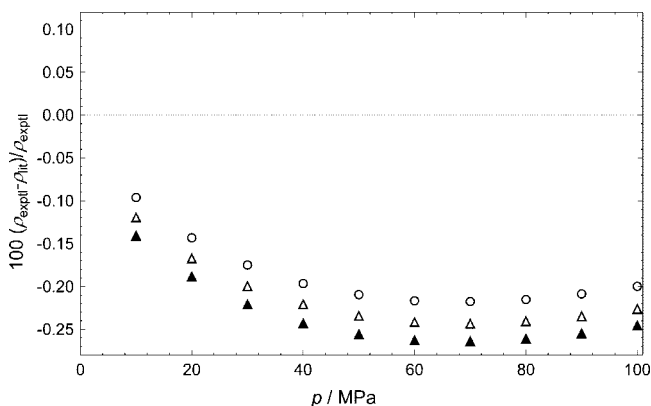
Figure 3. Comparison of densities for 2-methyl-2,4-pentanediol as a function of pressure (*p*) shown as the deviation $100 \cdot (\rho_{exptl} - \rho_{lit.})/\rho_{exptl}$ between values of this work (ρ_{exptl}) and literature values ($\rho_{lit.}$) of McDuffie et al.[25] at the temperatures: ○, 298.15 K; △, 308.15 K; and ▲, 318.15 K.

hand, quite independently, a very good agreement between the densities for ethanol, heptane, and their binary mixtures estimated by one of us from speed of sound measurements[5] and those obtained from direct measurements has been reported.[36] In our opinion, both this fact and our earlier results show that the acoustic method used by us yields in point of fact reliable values of density under elevated pressures.

The heat capacities of 2-methyl-2,4-pentanediol 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 in comparison
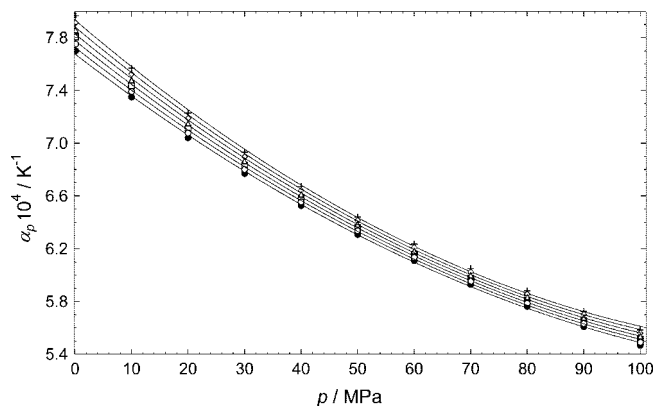
Figure 4. Isobaric coefficient of thermal expansion (α_p) for 2-methyl-2,4-pentanediol as a function of pressure (*p*) at the temperatures: ●, 293.15 K; ○, 298.15 K; □, 303.15 K; △, 308.15 K; ◇, 313.15 K; and +, 318.15 K. Lines − arbitrary.

with that of temperature (Table 7). Similar results have been obtained previously for 1-alkanols[1,5,6] and alkanediols.[7,8]

In turn (Table 8), it is observed that the dependency of the κ_S with respect to temperature is almost linear. The linearity of isobars increases with increasing pressure, and at the same time, the higher the pressure the smaller the temperature dependence. On the other hand, the dependency of the κ_S with respect to pressure has an evidently nonlinear character, and this nonlinearity of isotherms increases with increasing temperature. Generally, these dependencies are very similar to those reported previously for both butanediols[7] and propanediols.[8] However, it should be pointed out that the compressibility of 2-methyl-2,4-pentanediol is substantially higher than that of earlier investigated diols[7,8] due to its branching carbon chain. Also, temperature and pressure dependencies are considerable, especially in comparison with earlier investigated butane- and propanediols.[7,8]

It appears also that the similar temperature−pressure dependence shows κ_T. However, the respective values are translated by the term $T \cdot \alpha_p^2/(\rho \cdot c_p)$ which is practically almost temperature independent. Its contribution falls slightly as the pressure increases.

Simultaneously, both isentropic and isothermal compressibility depend significantly on pressure for pressures close to the atmospheric one, while with increasing pressure its effect on compressibility is gradually decreasing. Generally, both compressibilities increase with increasing temperature at constant pressure and decrease with increasing pressure at constant temperature.

As for the previous investigated alcohols,[6–8] the isobaric coefficients of thermal expansion increase with increasing temperature and decrease with increasing pressure monotonically (see Table 9 and Figure 4). Simultaneously, it can be seen evidently that with increasing pressure the influence of pressure on the temperature dependence of α_p decreases. Nevertheless, there is no crossing point of isotherms in the investigated temperature−pressure range (for example, such a crossing point has been reported for *n*-hexane at (65 ± 2) MPa[11]). For the diol under test, it is obviously possible that such a crossing point might exist at distinctly higher pressures because according to Randzio et al.[37] the crossing point in the case of 1-hexanol appears in the vicinity of 280 MPa (this singular point is however not very perceptible).

We pointed out that the overall uncertainties of κ_S, κ_T, and α_p obtained by an indirect method used in this work are in most

unfavorable conditions roughly estimated to be of $\pm$ 0.15 %, $\pm$ 0.5 %, and $\pm$ 1 %, respectively.

Summary

The pressure–temperature effects on the speeds of sound and related thermodynamic properties of 2-methyl-2,4-pentanediol are reported. Both fundamental material constants, i.e., the isobaric coefficients of thermal expansion and isothermal compressibilities, decrease with increasing pressure and decreasing temperature. Moreover, for pressures close to the atmospheric one, the volume properties (density, isobaric coefficient of thermal expansion, isentropic and isothermal compressibilities) depend significantly on pressure, while with increasing pressure its effect on these properties is gradually decreasing. In the case of isothermal and isentropic compressibility, the pressure dependence is generally very strong.

As an integral part of this work, a new temperature dependence of the density in the temperature range from (278.15 to 358.15) K and at atmospheric pressure for 2-methyl-2,4-pentanediol is reported. A new temperature dependence of the molar isobaric heat capacity in the temperature range from (284.15 to 358.15) K at atmospheric pressure is reported as well.

Acknowledgment

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