Study of the Acoustic and Thermodynamic Properties of 1,2- and 1,3-Propanediol 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-propanediol 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 the tested propanediol isomers have been measured in the temperature range from (283.15 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 a function of temperature and pressure have been calculated. The effects of pressure and temperature on the above quantities are discussed. A new temperature dependence of the heat capacity for 1,3-propanediol is reported too.

Introduction

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 mainly to associating liquids that are key substances in the chemical industry. Their structure and thermodynamics are still not properly understood.

Although in the last decades the acoustic method has found wide acceptance as a satisfactory and relatively simple tool for determining thermodynamic properties of compressed liquids, the experimental data of the speed of sound are still rather scarce. Moreover, unfortunately, some of original papers are available with difficulty. It is worthy of notice that publications until 1997/98 have been summarized in a review article by Oakley et al.[1]

This work is part of a continuing study of associated hydroxyl liquids by means of the acoustic method. In previous papers, the results for some 1-alkanols[2,3] and alkanediols[4] have been reported. The present study is aimed at the effects of pressure and temperature on the speed of sound in 1,2- and 1,3-propanediol and provides 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. An integral part of this study is the results of the density measurements of both propanediols at atmospheric pressure and temperatures ranging from (283.15 to 363.15) K. To the best of our knowledge, the speeds of sound under elevated pressures for 1,2-propanediol have not been reported yet, and for 1,3-propanediol only one data set exists.[5] In turn, the densities and speeds of sound at atmospheric pressure reported in the literature are rather scattered.

Experimental Section

Materials. 1,2- and 1,3-propanediol used in this study were supplied by Fluka and were used without further purification. According to the supplier, the purity of the materials on mass fraction was > 0.995 and > 0.990, respectively, while the water contents declared by the supplier were < $1 \cdot 10^{-3}$. In practice, the mass fractions of water in both the 1,2- and 1,3-propanediol determined in our laboratory by the Karl Fischer method were $2.6 \cdot 10^{-4}$ and $3.3 \cdot 10^{-4}$, respectively. The refractive indexes n_D (T = 298.15 K) measured with an Abbe refractometer RL3 (uncertainty ± 0.0002) were 1.4310 and 1.4380 for 1,2- and 1,3-propanediol, respectively. These results are in reasonable agreement with the literature data[6–10] since the average absolute deviations (AAD = $(100/n) \Sigma_{i=1}^{n} |n_{D,\mathrm{exptl}} - n_{D,\mathrm{lit}}/n_{D,\mathrm{exptl}}|_i$) are of 0.018 % and 0.026 %, respectively. Each sample was degassed in an ultrasonic cleaner just before the all measurements reported in this work.

Methods and Apparatus. The speed of sound at a frequency of 2 MHz was 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 were used. Both sets operate on the principle of the pulse-echo-overlap method that has been applied in our laboratory for many years.[11] A detailed description of the high-pressure device and the method of the speed of sound measurements can be found in previous papers.[12,13]

The pressure was measured with a strain gauge measuring system (Hottinger Baldwin System P3MD) with an uncertainty better than 0.15 %. The temperature (against the 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 ± 10 mK was achieved. Redistilled and degassed (by boiling) water was used as the standard for the calibration of the apparatus. Its electrolytic conductivity was $1 \cdot 10^{-4}\ \Omega^{-1} \cdot \mathrm{m}^{-1}$. The values of the speed of sound in water at atmospheric pressure were taken from the polynomial proposed by Marczak[14] and, at elevated pressures, from the Kell and Whalley polynomial.[15]

The repeatability of the measured speeds of sound was better than ± 0.02 % at atmospheric pressure and ± 0.04 % under

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Table 1. Speed of Sound (u) in 1,2- and 1,3-Propanediol 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-Propanediol			
0.1	292.92	1523.06	298.20	1508.28	303.18	1494.24
15.20	292.88	1578.73	298.16	1564.23	303.14	1551.04
30.39	292.88	1628.53	298.16	1615.07	303.14	1602.40
45.59	292.87	1674.42	298.15	1661.61	303.14	1649.62
60.79	292.87	1717.76	298.15	1705.21	303.13	1693.50
75.99	292.88	1758.52	298.15	1746.52	303.14	1735.39
91.18	292.88	1797.27	298.16	1785.61	303.14	1774.80
101.32	292.87	1821.92	298.16	1810.54	303.13	1799.90
0.1	308.17	1480.13	313.35	1465.43		
15.20	308.13	1537.72	313.31	1524.19		
30.39	308.13	1589.54	313.31	1576.37		
45.59	308.13	1637.57	313.31	1624.98		
60.79	308.12	1681.97	313.31	1669.92		
75.99	308.12	1724.11	313.31	1712.59		
91.18	308.12	1763.99	313.31	1752.77		
101.32	308.12	1789.33	313.31	1778.45		
			1,3-Propanediol			
0.1	292.91	1636.55	298.17	1624.49	303.15	1613.15
15.20	292.89	1681.16	298.17	1668.66	303.16	1657.61
30.39	292.88	1721.74	298.17	1709.92	303.16	1698.95
45.59	292.89	1760.33	298.17	1748.79	303.15	1738.57
60.79	292.89	1796.98	298.17	1786.04	303.15	1775.99
75.99	292.89	1832.24	298.16	1821.36	303.15	1811.65
91.18	292.89	1865.89	298.16	1855.40	303.15	1845.84
101.32	292.89	1887.83	298.16	1877.23	303.14	1868.05
0.1	308.13	1601.87	313.12	1590.54	318.30	1578.87
15.20	308.15	1646.58	313.14	1635.79	318.32	1624.63
30.39	308.15	1688.42	313.13	1678.01	318.31	1667.26
45.59	308.15	1728.41	313.13	1718.16	318.31	1707.96
60.79	308.15	1766.02	313.13	1756.39	318.31	1746.29
75.99	308.15	1801.97	313.13	1792.63	318.31	1783.06
91.18	308.15	1836.57	313.12	1827.41	318.31	1818.05
101.32	308.15	1858.78	313.12	1849.73	318.31	1840.61

Table 2. Speeds of Sound (u_0) in 1,2- and 1,3-Propanediol at Atmospheric Pressure and Various Temperatures (T)

	1,2-propanediol (u_0/m·s^{-1})		1,3-propanediol (u_0/m·s^{-1})	
T/K	exptl	lit.	exptl	lit.
293.15	1522.42	1522.6[16]	1635.99	
298.15	1508.41	1508.2,[16] 1500.1,[6] 1509.5[10]	1624.55	1636.1,[6] 1624.4[10]
303.15	1494.33	1493.8[16]	1613.16	1606[5]
308.15	1480.19	1479.4,[16] 1488.9[6]	1601.80	1616.0[6]
313.15	1465.98	1465.0[16]	1590.48	
318.15	1451.72[a]	1450.6,[16] 1438.1[6]	1579.20	1599.2[6]

[a] Extrapolated value.

elevated pressures. The uncertainty was estimated to be better than ± 0.5 m·s^{-1} and ± 1 m·s^{-1}, respectively.

The densities at atmospheric pressure were measured by means of a vibrating tube densimeter DMA 5000 (Anton Paar). The uncertainty was estimated to be better than ± 5·10^{-2} kg·m^{-3}, whereas the repeatability was estimated to be better than ± 5·10^{-3} kg·m^{-3}. The instrument was calibrated with air and redistilled, freshly degassed (by boiling) water with the above electrolytic conductivity. All the results of density measurements presented here include viscosity corrections. More experimental details can be found in our previous papers.[2–4]

Measurement Results

Speeds of Sound. The experimental speeds of sound in 1,2- and 1,3-propanediol have been measured at pressures up to 101 MPa within the temperature range from (293 to 313) K and from (293 to 318) K, respectively. 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 dependences of the speeds of sound under atmospheric pressure:

$$u_0 = \sum_{j=0}^{2} b_j T^j \qquad (1)$$

The regression coefficients b_j determined by the least-squares method are reported in Table 4. The backward stepwise rejection procedure was used to reduce the number of nonzero coefficients. 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.

Unexpectedly, the literature data on the speed of sound of propanediols at atmospheric pressure are very limited. Moreover, reported values are very scattered. As seen from Table 2, the agreement between results reported in this work and the values extracted from the paper of Orge et al.[10] is satisfactory; the deviations for 1,2- and 1,3-propanediol at $T = 298.15$ K are -0.072 % and $+0.0092$ %, respectively. Our results for 1,2-propanediol are also in good agreement with relatively old data of Marks[16] (reported in the form of a linear equation). In this case, an average absolute deviation (AAD $= (100/n)\Sigma_{i=1}^{n}|u_{0,\text{exptl}} - u_{0,\text{lit}}/u_{0,\text{exptl}}|_i$) was found to be 0.044 %. On the other hand, very poor agreement with the results of George and Sastry[6] (uncertainty declared by them is ± 1.6 m·s^{-1}) is observed. Deviations up to +0.94 % and up to −1.3 % are found here for 1,2- and 1,3-propanediol, respectively. The George and Sastry speeds of sound are generally very scattered (misprint?) and are in our opinion only slightly reliable. In our opinion, the differences are related most probably to the purity and relatively high viscosity of the diols as well as maybe to the measuring method. Also, hygroscopicity in the case of 1,2-propanediol cannot be neglected. We would like to point out that some of the literature data have been omitted consciously in Table 2, e.g., the data of Sastry and Patel[17] for 1,2-propanediol because of very large deviations coming up to 1.1 % at $T = 298.15$ K and even 1.8 % at $T = 308.15$ K.

As was to be expected, for a given pressure, the speed of sound in the liquids under testing is decreasing almost linearly with increasing temperature, while the pressure dependencies at constant temperatures are evidently nonlinear (see Table 1). Moreover, with increasing pressure its effect on the speed of sound becomes smaller. The results are very similar to those reported previously for 1,2- and 1,3-butanediol.[4] From this reason, a graphic presentation of the $u(p,T)$ surfaces are not shown. The form of the equation used for smoothing out the u, p, and T values is given in the next section.

The speeds of sound for 1,3-propanediol reported by us are compared with those reported by Sysoev and Otpuschennikov[5] at the temperature 303.15 K. The AAD was found to be 0.27 %. It is of the order of uncertainty declared by Sysoev and Otpuschennikov, i.e., for pressures up to 294 MPa of 0.1 % and for higher pressures of (0.3 to 0.4)%. For comparison, the Sysoev and Otpuschennikov data for pressures up to 834 MPa at the above-mentioned temperature were smoothed by means of a third-order polynomial ($u = 1616.6 + 265.75\cdot(p/100) - 23.791\cdot(p/100)^2 + 1.160\cdot(p/100)^3$, standard deviation $\delta(u) = \pm 5$ m·s^{-1}).

Densities at Atmospheric Pressure. The experimental densities ρ_0 of both the propanediols were measured at atmospheric pressure in the temperature range from (283.15 to 363.15) K. The results are listed in Table 3. In contrast to the speed of

Table 3. Densities (ρ_0) at Atmospheric Pressure and Various Temperatures (T) for 1,2- and 1,3-Propanediol

1,2-propanediol		1,3-propanediol	
T/K	ρ_0/kg·m^{-3}	T/K	ρ_0/kg·m^{-3}
283.156	1043.426	283.156	1059.093
288.155	1039.844	288.154	1056.002
293.159	1036.214	293.156	1052.891
298.156	1032.544	298.155	1049.779
303.156	1028.834	303.156	1046.650
308.155	1025.088	308.156	1043.516
313.155	1021.300	313.155	1040.362
318.156	1017.476	318.155	1037.193
323.155	1013.610	323.155	1034.003
328.156	1009.708	328.156	1030.793
333.155	1005.758	333.152	1027.556
338.156	1001.772	338.154	1024.298
343.155	997.745	343.155	1021.012
348.152	993.675	348.151	1017.691
353.155	989.560	353.155	1014.340
358.151	985.405	358.152	1010.955
363.149	981.219	363.147	1007.539

Table 4. 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 (283.15 to 363.15) K) Together with Mean Deviations (δ)

	b_o	b_1	b_2	δ
		1,2-Propanediol		
u_0/m·s^{-1}	2233.657	−2.05569	$-1.2638 \cdot 10^{-3}$	0.01[a]
ρ_0/kg·m^{-3}	1180.652	$-2.56233 \cdot 10^{-1}$	$-8.06643 \cdot 10^{-4}$	0.005[b]
		1,3-Propanediol		
u_0/m·s^{-1}	2374.405	−2.74703	$7.7818 \cdot 10^{-4}$	0.02[a]
ρ_0/kg·m^{-3}	1196.865	$-3.64905 \cdot 10^{-1}$	$-4.30349 \cdot 10^{-4}$	0.036[b]

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

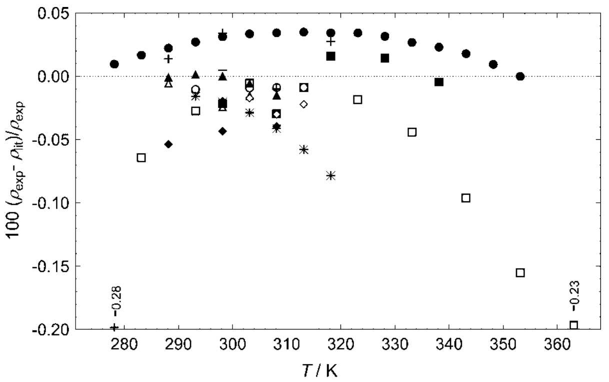

Figure 1. Comparison of densities for 1,2-propanediol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (\rho_{\text{exptl}} - \rho_{\text{lit}})/\rho_{\text{exptl}}$ between values of this work (ρ_{exptl}) and literature values (ρ_{lit}) of: ■, George and Sastry;[6] Δ, Riddick et al.;[7] ▲, Marks;[16] □, Zhuravlev;[18] ●, Marchetti et al.;[19] +, Geyer et al.;[20] ♦, Geyer et al.;[21] ○, Kapadi et al.;[22] ∗, Nain;[23] ◊, Sastry and Patel;[17] -, Orge et al.;[10] and ×, Arce et al.[8]

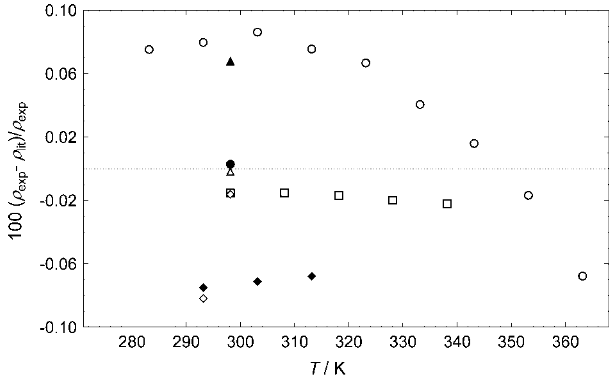

Figure 2. Comparison of densities for 1,3-propanediol as a function of temperature at atmospheric pressure shown as the deviation $100 \cdot (\rho_{\text{exptl}} - \rho_{\text{lit}})/\rho_{\text{exptl}}$ between values of this work (ρ_{exptl}) and literature values (ρ_{lit}) of: □, George and Sastry;[6] ◊, Riddick et al.;[7] ○, Zhuravlev;[18] Δ, Arce et al.;[8] ●, Orge et al.;[10] ▲, Nakanishi et al.;[24] and ♦, Czechowski et al.[25]

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

j	a_{1j}	a_{2j}	a_{3j}	$\delta(u)$/m·s^{-1}
		1,2-Propanediol		
0	0.380452	$2.87538 \cdot 10^{-4}$		0.18
1				
2	$-1.41827 \cdot 10^{-6}$		$-8.04623 \cdot 10^{-13}$	
		1,3-Propanediol		
0	0.408172	$4.13017 \cdot 10^{-4}$		0.24
1				
2	$-8.68421 \cdot 10^{-7}$	$-1.56267 \cdot 10^{-9}$		

Table 6. Densities (ρ) for 1,2- and 1,3-Propanediol 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
			1,2-Propanediol			
0.1[a]	1036.22	1032.55	1028.84	1025.10	1021.31	1017.48
10	1040.95	1037.38	1033.77	1030.12	1026.44	
20	1045.52	1042.03	1038.51	1034.95	1031.36	
30	1049.89	1046.08	1043.04	1039.56	1036.06	
40	1054.08	1050.75	1047.38	1043.98	1040.55	
50	1058.13	1054.86	1051.56	1048.23	1044.87	
60	1062.03	1058.82	1055.59	1052.32	1049.03	
70	1065.80	1062.66	1059.48	1056.27	1053.04	
80	1069.46	1066.37	1063.24	1060.10	1056.92	
90	1073.01	1069.96	1066.89	1063.80	1060.68	
100	1076.45	1073.46	1070.44	1067.39	1064.32	
			1,3-Propanediol			
0.1[a]	1052.91	1049.81	1046.70	1043.56	1040.39	1037.21
10	1057.00	1053.95	1050.89	1047.80	1044.70	1041.57
20	1060.96	1057.97	1054.96	1051.94	1048.89	1045.83
30	1064.80	1061.86	1058.90	1055.93	1052.94	1049.93
40	1068.51	1065.62	1062.72	1059.79	1056.85	1053.90
50	1072.11	1069.27	1066.41	1063.54	1060.65	1057.74
60	1075.61	1072.82	1070.00	1067.17	1064.33	1061.47
70	1079.02	1076.26	1073.49	1070.71	1067.90	1065.09
80	1082.34	1079.62	1076.89	1074.14	1071.38	1068.61
90	1085.57	1082.89	1080.20	1077.49	1074.77	1072.03
100	1088.73	1086.09	1083.43	1080.76	1078.07	1075.37

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

sound data, the literature density data are numerous (especially for 1,2-propanediol). However, the published values are rather scattered, especially below and above room temperature (Figure 1 and 2). Those discrepancies are caused mainly by systematic errors related to an apparatus, its calibration procedure, preparation of liquids, and its purity (in particular water contents because especially 1,2-propanediol absorbs water very readily during storing or handling). For example, recently reported Nain[23] densities have been measured pycnometrically; however, samples have not been (most probably) degassed (the formation of bubbles is a frequent source of errors, which increase with increasing temperature; see Figure 1), and a buoyancy correction is lacking. Another example included the results of Kapadi et al.[22a] and objections expressed by Linek[22b] regarding the calibration procedure (the vibrating-tube densimetry) of Kapadi et al. A comparison of the densities reported in this work with the literature values (mostly polythermal data sets) results in an average absolute deviation (AAD $= (100/n)\Sigma_{i=1}^{n}|\rho_{0,\text{exptl}} - \rho_{0,\text{lit}}/\rho_{0,\text{exptl}}|_i$) of 0.030 % and 0.045 % for 1,2-propanediol and 1,3-propanediol, respectively. The agreement in the vicinity of room temperatures (288.15, 293.15, 298.15, and 303.15 K) is better only in the case of 1,2-propanediol. The AADs here are of 0.018 % and 0.049 % for 1,2- and 1,3-propanediol, respectively. Generally, this comparison reveals that the experimental uncertainties given in the literature sources are very often considerably overestimated.

As seen in Figure 1, for 1,2-propanediol the best agreement over the whole temperature range is with the data of Marchetti et al.[19] and the relatively old data reported by Marks[16] (in the form of a linear equation). In the case of 1,3-propanediol, the best agreements shown are with the data of George and Sastry[6] (Figure 2). On the contrary, the data of Zhuravlev[18] show the greatest deviations in both cases, especially at higher temperatures. Thus, it seems that the above data are not very reliable. It should be noted here that apart from isothermal data some polythermal data have also been consciously omitted such as, for example, those reported by Sun and Teja[27] for 1,2-propanediol. Here, the systematic deviations up to −0.19 % are observed. However, these discrepancies are of the order of uncertainty (0.2 %) claimed realistic enough by the authors.

The densities ρ_0 of both propanediols 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 in the case of the speed of sound. The corresponding values are given in Table 4. In the case of 1,2-propanediol, the fit is excellent and the mean deviation does not exceed the estimated repeatability. Unfortunately, the fit is worse in the case of 1,3-propanediol, and we have no plausible explanation for the above deviations.

Calculations of Material Constants at Elevated Pressures

The detailed description of the calculation algorithm was presented in the previous works,[2,28] and therefore only a brief summarization is given below.

The acoustic method is based on the speeds of sound measured as a function of temperature and pressure as well as on the density and heat capacity measured as functions of temperature at atmospheric pressure.[29–32] Simultaneously, in the assumed absence of the sound wave absorption, the speed of sound may be regarded as a thermodynamic quantity. It is worthy of notice that Sun et al.[30] have claimed that the accuracy of the density attained by the acoustic method is much better than that of direct measurements. Simultaneously, the values of the heat capacities obtained in this way seem to be less reliable than the values of densities.[2,28,30] The respective uncertainties are estimated to be better than ± 0.02 % and ± 0.3 % for the density and heat capacity, respectively.

In the calculations, a modified numerical procedure proposed by Sun et al.,[30] based on the earlier suggestions of Davies and Gordon,[29] has been applied. As in previous papers from our laboratory,[2–4,33] the equation suggested by Sun et al.[30] 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.

Table 7. Molar Isobaric Heat Capacities (C_p) for 1,2- and 1,3-Propanediol 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-Propanediol			
0.1[a]	187.83	190.09	192.36	194.66	196.96	
10	187.3	189.5	191.8	194.1	196.4	
20	186.8	189.0	191.3	193.5	195.8	
30	186.4	188.6	190.8	193.0	195.3	
40	185.9	188.1	190.3	192.6	194.8	
50	185.5	187.7	189.9	192.1	194.3	
60	185.1	187.3	189.5	191.7	193.9	
70	184.8	186.9	189.1	191.3	193.5	
80	184.4	186.5	188.7	190.9	193.1	
90	184.1	186.2	188.3	190.5	192.7	
100	183.7	185.9	188.0	190.1	192.3	
			1,3-Propanediol			
0.1[b]	174.45	176.62	178.81	181.04	183.29	185.57
10	174.2	176.3	178.5	180.7	183.0	185.2
20	173.9	176.0	178.2	180.4	182.6	184.9
30	173.6	175.7	177.9	180.1	182.3	184.6
40	173.3	175.5	177.6	179.8	182.0	184.3
50	173.1	175.2	177.4	179.6	181.8	184.0
60	172.9	175.0	177.1	179.3	181.5	183.7
70	172.6	174.7	176.9	179.1	181.2	183.5
80	172.4	174.5	176.6	178.8	181.0	183.2
90	172.2	174.3	176.4	178.6	180.8	183.0
100	172.0	174.1	176.2	178.3	180.5	182.7

[a] Zábranský et al.[32] [b] Calculated from the equation presented in this work.

Reference densities and specific 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. In the calculations, the temperature dependence of the isobaric heat capacity of 1,2-propanediol at atmospheric pressure reported by Zábranský et al.[34] was used. In the case of 1,3-propanediol, the data recommended by Zábranský et al.[34] have been compiled with data from DETHERM databases.[35] The agreement of both sets is excellent. The mean deviation from the regression line is ± 1.7 J·kg^{-1}·K^{-1} for specific isobaric heat capacity c_p (or ± 0.13 J·mol^{-1}·K^{-1} for molar isobaric heat capacity C_p). In consequence, a modified temperature dependence of the specific isobaric heat capacity was obtained, $c_p/\text{J·kg}^{-1}\text{·K}^{-1} = 1405.8 + 11.6625 \cdot 10^{-3} \cdot T^2 - 4.5825 \cdot 10^{-6} \cdot T^3$, for the temperature range from (249.48 to 483.15) K and used in subsequent calculations.

Finally, the procedure gives the isobars of density and isobaric heat capacity in the form of a polynomial similar to eqs 1 and 2. The density and isobaric heat capacity values calculated in this way are listed in Tables 6 and 7, respectively.

Using obtained densities and heat capacities as functions of temperature and pressure, the isobaric coefficients of thermal expansion, α_p, isentropic and isothermal compressibilities, κ_S and κ_T, and internal pressures, P_{int}, were calculated from the formulas

$$\alpha_p = -\rho^{-1}(\partial\rho/\partial T)_p \tag{4}$$

$$\kappa_S = (\rho \cdot u^2)^{-1} \tag{5}$$

$$\kappa_T = \kappa_S + \alpha_p^2 \cdot T \cdot (\rho \cdot c_p)^{-1} \tag{6}$$

$$P_{\text{int}} = T \cdot \alpha_p \cdot \kappa_T^{-1} - p \tag{7}$$

Obviously, at low pressures, mostly at atmospheric pressure, where $p << T \cdot \alpha_p \cdot \kappa_T^{-1}$, the second term in equation 7 can be neglected without significant error. However, it must be included

Table 8. Isentropic Compressibilities (κ_S) for 1,2- and 1,3-Propanediol 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-Propanediol			
0.1[a]	416.37	425.65	435.27	445.24	455.60	
10	395.1	403.4	412.0	420.9	430.0	
20	376.5	384.0	391.7	399.7	407.9	
30	360.1	366.9	374.0	381.2	388.6	
40	345.4	351.7	358.2	364.8	371.6	
50	332.2	338.0	344.0	350.1	356.3	
60	320.2	325.6	331.1	336.8	342.6	
70	309.2	314.2	319.4	324.6	330.0	
80	299.1	303.8	308.6	313.5	318.5	
90	289.7	294.1	298.6	303.2	307.9	
100	281.0	285.1	289.4	293.7	298.1	
			1,3-Propanediol			
0.1[a]	354.84	360.92	367.13	373.48	379.97	386.60
10	341.3	346.9	352.7	358.6	364.6	370.7
20	328.9	334.1	339.5	344.9	350.5	356.1
30	317.5	322.4	327.4	332.5	337.7	342.9
40	307.1	311.7	316.4	321.2	326.0	330.9
50	297.6	301.9	306.3	310.7	315.2	319.8
60	288.7	292.8	296.9	301.1	305.3	309.6
70	280.4	284.3	288.2	292.1	296.1	300.1
80	272.7	276.4	280.0	283.7	287.5	291.3
90	265.5	269.0	272.4	275.9	279.5	283.0
100	258.8	262.0	265.3	268.6	271.9	275.3

[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-Propanediol at Various Temperatures (T) and Pressures (p)

	$\alpha_p 10^4$/K^{-1} at T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			1,2-Propanediol			
0.1[a]	7.04	7.14	7.24	7.35	7.46	7.56
10	6.83	6.92	7.02	7.12	7.21	
20	6.64	6.72	6.81	6.91	7.00	
30	6.46	6.54	6.63	6.71	6.80	
40	6.30	6.38	6.46	6.54	6.62	
50	6.15	6.23	6.30	6.38	6.46	
60	6.01	6.08	6.16	6.23	6.31	
70	5.88	5.95	6.02	6.09	6.17	
80	5.76	5.83	5.90	5.97	6.03	
90	5.65	5.71	5.78	5.84	5.91	
100	5.54	5.60	5.67	5.73	5.80	
			1,3-Propanediol			
0.1[a]	5.89	5.94	6.00	6.05	6.11	6.17
10	5.75	5.80	5.85	5.91	5.96	6.02
20	5.62	5.67	5.72	5.77	5.82	5.88
30	5.50	5.55	5.60	5.65	5.70	5.75
40	5.39	5.44	5.48	5.53	5.58	5.62
50	5.29	5.33	5.37	5.42	5.47	5.51
60	5.19	5.23	5.27	5.32	5.36	5.40
70	5.09	5.13	5.18	5.22	5.26	5.31
80	5.00	5.05	5.09	5.13	5.17	5.21
90	4.92	4.96	5.00	5.04	5.08	5.12
100	4.84	4.88	4.92	4.96	5.00	5.04

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

Table 10. Isothermal Compressibilities (κ_T) for 1,2-, and 1,3-Propanediol 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-Propanediol			
0.1[a]	473	485	496	509	521	
10	448	459	469	480	492	
20	427	436	446	456	466	
30	408	416	425	434	443	
40	391	398	406	415	423	
50	375	382	390	398	405	
60	361	368	375	382	389	
70	348	355	361	368	374	
80	337	343	349	355	361	
90	326	331	337	343	349	
100	316	321	326	332	337	
			1,3-Propanediol			
0.1[a]	397	404	411	419	427	434
10	381	388	395	402	409	416
20	367	373	380	386	393	399
30	354	360	366	372	378	384
40	342	348	353	359	365	370
50	331	336	341	347	352	358
60	321	326	331	336	341	346
70	311	316	321	325	330	335
80	303	307	311	316	320	325
90	294	299	303	307	311	315
100	287	291	295	299	303	307

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

Table 11. Internal Pressure (P_{int}) for 1,2- and 1,3-Propanediol 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-Propanediol			
0.1[a]	436	439	442	445	448	
10	436	440	443	447	450	
20	436	440	444	447	451	
30	435	439	443	447	451	
40	433	437	442	446	450	
50	431	435	440	445	449	
60	428	433	438	443	447	
70	425	430	436	441	446	
80	422	427	433	438	443	
90	418	424	430	435	441	
100	415	421	427	433	438	
			1,3-Propanediol			
0.1[a]	435	438	442	445	448	451
10	432	436	440	443	447	450
20	429	433	437	441	444	448
30	426	430	434	438	442	446
40	422	426	431	435	439	443
50	418	423	427	432	436	440
60	414	419	423	428	433	437
70	409	414	419	424	429	434
80	405	410	415	420	425	430
90	400	405	411	416	421	427
100	395	401	406	412	417	423

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

at high pressures. The respective values obtained by the use of eqs 4, 5, 6, and 7 are presented in Tables 8, 9, 10, and 11.

The densities of both the propanediols increase monotonically with increasing pressure and decreasing temperature (similarly to 1,2- and 1,3-butanediol[4]). 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 (Table 6). In contrary to the atmospheric pressure, both for 1,2-propanediol and 1,3-propanediol, only a limited data set for comparison at elevated pressures has been found in the literature. Available data on the compressed liquid density and related quantities published until the year 1996 were summarized and critically evaluated by Cibulka et al.[36] Three data sets for 1,2-propanediol[37–39] and three for 1,3-propanediol[37,39,40] have been taken into account for estimation of the parameters of the Tait equation. In the case of 1,2-propanediol, the agreement of results reported in this work with values calculated by the use of the Tait equation with parameters

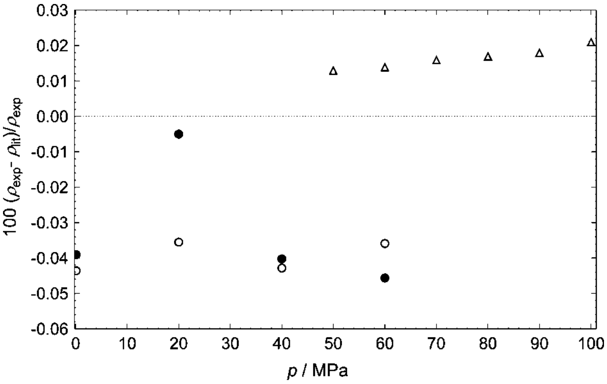

Figure 3. Comparison of densities for 1,2-propanediol as a function of pressure (p) shown as the deviation $100\cdot(\rho_{\text{exptl}} - \rho_{\text{lit}})/\rho_{\text{exptl}}$ between values obtained in this work by means of the acoustic method (ρ_{exptl}) and literature values (ρ_{lit}) of Geyer et al.[21] at the temperatures ○, 298.15 K; and ●, 308.15 K; as well as values obtained from the Tait equation reported by Cibulka et al.[36] (with parameters based only on Miyamoto et al.[39] data) at the temperature Δ, 298.15 K.

given by Cibulka et al. (based on three data sets[37–39]) and our density data at atmospheric pressure (as reference density) is poor (adequate AAD = 0.30 %). At $T = 298.15$ K only, the agreement is a little better (AAD = 0.28 %) but still unsatisfactory. In turn, the use of the Tait equation with parameters based only on Miyamoto and co-workers'[39] isothermal data ($T = 298.15$ K, Aime method) yields AAD = 0.017 % (Figure 3). Thus, taking into account also previous considerations of Cibulka et al.,[36] the relatively old data of Bridgman[37] (variable volume cell with bellows) seem to be, as a matter of fact, less reliable (especially in higher temperatures and pressures). The same is related to the isothermal ($T = 303.15$ K) data of Hamann and Smith[38] (Aime method). Therefore, the above data are omitted in the comparison presented in Figure 3. As seen from Figure 3, the values of density estimated by us for 1,2-propanediol are in good agreement with those obtained by Geyer et al.[21] (vibrating tube densimeter). The comparison under elevated pressures gives an AAD = 0.024 % (including the results at atmospheric pressure, the AAD is 0.021 %). However, the deviations show in both cases a rather systematic shift (Figure 3).

Similarly, as in the case of 1,2-propanediol, the agreement between the values of the density of 1,3-propanediol estimated in this work and those calculated by the use of the Tait equation reported by Cibulka et al.[36] (with parameters based on three data sets[37,39,40]) is rather unsatisfactory (AAD = 0.058 %). Simultaneously, the higher the temperature the higher the deviations. For instance, at $T = 298.15$ K, AAD = 0.017 %, whereas at $T = 318.15$ K, AAD = 0.1 %, which indicates that the Bridgmann[37] data, as was already mentioned, are controversial. For 1,3-propanediol, similarly as in the case of 1,2-propanediol, the best fit is obtained when the Tait equation with parameters based only on Miyamoto and co-workers'[39] isothermal data ($T = 298.15$ K, Aime method) is used. The agreement is excellent; the adequate AAD = 0.0093 % (Figure 4). It seems that the main reasons for deviations, as at the atmospheric pressure, are sample purity and the calibration procedure of the measuring devices used by the mentioned authors.

Recently, quite independently, a very good agreement between the densities of ethanol, heptane, and their binary mixtures determined by one of us from speed of sound measurements[41] and those obtained from direct measurements has been reported too.[42] Therefore, the acoustic method used by us yields in point of fact reliable values of the density under elevated pressures.

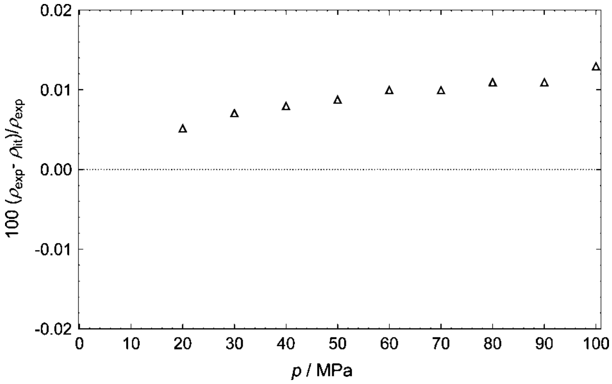

Figure 4. Comparison of densities for 1,3-propanediol as a function of pressure (p) shown as the deviation $100\cdot(\rho_{\text{exptl}} - \rho_{\text{lit}})/\rho_{\text{exptl}}$ between values obtained in this work by means of the acoustic method (ρ_{exptl}) and literature values (ρ_{lit}) obtained from the Tait equation reported by Cibulka et al.[36] (with parameters based only on Miyamoto et al.[39] data) at the temperature Δ, 298.15 K.

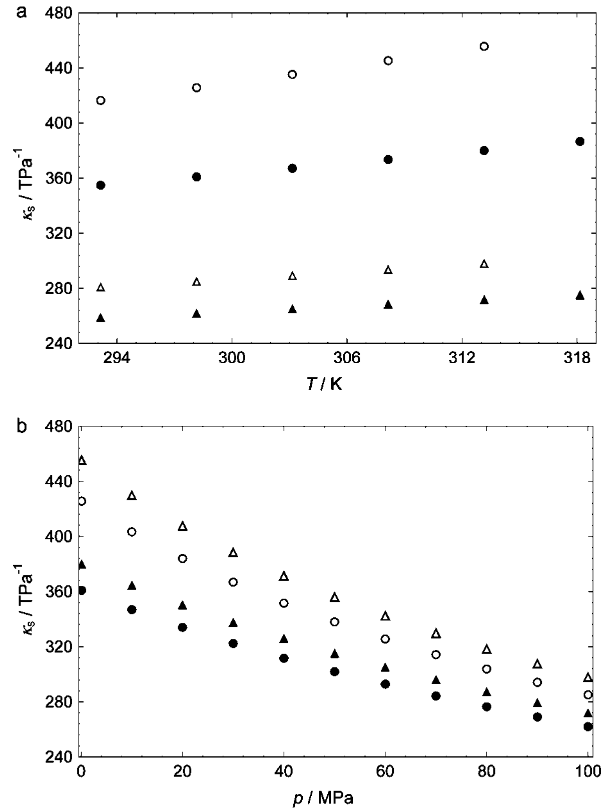

Figure 5. Isentropic compressibility (κ_S) as a function of (a) temperature (T) for 1,2-propanediol at the pressures ○, 0.1 MPa; and Δ, 100 MPa; as well as for 1,3-propanediol at ●, 0.1 MPa; and ▲, 100 MPa; and (b) pressure (p) for 1,2-propanediol at the temperatures ○, 298.15 K; and, ♦, 313.15 K; as well as for 1,3-propanediol at ●, 298.15 K; and ▲, 313.15 K.

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 previous investigated butanediols[4] as well as 1-alkanols.[2,3,41]

In turn, the dependency of the κ_S on temperature is almost linear (Table 8 and Figure 5). The linearity of the isobars increases with increasing pressure. At the same time, with increasing pressure the effect of temperature on κ_S decreases. On the other hand, the dependency of the κ_S on pressure is evidently nonlinear, and the nonlinearity of the κ_S isotherms

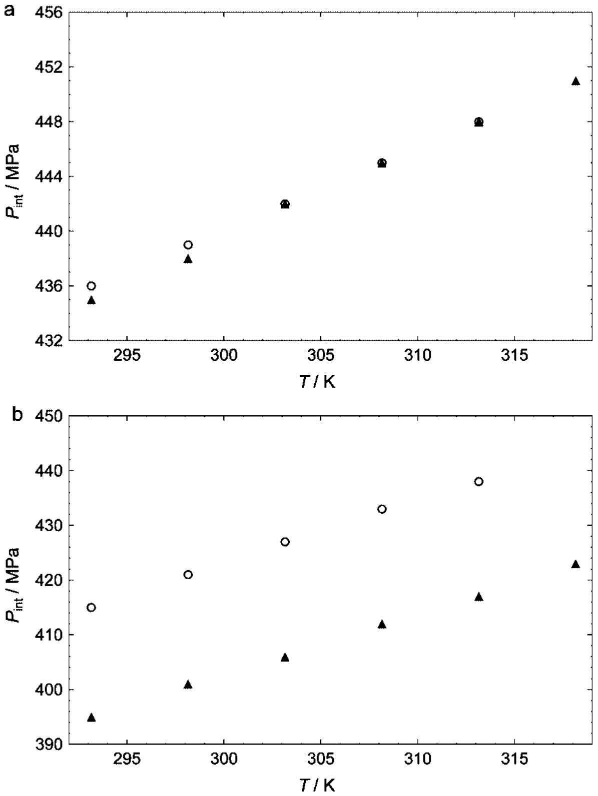

Figure 6. Internal pressure (P_{int}) as a function of temperature (T) for ○, 1,2-propanediol; and ▲, 1,3-propanediol at the pressures: (a) $p = 0.1$ MPa and (b) $p = 100$ MPa.

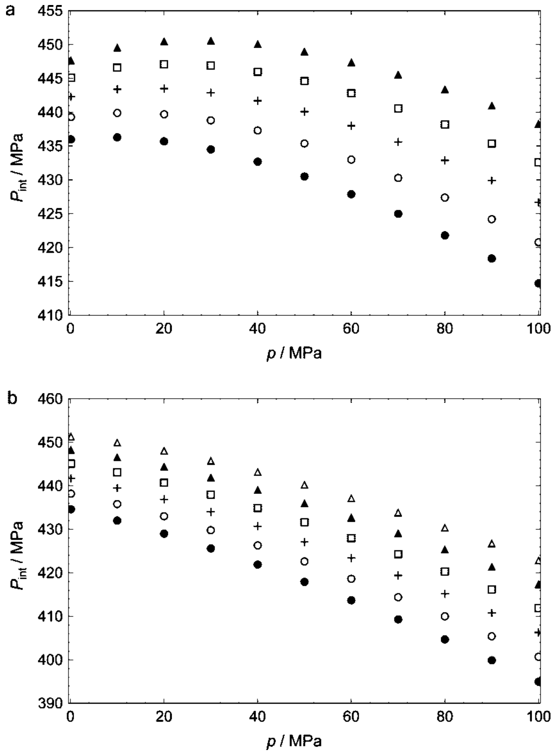

Figure 7. Internal pressure (P_{int}) as a function of pressure (p) for (a) 1,2-propanediol at the temperatures ●, 293.15 K; ○, 298.15 K; +, 303.15 K; □, 308.15 K; and ▲, 313.15 K and for (b) 1,3-propanediol at the temperatures ●, 293.15 K; ○, 298.15 K; +, 303.15 K; □, 308.15 K; ▲, 313.15 K; and Δ, 318.15 K.

increases with increasing temperature. Generally, the isentropic compressibility increases with increasing temperature at constant pressure and decreases with increasing pressure at constant temperature.

The shape of the isobars and isotherms of the isentropic compressibility is identical to that observed for the isothermal compressibility. However, the curves are translated by the term $T \cdot \alpha_p^2 / p \cdot c_p$ 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 gradually decreases with increasing pressure. The isothermal compresssibility at atmospheric pressure obtained in this work for both diols agrees with the values reported by Kartsev et al.[26] The average absolute deviations (AAD $= (100/n)\,\Sigma_{i=1}^{n}|\kappa_{T,0,\text{exptl}} - \kappa_{T,0,\text{lit}}/\kappa_{T,0,\text{exptl}}|_i$) are 0.62 % and 0.73 % for 1,2- and 1,3-propanediol, respectively. They do not exceed the uncertainty of 1 % declared by the above-mentioned authors.

The overall uncertainties of the isentropic and isothermal compressibilities reported in this work are estimated to be ± 0.15 % and ± 0.3 %, respectively.

The isobaric coefficient of thermal expansion decreases monotonically with increasing pressure and increases monotonically with increasing temperature. Because of the similarity to 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. The estimated uncertainty of the thermal expansion coefficient is ± 1 %.

As for the previous investigated butanediols,[4] the internal pressure increases linearly with temperature along the isobars (Table 11 and Figure 6). Simultaneously, the higher the pressure the greater the temperature coefficients of internal pressure $(\mathrm{d}P_{\text{int}}/\mathrm{d}T)_p$. Moreover, taking into account the uncertainty of the internal pressure equal to ± 1 %, there is not a significant difference between the temperature dependence of internal pressure for the tested diols (Figure 6). It is interesting because the polarity of 1,3-propanediol is, however, a little higher; i.e., dipole moments at $T = 298.15$ K are equal to 2.50 D and 2.25 D for 1,3-propanediol and 1,2-propanediol, respectively.[18]

The internal pressure of 1,3-propanediol also decreases monotonically with increasing pressure (Table 11 and Figure 7). For 1,2-propanediol, however, the pressure dependence of internal pressure shows a maximum. The maxima of the P_{int} isotherms for 1,2-propanediol are shifted toward higher pressures with increasing temperature; i.e., for $T = 293.15$ K, the maximum is observed at about 10 MPa, whereas for $T = 313.15$ K, it is in the vicinity of 30 MPa. It is very interesting that such behavior for various liquids was observed.[3,43]

It should be noted that a very interesting similarity of P_{int} is observed for 1,2-propanediol studied in this work and 1,3-butanediol studied previously.[4] It seems that this similarity arises from a relatively small difference between both the speeds of sound and isentropic compressibilities. 1,2-Propanediol and 1,3-butanediol contain single primary and secondary alcohol groups and differ structurally only in the addition of a CH_2 group to the carbon chain of the latter.

Summary

The pressure−temperature effects on the speeds of sound and related thermodynamic properties of 1,2- and 1,3-propanediol are reported.

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-propanediol than for 1,3-propanediol. 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 in the temperature range from (283.15 to 363.15) K at atmospheric pressure is reported for the diols under test. A new temperature dependence (by compilation of the two various literature data sets) of the heat capacity for 1,3-propanediol is reported too.

Acknowledgment

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