Study of the Effects of Temperature and Pressure on the Thermodynamic and Acoustic Properties of Pentan-1-ol, 2-Methyl-2-butanol, and Cyclopentanol in the Pressure Range from (0.1 to 100) MPa and Temperature from (293 to 318) K

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The speeds of sound in pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol were measured within the temperatures from $T =$ (293 to 318) K and at pressures up to 101 MPa. The densities have been measured in the same temperature range under atmospheric pressure. The densities, isobaric heat capacities, isobaric thermal expansions, and isentropic and isothermal compressibilities as functions of temperature and pressure were calculated using the speeds of sound under elevated pressures together with the densities and heat capacities at atmospheric pressure. The effects of temperature and pressure on the isobaric heat capacity, isobaric thermal expansion, and isothermal compressibility of pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol are compared and discussed.

Introduction

The impact of temperature and pressure on the thermodynamic properties of alcohols should be analyzed taking into account the effects of the breaking and making of the H-bonds, nonspecific interactions, and the packing of molecules. The capability of the formation of the hydrogen bonds and the type of the formed associates depend on the chain structure and the position of the hydroxyl group in the alcohol molecules. In this work, pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol were chosen to study the influence of the above effects on the thermodynamic properties and their dependence on temperature and pressure. The pentanols have been often selected for this study because they are the heaviest of the alcohols that are easily available in sufficient purity.[1] Promising preliminary results obtained for some isomeric pentanols[2] tempted me to continue the research. The temperature dependences of heat capacities of pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol in the wide range of temperatures have been analyzed previously.[3]

The thermodynamic properties of liquids under high pressure are of considerable interest from both fundamental as well as practical points of view. In particular, it refers to associating liquids which are key substances in the industrial processes, but their structure and thermodynamics are still not properly understood. The thermodynamic and acoustic properties under high pressure have been reported mainly for alkan-1-ols. Relatively few data are available in the literature for branched and cyclic alcohols.[4,5] Recently, Cerdeiriña et al.[6,7] and González-Salgado et al.[8] reported the thermodynamic and acoustic properties under high pressure for pentan-3-ol, 3-methyl-3-pentanol, and 3-ethyl-3-pentanol.

The speeds of sound in primary alcohols under elevated pressures have been measured by Sysoev and Otpuschennikov and published in Nauchnye Trudy (Kurskioei Gosudarstvennyoei Pedagogicheskioei Institute).[5] Khasanshin[9] published a correlation equation for the speed of sound of akan-1-ols with the carbon atoms in the chain ranging from 4 to 12 for pressures from $p =$ (0.1 to 100) MPa and for six temperatures from $T =$ (303.15 to 453.15) K determined at 20 K steps. To this end, the above-mentioned experimental data were used. Boned et al.[10] published new experimental densities of pentan-1-ol at temperatures from $T =$ (293.15 to 403.15) K and pressures up to 140 MPa. They also completed and analyzed literature where $p\rho T$ data for pentan-1-ol had been reported up to now. Additionally, Khasanshin[11] published a correlation equation between the density and the number of carbon atoms ranging from 4 to 10 for pressures up to 50 MPa at $T =$ (293.15 and 298.15) K. To the best of my knowledge, speeds of sound in 2-methyl-2-butanol and cyclopentanol have never been measured under high pressure. Densities of 2-methyl-2-butanol at $T =$ (293.15 and 298.15) K and pressures from $p =$ (1 to 7) MPa were reported by Cibulka et al.[4] Wisotzki and Würflinger[12] obtained pVT data for cyclopentanol in the temperature range from $T =$ (273.3 to 324.9) K and at pressures up to 230 MPa.

This work is a part of systematic studies of thermodynamic properties of alcohols under high pressure using the acoustic method. Acoustic and thermodynamic properties of ethanol, propan-1-ol, hexan-1-ol, heptan-1ol, octan-1-ol, nonan-1-ol, and decan-1-ol at pressures up to 100 MPa have been presented earlier.[13−16] In this paper, new experimental speeds of sound in pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol in the temperature range from $T =$ (293 to 318) K and at pressures up to 101 MPa are reported. The densities have been measured within the same temperature range under atmospheric pressure. The densities and isobaric heat capacities of the alcohols under test for the temperature range from $T =$ (293 to 318) K and for pressures from $p =$ (0.1 to 100) MPa have been calculated using the speeds of sound under elevated pressures together with the densities and isobaric heat capacities at atmospheric pressure. The method based on the suggestion of Davis and Gordon[17] with a numerical procedure proposed by Sun et al.[18] was applied for calculations. Furthermore, the measured speeds of sound and calculated densities and isobaric heat capacities have been used for the calculation of the adiabatic and isothermal compressibilities and isobaric thermal expansion. The effects of temperature and pressure on the thermodynamic properties of

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Table 1. Comparison of the Speeds of Sound, u, and Densities, ρ, Obtained in This Work at $T = 298.15$ K under Atmospheric Pressure with Those Reported in the Literature

component	exptl	lit.	
pentan-1-ol	u/m·s^{-1}	1275.24	1274.42,[19] 1275.18,[20] 1275.5,[21] 1275.6[22]
	ρ/kg·m^{-3}	810.84	810.83,[23] 810.85,[24] 810.93,[21] 810.96[25]
2-methyl-2-butanol	u/m·s^{-1}	1177.79	1178.44,[19] 1179.02[26]
	ρ/kg·m^{-3}	804.32[a]	804.25,[27] 804.257,[28] 804.33,[29,30] 804.37[31]
cyclopentanol	u/m·s^{-1}	1435.11	–
	ρ/kg·m^{-3}	942.86[a]	942.84,[27] 942.91,[32] 942.97[31]

[a] Published in the previous work.[3]

Table 2. Speed of Sound, u, in Alcohols Measured at Pressures up to 101 MPa within the Temperature Range from $T = (293$ to $318)$ K

T/K	p/MPa	u/m·s^{-1}	T/K	p/MPa	u/m·s^{-1}	T/K	p/MPa	u/m·s^{-1}
Pentan-1-ol			2-Methyl-2-butanol			Cyclopentanol		
292.81	0.10	1293.90	292.90	0.10	1196.68	292.86	0.10	1454.43
292.95	15.20	1371.49	292.86	15.20	1290.79	292.85	15.20	1519.52
292.96	30.40	1439.68	292.86	30.39	1369.65	292.85	30.39	1576.30
292.91	45.59	1501.59	292.86	45.59	1440.87	292.85	45.59	1629.14
292.91	60.81	1558.29	292.86	60.79	1505.95	292.85	60.79	1677.79
292.88	76.01	1611.23	292.86	75.99	1566.11	292.85	75.99	1723.91
292.88	91.21	1659.95	292.86	91.18	1623.13	292.85	91.18	1767.22
292.88	101.33	1691.40	292.86	101.32	1658.53	292.85	101.32	1794.98
298.18	0.10	1275.13	298.17	0.10	1177.76	298.17	0.10	1435.02
297.94	15.20	1355.47	298.15	15.20	1274.22	298.14	15.20	1500.37
297.93	30.40	1424.76	298.15	30.39	1354.40	298.14	30.39	1557.78
297.93	45.60	1487.07	298.15	45.59	1426.29	298.14	45.59	1611.51
297.93	60.80	1544.35	298.15	60.79	1491.48	298.14	60.79	1660.96
297.93	75.99	1597.60	298.15	75.99	1551.92	298.14	75.99	1707.20
297.93	91.19	1647.33	298.15	91.18	1608.65	298.14	91.18	1751.19
297.93	101.34	1678.66	298.15	101.32	1644.42	298.14	101.32	1779.31
303.15	0.10	1257.97	303.15	0.10	1159.80	303.15	0.10	1416.87
303.06	15.20	1339.33	303.14	15.20	1258.55	303.12	15.20	1482.15
303.06	30.41	1409.73	303.13	30.39	1339.71	303.12	30.39	1540.43
303.05	45.60	1472.84	303.13	45.59	1412.26	303.12	45.59	1595.06
303.10	60.79	1530.59	303.14	60.79	1478.06	303.12	60.79	1645.63
303.10	76.00	1584.09	303.14	75.99	1538.62	303.12	75.99	1692.59
303.06	91.18	1634.58	303.13	91.18	1595.59	303.12	91.18	1737.24
303.06	101.33	1666.32	303.13	101.32	1631.38	303.12	101.32	1765.46
308.13	0.10	1240.94	308.12	0.10	1141.91	308.13	0.10	1398.71
308.08	15.20	1323.46	308.12	15.20	1242.61	308.11	15.20	1464.83
308.08	30.40	1394.79	308.12	30.39	1324.91	308.11	30.39	1524.45
308.04	45.60	1459.02	308.12	45.59	1398.03	308.11	45.59	1579.44
308.06	60.80	1517.53	308.12	60.79	1464.69	308.11	60.79	1630.62
308.05	76.00	1571.63	308.12	75.99	1525.64	308.11	75.99	1678.03
308.06	91.21	1622.45	308.12	91.18	1582.62	308.12	91.18	1722.96
308.06	101.33	1654.25	308.12	101.32	1618.96	308.11	101.32	1751.59
313.11	0.10	1224.06	313.10	0.10	1123.98	313.12	0.10	1380.61
313.04	15.21	1308.45	313.11	15.20	1226.63	313.09	15.20	1447.62
313.03	30.40	1380.74	313.11	30.39	1310.06	313.09	30.39	1508.35
313.05	45.60	1445.47	313.10	45.59	1384.09	313.09	45.59	1563.96
313.03	60.79	1504.83	313.10	60.79	1451.15	313.09	60.79	1616.12
313.03	75.99	1559.24	313.10	75.99	1512.77	313.09	75.99	1664.14
313.03	91.19	1610.72	313.10	91.18	1569.88	313.09	91.18	1709.54
313.02	101.34	1642.93	313.11	101.32	1606.18	313.09	101.32	1738.58
318.68	0.10	1205.45	318.29	0.10	1105.29	318.29	0.10	1361.75
318.52	15.20	1292.04	318.18	15.20	1210.40	318.19	15.20	1430.75
318.52	30.40	1365.43	318.19	30.39	1295.23	318.20	30.39	1492.37
318.51	45.59	1431.27	318.19	45.59	1370.11	318.19	45.59	1548.63
318.50	60.80	1491.19	318.18	60.79	1437.90	318.19	60.79	1601.42
318.49	76.00	1546.38	318.18	75.99	1499.85	318.19	75.99	1650.30
318.49	91.20	1598.10	318.19	91.18	1557.15	318.20	91.18	1695.85
318.51	101.33	1630.77	318.18	101.32	1593.86	318.19	101.32	1725.29

pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol are compared and discussed.

Experimental Section

Chemicals. Pentan-1-ol from Lancaster (0.98+ mass fraction purity, $C_5H_{11}OH$), 2-methyl-2-butanol from Aldrich (minimum 0.99 mass fraction purity, $C_2H_5C(CH_3)_2OH$), and cyclopentanol from Fluka (minimum 0.99 mass fraction purity, C_5H_9OH) were used. Because of the lower purity of pentan-1-ol, the content of the main component was checked by gas chromatography, mass spectra, and IR spectra. The content of the main component was found to be 0.993 mass fraction. All alcohols were dried over molecular sieves of 0.3 nm. The mass fraction of water, determined by the Karl Fischer method, was less than $2 \cdot 10^{-4}$ for 2-methyl-2-butanol and $1 \cdot 10^{-4}$ for pentan-1-ol and cyclopentanol. The purity of these chemicals was tested by comparison of the density and speed of sound with literature values (Table 1).

Table 3. Densities, ρ, of Alcohols Measured within the Temperature Range from $T = (293$ to $318)$ K at Atmospheric Pressure

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
Pentan-1-ol		2-Methyl-2-butanol		Cyclopentanol	
293.150	814.500	293.154	808.891	293.154	946.792
298.150	810.840	298.155	804.300	298.154	942.856
303.149	807.155	303.156	799.660	303.156	938.874
308.153	803.442	308.156	794.954	308.155	934.843
313.148	799.705	313.155	790.176	313.155	930.754
318.151	795.912	318.154	785.312	318.148	926.613

Table 4. Coefficients of Polynomial (1) for the Speed of Sound and Density under Atmospheric Pressure within the Temperature Range (293 to 318) K and Mean Deviations from the Regression Line

component	c_0 / m·s^{-1}	c_1 / m·s^{-1}·K^{-1}	$c_2 \cdot 10^3$ / m·s^{-1}·K^{-2}	δu_0 / m·s^{-1}
pentan-1-ol	2626.764	−5.592810	3.55451	0.009
2-methyl-2-butanol	2250.871	−3.599128	–	0.023
cyclopentanol	2521.355	−3.643279	–	0.039
	ρ_0 / kg·m^{-3}	ρ_1 / kg·m^{-3}·K^{-1}	$\rho_2 \cdot 10^3$ / kg·m^{-3}·K^{-2}	$\delta\rho$ / kg·m^{-3}
pentan-1-ol	974.153	−0.3616732	−0.624084	0.006
2-methyl-2-butanol	941.397	–	−1.542083	0.014
cyclopentanol	1084.253	−0.1572318	−1.063198	0.004

Ultrasonic Speed Measurements. The speed of sound at a frequency of 2 MHz was measured at atmospheric and elevated pressures using two measuring sets operating on the principle of the pulse-echo-overlap method. Two measuring vessels of the same acoustic path and construction (a single transmitting−receiving ceramic transducer and an acoustic mirror) have been used. One of them was destined for measurements under atmospheric pressure, the other one for measurements under high pressure. The pressure was provided by a hand-operated hydraulic press and was measured with a strain gauge measuring system (Hottinger Baldwin System P3MD) with accuracy 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 and resolution of 0.001 K. All temperatures reported in this work are expressed in the International Temperature Scale of 1990 (ITS-90).

Redistilled water, degassed by boiling just before measurements, was used as the standard liquid for determining the ultrasonic path length. The electrolytic conductivity of water was $1 \cdot 10^{-4}$ S·m^{-1}. The speed of sound in water under atmospheric pressure was calculated from the polynomial of Marczak,[33] while for higher pressures the equation of Kell and Whalley[34] was used. The repeatability of the measured speeds of sound was better than ± 0.02 % at atmospheric pressure and ± 0.04 % under high pressure. The uncertainties under atmospheric and high pressure were estimated to be better than ± 0.5 m·s^{-1} and ± 1 m·s^{-1}, respectively. Other details of the high-pressure device and the method of the speed of sound measurements can be found in the previous papers.[35,36]

Density Measurements. The densities at atmospheric pressure were measured using a vibrating-tube densimeter (Anton Paar

Table 5. Coefficients of Equation 2 and Mean Deviations from the Regression Line δu

component	j	a_{1j} / K^{-j}·MPa·s·m^{-1}	a_{2j} / K^{-j}·MPa·s^2·m^{-2}	a_{3j} / K^{-j}·MPa·s^3·m^{-3}	δu / m·s^{-1}
pentan-1-ol	0	0.2798800032	$2.65356912 \cdot 10^{-4}$	–	0.17
	1	–	$-2.60109240 \cdot 10^{-7}$	–	
	2	$-1.17395556 \cdot 10^{-6}$	–	–	
2-methyl-2-butanol	0	0.2461770385	$1.78385484 \cdot 10^{-4}$	$-1.69299925 \cdot 10^{-7}$	0.36
	1	–	–	$4.54474877 \cdot 10^{-10}$	
	2	$-1.18466308 \cdot 10^{-6}$	–	–	
cyclopentanol	0	0.3088901939	$3.48700649 \cdot 10^{-4}$	–	0.49
	1	–	–	–	
	2	$-9.97555440 \cdot 10^{-7}$	$-1.51550450 \cdot 10^{-9}$	–	

Table 6. Calculated Densities, ρ, of Alcohols at Pressures up to 100 MPa and within the Temperature Range from T = (293 to 318) K

	ρ/kg·m^{-3}					
	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
	Pentan-1-ol					
0.1[a]	814.50	810.84	807.16	803.44	799.70	795.92
10	821.13	817.65	814.14	810.61	807.04	803.45
20	827.33	824.00	820.64	817.25	813.84	810.41
30	833.11	829.91	826.67	823.42	820.14	816.84
40	838.54	835.45	832.33	829.19	826.02	822.83
50	843.66	840.67	837.65	834.61	831.55	828.47
60	848.52	845.62	842.70	839.75	836.78	833.78
70	853.15	850.33	847.49	844.62	841.73	838.82
80	857.57	854.83	852.06	849.27	846.46	843.62
90	861.80	859.13	856.44	853.72	850.97	848.21
100	865.87	863.26	860.63	857.98	855.30	852.60
	2-Methyl-2-butanol					
0.1[a]	808.88	804.32	799.68	794.97	790.18	785.31
10	816.69	812.36	807.98	803.52	799.00	794.41
20	823.84	819.72	815.53	811.28	806.98	802.61
30	830.42	826.46	822.44	818.37	814.24	810.06
40	836.52	832.70	828.83	824.91	820.94	816.91
50	842.23	838.54	834.79	831.00	827.16	823.28
60	847.60	844.02	840.39	836.71	832.99	829.23
70	852.67	849.19	845.67	842.10	838.48	834.83
80	857.49	854.10	850.67	847.19	843.68	840.12
90	862.07	858.76	855.42	852.03	848.61	845.14
100	866.44	863.22	859.95	856.65	853.31	849.93
	Cyclopentanol					
0.1[a]	946.79	942.86	938.88	934.84	930.76	926.61
10	952.27	948.47	944.64	940.75	936.81	932.83
20	957.48	953.81	950.10	946.35	942.55	938.70
30	962.43	958.87	955.27	951.63	947.95	944.23
40	967.13	963.68	960.18	956.65	953.08	949.47
50	971.63	968.27	964.87	961.43	957.95	954.44
60	975.94	972.66	969.34	965.99	962.61	959.19
70	980.08	976.88	973.64	970.37	967.07	963.73
80	984.06	980.93	977.77	974.58	971.35	968.09
90	987.91	984.85	981.75	978.63	975.47	972.28
100	991.63	988.63	985.60	982.54	979.44	976.32

[a] Calculated from eq 1.

Table 7. Calculated Isobaric Molar Heat Capacities, C_p, of Alcohols at Pressures up to 100 MPa and within the Temperature Range from T = (293 to 318) K

	C_p/J·mol^{-1}·K^{-1}					
	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
	Pentan-1-ol					
0.1[a]	204.25	208.14	212.24	216.52	220.95	225.50
10	203.32	207.20	211.26	215.49	219.87	224.40
20	202.50	206.36	210.38	214.57	218.92	223.43
30	201.75	205.58	209.58	213.74	218.06	222.54
40	201.05	204.87	208.84	212.97	217.27	221.72
50	200.40	204.19	208.14	212.25	216.52	220.95
60	199.78	203.55	207.48	211.56	215.81	220.22
70	199.17	202.93	206.83	210.90	215.12	219.51
80	198.59	202.32	206.21	210.26	214.46	218.83
90	198.02	201.74	205.60	209.63	213.81	218.16
100	197.46	201.16	205.01	209.01	213.18	217.50
	2-Methyl-2-butanol					
0.1[b]	242.22	247.44	252.80	258.20	263.48	268.52
10	240.32	245.55	250.82	256.06	261.22	266.23
20	238.68	243.88	249.06	254.20	259.27	264.24
30	237.22	242.38	247.49	252.56	257.55	262.47
40	235.89	241.01	246.07	251.07	256.00	260.86
50	234.68	239.75	244.76	249.71	254.59	259.40
60	233.55	238.58	243.55	248.45	253.28	258.04
70	232.50	237.49	242.42	247.28	252.06	256.78
80	231.52	236.47	241.36	246.18	250.92	255.60
90	230.59	235.51	240.36	245.14	249.85	254.49
100	229.71	234.60	239.42	244.17	248.84	253.44
	Cyclopentanol					
0.1[b]	177.54	181.81	186.22	190.71	195.27	199.87
10	176.62	180.89	185.25	189.69	194.21	198.79
20	175.78	180.03	184.36	188.76	193.24	197.79
30	175.02	179.24	183.54	187.91	192.36	196.88
40	174.31	178.51	182.78	187.13	191.55	196.04
50	173.65	177.82	182.07	186.39	190.79	195.26
60	173.03	177.18	181.41	185.71	190.08	194.53
70	172.44	176.57	180.78	185.06	189.41	193.83
80	171.88	175.99	180.18	184.44	188.77	193.17
90	171.34	175.44	179.61	183.85	188.16	192.54
100	170.82	174.90	179.06	183.28	187.57	191.94

[a] Values from ref 41. [b] Values from ref 3.

DMA 5000). The densimeter was calibrated with air and redistilled water of electrolytic conductivity as above and degassed by boiling just before the measurements. The uncertainty of the density measurements was 0.05 kg·m^{-3}, whereas the repeatability was estimated to be better than 0.005 kg·m^{-3}.

Measurement Results

The ultrasonic speeds in pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol have been measured from T = (293 to 318) K in about 5 K steps and under the pressures of about (0.1, 15, 30, 45, 60, 75, 90, and 101) MPa. The experimental values are listed in Table 2. The densities for the alcohols under test were measured under atmospheric pressure within the same temperature range. The experimental values are collected in Table 3.

The dependencies of the speed of sound and density on temperature at atmospheric pressure were approximated by second-order polynomials of the type

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

where y is the speed of sound, u_0, or density, ρ, at atmospheric pressure p_0 and b_j are the polynomial coefficients ($b_j = c_j$ for the speed of sound and $b_j = \rho_j$ for the density) calculated by the least-squares method. The backward stepwise rejection

Table 8. Isentropic Compressibilities, κ_S, of Alcohols at Pressures up to 100 MPa and within the Temperature Range from T = (293 to 318) K

$\kappa_S \cdot 10^9$/Pa^{-1}						
	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Pentan-1-ol			
0.1	0.7347	0.7584	0.7829	0.8083	0.8347	0.8621
10	0.6731	0.6929	0.7132	0.7342	0.7557	0.7779
20	0.6227	0.6396	0.6569	0.6747	0.6928	0.7113
30	0.5808	0.5956	0.6106	0.6259	0.6415	0.6573
40	0.5452	0.5582	0.5715	0.5849	0.5985	0.6123
50	0.5145	0.5261	0.5379	0.5498	0.5618	0.5740
60	0.4875	0.4980	0.5086	0.5193	0.5301	0.5409
70	0.4637	0.4732	0.4828	0.4925	0.5022	0.5120
80	0.4424	0.4511	0.4599	0.4687	0.4775	0.4863
90	0.4233	0.4313	0.4393	0.4473	0.4554	0.4635
100	0.4059	0.4133	0.4207	0.4281	0.4355	0.4429
			2-Methyl-2-butanol			
0.1	0.8646	0.8963	0.9297	0.9649	1.0021	1.0414
10	0.7720	0.7970	0.8231	0.8504	0.8788	0.9085
20	0.7007	0.7214	0.7428	0.7650	0.7880	0.8118
30	0.6438	0.6613	0.6795	0.6982	0.7175	0.7373
40	0.5968	0.6120	0.6277	0.6439	0.6605	0.6775
50	0.5571	0.5706	0.5844	0.5985	0.6131	0.6280
60	0.5230	0.5350	0.5473	0.5599	0.5728	0.5860
70	0.4931	0.5040	0.5151	0.5265	0.5381	0.5499
80	0.4668	0.4767	0.4868	0.4971	0.5077	0.5185
90	0.4434	0.4524	0.4617	0.4712	0.4808	0.4907
100	0.4223	0.4307	0.4392	0.4480	0.4569	0.4659
			Cyclopentanol			
0.1	0.5001	0.5150	0.5305	0.5468	0.5638	0.5816
10	0.4693	0.4825	0.4962	0.5105	0.5253	0.5408
20	0.4428	0.4546	0.4668	0.4795	0.4926	0.5063
30	0.4198	0.4304	0.4414	0.4528	0.4645	0.4767
40	0.3996	0.4093	0.4192	0.4295	0.4401	0.4509
50	0.3817	0.3905	0.3996	0.4089	0.4185	0.4283
60	0.3656	0.3737	0.3820	0.3906	0.3993	0.4082
70	0.3511	0.3586	0.3662	0.3741	0.3820	0.3902
80	0.3379	0.3448	0.3519	0.3591	0.3664	0.3739
90	0.3258	0.3323	0.3388	0.3455	0.3522	0.3591
100	0.3147	0.3207	0.3268	0.3330	0.3393	0.3456

Table 9. Calculated Isobaric Thermal Expansions, α_p, of Alcohols at Pressures up to 100 MPa and within the Temperature Range from T = (293 to 318) K

$\alpha_p \cdot 10^3$/K^{-1}						
	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Pentan-1-ol			
0.1	0.8933	0.9050	0.9169	0.9289	0.9410	0.9533
10	0.8448	0.8551	0.8655	0.8760	0.8866	0.8973
20	0.8033	0.8126	0.8220	0.8315	0.8411	0.8508
30	0.7673	0.7759	0.7847	0.7935	0.8025	0.8115
40	0.7355	0.7437	0.7521	0.7605	0.7689	0.7775
50	0.7072	0.7151	0.7231	0.7312	0.7394	0.7476
60	0.6815	0.6893	0.6971	0.7050	0.7129	0.7210
70	0.6582	0.6658	0.6735	0.6813	0.6891	0.6970
80	0.6368	0.6443	0.6520	0.6597	0.6674	0.6753
90	0.6170	0.6245	0.6321	0.6398	0.6475	0.6553
100	0.5986	0.6062	0.6138	0.6215	0.6292	0.6370
			2-Methyl-2-butanol			
0.1	1.1177	1.1433	1.1692	1.1955	1.2223	1.2495
10	1.0504	1.0723	1.0946	1.1173	1.1402	1.1636
20	0.9949	1.0144	1.0342	1.0543	1.0747	1.0954
30	0.9481	0.9658	0.9838	1.0021	1.0206	1.0394
40	0.9077	0.9241	0.9407	0.9575	0.9745	0.9917
50	0.8722	0.8874	0.9029	0.9185	0.9344	0.9504
60	0.8406	0.8549	0.8694	0.8840	0.8989	0.9139
70	0.8121	0.8256	0.8393	0.8531	0.8671	0.8813
80	0.7863	0.7991	0.8120	0.8251	0.8384	0.8518
90	0.7626	0.7748	0.7871	0.7996	0.8122	0.8249
100	0.7408	0.7524	0.7642	0.7761	0.7881	0.8002
			Cyclopentanol			
0.1	0.8245	0.8392	0.8540	0.8691	0.8843	0.8998
10	0.7912	0.8046	0.8181	0.8317	0.8455	0.8595
20	0.7614	0.7737	0.7860	0.7985	0.8112	0.8240
30	0.7347	0.7461	0.7575	0.7691	0.7808	0.7926
40	0.7106	0.7212	0.7319	0.7427	0.7536	0.7646
50	0.6886	0.6986	0.7086	0.7188	0.7291	0.7395
60	0.6684	0.6779	0.6875	0.6971	0.7069	0.7167
70	0.6498	0.6589	0.6681	0.6773	0.6866	0.6960
80	0.6327	0.6414	0.6502	0.6590	0.6680	0.6770
90	0.6167	0.6251	0.6336	0.6422	0.6508	0.6595
100	0.6017	0.6099	0.6182	0.6265	0.6349	0.6434

procedure was used to reduce the number of nonzero coefficients. The coefficients and the mean deviations from the regression lines are given in Table 4.

The equation suggested by Sun et al.[37] was chosen for smoothing out the speed of sound, pressure, and temperature

$$p - p_0 = \sum_{i=1}^{m} \sum_{j=0}^{n} a_{ij} (u - u_0)^i T^j \qquad (2)$$

where a_{ij} are the polynomial coefficients calculated by the least-squares method; u is the speed of sound at $p > 0.1$ MPa; and u_0 is the speed calculated from eq 1. The coefficients a_{ij} and the mean deviations from the regression lines are given in Table 5. The stepwise rejection procedure was used to reduce the number of the nonzero coefficients.

The speeds of sound in pentan-1-ol reported in this work are compared with those calculated by the correlation equation proposed by Khasanshin.[9] The absolute average deviation (AAD $= (100/n)\sum_{i=1}^{n} |u_{\mathrm{lit},i}/u_{\mathrm{exp},i} - 1|$) was found to be 0.08 %.

Density, Isobaric Heat Capacity, and Derived Thermodynamic Properties under Elevated Pressures

The densities and isobaric heat capacities as functions of temperature and pressure were calculated using the experimental speeds of sound under high pressures together with the densities and heat capacities at atmospheric pressure. Details of the algorithm were discussed in previous works.[15,38] The uncertainty of the measured speed of sound causes the uncertainties of ± 0.02 % in the densities and ± 0.3 % in the isobaric heat capacities calculated.[15,16,38,39] Taking into account the AADs between results obtained in our laboratory and those measured directly by a vibrating-tube densimeter, the overall uncertainty of density and isobaric heat capacity under elevated pressures was found to be ± 0.05 % and ± 1 %, respectively.[40] The values of heat capacities obtained by the above method may be less reliable than the values of densities, which results from the principles of the method.

The densities and isobaric heat capacities of pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol were determined for temperatures from T = (293 to 318) K and for pressures up to 100 MPa. In the calculations, the experimental speeds of sound under elevated pressures have been used, together with the densities and heat capacities at atmospheric pressure. The temperature dependence of the isobaric heat capacity was taken from the literature: the polynomial reported by Zábranský et al.[41] was used for pentan-1-ol, while for 2-methyl-2-butanol and cyclopentanol the polynomials reported by Dzida and Góralski[3] were applied. The calculated density and isobaric heat capacity values are listed in Tables 6 and 7, respectively.

The densities of pentan-1-ol calculated in this work by the acoustic method were compared with the values critically evaluated and correlated by Cibulka and Ziková,[42] measured

Table 10. Isothermal Compressibilities, κ_T, of Alcohols at Pressures up to 100 MPa and within the Temperature Range from $T = (293$ to 318) K

	$\kappa_T \cdot 10^9$/Pa^{-1}					
	T/K					
p/MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Pentan-1-ol			
0.1	0.8587	0.8859	0.9140	0.9431	0.9731	1.0041
10	0.7836	0.8063	0.8296	0.8535	0.8780	0.9032
20	0.7223	0.7417	0.7615	0.7818	0.8024	0.8235
30	0.6713	0.6883	0.7055	0.7231	0.7409	0.7589
40	0.6281	0.6432	0.6584	0.6738	0.6895	0.7052
50	0.5909	0.6044	0.6180	0.6318	0.6457	0.6596
60	0.5583	0.5706	0.5829	0.5953	0.6078	0.6203
70	0.5296	0.5407	0.5520	0.5633	0.5746	0.5859
80	0.5039	0.5142	0.5245	0.5349	0.5452	0.5556
90	0.4809	0.4904	0.4999	0.5095	0.5190	0.5285
100	0.4601	0.4689	0.4778	0.4866	0.4954	0.5042
			2-Methyl-2-butanol			
0.1	1.0294	1.0689	1.1104	1.1540	1.2001	1.2490
10	0.9172	0.9485	0.9811	1.0152	1.0508	1.0880
20	0.8308	0.8566	0.8835	0.9114	0.9404	0.9705
30	0.7617	0.7837	0.8065	0.8301	0.8546	0.8798
40	0.7047	0.7239	0.7437	0.7641	0.7852	0.8069
50	0.6566	0.6735	0.6910	0.7090	0.7275	0.7466
60	0.6152	0.6304	0.6460	0.6620	0.6785	0.6955
70	0.5791	0.5928	0.6069	0.6214	0.6363	0.6515
80	0.5473	0.5598	0.5726	0.5858	0.5993	0.6132
90	0.5190	0.5305	0.5422	0.5543	0.5667	0.5794
100	0.4935	0.5042	0.5150	0.5262	0.5376	0.5493
			Cyclopentanol			
0.1	0.6022	0.6205	0.6395	0.6593	0.6799	0.7014
10	0.5633	0.5794	0.5961	0.6134	0.6313	0.6500
20	0.5298	0.5441	0.5589	0.5742	0.5901	0.6065
30	0.5007	0.5136	0.5269	0.5406	0.5547	0.5693
40	0.4753	0.4869	0.4989	0.5113	0.5240	0.5370
50	0.4527	0.4633	0.4742	0.4855	0.4970	0.5087
60	0.4325	0.4422	0.4522	0.4625	0.4730	0.4837
70	0.4142	0.4232	0.4325	0.4419	0.4515	0.4613
80	0.3977	0.4060	0.4146	0.4232	0.4321	0.4411
90	0.3826	0.3903	0.3983	0.4063	0.4145	0.4228
100	0.3687	0.3760	0.3834	0.3909	0.3985	0.4062

by Boned et al.[10] using a vibrating-tube densimeter, and calculated from the correlation equation proposed by Khasanshin.[11] The AAD values were found to be 0.027 %, 0.024 %, and 0.035 %, respectively. Wisotzki and Würflinger[12] measured specific volume of cyclopentanol using a high-pressure dilatometer. The AAD value is 0.090 % for all results reported in the pressure range from $p = (0.1$ to 100) MPa and temperatures

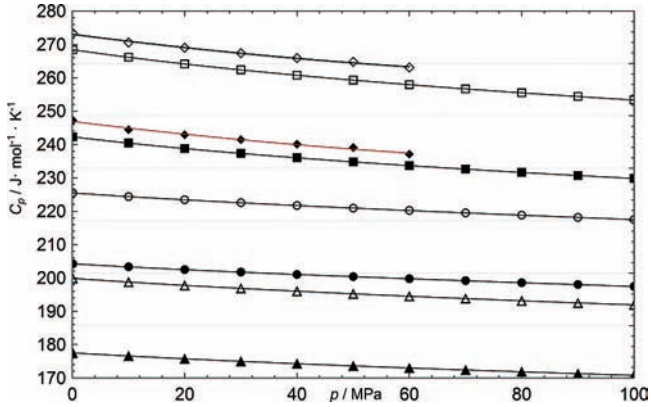

Figure 1. Isobaric molar heat capacity of cyclopentanol at ▲, $T = 293.15$ K and Δ, $T = 318.15$ K; pentan-1-ol at ●, $T = 293.15$ K and ○, $T = 318.15$ K; 2-methyl-2-butanol at ■, $T = 293.15$ K and □, $T = 318.15$ K; and pentan-3-ol[7] at ◆, $T = 293.15$ K and ◇, $T = 318.15$ K. Lines calculated from the empirical function: $C_p = \sum_{i=0}^{3} a_i p^i$.

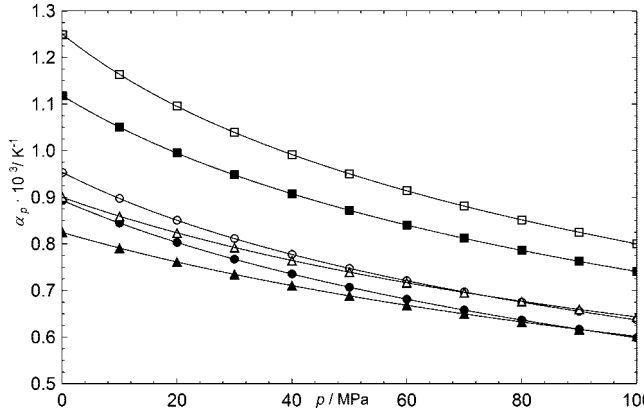

Figure 2. Isobaric thermal expansion of cyclopentanol at ▲, $T = 293.15$ K and Δ, $T = 318.15$ K; pentan-1-ol at ●, $T = 293.15$ K and ○, $T = 318.15$ K; 2-methyl-2-butanol at ■, $T = 293.15$ K and □, $T = 318.15$ K. Lines calculated from the empirical function: $\alpha_p = \sum_{i=0}^{3} a_i p^i$.

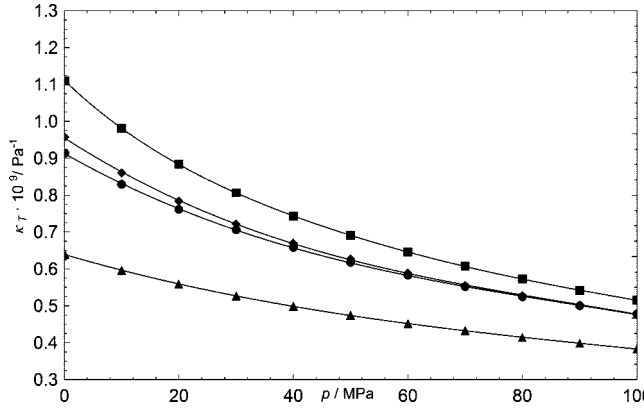

Figure 3. Isothermal compressibity of ▲, cyclopentanol; ●, pentan-1-ol; ■, 2-methyl-2-butanol; and ◆, pentan-3-ol[8] at $T = 303.15$ K. Lines calculated from the empirical function: $\kappa_T = \sum_{i=0}^{3} a_i p^i$.

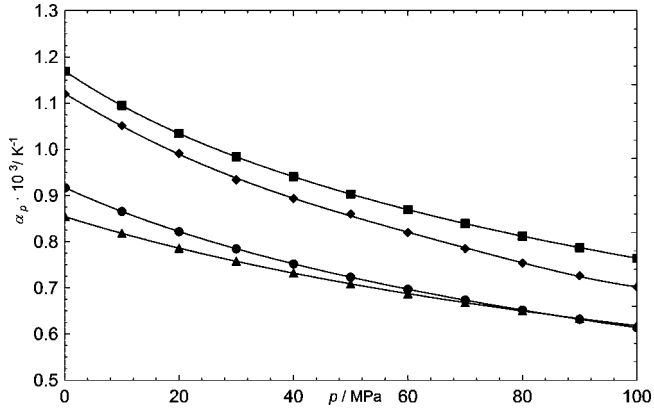

Figure 4. Isobaric thermal expansion of ▲, cyclopentanol; ●, pentan-1-ol; ■, 2-methyl-2-butanol; and ◆, pentan-3-ol* at $T = 303.15$ K. *, calculated from densities reported in ref 8. Lines calculated from the empirical function: $\alpha_p = \sum_{i=0}^{3} a_i p^i$.

from $T = (293.15$ to 318.15) K. After critical analysis of results obtained by them, I found that AAD was 0.042 % when I rejected results for $T = 303$ K. A comparison of the densities of 2-methyl-2-butanol at $p = 10$ MPa obtained in this work for the whole temperature range and those correlated by Cibulka et al.[4] resulted in an AAD value of 0.017 %.

From the densities and speeds of sound, the adiabatic compressibilities were calculated by the Laplace formula: $\kappa_S = (\rho u^2)^{-1}$. Results of the calculations are given in Table 8.

The isothermal compressibility was calculated from the adiabatic one by the well-known relationship

$$\kappa_T = \kappa_S + \frac{\alpha_p^2 VT}{C_p} \quad (3)$$

where α_p is the isobaric thermal expansion calculated from the definition: $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$. The values of the isobaric thermal expansion and the isothermal compressibility are listed in Tables 9 and 10, respectively. Boned et al.[10] calculated the isobaric thermal expansion of pentan-1-ol in two different ways: using temperature dependence of the densities $\rho_p(T)$ or of the molar volumes $V_p(T)$ for each pressure. In this work, the isobaric thermal expansion was calculated using $\rho_p(T)$ for each pressure. The comparison between the isobaric thermal expansions obtained in this work and those calculated by Boned et al.[10] using $\rho_p(T)$ dependence gives AAD = 1.49 %. The uncertainty declared by Boned et al.[10] is 3 %. The comparison between the isothermal compressibilities of pentan-1-ol calculated in this work from eq 3 and calculated by Boned et al.[10] using the Tait-like equation gives AAD = 1.33 %. The uncertainty for the isothermal compressibility declared by the authors[10] is 1 %.

Since association is connected with a negative volume effect, this suggests an increase in association with increasing pressure and thereby a shift of the association equilibrium toward associated species ($(\partial \ln K/\partial p)_T > 0$). Additionally, the isothermal compression of liquid reduces the free volume and the amplitude of molecular vibrations. This suggests that the structural contributions and nonspecific interactions, connected with the change of intermolecular distances in the compressed liquid, play also important role.

Because of the relation between the isobaric heat capacity and entropy ($C_p = T(\partial S/\partial T)_p$), the isobaric heat capacity is an approximated indicator of the molecular structure. Cerdeiriña et al.[6,7] examined the effects of temperature and pressure on heat capacities of linear and branched alcohols. They pointed out that association affects the effect of temperature on the heat capacity, while the association contribution to $(\partial C_p/\partial p)_T$ is significantly less important than the nonspecific one.[7] Forsman et al.[43] analyzed pressure dependence of heptane, propan-1-ol, and propan-2-ol. They proposed that three factors control the variation of heat capacity with pressure: the free volume for molecular vibration, intramolecular vibration, and rotational degrees of freedom. Isothermal compression of a liquid reduces the free volume and the amplitude of molecular vibrations independently of the shape of the molecules, while changes in rotation depend significantly on their symmetry. Thus, probably rotations around the long axis of the linear molecule such as heptane do not remain, affected very much by compression, while for propan-2-ol, rotation can be hindered under high pressure. The isobaric heat capacity decreases with increasing pressure and increases with increasing temperature; however, the effect of pressure on this quantity is rather small in comparison with that of temperature. Results obtained in this work show that the effect of pressure on heat capacity, and also on isobaric thermal expansion and isothermal compressibility, is more pronounced for, weakly associated, tertiary 2-methyl-2-butanol than for pentan-1-ol and cyclopentanol (Figures 1, 2, and 3).

On the basis of the thermodynamic relation $(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p$, the pressure−temperature behavior of the isobaric thermal expansion can be analyzed as a macroscopic manifestation of the effects existing at the molecular level.[44−47] The isotherms of isobaric thermal expansion cross each other at high pressure. The crossing point of isobaric thermal expansion is characteristic for simple liquids. For example, the isotherms of α_p of hexane cross each other at $p = (65 \pm 2)$ MPa.[45] For associated liquids, a shift of the crossing points toward the higher pressure region was observed. For example, for hexan-1-ol the crossing point appears in the vicinity of $p = 280$ MPa; however, for water the crossing point is observed nearby $p = 450$ MPa.[46] Moreover, this specific behavior of isobaric thermal expansion was also observed for more complicated systems such as petroleum diesel oil and biodiesel fuel.[48]

The isobaric thermal expansion and isothermal compressibility depend significantly on pressure in the vicinity of the atmospheric pressure, while with increasing pressure the effect gradually decreases. This effect is the most significant for isothermal compressibility of 2-methyl-2-butanol, in contrast to the close-packed cyclopentanol which is less compressible (Figure 3). Moreover, pressure dependence of heat capacity and the isobaric thermal expansion of 2-methyl-2-butanol is similar to that of pentan-3-ol (Figures 1 and 4). In the previous work,[3] the temperature dependencies of the heat capacities under atmospheric pressure were reported for 2-methyl-2-butanol and cyclopentanol, and the physicochemical properties of pentan-1-ol, cyclopentanol, 2-methyl-2-butanol, and pentan-3-ol were compared and discussed. It was found that under atmospheric pressure temperature dependence of heat capacity for 2-methyl-2-butanol is the most similar to that for pentan-3-ol, particularly at high temperatures, and heat capacity of cyclopentanol is low in comparison with other pentanols. Concluding, pressure dependence of the isobaric heat capacities and the isobaric thermal expansions also qualitatively confirms similarities and dissimilarities of physicochemical properties of pentan-1-ol, cyclopentanol, 2-methyl-2-butanol, and pentan-3-ol.

Summary

The speeds of sound in pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol were measured within the temperatures from $T = (293$ to $318)$ K and at pressures up to 101 MPa. The densities of the liquids under test have been measured within the same temperature range under atmospheric pressure. From the measurement results, the pressure and temperature dependence of the density and isobaric heat capacity have been determined using the modified method of Davis and Gordon.[7] This enables the determination of the isothermal and adiabatic compressibility and the isobaric thermal expansion as a function of temperature and pressure. The obtained results qualitatively confirm similarities and dissimilarities of physicochemical properties of pentan-1-ol, cyclopentanol, 2-methyl-2-butanol, and pentan-3-ol.

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