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Speeds of Sound, Densities, Isobaric Thermal Expansion, Compressibilities, and Internal Pressures of Heptan-1-ol, Octan-1-ol, Nonan-1-ol, and Decan-1-ol at Temperatures from (293 to 318) K and Pressures up to 100 MPa

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The speeds of sound in heptan-1-ol, octan-1-ol, and nonan-1-ol at pressures up to 101 MPa and in decan-1-ol at pressures up to 76 MPa have been measured within the temperature range of (293 to 318) K. The densities have been measured in the same temperature range under atmospheric pressure. The densities, isobaric heat capacities, isentropic and isothermal compressibilities, isobaric thermal expansions, and internal pressures as functions of temperature and pressure have been calculated using the experimental results and the literature isobaric heat capacities for the atmospheric pressure. A modified method, based on the suggestion of Davis and Gordon (*J. Chem. Phys*. **1967**, *46*, 2650−2660), has been applied. The effect of pressure and temperature on the isothermal compressibility, isobaric thermal expansion, isobaric heat capacity, and internal pressure is discussed.

Introduction

Thermodynamic properties of simple organic liquids are of considerable interest from both the theoretical as well as the practical point of view. In the petrochemical industry, an important point of interest is the influence of "bio" additives to mineral fuels and greases such as alcohols or esters. Alkan-1-ols belong to the liquids most frequently studied under atmospheric and also higher pressures. However, the thermodynamic and acoustic properties have been reported mainly for alcohols with 1 to 5 carbon atoms in the chain. Relatively few data are available in the literature[1,2] for higher alkan-1-ols. Besides, the available results are rather incomplete. The speeds of sound in primary alcohols under elevated pressures have been measured by Sysoev and Otpuschennikov and published in Nauchnye Trudy (Kurskiœi Gosudarstvennyœi Pedagogicheskiœi Institute).[2] Unfortunately, these articles are not available. Khasanshin[3] 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 (0.1 to 100) MPa and for six temperatures from (303.15 to 453.15) K determined at 20 K steps. Plantier et al.[4] reported the speed of sound in octan-1-ol at pressures up to 50 MPa and temperatures ranging from (303.15 to 373.15) K every 10 K. This work is a part of systematic studies of thermodynamic properties of organic liquids under elevated pressures using the acoustic method. Acoustic and thermodynamic properties of ethanol, propan-1-ol, and hexan-1-ol at elevated pressures have been presented earlier.[5−7] In this paper, new measurements of the speed of sound in heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol in the temperature range from (293 to 318) K are reported. The speeds have been measured under pressures up to 101 MPa for heptan-1-ol, octan-1-ol, and nonan-1-ol and up to 76 MPa for decan-1-ol. The densities have been measured within the same temperature range under atmospheric pressure. The densities and isobaric heat capacities of heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol for the temperature range from (293 to 318) K and at pressures up to 100 MPa for the first three alcohols and up to 70 MPa for the latter one have been calculated using the speeds of sound under elevated pressures together with the densities and isobaric heat capacities at atmospheric pressure. To this end, the method based on the suggestion of Davis and Gordon[8] with a numerical procedure proposed by Sun et al.[9] was applied. 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, isobaric thermal expansion, and internal pressures. The effect of temperature and pressure on the isothermal compressibility, isobaric thermal expansion, isobaric heat capacity, and internal pressure is discussed. To the best of my knowledge, these properties have never been investigated in that pressure range.

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

component		exp.	lit.
heptan-1-ol	u/m·s^{-1}	1327.27	1327.57,[10] 1330[11]
	ρ/kg·m^{-3}	818.80	818.52,[12] 818.78,[13] 818.9[11]
octan-1-ol	ρ/m·s^{-1}	1347.32	1347.18,[14] 1347.43,[15] 1347.5[16]
	ρ/kg·m^{-3}	821.62	821.60,[13] 821.68,[17] 821.79,[15] 822.3[18]
nonan-1-ol	u/m·s^{-1}	1364.64	1364.41,[19] 1364.70[20]
	ρ/kg·m^{-3}	824.24	824.02,[12] 824.271,[20] 824.47[21]
decan-1-ol	u/m·s^{-1}	1379.69[a]	1375.84,[15] 1380.2,[15] 1384[15]
	ρ/kg·m^{-3}	826.37	826.23,[20] 826.3,[15] 826.57,[15] 826.8[18]

[a] Published in a previous work.[22]

Experimental Section

Chemicals. Heptan-1-ol was from Fluka with a minimum mass fraction 99 % of $C_7H_{15}OH$, octan-1-ol was from Lancaster with a minimum mass fraction 99 % of $C_8H_{17}OH$, nonan-1-ol was from Alfa Aesar with a minimum mass fraction 99 % of $C_9H_{19}OH$, and decan-1-ol was from Aldrich with a minimum mass fraction 99 % of $C_{10}H_{21}OH$. All the alcohols were dried over 0.3 nm molecular sieves. The concentration of water was determined by the Karl Fisher method. The mass fraction of water was less than $2 \cdot 10^{-7}$ for nonan-1-ol and decan-1-ol and

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

heptan-1-ol			octan-1-ol			nonan-1-ol			dacan-1-ol		
T/K	*p*/MPa	*u*/m·s^{-1}	*T*/K	*p*/MPa	*u*/m·s^{-1}	*T*/K	*p*/MPa	*u*/m·s^{-1}	*T*/K	*p*/MPa	*u*/m·s^{-1}
292.89	0.10	1345.37	292.92	0.10	1365.25	292.88	0.10	1382.77	293.10	0.10	1397.23[a]
292.78	15.20	1421.66	292.77	15.23	1440.32	292.87	15.20	1456.67	292.91	15.20	1470.57
292.77	30.39	1487.31	292.77	30.43	1505.21	292.87	30.39	1520.79	292.90	30.39	1533.84
292.77	45.59	1546.94	292.83	45.61	1564.06	292.86	45.59	1579.55	292.96	45.59	1592.01
292.77	60.79	1602.64	292.78	60.80	1619.26	292.87	60.79	1633.97	292.86	60.79	1646.34
292.76	75.99	1654.15	292.77	76.01	1670.06	292.87	75.99	1684.39	298.07	0.10	1379.96[a]
292.77	91.18	1701.99	292.79	91.20	1717.80	292.86	91.18	1731.84	297.95	15.20	1453.77
292.77	101.32	1732.68	292.83	96.12	1732.99	292.86	101.32	1762.05	297.96	30.39	1518.00
298.17	0.10	1327.21	298.20	0.10	1347.13	298.18	0.10	1364.56	297.98	45.59	1576.76
298.06	15.20	1404.93	298.19	15.20	1422.59	297.96	15.20	1440.24	297.96	60.79	1631.39
298.06	30.39	1471.77	298.13	30.41	1488.81	297.96	30.39	1505.39	297.95	66.24	1649.80
298.06	45.59	1532.30	298.09	45.61	1548.80	297.96	45.59	1564.54	297.96	69.30	1660.02
298.06	60.79	1588.18	298.09	60.84	1604.63	297.95	60.79	1619.98	297.99	71.85	1668.22
298.06	75.99	1640.40	298.07	76.04	1656.52	297.96	75.99	1670.69	297.99	73.52	1673.62
298.06	91.18	1688.89	298.07	91.19	1703.92	297.95	91.18	1718.71	297.99	74.70	1677.61
298.06	101.32	1719.64	298.07	97.84	1724.34	297.95	101.32	1749.18	298.00	75.99	1681.72
303.14	0.10	1310.24	303.18	0.10	1330.19	303.16	0.10	1347.52	303.04	0.10	1362.82[a]
302.94	15.20	1389.45	303.27	15.20	1406.24	302.94	15.20	1424.28	302.92	15.20	1436.75
302.94	30.39	1457.34	303.28	30.41	1473.29	302.94	30.39	1490.24	303.08	30.39	1501.48
302.94	45.59	1518.74	303.27	45.60	1533.86	302.93	45.59	1550.12	303.11	45.59	1560.98
302.94	60.79	1575.32	303.26	60.82	1590.15	302.93	60.79	1606.05	303.02	60.79	1616.95
302.95	75.99	1628.00	303.15	76.00	1642.79	302.93	75.99	1657.58	303.03	66.24	1635.74
302.94	91.18	1676.97	303.16	91.20	1691.22	302.93	91.18	1705.79	303.05	69.23	1645.65
302.94	101.32	1708.00	303.20	101.34	1722.27	302.93	101.32	1736.67	303.03	71.56	1653.45
308.12	0.10	1293.20	308.16	0.10	1313.30	308.14	0.10	1330.57	303.04	73.60	1660.21
307.94	15.20	1373.96	308.19	15.21	1390.70	307.92	15.20	1408.48	303.15	74.79	1664.07
307.94	30.39	1442.79	308.17	30.40	1458.76	307.91	30.39	1475.46	303.09	75.99	1667.77
307.94	45.59	1505.03	308.18	45.60	1520.26	307.91	45.59	1535.97	308.04	0.10	1345.82[a]
307.93	60.79	1561.90	308.18	60.79	1576.82	307.91	60.79	1592.39	308.09	15.20	1420.03
307.94	75.99	1615.55	308.17	76.02	1629.97	307.92	75.99	1644.67	307.97	30.39	1486.61
307.93	91.18	1664.79	308.12	91.20	1679.20	307.92	91.18	1693.20	307.98	45.59	1546.89
307.94	101.32	1695.96	308.16	91.21	1679.14	307.92	101.32	1724.32	307.96	60.79	1603.08
313.09	0.10	1276.31	308.12	101.32	1710.26	313.11	0.10	1313.75	307.95	65.86	1620.93
312.91	15.20	1358.87	313.15	0.10	1296.46	312.91	15.20	1392.75	307.96	68.85	1631.26
312.90	30.39	1428.71	313.26	15.20	1375.07	312.91	30.39	1460.82	307.96	71.38	1639.82
312.90	45.59	1491.58	313.26	30.39	1443.89	312.91	45.59	1522.18	307.94	73.31	1646.24
312.90	60.79	1549.07	313.26	45.59	1506.12	312.91	60.79	1578.93	307.93	74.72	1650.91
312.90	75.99	1603.13	313.28	60.79	1563.47	312.91	75.99	1631.98	307.92	75.99	1655.12
312.90	91.18	1653.05	313.23	76.00	1616.59	312.91	91.18	1681.12	313.01	0.10	1329.03[a]
312.91	101.32	1684.72	313.22	91.20	1666.84	312.91	101.32	1712.28	313.06	15.20	1404.47
318.37	0.10	1258.57	313.22	101.34	1697.76	318.29	0.10	1296.33	313.03	30.39	1471.90
318.30	15.20	1342.76	318.33	0.10	1279.15	318.39	15.20	1375.92	313.01	45.59	1532.53
318.29	30.39	1413.60	318.83	15.20	1357.83	318.39	30.39	1444.81	313.00	60.79	1589.39
318.29	45.59	1477.46	318.84	30.39	1427.84	318.39	45.59	1507.26	313.00	65.98	1607.83
318.29	60.79	1535.46	318.82	45.60	1491.03	318.38	45.59	1507.34	313.00	69.20	1618.90
318.29	75.99	1590.00	318.82	60.79	1549.17	318.38	60.79	1564.64	313.03	72.90	1631.48
318.29	91.18	1640.62	318.82	75.99	1603.39	318.38	75.99	1618.27	313.04	75.99	1641.73
318.29	101.32	1672.37	318.83	91.18	1653.69	318.39	91.18	1667.79	318.18	0.10	1311.69[a]
			318.82	101.33	1684.88	318.38	91.18	1667.82	318.36	15.20	1387.67
						318.38	101.32	1699.14	318.44	30.39	1455.97
									318.45	30.39	1455.89
									318.44	45.59	1517.70
									318.41	60.79	1575.13
									318.40	65.95	1593.73
									318.43	72.66	1617.01
									318.43	73.87	1621.06
									318.43	75.99	1628.22

[a] Published in a previous work.[22]

less than $3{\cdot}10^{-7}$ for heptan-1-ol and octan-1-ol. Each sample was degassed in an ultrasonic cleaner just before the measurement. The purity of these chemicals was tested by comparing the densities and speeds of sound with literature values (Table 1).

Ultrasonic Speed Measurements. The speed of sound in liquids under test has been measured at atmospheric and higher pressures using two measuring sets designed and constructed in our laboratory. Two measuring vessels of the same acoustic path and construction have been used: one of them destined for measurements under atmospheric pressure, the other one for measurements under elevated pressures. A single transmitting−receiving ceramic transducer operating at 2 MHz and an acoustic mirror have been applied. The measuring sets operate on the principle of the pulse−echo−overlap method. 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).

Re-distilled 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,[23] while for higher pressures the equation of Kell and Whalley[24] was used. The uncertainty of the speed of sound measurements was estimated to be 0.03 % at atmospheric pressure, 0.04 % under pressures up to 60 MPa, and 0.05 % under pressures from (60 to 101) MPa. Other details of the high-pressure device and the method of the speed of sound measurements can be found in a previous paper.[25]

Density Measurements. The densities at atmospheric pressure were measured using a vibrating tube densimeter Anton Paar DMA 5000. The densimeter was calibrated with air and re-

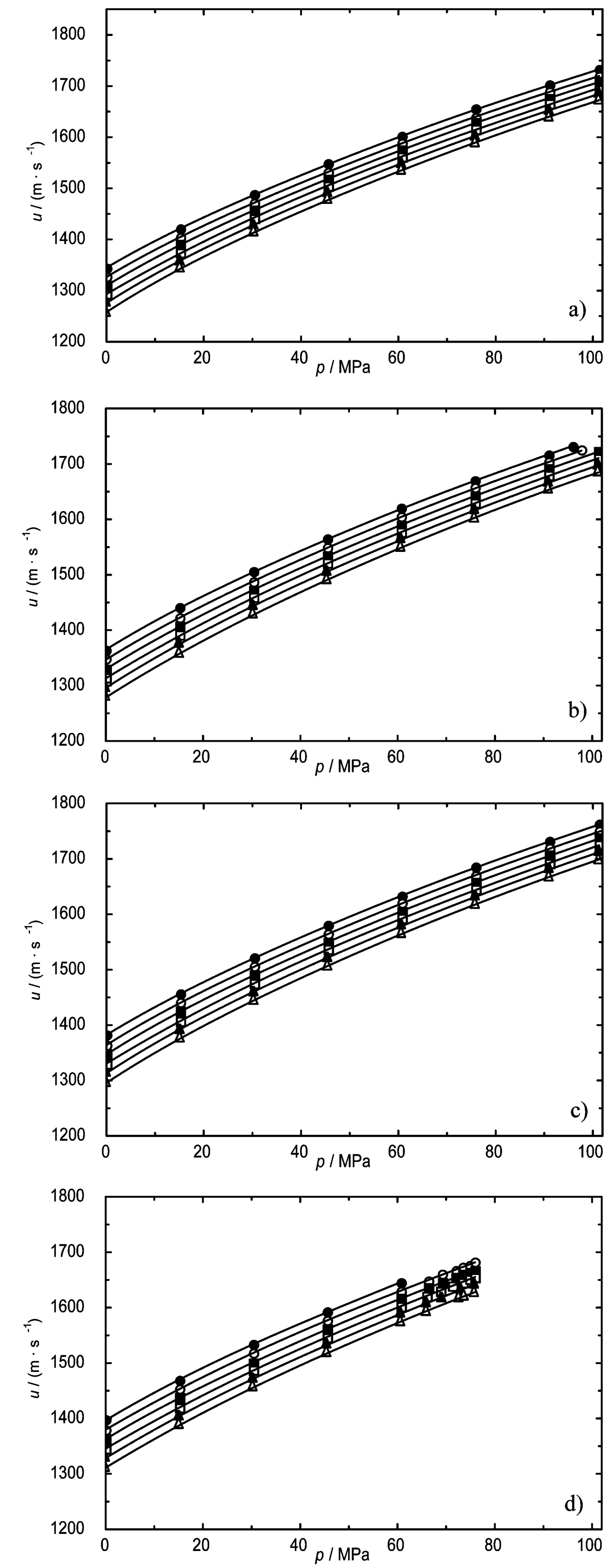

Figure 1. Speed of sound in (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $u = \sum_{i=0}^{3} a_i p^i$.

distilled 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}.

Table 3. Densities of Alcohols Measured within the Temperature Range of (293 to 318) K at Atmospheric Pressure

heptan-1-ol		octan-1-ol		nonan-1-ol		dacan-1-ol	
T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
293.151	822.297	293.151	825.048	293.155	827.660	293.150	829.758
298.150	818.796	298.148	821.636	298.155	824.239	298.150	826.370
303.152	815.269	303.151	818.173	303.156	820.800	303.150	822.950
308.150	811.724	308.149	814.675	308.155	817.345	308.150	819.570
313.152	808.158	313.149	811.171	313.153	813.868	313.150	816.120
318.151	804.546	318.149	807.654	318.150	810.376	318.150	812.634

Table 4. Coefficients of Polynomial (1) for the Speed of Sound and Density under Atmospheric Pressure within the Temperature Range of (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_2·10^3/ m·s^{-1}·K^{-2}	δu_0/ m·s^{-1}	ρ_0/ kg·m^{-3}	ρ_1/ kg·m^{-3}·K^{-1}	ρ_2·10^4/ kg·m^{-3}·K^{-2}	$\delta\rho$/ kg·m^{-3}
heptan-1-ol	2497.354	−4.416949	1.65176	0.04	983.002	−0.3993296	−5.07848	0.006
octan-1-ol	2560.249	−4.714394	2.16735	0.02	983.294	−0.3955131	−4.92143	0.01
nonan-1-ol	2555.809	−4.560609	1.89642	0.002	995.338	−0.4618601	−3.75632	0.001
decan-1-ol	2696.695	−5.376703	3.21792	0.02	989.849	−0.4188373	−4.34218	0.02

Results

The ultrasonic speeds in heptan-1-ol, octan-1-ol, and nonan-1-ol have been measured from (293 to 318) K in about 5 K steps and under the pressures about (0.1, 15, 30, 45, 60, 75, 90, and 101) MPa. The ultrasonic speeds in decan-1-ol have been measured under the pressures about (0.1, 15, 30, 45, 60, and 76) MPa. The experimental values are listed in Table 2 and presented in Figure 1. 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); 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 procedure was used to reduce the number of non-zero coefficients. The coefficients and the mean deviations from the regression lines are given in Table 4.

Since the sensitivity of the pressure gauge is lower than that of both the ultrasonic measuring set and the thermometer, the equation suggested by Sun et al.[26] was chosen in this work for smoothing out the speed of sound, pressure, and temperature:

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

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 non-zero coefficients.

The speeds of sound in octan-1-ol reported in this work are compared with those reported by Plantier et al.[4] The absolute average deviation (AAD $= (100/n)\sum_{i=1}^{n} |u_{\mathrm{lit},i}/u_{\mathrm{exp},i} - 1|$) was

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

component	j	a_{1j}/ $K^{-j}\cdot MPa\cdot s\cdot m^{-1}$	a_{2j}/ $K^{-j}\cdot MPa\cdot s^2\cdot m^{-2}$	a_{3j}/ $K^{-j}\cdot MPa\cdot s^3\cdot m^{-3}$	δu/ $m\cdot s^{-1}$
heptan-1-ol	0	0.4261233304	$2.06383455\cdot 10^{-4}$		0.31
	1	$-8.23147105\cdot 10^{-4}$			
	2			$-2.76888747\cdot 10^{-13}$	
octan-1-ol	0	0.2803665851	$3.16738349\cdot 10^{-4}$		0.28
	1		$-4.20983029\cdot 10^{-7}$		
	2	$-1.04835117\cdot 10^{-6}$			
nonan-1-ol	0	0.2823007509	$3.19513200\cdot 10^{-4}$		0.31
	1		$-4.18349839\cdot 10^{-7}$		
	2	$-1.05123867\cdot 10^{-6}$			
decan-1-ol	0	0.2594264772	$3.33303397\cdot 10^{-4}$		0.25
	1				
	2	$-7.41555104\cdot 10^{-7}$	$-1.58502851\cdot 10^{-9}$		

Table 6. Calculated Densities of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

p	$\rho/kg\cdot m^{-3}$					
	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1[a]	822.30	818.80	815.27	811.73	808.15	804.55
10	828.43	825.08	821.71	818.32	814.91	811.47
20	834.20	830.97	827.73	824.47	821.2	817.90
30	839.60	836.48	833.36	830.21	827.05	823.88
40	844.69	841.68	838.65	835.60	832.54	829.47
50	849.52	846.59	843.65	840.70	837.73	834.75
60	854.11	851.26	848.40	845.53	842.64	839.74
70	858.50	855.72	852.93	850.13	847.32	844.49
80	862.70	859.99	857.27	854.53	851.79	849.03
90	866.73	864.08	861.42	858.75	856.07	853.37
100	870.61	868.02	865.42	862.80	860.18	857.54
			Octan-1-ol			
0.1[a]	825.06	821.62	818.17	814.68	811.18	807.65
10	831.02	827.73	824.42	821.08	817.73	814.36
20	836.63	833.46	830.28	827.07	823.85	820.62
30	841.90	838.84	835.76	832.67	829.56	826.44
40	846.87	843.91	840.93	837.94	834.93	831.91
50	851.59	848.71	845.82	842.91	840.00	837.07
60	856.08	853.28	850.47	847.64	844.81	841.96
70	860.38	857.65	854.90	852.15	849.39	846.61
80	864.49	861.83	859.15	856.46	853.76	851.05
90	868.44	865.84	863.22	860.60	857.96	855.31
100	872.25	869.70	867.14	864.57	861.99	859.40
			Nonan-1-ol			
0.1[a]	827.66	824.24	820.80	817.35	813.87	810.38
10	833.48	830.20	826.91	823.59	820.27	816.92
20	838.97	835.81	832.64	829.45	826.25	823.04
30	844.12	841.07	838.01	834.93	831.84	828.74
40	849.00	846.04	843.07	840.09	837.10	834.09
50	853.62	850.75	847.87	844.97	842.07	839.15
60	858.03	855.23	852.43	849.62	846.79	843.95
70	862.24	859.52	856.79	854.05	851.29	848.53
80	866.28	863.63	860.96	858.29	855.60	852.90
90	870.16	867.57	864.97	862.35	859.73	857.09
100	873.91	871.37	868.82	866.27	863.70	861.11
			Decan-1-ol			
0.1[a]	829.75	826.37	822.97	819.55	816.11	812.64
10	835.44	832.20	828.94	825.66	822.37	819.05
20	840.81	837.69	834.56	831.40	828.24	825.05
30	845.86	842.85	839.82	836.78	833.73	830.66
40	850.64	847.72	844.79	841.85	838.90	835.93
50	855.17	852.35	849.51	846.65	843.79	840.91
60	859.50	856.75	853.99	851.22	848.44	845.64
70		860.97	858.28	855.58	852.87	850.14

[a] Calculated from eq 1.

Table 7. Calculated Isobaric Molar Heat Capacities of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

p	$C_p/J\cdot mol^{-1}K^{-1}$					
	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1[a]	268.13	272.98	278.01	283.17	288.44	293.77
10	267.10	271.94	276.92	282.03	287.26	292.57
20	266.20	271.02	275.97	281.04	286.22	291.52
30	265.40	270.20	275.12	280.16	285.31	290.58
40	264.67	269.45	274.35	279.36	284.49	289.73
50	264.01	268.77	273.64	278.63	283.73	288.96
60	263.39	268.13	272.98	277.95	283.04	288.24
70	262.81	267.54	272.37	272.37	282.39	287.57
80	262.27	266.98	271.79	276.73	281.77	286.93
90	261.75	266.44	271.25	276.16	281.19	286.34
100	261.26	265.93	270.72	275.62	280.63	285.76
			Octan-1-ol			
0.1[a]	297.51	303.47	309.49	315.55	321.64	327.72
10	296.41	302.34	308.32	314.33	320.37	326.43
20	295.45	301.35	307.29	313.26	319.27	325.30
30	294.59	300.47	306.38	312.32	318.29	324.29
40	293.82	299.67	305.55	311.47	317.41	323.38
50	293.11	298.94	304.80	310.69	316.61	322.56
60	292.45	298.26	304.10	309.97	315.87	321.79
70	291.84	297.63	303.45	309.30	315.17	321.08
80	291.25	297.03	302.83	308.66	314.52	320.40
90	290.70	296.45	302.24	308.05	313.89	319.76
100	290.16	295.90	301.67	307.47	313.29	319.14
			Nonan-1-ol			
0.1[a]	332.80	337.57	342.85	348.57	354.65	361.04
10	331.70	336.49	341.72	347.36	353.40	359.79
20	330.74	335.52	340.71	346.31	352.30	358.68
30	329.88	334.64	339.80	345.36	351.32	357.68
40	329.10	333.84	338.97	344.50	350.43	356.77
50	328.37	333.09	338.19	343.70	349.61	355.92
60	327.68	332.38	337.46	342.95	348.83	355.12
70	327.03	331.70	336.77	342.23	348.09	354.36
80	326.40	331.06	336.10	341.54	347.38	353.63
90	325.79	330.43	335.45	340.87	346.70	352.92
100	325.19	329.81	334.82	340.22	346.03	352.24
			Decan-1-ol			
0.1[b]	367.12	372.61	378.31	378.31	390.31	396.62
10	365.90	371.34	376.99	382.85	388.90	395.17
20	364.80	370.21	375.83	381.64	387.66	393.88
30	363.82	369.20	374.78	380.56	386.54	392.73
40	362.93	368.28	373.83	379.58	385.53	391.68
50	362.10	367.42	372.94	378.67	384.59	390.71
60	361.32	366.62	372.11	377.81	383.71	389.81
70		365.85	371.33	371.33	382.87	388.94

[a] Values from ref 29. [b] Values from ref 22.

found to be 0.06 %, which does not exceed the uncertainty of 0.2 % reported by them. A comparison of the speeds of sound in heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol at 303.15 K obtained in this experiment for the whole pressure range with calculated by the correlation equation proposed by Khasanshin[4] resulted in AAD values of 0.04 %, 0.03 %, 0.06 %, and 0.04 %, respectively.

Density, Isobaric Heat Capacity, and Derived Thermodynamic Properties under Elevated Pressures. The densities and isobaric heat capacities of heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol were determined for temperatures from (293 to 318) K and for pressures up to 100 MPa for the first three alkanols and up to 70 MPa for the latter one. Details of the algorithm were discussed in previous works.[27,28] 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 polynomials reported by Zábranský et al.[29] were used for heptan-1-ol, octan-1-ol, and nonan-1ol, while for decan-1-ol the polynomial reported by Dzida and Góralski[22] was applied. The calculated density and isobaric heat capacity values are listed in Tables 6 and 7, respectively. The uncertainty of the measured speeds of sound cause a maximum error of 0.02 % in the densities calculated for elevated pressures. The quality of the densities, obtained in this work, was checked by comparisons: (a) with the densities of octan-1-ol and decan-1-ol measured by Matsuo and Makita[18] by means of a vibrating densimeter at 298.15 K and pressures up to 40 MPa (the AAD values were found to be 0.07 % and 0.05 % for octan-1-ol and decan-1-ol, respectively, at atmospheric pressure as well as higher pres-

Table 8. Isentropic Compressibilities of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

p	$\kappa_S \cdot 10^9$/Pa^{-1}					
	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1	0.6728	0.6933	0.7146	0.7367	0.7598	0.7838
10	0.6201	0.6373	0.6551	0.6734	0.6924	0.7120
20	0.5767	0.5915	0.6067	0.6224	0.6384	0.6550
30	0.5403	0.5533	0.5666	0.5802	0.5941	0.6084
40	0.5092	0.5207	0.5325	0.5445	0.5567	0.5693
50	0.4821	0.4924	0.5029	0.5137	0.5246	0.5358
60	0.4582	0.4675	0.4770	0.4867	0.4966	0.5066
70	0.4369	0.4454	0.4541	0.4629	0.4718	0.4809
80	0.4177	0.4256	0.4335	0.4416	0.4497	0.4580
90	0.4004	0.4077	0.4150	0.4224	0.4298	0.4374
100	0.3847	0.3914	0.3981	0.4049	0.4118	0.4188
			Octan-1-ol			
0.1	0.6510	0.6705	0.6907	0.7117	0.7334	0.7560
10	0.6018	0.6185	0.6357	0.6534	0.6717	0.6905
20	0.5609	0.5754	0.5902	0.6055	0.6212	0.6373
30	0.5263	0.5391	0.5522	0.5655	0.5792	0.5932
40	0.4965	0.5079	0.5196	0.5315	0.5436	0.5559
50	0.4706	0.4809	0.4913	0.5020	0.5128	0.5237
60	0.4477	0.4570	0.4665	0.4761	0.4858	0.4956
70	0.4272	0.4358	0.4444	0.4531	0.4619	0.4709
80	0.4089	0.4167	0.4246	0.4326	0.4407	0.4488
90	0.3923	0.3995	0.4068	0.4141	0.4215	0.4289
100	0.3771	0.3838	0.3906	0.3973	0.4041	0.4110
			Nonan-1-ol			
0.1	0.6328	0.6515	0.6709	0.6911	0.7120	0.7338
10	0.5860	0.6020	0.6186	0.6357	0.6534	0.6716
20	0.5469	0.5609	0.5753	0.5901	0.6053	0.6209
30	0.5138	0.5262	0.5389	0.5519	0.5652	0.5788
40	0.4853	0.4964	0.5077	0.5193	0.5311	0.5431
50	0.4604	0.4704	0.4806	0.4910	0.5016	0.5123
60	0.4384	0.4475	0.4568	0.4661	0.4757	0.4853
70	0.4188	0.4271	0.4355	0.4441	0.4527	0.4615
80	0.4011	0.4087	0.4165	0.4243	0.4322	0.4402
90	0.3851	0.3921	0.3993	0.4065	0.4138	0.4211
100	0.3705	0.3770	0.3836	0.3903	0.3970	0.4038
			Decan-1-ol			
0.1	0.6175	0.6357	0.6546	0.6741	0.6942	0.7151
10	0.5732	0.5890	0.6053	0.6221	0.6394	0.6571
20	0.5359	0.5498	0.5640	0.5787	0.5936	0.6090
30	0.5041	0.5165	0.5291	0.5420	0.5552	0.5686
40	0.4766	0.4877	0.4990	0.5105	0.5222	0.5341
50	0.4525	0.4626	0.4728	0.4831	0.4936	0.5042
60	0.4312	0.4404	0.4496	0.4590	0.4684	0.4780
70		0.4205	0.4290	0.4375	0.4461	0.4547

sures); (b) with densities calculated from the speeds of sound reported by Plantier et al.[4] for octan-1-ol at (303.15 and 313.15) K and pressures up to 50 MPa (the AAD values are 0.07 % and 0.06 % for (303.15 and 313.15) K, respectively, at atmospheric and higher pressures), and (c) with densities calculated by Khasanshin,[30] who published correlation equations between the density and the number of carbon atoms ranging from 4 to 10 for pressures up to 50 MPa at (293.15 and 298.15) K (the AAD values are 0.04 %, 0.04 %, 0.02 %, and 0.05 % for heptan-1-ol, octan-1-ol, nonan-1ol, and decan-1-ol, respectively). The above discrepancies are of order of uncertainty declared by Matsuo and Makita[18] (± 0.06 %) and Plantier et al.[4] (0.1 %). The values of measured speeds of sound and calculated densities of the alcohols under test are generally in a very good agreement with the literature ones providing a high quality of the obtained thermodynamic properties determined. Unfortunately, the quality of the isobaric heat capacities obtained from the ultrasonic measurements is worse than that of the densities which results from the principles of the method.[28]

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:

$$\kappa_T = \kappa_S + \frac{\alpha_p^{\,2} V T}{C_p} \tag{3}$$

Table 9. Calculated Isobaric Thermal Expansion of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

p	$\alpha_p \cdot 10^3$/K^{-1}					
	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1	0.8477	0.8575	0.8675	0.8775	0.8877	0.8980
10	0.8061	0.8145	0.8230	0.8315	0.8402	0.8489
20	0.7704	0.7777	0.7852	0.7927	0.8003	0.8079
30	0.7393	0.7459	0.7526	0.7526	0.7662	0.7731
40	0.7119	0.7180	0.7241	0.7302	0.7365	0.7427
50	0.6875	0.6931	0.6987	0.7044	0.7102	0.7160
60	0.6654	0.6706	0.6759	0.6759	0.6867	0.6921
70	0.6453	0.6503	0.6553	0.6603	0.6654	0.6706
80	0.6269	0.6316	0.6364	0.6412	0.6461	0.6510
90	0.6099	0.6145	0.6191	0.6237	0.6284	0.6331
100	0.5942	0.5986	0.6031	0.6076	0.6121	0.6167
			Octan-1-ol			
0.1	0.8291	0.8386	0.8481	0.8578	0.8676	0.8774
10	0.7896	0.7977	0.8058	0.8141	0.8224	0.8308
20	0.7552	0.7623	0.7694	0.7767	0.7839	0.7913
30	0.7252	0.7315	0.7379	0.7443	0.7508	0.7574
40	0.6985	0.7043	0.7101	0.7159	0.7219	0.7278
50	0.6746	0.6799	0.6853	0.6907	0.6962	0.7017
60	0.6530	0.6580	0.6630	0.6681	0.6732	0.6784
70	0.6333	0.6380	0.6428	0.6476	0.6525	0.6574
80	0.6152	0.6198	0.6243	0.6290	0.6336	0.6383
90	0.5985	0.6029	0.6074	0.6119	0.6164	0.6209
100	0.5831	0.5874	0.5917	0.5961	0.6005	0.6049
			Nonan-1-ol			
0.1	0.8241	0.8321	0.8402	0.8483	0.8565	0.8649
10	0.7854	0.7923	0.7992	0.8063	0.8134	0.8205
20	0.7516	0.7577	0.7639	0.7701	0.7764	0.7827
30	0.7218	0.7274	0.7330	0.7386	0.7444	0.7501
40	0.6953	0.7004	0.7057	0.7109	0.7162	0.7216
50	0.6714	0.6763	0.6812	0.6862	0.6912	0.6962
60	0.6496	0.6543	0.6591	0.6638	0.6687	0.6735
70	0.6297	0.6343	0.6389	0.6435	0.6482	0.6529
80	0.6114	0.6159	0.6204	0.6250	0.6296	0.6342
90	0.5944	0.5989	0.6033	0.6079	0.6124	0.6170
100	0.5786	0.5830	0.5875	0.5920	0.5965	0.6011
			Decan-1-ol			
0.1	0.8116	0.8303	0.8288	0.8376	0.8464	0.8554
10	0.7735	0.7810	0.7885	0.7962	0.8038	0.8116
20	0.7400	0.7466	0.7533	0.7601	0.7669	0.7739
30	0.7103	0.7163	0.7224	0.7286	0.7348	0.7411
40	0.6838	0.6894	0.6950	0.7007	0.7065	0.7123
50	0.6598	0.6651	0.6705	0.6758	0.6813	0.6867
60	0.6381	0.6431	0.6482	0.6534	0.6585	0.6638
70		0.6230	0.6280	0.6329	0.6380	0.6430

where α_p is the isobaric thermal expansion calculated from 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.

The exact thermodynamic isothermal volume dependence of internal energy (i.e., the internal pressure) was derived from the basic thermodynamic relation $dU = T\,dS - p\,dV$ as follows:

$$p_{\text{int}} \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{4}$$

where $(\partial p/\partial T)_V$ is the thermal pressure coefficient. Equation 4 can be rewritten in the following form:

$$p = T\left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \tag{5}$$

Thus, two definitions of the internal pressure can be found in the literature: one as given by eq 4[31−43] or multiplied by −1.[44−48] The total pressure of the system consists of two parts. The first term on the right-hand side represents the kinetic pressure due to the thermal motion. The second one is the static pressure called the internal pressure due to intermolecular energy. The latter can be positive, negative, or, as in the case of ideal gas, zero.

Table 10. Isothermal Compressibilities of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

	$\kappa_T \cdot 10^9$/Pa^{-1}					
p	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1	0.7838	0.8073	0.8316	0.8567	0.8828	0.9099
10	0.7202	0.7398	0.7599	0.7807	0.8021	0.8242
20	0.6678	0.6846	0.7018	0.7195	0.7376	0.7562
30	0.6239	0.6386	0.6536	0.6690	0.6847	0.7007
40	0.5864	0.5994	0.6127	0.6263	0.6401	0.6541
50	0.5538	0.5655	0.5774	0.5895	0.6018	0.6143
60	0.5252	0.5358	0.5465	0.5574	0.5685	0.5797
70	0.4997	0.5094	0.5192	0.5291	0.5392	0.5493
80	0.4769	0.4858	0.4947	0.5038	0.5130	0.5223
90	0.4563	0.4645	0.4727	0.4811	0.4895	0.4981
100	0.4375	0.4451	0.4528	0.4605	0.4683	0.4762
			Octan-1-ol			
0.1	0.7579	0.7800	0.8028	0.8265	0.8511	0.8765
10	0.6985	0.7172	0.7365	0.7564	0.7770	0.7981
20	0.6490	0.6652	0.6818	0.6990	0.7165	0.7345
30	0.6072	0.6215	0.6361	0.6510	0.6663	0.6819
40	0.5714	0.5841	0.5971	0.6103	0.6237	0.6375
50	0.5402	0.5516	0.5632	0.5751	0.5871	0.5993
60	0.5127	0.5231	0.5336	0.5443	0.5551	0.5660
70	0.4882	0.4977	0.5073	0.5170	0.5268	0.5367
80	0.4663	0.4750	0.4838	0.4927	0.5016	0.5107
90	0.4464	0.4545	0.4626	0.4708	0.4790	0.4873
100	0.4284	0.4359	0.4434	0.4510	0.4586	0.4662
			Nonan-1-ol			
0.1	0.7370	0.7585	0.7806	0.8034	0.8269	0.8511
10	0.6803	0.6987	0.7175	0.7367	0.7565	0.7767
20	0.6330	0.6489	0.6652	0.6819	0.6988	0.7161
30	0.5929	0.6071	0.6214	0.6360	0.6508	0.6659
40	0.5585	0.5711	0.5839	0.5969	0.6101	0.6234
50	0.5284	0.5398	0.5514	0.5631	0.5749	0.5868
60	0.5019	0.5123	0.5228	0.5334	0.5441	0.5548
70	0.4782	0.4878	0.4974	0.5071	0.5168	0.5266
80	0.4570	0.4658	0.4747	0.4836	0.4925	0.5014
90	0.4378	0.4459	0.4542	0.4624	0.4706	0.4788
100	0.4203	0.4279	0.4355	0.4432	0.4508	0.4584
			Decan-1-ol			
0.1	0.7178	0.7388	0.7605	0.7827	0.8057	0.8294
10	0.6640	0.6822	0.7008	0.7199	0.7395	0.7596
20	0.6187	0.6346	0.6509	0.6674	0.6844	0.7018
30	0.5802	0.5943	0.6087	0.6232	0.6382	0.6534
40	0.5469	0.5595	0.5724	0.5854	0.5987	0.6121
50	0.5178	0.5292	0.5408	0.5525	0.5645	0.5765
60	0.4921	0.5025	0.5130	0.5236	0.5344	0.5453
70		0.4787	0.4884	0.4980	0.5079	0.5177

Table 11. Internal Pressure of Alcohols at Pressures up to 100 MPa and within the Temperature Limits of (293 and 318) K

	$p_{int} \cdot 10^{-6}$/Pa					
p	T/K					
MPa	293.15	298.15	303.15	308.15	313.15	318.15
			Heptan-1-ol			
0.1	317.0	316.6	316.2	315.5	314.8	313.9
10	318.1	318.3	318.3	318.2	318.0	317.7
20	318.2	318.7	319.2	319.5	319.8	319.9
30	317.4	318.3	319.1	319.8	320.4	321.0
40	315.9	317.1	318.2	319.3	320.3	321.2
50	313.9	315.4	316.8	318.2	319.5	320.8
60	311.4	313.2	314.9	316.6	318.2	319.8
70	308.5	310.6	312.6	314.6	316.5	318.4
80	305.3	307.7	310.0	312.2	314.4	316.6
90	301.8	304.4	307.0	309.5	312.0	314.4
100	298.1	301.0	303.8	306.6	309.3	312.0
			Octan-1-ol			
0.1	320.6	320.4	320.1	319.7	319.1	318.4
10	321.4	321.6	321.7	321.6	321.5	321.2
20	321.2	321.7	322.1	322.4	322.6	322.8
30	320.1	320.9	321.7	322.3	322.9	323.4
40	318.4	319.5	320.5	321.5	322.4	323.3
50	316.1	317.5	318.9	320.1	321.4	322.5
60	313.4	315.1	316.7	318.3	319.8	321.3
70	310.3	312.2	314.1	316.0	317.9	319.7
80	306.8	309.0	311.2	313.4	315.6	317.7
90	303.0	305.5	308.0	310.5	312.9	315.4
100	299.0	301.8	304.5	307.3	310.0	312.8
			Nonan-1-ol			
0.1	327.7	327.0	326.2	325.3	324.3	323.2
10	328.4	328.1	327.7	327.2	326.7	326.1
20	328.1	328.1	328.1	328.0	327.9	327.7
30	326.9	327.2	327.6	327.9	328.1	328.4
40	325.0	325.7	326.3	327.0	327.6	328.3
50	322.5	323.5	324.5	325.5	326.5	327.5
60	319.5	320.8	322.2	323.5	324.9	326.2
70	316.0	317.7	319.4	321.1	322.8	324.5
80	312.2	314.2	316.2	318.3	320.3	322.4
90	308.0	310.4	312.7	315.1	317.5	319.9
100	303.6	306.2	308.9	311.6	314.4	317.2
			Decan-1-ol			
0.1	331.3	330.9	330.3	329.6	328.9	328.0
10	331.5	331.3	331.1	330.8	330.4	329.9
20	330.6	330.7	330.8	330.9	330.8	330.7
30	328.8	329.3	329.7	330.1	330.4	330.7
40	326.4	327.2	328.0	328.7	329.4	330.0
50	323.4	324.6	325.6	326.7	327.7	328.8
60	320.0	321.4	322.8	324.2	325.6	327.0
70		317.9	319.6	321.4	323.1	324.9

The thermal pressure coefficient and thereby the internal pressure are related to the isothermal compressibility and isobaric thermal expansion in the following way:

$$p_{int} = \frac{T\alpha_p}{\kappa_T} - p \qquad (6)$$

Therefore the internal pressures have been calculated using the corresponding κ_T and α_p values. The values of the internal pressures of the alcohols under test are collected in Table 11. The uncertainty of internal pressures obtained in this work is estimated to be better than $\pm$ 1 %.

The results of the calculations are shown in Figures 2 to 6. For clarity the lines and points are presented.

The densities of all the alcohols increase monotonically with increasing pressure and decreasing temperature (Figure 2). 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. The effects of pressure and temperature on the isobaric heat capacity of the alcohols under test are shown in Figure 3. 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 (Figures 4 and 5). The increase of the volume with temperature becomes lower with increasing pressure due to stronger hydrogen bonds caused by the σ-bond cooperativity. The increase in the association with increasing pressure is indicated also by the decreasing of isobaric heat capacities. 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. Association of alcohol molecules provides an increase of the molecular order. Moreover the isothermal compression of liquid reduces the free volume and the amplitude of molecular vibrations. The effect of pressure on the volume was found to increase with increasing temperature, which is related doubtless to the increasing number of broken hydrogen bonds that makes the system more elastic. However the volume change due to the formation of hydrogen bonds is not too large as compared to the molar volume. This suggests that probably the nonspecific interactions and structural contributions, connected with the change of intermolecular distances in the compressed liquid, play also important role.

Moreover with increasing pressure, the influence of pressure on the temperature dependence of isobaric thermal expansion and isothermal compressibility decreasing. It demonstrates the existence a possible crossing point of isotherms at higher pressures. The crossing point of isobaric thermal expansion is characteristic for simple liquids; for isothermal compressibility

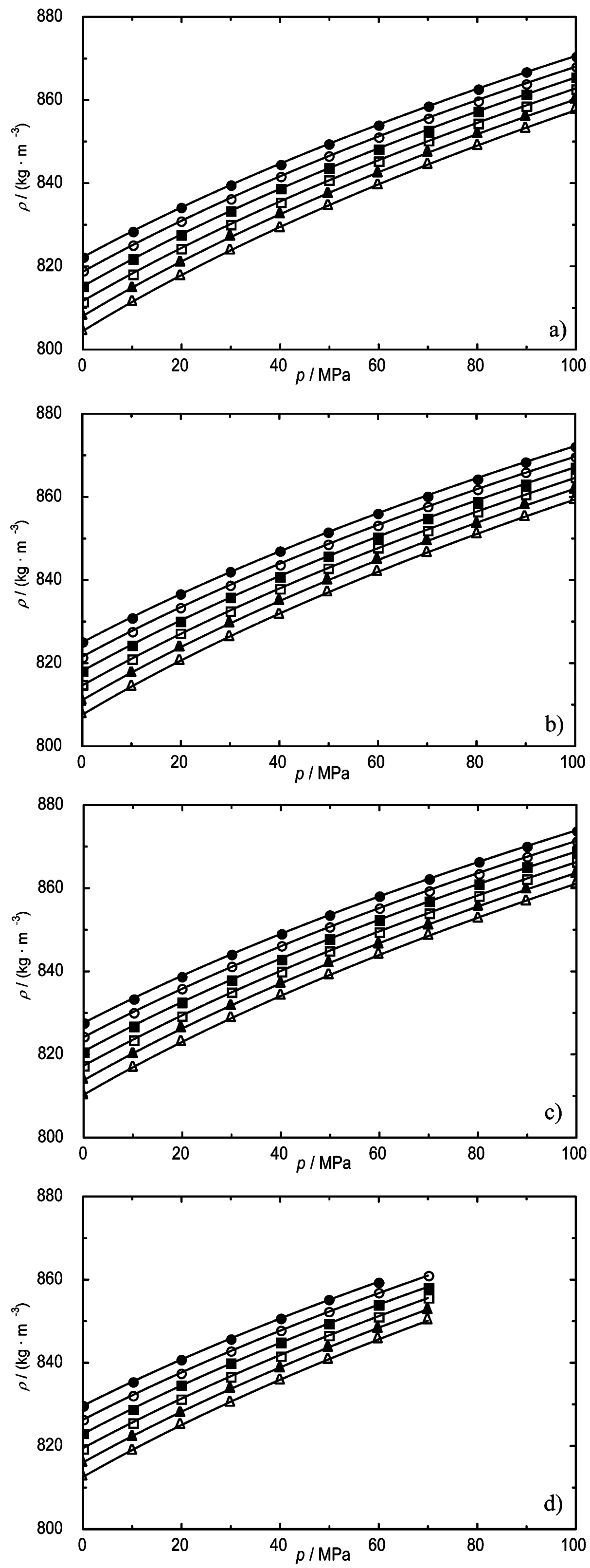

Figure 2. Densities of (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $\rho = \sum_{i=0}^{3} a_i p^i$.

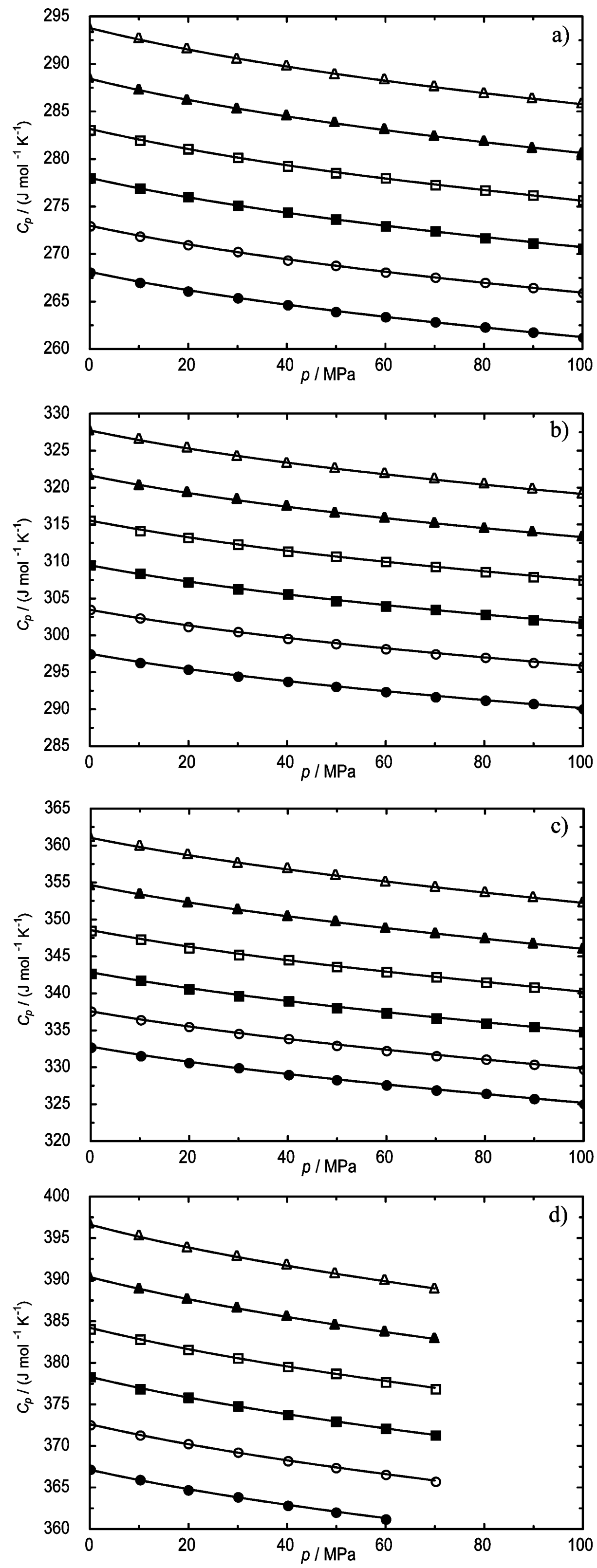

Figure 3. Isobaric molar heat capacities of (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $C_p = \sum_{i=0}^{3} a_i p^i$.

this effect was not observed.[49,50] Randzio et al.[50] suggested the correlation between the pressure of the crossing point of α_p and the nature of liquids. For example the isotherms of α_p of hexane cross each other at 65 ± 2 MPa.[49] 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 280 MPa; however, for water the crossing point is observed close to 450 MPa.[50] Therefore, the determination of the isobaric thermal expansion of the alcohols under

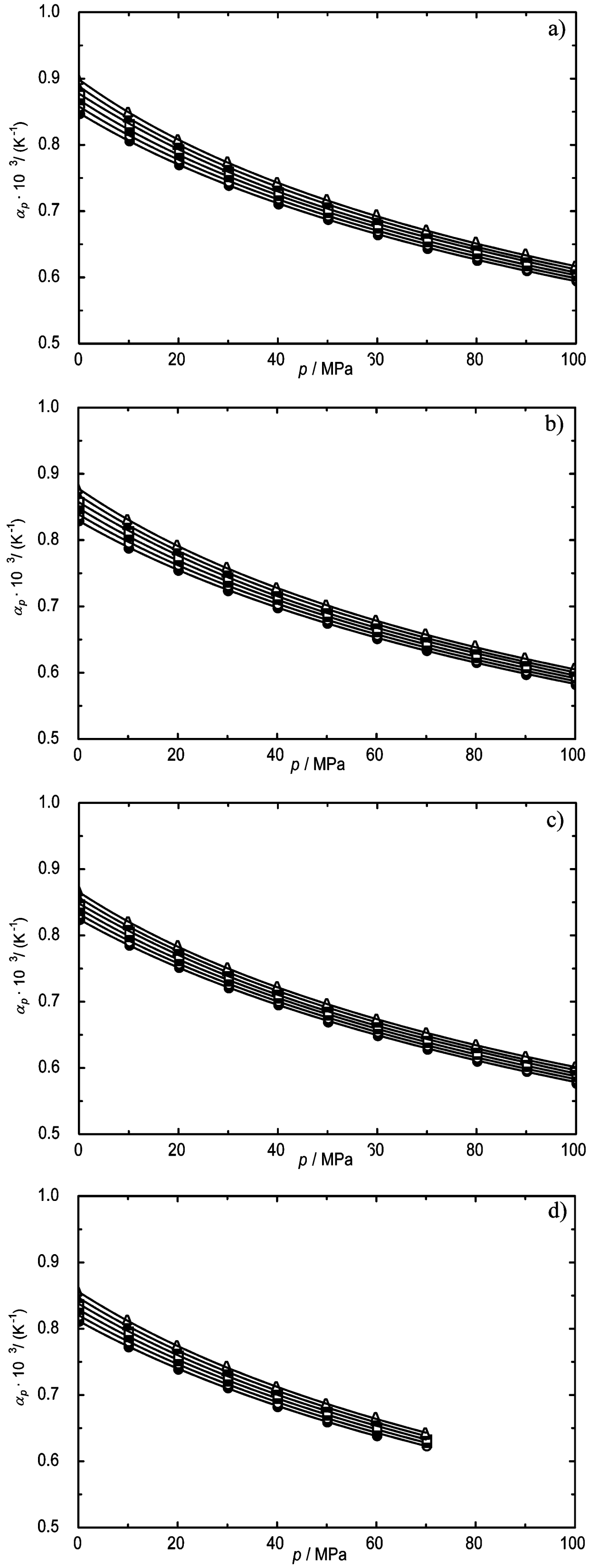

Figure 4. Isobaric thermal expansion of (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $\alpha_p = \sum_{i=0}^{3} a_i p^i$.

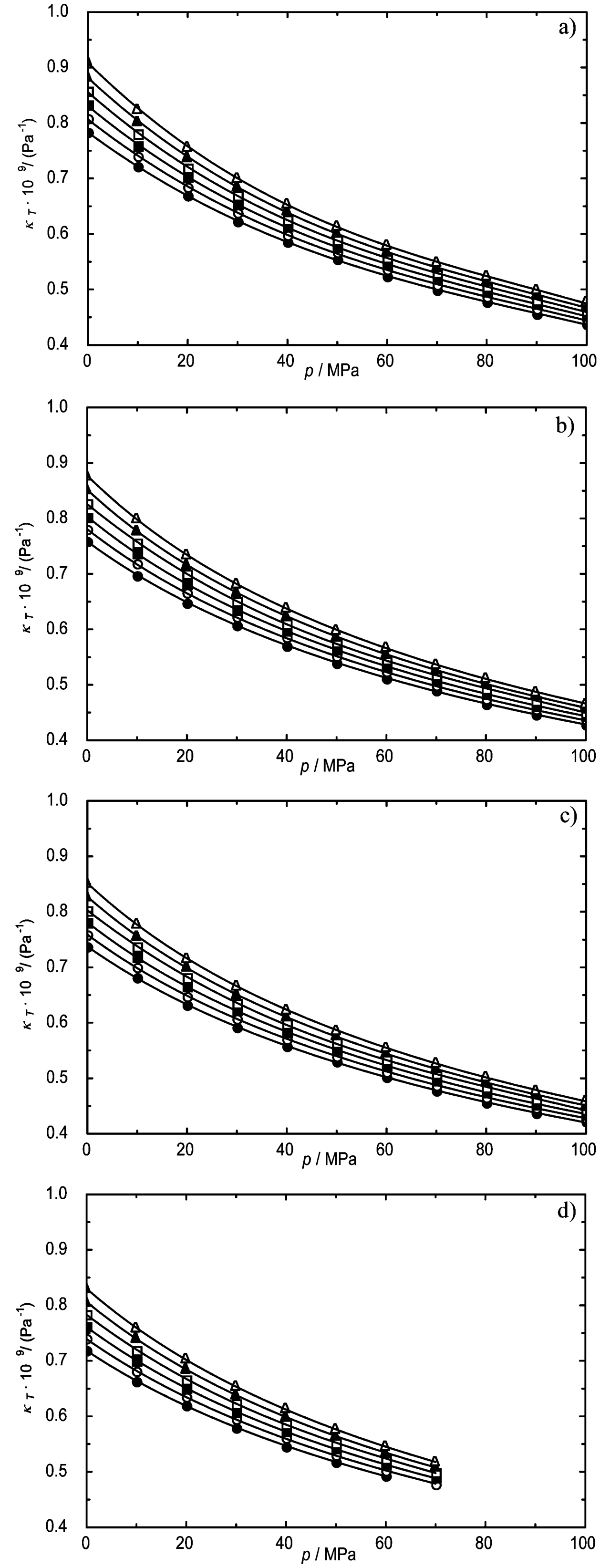

Figure 5. Isothermal compressibity of (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $\kappa_T = \sum_{i=0}^{3} a_i p^i$.

test in the wider temperature and pressure ranges seems to be of interest.

Molecular interactions related to the work of intermolecular forces that accompanying the volume change are also manifested in the internal pressure.[51] The internal pressure of liquids is a sum of the repulsion and attraction forces between molecules of the liquid.[35,36,39] Since $(\partial p/\partial T)_V = (\partial S/\partial V)_T$, the internal

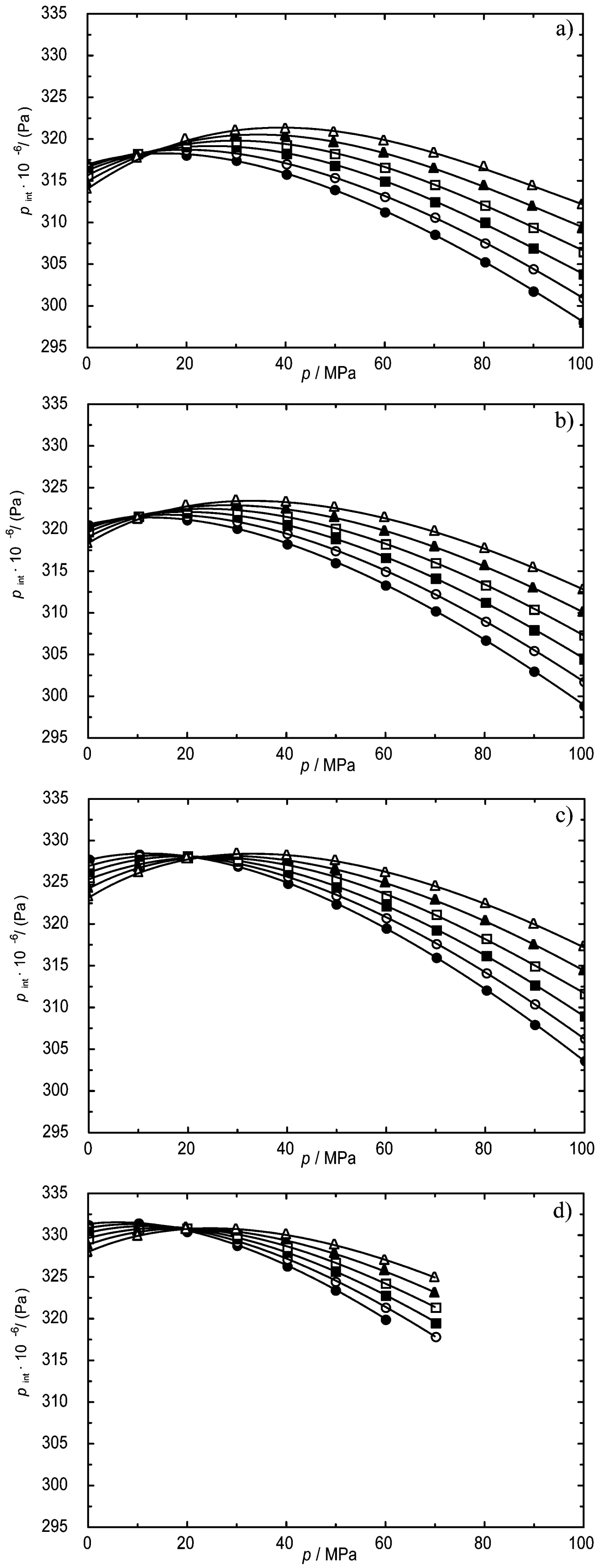

Figure 6. Internal pressure of (a) heptan-1-ol, (b) octan-1-ol, (c) nonan-1-ol, and (d) decan-1-ol: ●, 293.15 K; ○, 298.15 K; ■, 303.15 K; □, 308.15 K; ▲, 313.15 K; △, 318.15 K. Lines calculated from empirical function: $p_{\text{int}} = \sum_{i=0}^{3} a_i p^i$.

pressure is related to the isothermal change of entropy per unit volume and can be discussed in terms of order in liquids resulting from isothermal expansion. A very interesting pressure and temperature dependence of the internal pressure of the alcohols under test was observed (Figure 6). A crossing point of the isotherms exists for all of the alcohols studied. The pressure of the crossing point is characteristic for each alcohol and is observed at rather low pressures up to 22 MPa. The internal pressure decreases with increasing temperature at pressures up to the crossing point, and then it increases with the increase of temperature. Moreover, the internal pressure as a function of pressure shows a maximum (i.e., the internal pressure first increases with increasing pressure and then it decreases). With increasing temperature the maximum moves toward higher pressures. The existence of a maximum of the pressure dependence of the internal pressure was reported in the literature.[41,52] Under low pressures, as the temperature is increasing, the repulsive part of the internal pressure becomes more predominant, but at constant temperature the resultant forces under low-pressure conditions are attractive. A change in the molar volume is always accompanied by a corresponding change in the mean molecular distance. As the pressure increases the repulsive forces become predominant. Thus at high pressures, the increasing temperature causes an increase of the internal pressure at high pressures. The internal pressure increases with pressure and decreases with temperature due to the shift of the thermodynamic equilibrium of association. However, the decrease of internal pressure with increasing pressure and the increase with increasing temperature suggest that the possible nonspecific interactions, connected with the variation of intermolecular distances in the compressed liquid, play also an important role. Kartsev et al.[45−48] showed that the temperature coefficient of internal pressure is sensitive to the structural organization of the liquid and reflects the character of the interactions. According to the sign of the temperature coefficient of the internal pressure, liquids can be classified as not hydrogen-bonded or weakly associated and hydrogen-bonded.[48] Alcohols are characterized also by the inversion of the temperature dependence of the internal pressure.[45] For the alcohols under test, such an inversion is observed at temperatures higher than 318.15 K.[45]

However to the best of my knowledge, a reliable molecular theory of the internal pressure has not been worked out yet. Thus, I decided to postpone further discussion of the internal pressure until necessary data for liquids and liquid mixtures at elevated pressures are available.

Summary

The speeds of sound in heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol have been measured at temperatures from (293to 318) K and at pressures up to 101 MPa for heptan-1-ol, octan-1-ol, and nonan-1-ol and up to 76 MPa for decan-1-ol. 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.[8] This enables the determination of the isothermal and adiabatic compressibility, the isobaric thermal expansion, and the internal pressure as a function of temperature and pressure. A simple association model qualitatively explains the pressure and temperature dependence of the volumetric properties of alcohols. Interesting temperature and pressure dependences of the internal pressure of the alcohols under test have been observed.

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