Study of the Effects of Temperature and Pressure on the Thermodynamic and Acoustic Properties of 2-Methyl-1-butanol at Temperatures from 293 K to 318 K and Pressures up to 100 MPa

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Abstract   The speeds of sound in 2-methyl-1-butanol were measured at temperatures from 293 K to 318 K and pressures up to 101 MPa. The densities were measured in the same temperature range under atmospheric pressure. The isobaric specific heat capacities were measured at atmospheric pressure and temperatures from 284 K to 355 K. The densities, isobaric heat capacities, isobaric thermal expansions, isentropic compressibilities, isothermal compressibilities, and internal pressures as functions of temperature and pressure were calculated using the experimental 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 thermal expansion and internal pressure of 2-methyl-1-butanol are discussed and compared with those of pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol.

Keywords   Density · Heat capacity · High pressure · Internal pressure · 2-Methyl-1-butanol · Speed of sound

1 Introduction

A knowledge of the thermodynamic properties of pure organic liquids is of practical interest to industries in different fields, such as chemical, pharmaceutical industries, and food technology, because the applied industrial procedures are influenced by the temperature and pressure dependences of the used liquids. 2-methyl-1-butanol is a main component of fusel oils which are by-products of biomass fermentation [1].

Dedicated to Professor Dr. Stefan Ernst on the occasion of his 75th Birthday.

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A higher concentration of fusel oils masks the wine aroma, for example, 2-methyl-1-butanol shows aroma descriptors as nail polish and fuel alcohols [2]. 2-methyl-1-butanol was selected as one of the chemical descriptors that confirms whiskey authenticity, the content of it differentiates, for example, scotch whiskey from Irish whiskey and bourbons [3].

Isomeric pentanols were often chosen to study the influence of the chain structure and the position of the hydroxyl group in the alcohol molecule on the capability of the formation of the hydrogen bonds and the type of the formed associates.

This study is a part of systematic investigations of thermodynamic and acoustic properties of pentanols under high pressures. The pressure and temperature dependences of thermodynamic and acoustic properties of pentan-1-ol, 2-methyl-2-butanol, and cyclopentanol have been studied previously [4–7]. Promising preliminary results obtained for 2-methyl-1-butanol [7] made me to continue the research.

In this article new experimental speeds of sound in 2-methyl-1-butanol in the temperature range from 293 K to 318 K and pressures up to 101 MPa are reported. To the best of my knowledge, speeds of sound in 2-methyl-1-butanol have never been measured under high pressures. Additionally, the densities and isobaric specific heat capacities were measured under atmospheric pressure in the temperature range from 293 K to 318 K and 284 K to 355 K, respectively. Using the experimental results, the densities and isobaric heat capacities of the alcohol under test for temperatures from 293 K to 318 K and for pressures up to 100 MPa were calculated. A method based on the suggestion of Davis and Gordon [8] with a numerical procedure proposed by Sun et al. [9] was applied for calculations. Densities of 2-methyl-1-butanol at 293.15 K and 298.15 K and pressures from 1 MPa to 7 MPa have been reported by Cibulka et al. [10].

The measured speeds of sound and calculated densities and isobaric heat capacities were used for calculation of adiabatic compressibilities, isothermal compressibilities, isobaric thermal expansions, and internal pressures. The effects of temperature and pressure on the isobaric thermal expansion and internal pressure of 2-methyl-1-butanol are discussed and compared with those of pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol.

2 Measurements

2.1 Specimens

2-Methyl-1-butanol was obtained from Aldrich, with 0.99+ mass fraction purity $C_2H_5CH(CH_3)CH_2OH$. Alcohol was dried over molecular sieves of 0.3 nm. The mass fraction of water, determined by the Karl–Fischer method, was less than 3×10^{-4}. The purity of 2-methyl-1-butanol was tested by comparing the density, speed of sound, refractive index, and molar heat capacity with literature values (Table 1).

2.2 Ultrasonic Speed

The speed of sound at a frequency of 2 MHz was measured at atmospheric and elevated pressures using two measuring sets operate on the principle of the pulse-echo-overlap

Table 1 Comparison of the speed of sound, u; density, ρ; refractive index, n_D; and isobaric molar heat capacity, C_p of 2-methyl-1-butanol obtained in this study at 298.15 K under atmospheric pressure with those reported in the literature

	Experimental	Literature
Speed of sound (m · s^{-1})	1253.09	1253 [11], 1253.29 [12]
Density (kg · m^{-3})	815.02	814.87 [11,12], 815.02 [13], 815.09 [14]
Refractive index	1.4086	1.4086 [12], 1.40872 [12]
Molar heat capacity (J · mol^{-1} · K^{-1})	213.88	212.16 [15], 215.0 [16]

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 used for measurements under atmospheric pressure, the other one for measurements under high pressures.

2.2.1 Pressures

The pressure was provided by a hand-operated hydraulic press and was measured with a strain-gauge measuring system (Hottinger Baldwin System P3MD) with an uncertainty better than 0.15 %. A stability of ± 0.03 MPa during the measurement was achieved.

2.2.2 Temperatures

The temperature was measured using an Ertco Hart 850 platinum resistance thermometer (NIST certified) with an uncertainty of ± 0.05 K and a resolution of 0.001 K. During the measurements, the stability of the temperature was ± 0.005 K and ± 0.01 K at atmospheric and high pressures, respectively. All the temperatures reported in this study are expressed on 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 1×10^{-4} S · m^{-1}. The speed of sound in water under atmospheric pressure was calculated from the polynomial of Marczak [17], while for high pressures, the equation of Kell and Whalley [18] was used.

2.2.3 Uncertainties

The repeatability of the measured speeds of sound was better than ± 0.02 % at atmospheric pressure and ± 0.04 % under high pressures. The uncertainties under atmospheric and high pressures 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 previous articles [19,20].

2.3 Density

The densities at atmospheric pressure were measured using a vibrating-tube densimeter Anton Paar DMA 5000. The densimeter was calibrated with air and re-distilled water of electrolytic conductivity as above and degassed by boiling just before the measurements.

2.3.1 Uncertainties

The uncertainty of the density measurements was $0.05 \, kg \cdot m^{-3}$, whereas the repeatability was estimated to be better than $0.005 \, kg \cdot m^{-3}$.

2.4 Specific Heat Capacity

The specific isobaric heat capacity was measured by a high sensitivity differential scanning calorimeter Micro DSC III, manufactured by Setaram and based on the Tian–Calvet principle.

2.4.1 Uncertainties

The uncertainty of the measurements was estimated to be 0.15 %. More details of the measuring set, calibration, and measurement procedure can be found in [21].

3 Results and Discussion

The speeds of sound in 2-methyl-1-butanol were measured from 293 K to 318 K in about 5 K increments and under pressures of about 0.1 MPa, 15 MPa, 30 MPa, 45 MPa, 60 MPa, 75 MPa, 90 MPa, and 101 MPa. The experimental values are listed in Table 2. The temperature dependences of the speeds of sound in the liquid under test are shown in Fig. 1. The speed of sound in 2-methyl-1-butanol decreases almost linearly with increasing temperature and with increasing pressure the influence of temperature on the speed of sound decreases.

The densities of the alcohol under test were measured under atmospheric pressure within the same temperature range. The experimental values are shown in Table 3.
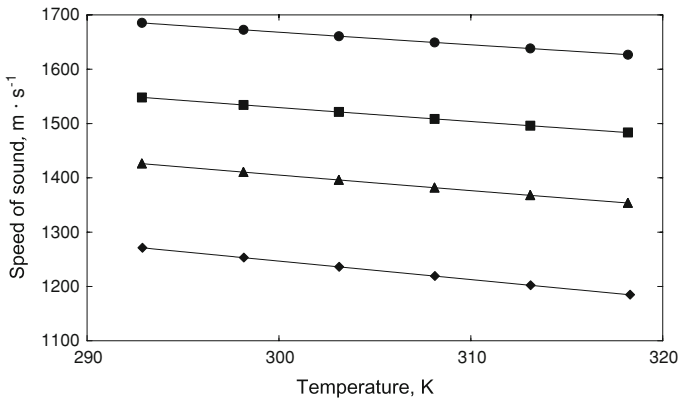
The isobaric specific heat capacities were measured at atmospheric pressure and temperatures from 284 K to 355 K in about 0.02 K increments. Thus, it has given ca. 3180 experimental points. Therefore, the values of the isobaric specific heat capacity for every 5 K are shown in Table 4.

The dependences of the speed of sound, density, and isobaric specific heat capacity on temperature at atmospheric pressure were approximated by the following polynomials of the type:

$$y = \sum_{j=0}^{n} b_j T^j,$$ (1)

Table 2 Experimental speeds of sound, u, in 2-methyl-1-butanol measured at pressures up to 101 MPa within the temperature range from 293 K to 318 K

Temperature (K)	Pressure (MPa)	Speed of sound $(m \cdot s^{-1})$	Temperature (K)	Pressure (MPa)	Speed of sound $(m \cdot s^{-1})$	Temperature (K)	Pressure (MPa)	Speed of sound $(m \cdot s^{-1})$
292.89	0.10	1271.16	303.15	0.10	1236.01	313.12	0.10	1202.13
292.86	15.20	1355.50	303.13	15.20	1323.42	313.11	15.20	1292.81
292.86	30.39	1426.09	303.12	30.39	1396.12	313.10	30.39	1367.72
292.86	45.59	1489.75	303.12	45.59	1461.70	313.10	45.59	1434.86
292.86	60.79	1548.13	303.12	60.79	1521.30	313.10	60.79	1495.96
292.86	75.99	1602.52	303.12	75.99	1576.62	313.10	75.99	1552.10
292.86	91.18	1653.28	303.12	91.18	1628.35	313.10	91.18	1604.92
292.86	101.32	1685.32	303.12	101.32	1660.84	313.10	101.32	1638.14
298.17	0.10	1253.01	308.14	0.10	1219.02	318.31	0.10	1184.65
298.16	15.20	1338.81	308.12	15.20	1308.02	318.18	15.20	1277.52
298.15	30.39	1410.68	308.12	30.39	1381.77	318.19	30.39	1353.75
298.15	45.59	1475.28	308.12	45.59	1448.04	318.18	45.59	1421.73
298.15	60.79	1534.30	308.12	60.79	1508.55	318.19	60.79	1483.43
298.15	75.99	1588.97	308.12	75.99	1564.09	318.19	75.99	1539.94
298.15	91.18	1640.43	308.12	91.18	1616.64	318.18	91.18	1593.24
298.15	101.32	1672.51	308.12	101.32	1649.31	318.19	101.32	1626.83

Fig. 1 Speeds of sound in 2-methyl-1-butanol plotted against temperature at elevated pressures: (♦) 0.1 MPa, (▲) 30.39 MPa, (■) 60.79 MPa, (●) 101.32 MPa. Lines calculated from Eq. 1

where y is the speed of sound, u_0, density, ρ, or isobaric specific heat capacity, C_p, at atmospheric pressure p_0, b_j are the polynomial coefficients ($b_j = c_j$ for the speed of sound, $b_j = \rho_j$ for the density, and $b_j = h_j$ for the isobaric specific heat capacity)

Table 3 Experimental densities, ρ, of 2-methyl-1-butanol measured within temperature range from 293 K to 318 K at atmospheric pressure

Temperature (K)	Density (kg · m^{-3})
293.15	818.73
298.16	815.01
303.16	811.25
308.16	807.44
313.16	803.58
318.16	799.66

Table 4 Experimental isobaric molar heat capacities, C_p, of 2-methyl-1-butanol within the temperature range from 284 K to 355 K at atmospheric pressure

Temperature (K)	Molar heat capacity (J · mol^{-1} · K^{-1})	Temperature (K)	Molar heat capacity (J · mol^{-1} · K^{-1})
284.14	200.72	323.14	240.70
288.15	204.34	328.15	246.21
293.14	209.01	333.14	251.55
298.14	213.91	338.16	256.80
298.16	213.94	343.15	261.79
303.15	218.98	348.14	266.64
308.14	224.32	353.15	271.18
313.16	229.74	355.12	272.93
318.15	235.20		

Table 5 Coefficients of polynomial, Eq. 1, for the speed of sound, density, and isobaric specific heat capacity

c_0 (m · s^{-1})	c_1 (m · s^{-1} · K^{-1})	$c_2 \times 10^3$ (m · s^{-1} · K^{-2})		δu_0^{a} (m · s^{-1})
2410.184	−4.335227	1.52383		0.009
ρ_0 (kg · m^{-3})	ρ_1 (kg · m^{-3} · K^{-1})	$\rho_2 \times 10^4$ (kg · m^{-3} · K^{-2})		$\delta \rho^{\mathrm{a}}$ (kg · m^{-3})
950.553	−0.1613741	−9.83439		0.005
h_0 (J · kg^{-1} · K^{-1})	h_1 (J · kg^{-1} · K^{-2})	h_2 (J · kg^{-1} · K^{-3})	$h_2 \times 10^4$ (J · kg^{-1} · K^{-4})	δC_p^{a} (J · kg^{-1} · K^{-1})
23434.67	−219.567	0.725587	−7.56292	0.53

$^{\mathrm{a}}$ Mean deviations from the regression line

calculated by the least-squares method. The backward stepwise rejection procedure was used to reduce the number of non-zero coefficients. The coefficients and standard deviations from the regression lines are given in Table 5.

Table 6 Coefficients of Eq. 2

	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^{a} (m · s^{-1})
j				
0	0.3823270481	$2.10030612 \times 10^{-4}$	–	0.31
1	$-7.46113765 \times 10^{-4}$	–	–	
2	–	–	$-4.39070698 \times 10^{-13}$	

[a] Mean deviations from the regression line

The dependences of the speed of sound on pressure and temperature were approximated by the equation suggested by Sun et al. [22]:

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

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 6. The stepwise rejection procedure was used to reduce the number of non-zero coefficients.

The densities and isobaric heat capacities of 2-methyl-1-butanol were determined for temperatures from 293 K 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. Details of the algorithm were discussed in previous studies [23,24]. The uncertainty of the measured speeds of sound causes uncertainties of ± 0.02 % in the calculated densities and ± 0.3 % in the calculated isobaric heat capacities [23–26]. Taking into account the absolute average deviations (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 calculated for high pressures was found to be ± 0.05 % and ± 1 %, respectively, [27]. Tables 7 and 8 list the calculated densities and isobaric heat capacities, respectively. The densities of 2-methyl-1-butanol up to 7 MPa for 293.15 K and 298.15 K obtained in this study were compared with correlation by Cibulka et al. [10]. AAD $= (100/n) \sum_{i=1}^{n} \left| \rho_{lit,i}/\rho_{\exp,i} - 1 \right|$) was found to be 0.019 %.

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 9.

The isothermal compressibilities were calculated using the well-known relationship:

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

Table 7 Calculated densities, ρ, of 2-methyl-1-butanol at pressures up to 100 MPa and within the temperature range from 293 K to 318 K

Pressure (MPa)	Density (kg · m^{-3})					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	818.73	815.02	811.25	807.44	803.58	799.67
10	825.54	822.01	818.43	814.81	811.14	807.43
20	831.87	828.49	825.06	821.60	818.10	814.55
30	837.75	834.50	831.21	827.88	824.51	821.11
40	843.26	840.12	836.95	833.73	830.49	827.20
50	848.46	845.42	842.34	839.24	836.09	832.92
60	853.37	850.43	847.44	844.43	841.38	838.30
70	858.05	855.19	852.29	849.36	846.40	843.40
80	862.51	859.72	856.90	854.05	851.17	848.25
90	866.78	864.06	861.31	858.53	855.72	852.87
100	870.88	868.22	865.54	862.82	860.07	857.29

[a] Calculated from Eq. 1

Table 8 Calculated isobaric molar heat capacities, C_p, of 2-methyl-1-butanol at pressures up to 100 MPa and in the temperature range from 293 K to 318 K

Pressure (MPa)	Isobaric molar heat capacity (J · mol^{-1} · K^{-1})					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1[a]	208.97	213.88	219.01	224.31	229.72	235.20
10	207.8	212.7	217.8	223.0	228.3	233.8
20	206.7	211.6	216.6	221.8	227.1	232.5
30	205.7	210.6	215.6	220.7	226.0	231.4
40	204.9	209.7	214.6	219.7	225.0	230.3
50	204.0	208.8	213.8	218.8	224.0	229.3
60	203.3	208.0	212.9	218.0	223.1	228.4
70	202.5	207.3	212.1	217.1	222.3	227.5
80	201.8	206.5	211.4	216.4	221.5	226.7
90	201.1	205.8	210.6	215.6	220.7	225.9
100	200.5	205.1	209.9	214.9	219.9	225.1

[a] Calculated from Eq. 1

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 isothermal compressibility are listed in Tables 10 and 11, respectively.

Table 9 Calculated isentropic compressibilities, κ_S, of 2-methyl-1-butanol at pressures up to 100 MPa and in the temperature range from 293 K to 318 K

Pressure (MPa)	Isentropic compressibility $\times 10^9 (\mathrm{Pa}^{-1})$					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1	0.7570	0.7814	0.8069	0.8335	0.8613	0.8903
10	0.6882	0.7081	0.7288	0.7502	0.7724	0.7954
20	0.6336	0.6504	0.6678	0.6857	0.7042	0.7232
30	0.5890	0.6035	0.6185	0.6339	0.6497	0.6659
40	0.5514	0.5643	0.5774	0.5908	0.6046	0.6187
50	0.5192	0.5307	0.5423	0.5542	0.5664	0.5788
60	0.4912	0.5015	0.5119	0.5226	0.5334	0.5445
70	0.4664	0.4757	0.4852	0.4948	0.5046	0.5145
80	0.4444	0.4528	0.4614	0.4701	0.4790	0.4880
90	0.4245	0.4323	0.4401	0.4481	0.4561	0.4643
100	0.4065	0.4137	0.4209	0.4282	0.4355	0.4430

Table 10 Calculated isobaric thermal expansions, α_p, of 2-methyl-1-butanol at pressures up to 100 MPa and in the temperature range from 293 K to 318 K

Pressure (MPa)	Isobaric thermal expansion $\times 10^3 (\mathrm{K}^{-1})$					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1	0.901	0.918	0.934	0.950	0.967	0.984
10	0.851	0.865	0.880	0.895	0.909	0.924
20	0.809	0.822	0.835	0.848	0.862	0.875
30	0.773	0.785	0.797	0.809	0.821	0.834
40	0.741	0.752	0.763	0.775	0.786	0.798
50	0.712	0.723	0.734	0.745	0.756	0.767
60	0.687	0.697	0.708	0.718	0.728	0.739
70	0.664	0.674	0.684	0.694	0.704	0.714
80	0.643	0.653	0.662	0.672	0.682	0.692
90	0.624	0.633	0.642	0.652	0.661	0.671
100	0.606	0.615	0.624	0.633	0.643	0.652

The overall uncertainties of κ_S, κ_T, α_p, and p_{int} obtained by an indirect method are estimated to be ± 0.15 %, ± 0.5 %, ± 1 %, and ± 1 %, respectively [27].

Based on the thermodynamic relation $\left[T \left(\partial S / \partial T \right)_p / \partial p \right]_T = -T (\partial^2 V / \partial T^2)_p$, the pressure–temperature behavior of the thermal expansion can be analyzed as a macroscopic manifestation of the effects existing at the molecular level. Thus, the pressure dependence of the isobaric thermal expansions qualitatively confirms similarities and

Table 11 Calculated isothermal compressibilities, κ_T, of 2-methyl-1-butanol at pressures up to 100 MPa and in the temperature range from 293 K to 318 K

Pressure (MPa)	Isothermal compressibility $\times 10^9 (Pa^{-1})$					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1	0.880	0.908	0.938	0.969	1.001	1.035
10	0.797	0.821	0.845	0.870	0.896	0.922
20	0.732	0.752	0.772	0.793	0.814	0.837
30	0.678	0.696	0.713	0.731	0.750	0.769
40	0.634	0.649	0.664	0.680	0.696	0.712
50	0.595	0.609	0.622	0.636	0.651	0.665
60	0.562	0.574	0.586	0.599	0.611	0.624
70	0.532	0.543	0.554	0.566	0.577	0.589
80	0.506	0.516	0.526	0.537	0.547	0.558
90	0.482	0.491	0.501	0.510	0.520	0.530
100	0.461	0.469	0.478	0.487	0.496	0.505
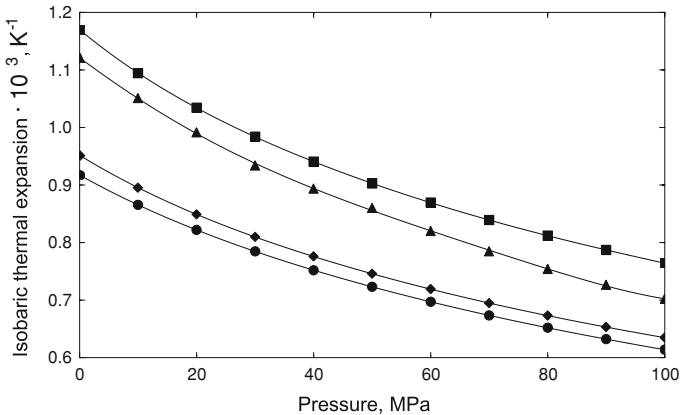
Fig. 2 Isobaric thermal expansion of (●) pentan-1-ol [6], (■) 2-methyl-2-butanol [6], (▲) pentan-3-ol*, and (♦) 2-methyl-1-butanol (this study) at $T = 303.15$ K. *Calculated from densities reported in Ref. [28]. Lines calculated from empirical function: $\alpha_p = \sum_{i=0}^{3} a_i p^i$

dissimilarities of physicochemical properties of 2-methyl-1-butanol, pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol (Fig. 2).

Molecular interactions related to the work of intermolecular forces that accompany the volume change are manifested in the internal pressure, i.e., the isothermal volume dependence of the internal energy:

Table 12 Calculated internal pressures, p_{int}, of 2-methyl-1-butanol at pressures up to 100 MPa and within the temperature range from 293 K to 318 K

Pressure (MPa)	Internal pressure $\times 10^{-6}$ (Pa)					
	Temperature (K)					
	293.15	298.15	303.15	308.15	313.15	318.15
0.1	300	301	302	302	302	303
10	303	304	306	307	308	309
20	304	306	308	310	311	313
30	304	306	309	311	313	315
40	303	306	308	311	314	316
50	301	304	308	311	314	317
60	299	302	306	310	313	317
70	296	300	304	308	312	316
80	293	297	302	306	310	314
90	289	294	299	304	308	313
100	285	291	296	301	306	311

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

where $(\partial p/\partial T)_V$ is the thermal pressure coefficient.

Since $(\partial p/\partial T)_V = (\partial S/\partial V)_T$, the internal 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.

In this study, the internal pressures, p_{int}, were calculated from the experimental speeds of sound, calculated densities, and heat capacities in the following way:

$$p_{int} = \frac{T\alpha_p}{\kappa_T} - p = \left[T\alpha_p\left(\frac{1}{\rho u^2} + \frac{\alpha_p^2 T}{\rho C_p}\right)^{-1}\right] - p. \tag{5}$$

The values of the internal pressure of 2-methyl-1-butanol are shown in Table 12.

The temperature and pressure dependence of the internal pressure of 2-methyl-1-butanol is compared with those of pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol in Fig. 3. Each isotherm of the internal pressure of 2-methyl-1-butanol and pentan-1-ol as a function of pressure shows a maximum in the temperature and pressure range under investigation. The pressure dependence of the internal pressure shows a maximum at 303.15 K, 313.15 K, and 323.15 K for pentan-3-ol. While, for 2-methyl-2-butanol this maximum exists only at 293.15 K, 298.15 K, and 303.15 K. With increasing temperature the maximum moves toward higher pressures. Thus, it is probably shifted to higher pressures for pentan-3-ol and 2-methyl-2-butanol at higher temperatures. The internal pressure of liquids is a sum of the attraction and repulsion forces between molecules

Fig. 3 Pressure dependences of internal pressure of (**a**) pentan-1-ol*, (**b**) 2-methyl-1-butanol (this study), (**c**) 2-methyl-2-butanol*, and (**d**) pentan-3-ol** at (◆) 293.15 K, (*) 298.15 K, (■) 303.15 K, (+) 308.15 K, (▲) 313.15 K, (●) 318.15 K, (○) 323.15 K, (□) 333.15 K, (◇) 343.15 K, (△) 353.15 K, (—) 363.15 K, (-) 368.15 K. Calculated from experimental data reported in: *Ref. [6] and **Ref. [28]. Lines calculated from empirical function: $p_{int} = \sum_{i=0}^{3} a_i \, p^i$
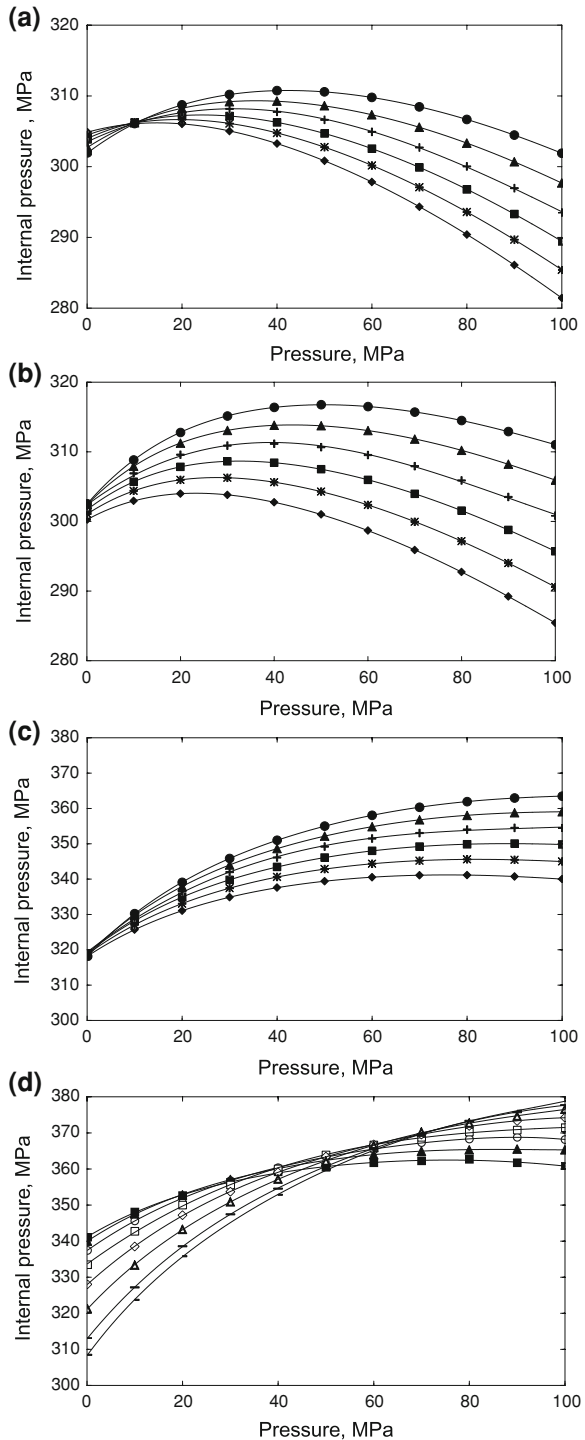
of the liquid. The attraction forces are related to dispersion, dipole–dipole, multipolar, and hydrogen-bonding interactions. With increasing pressure, the mean molecular distance decreases and the repulsive forces increase. Thus, the internal pressure first increases with increasing pressure and then it decreases.

It is known that the steric effects disturb the formation of hydrogen bonds; therefore, non-primary alcohols are weakly associated than a primary one. Hence, it seems that besides non-specific, physical interactions, probably the self-association capability affects also the effect of pressure on the internal pressure.

Kartsev et al. [29–32] pointed out that the temperature dependence of internal pressure is sensitive to the structural organization of the liquid and reflects the character of the interactions. They showed that the inversion of the temperature coefficient of the internal pressure at atmospheric pressure is characteristic for primary alcohols, i.e., sign reversal from (+) to (−). Such inversion is also observed for 2-methyl-2-butanol and pentan-3-ol (Fig. 4a). With increasing pressure, the temperature dependence of internal pressure changes (Fig. 4). It reflects the crossing point of the isotherms of the internal pressure. The crossing points of the internal pressure isotherms are observed for pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol. The internal pressure decreases with increasing temperature at pressures up to the crossing point, and then it increases with the increase of temperature. For pentan-1-ol all isotherms cross each other at one pressure (Fig. 3a). A similar temperature and pressure dependence was observed for other alkan-1-ols [25,33]. For pentan-3-ol, with increasing temperature the crossing point of each two neighboring isotherms moves toward higher pressure (Fig. 3d). For 2-methyl-2-butanol, the crossing point of each two neighboring isotherms appears at temperatures higher than 303.15 K (Fig. 3c), and it moves toward higher pressure with increasing temperature as in the case of pentan-3-ol. While, for 2-methyl-1-butanol, the crossing point is not observed, and the internal pressure increases with increasing temperature over the entire investigated pressure range (Fig. 3b). However, the temperature dependence of the internal pressure of 2-methyl-1-butanol under atmospheric pressure indicates that the crossing point probably appears at higher temperatures (Figs. 3b, 4a).

4 Summary

The speeds of sound in 2-methyl-1-butanol were measured at temperatures from 293 K to 318 K and at pressures up to 101 MPa. The densities and specific isobaric heat capacities of the liquid under test were measured under atmospheric pressure in the temperature range from 293 K to 318 K and 284 K to 355 K, respectively. From the measurement results, the pressure and temperature dependences of the density and isobaric heat capacity were determined using the modified method of Davis and Gordon [8]. This enabled the determination of the isothermal and adiabatic compressibility, the isobaric thermal expansion, and internal pressure as functions of temperature and pressure. The effects of temperature and pressure on the isobaric thermal expansion and internal pressure of 2-methyl-1-butanol were compared with those of pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol. The obtained results qualitatively confirm similarities
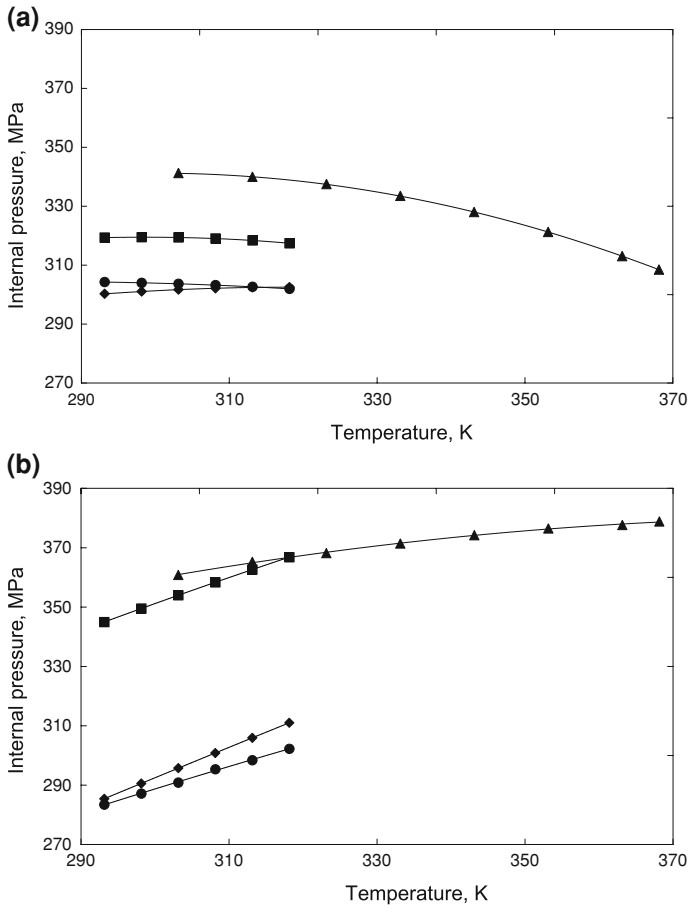
Fig. 4 Temperature dependences of internal pressure of (•) pentan-1-ol*, (■) 2-methyl-2-butanol*, (▲) pentan-3-ol**, and (♦) 2-methyl-1-butanol (this study) at (**a**) 0.1 MPa and (**b**) 100 MPa. Calculated from experimental data reported in: *Ref. [6] and **Ref. [28]. Lines calculated from empirical function: $p_{int} = \sum_{i=0}^{2} a_i T^i$

and dissimilarities of physicochemical properties of 2-methyl-1-butanol, pentan-1-ol, 2-methyl-2-butanol, and pentan-3-ol.

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