Int J Thermophys (2010) 31:26–41
DOI 10.1007/s10765-009-0610-6

Thermodynamic and Acoustic Properties of 1,3-Dibromopropane and 1,5-Dibromopentane within the Temperature Range From 293 K to 313 K at Pressures up to 100 MPa

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Received: 2 April 2009 / Accepted: 9 June 2009 / Published online: 24 June 2009

Abstract This study reports new experimental data of the speed of sound in liquid 1,3-dibromopropane and 1,5-dibromopentane from 293 K to 313 K at pressures up to 101 MPa, measured with a pulse–echo overlap method. The experimental results have been used to calculate densities, isobaric heat capacities, isobaric coefficient of thermal expansion, and isentropic and isothermal compressibilities as functions of temperature and pressure.

Keywords α, ω-Dibromoalkanes · Density · 1,5-Dibromopentane · 1,3-Dibromopropane · Heat capacity · High pressure · Speed of sound

1 Introduction

α, ω-Dibromoalkanes are compounds characterized by the so-called intramolecular proximity effect [1], that is, a change in the distance between two bromine atoms in the molecule provokes a change in the behavior and hence in the parameters of interaction with other molecular groups. A knowledge of the thermophysical properties of liquid halogenoalkanes is of high interest on account of their wide usage in science and industrial processes. Those properties are crucial for the design of chemical processes as well as for progress in thermodynamic theories of the liquid state. The heat capacities, speeds of sound, and densities as functions of temperature and pressure and

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their derivatives render some insight in the molecular structure of liquids and provide information on intermolecular interactions.

Unfortunately, basic properties of α, ω-dibromoalkanes, such as heat capacities, densities, and speeds of sound at atmospheric pressure, as well as under elevated pressures, are rather scarce in the literature. To the best of our knowledge, for the substances studied in this article, no experimental data corresponding to speed of sound, density, and heat capacity under high pressures are available in the accessible literature. This prompted us to continue our earlier calorimetric and acoustic study of pure halogenoalkanes [2–4] and their mixtures with aliphatic alkanes [5,6] and to expand it to the speed-of-sound measurements under elevated pressures.

The speeds of sound in 1,3-dibromopropane and 1,5-dibromopentane have been measured in the temperature range from 293 K to 313 K at pressures up to 100 MPa by the pulse–echo overlap method. The densities of 1,3-dibromopropane were measured in the same temperature range under atmospheric pressure. The experimental results have been used to calculate densities, isobaric heat capacities, the isobaric coefficient of thermal expansion, and isentropic and isothermal compressibilities as functions of temperature and pressure. A computational method originally developed by Davis and Gordon [7] and next modified by Sun et al. [8] was used for the calculations. The effects of pressure and temperature are discussed.

2 Measurements

2.1 Specimens

1,3-Dibromopropane (Lancaster, 98 %) and 1,5-dibromopentane (Lancaster, 97 %) were purified before use by fractional distillation, and the middle fraction (5 %) was collected in every case. The purities of the liquid samples of 1,3-dibromopropane and 1,5-dibromopentane checked by gas–liquid chromatography (GLC) were >99 %.

The mass fraction of water, determined by the Karl Fischer method, was $<5 \times 10^{-8}$ for 1,3-dibromopropane and 1,5-dibromopentane. Prior to the measurements, all the liquids were dried with molecular sieves (Type 3A, (1 mm to 2 mm) beads from Lancaster) and degassed in an ultrasonic cleaner.

The compounds of the homologous series of α, ω-dihalogenoalkanes are difficult to study due to their instability. In order to minimize the errors, the compounds were kept in dark glass flasks. The flasks were wrapped in aluminum foil and stored in a desiccator.

2.2 Speed of Sound

The details of the method and technique used to determine the speed of sound have been described previously [9,10], so that only a brief description will be given here.

The phase speed of the ultrasound at a frequency of 2 MHz was measured with a pulse–echo overlap apparatus designed and constructed in the Department of Physical Chemistry of the University of Silesia (electronic part and high-pressure ultrasonic cell). Two measuring vessels of the same acoustic path and construction (a single transmitting–receiving ceramic transducer and an acoustic mirror), one for the measurements under atmospheric pressure and another one for measurements under elevated pressures, have been used.

Our laboratory has developed apparatus to measure the speed of sound in liquids with a high accuracy. Prior to this study, the speed-of-sound measurement system had been used to study more than 20 liquids and liquid mixtures.

The ultrasonic apparatus was calibrated with redistilled and de-aerated (by multiple boiling) water as the standard liquid. Its electrolytic conductivity was $1 \times 10^{-4}\,\mathrm{S \cdot m^{-1}}$. The speeds of sound in water, calculated from the polynomial of Marczak [11] at atmospheric pressure and, at elevated pressures from the Kell and Whalley polynomial [12], were taken as true values.

In order to check the possible dispersion of the ultrasound speed in the liquid under test within the temperature and pressure ranges investigated, control measurements have been carried out on odd harmonic frequencies according to the following equation for the frequency of free vibrations of the transducer [13]:

$$f = (2n - 1)\,(c/2d))\,, \tag{1}$$

where c is the speed of longitudinal wave, d is the thickness of the transducer, and n is an integer =2,3. The differences observed are insignificant and do not exceed the measurement error, which indicates the absence of dispersion.

2.2.1 Pressure

The pressure was produced by using 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 %. The pressure fluctuations did not exceed ±0.02 MPa during a day.

2.2.2 Temperature

The temperature was measured with an Ertco Hart 850 platinum resistance thermometer (NIST certified) with an uncertainty of 0.05 K and a resolution of 0.001 K. The temperature fluctuations did not exceed ±0.005 K in a 30-min period of measurement and did not exceed ±0.01 K during a day. All the temperatures reported in this article are expressed on the ITS-90.

2.2.3 Uncertainties

The uncertainty of the pulse–echo overlap apparatus is limited mainly by the calibration procedure and is estimated to be of the order of $1\,\mathrm{dm \cdot s^{-1}}$ at atmospheric pressure and $1\,\mathrm{m \cdot s^{-1}}$ under elevated pressures. Higher accuracy is rather difficult to attain due to uncertainty in the speed of sound in reference liquids. That uncertainty is of the order of $5\,\mathrm{cm \cdot s^{-1}}$ in water [11], which is undoubtedly the best standard liquid available. The repeatability of the measured speeds of sound was better than ±0.02 % at atmospheric pressure and ±0.04 % under high pressures.

2.3 Density

The measurements of the densities, ρ, of the 1,3-dibromopropane were carried out using an Anton Paar densimeter (Model DMA 5000) operated in the static mode. The water used for the calibration of the densimeter was redistilled over alkaline $KMnO_4$ and de-aerated by multiple boiling. The apparatus was also tested with a density of known molality of aqueous NaCl.

2.3.1 Uncertainties

The uncertainty of the density measurements was $5 \times 10^{-2}\,\mathrm{kg \cdot m^{-3}}$.

3 Results, Calculations, and Discussion

The measurements of the speeds of sound of the substances studied were carried out within the temperature range from 293 K to 313 K with steps of about 5 K and under pressures from 0.1 MPa to 101 MPa with steps of about 15 MPa.

Densities for 1,3-dibromopropane have been measured within the temperature range from 293 K to 313 K under atmospheric pressure. The experimental data of the speeds of sound and densities are collected in Tables 1 and 2, respectively.

From speed-of-sound data, over the entire pressure range, and from a knowledge of the density at atmospheric pressure and heat capacity at atmospheric pressure, it is possible to calculate, through an iterative method [8], densities, and several thermodynamic properties such as the isobaric heat capacities, isobaric thermal expansion coefficient, and isentropic and isothermal compressibilities from atmospheric pressure up to 100 MPa. Numerical calculations are based on the following thermodynamic relations, where the first step is to solve a set of first-order differential equations for the density, ρ, and for the isobaric specific heat, C_p:

$$\Delta\rho = \int_{p_1}^{p_2} \left(\frac{1}{u^2} + \frac{\alpha_p^2 T}{C_p}\right) \mathrm{d}p \approx \int_{p_1}^{p_2} \frac{1}{u^2} \mathrm{d}p + \frac{\alpha_p^2 T}{C_p} \Delta p \tag{2}$$

and

$$\Delta C_p \approx -(T/\rho) \left[\alpha_p^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p\right] \Delta p, \tag{3}$$

where $\alpha_p = -\rho^{-1} (\partial\rho/\partial T)_p$ is the thermal expansion coefficient, C_p is the specific isobaric heat capacity, and $\Delta p = p_2 - p_1$.

Thus, to calculate the density at p_2, the values of ρ, α_p, and C_p at $p_1$should be known aside from the speed of ultrasound as a function of pressure.

Table 1 Speeds of sound, u, in 1,3-dibromopropane and 1,5-dibromopentane measured at pressures up to 101 MPa within the temperature range from 292 K to 313 K

1,3-Dibromopropane						1,5-Dibromopentane					
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 ($m \cdot s^{-1}$)	Temperature (K)	Pressure (MPa)	Speed of sound ($m \cdot s^{-1}$)
292.66	0.10	1078.91	302.95	60.79	1187.19	292.38	0.10	1149.48[a]	303.01	60.79	1270.04
292.72	15.20	1114.42	302.95	76.01	1216.70	292.53	15.21	1189.09	303.00	76.00	1301.95
292.78	30.40	1148.59	302.95	91.22	1244.54	292.48	30.40	1226.21	303.01	91.20	1331.80
292.79	45.60	1180.55	302.95	101.35	1262.26	292.50	45.60	1260.76	303.01	101.34	1350.72
292.80	60.81	1210.75	308.67	0.10	1035.28	292.52	60.80	1293.37	308.38	0.10	1105.79[a]
292.82	76.01	1239.13	308.05	15.21	1074.31	292.59	76.01	1324.36	308.03	15.21	1148.74
292.80	91.22	1265.80	308.05	30.41	1110.48	292.47	91.20	1353.98	308.03	30.41	1187.74
292.83	101.35	1283.00	308.05	45.62	1144.20	292.57	101.32	1372.23	308.03	45.59	1223.97
298.61	0.10	1062.56	308.05	60.82	1175.81	298.37	0.10	1133.01[a]	308.06	60.79	1257.88
298.07	15.21	1100.13	308.04	76.01	1205.62	298.03	15.21	1174.79	308.06	76.00	1290.08
298.05	30.40	1135.12	308.04	91.21	1233.73	298.02	30.41	1212.72	308.06	91.20	1320.46
298.04	45.60	1167.82	308.04	101.35	1251.75	298.01	45.60	1247.97	308.05	101.33	1340.01
298.04	60.81	1198.54	314.70	0.10	1019.02	298.00	60.80	1281.15	314.36	0.10	1089.74[a]
298.03	76.00	1227.51	313.41	15.23	1060.73	298.05	76.00	1312.60	313.20	15.21	1135.80
298.04	91.21	1254.97	313.41	30.41	1097.53	298.00	91.20	1342.44	313.20	30.41	1175.46
298.08	101.33	1272.43	313.41	45.61	1131.74	298.00	101.33	1361.63	313.17	45.61	1212.35
303.58	0.10	1049.01	313.41	60.80	1163.81	303.40	0.10	1119.29[a]	313.18	60.80	1246.82
302.95	15.21	1087.38	313.41	76.01	1194.03	303.01	15.20	1162.07	313.14	76.03	1279.29
302.95	30.41	1122.97	313.42	91.20	1222.60	303.01	30.40	1200.58	313.16	91.21	1310.12
302.95	45.60	1156.12	313.42	101.33	1240.83	303.02	45.60	1236.47	313.16	101.33	1329.99

[a] Values from our previous work [5]

Table 2 Densities, ρ, of 1,3-dibromopropane measured within temperature range from 293 K to 315 K at atmospheric pressure

Temperature (K)	Density ($\mathrm{kg \cdot m^{-3}}$)
292.55	1980.22
297.98	1970.59
303.07	1961.58
308.02	1952.84
314.58	1941.18

Table 3 Coefficients of Eq. 6 with their standard deviations and mean deviations from the regression line δ_i

1,3-dibromopropane			
u_0 ($\mathrm{m \cdot s^{-1}}$)	u_1 ($\mathrm{m \cdot s^{-1} \cdot K^{-1}}$)	u_2 ($\mathrm{m \cdot s^{-1} \cdot K^{-2}}$)	δu^{a} ($\mathrm{m \cdot s^{-1}}$)
2042.510 ± 22.305	-3.8282 ± 0.1470	0.001830 ± 0.000242	0.03
ρ_0 ($\mathrm{kg \cdot m^{-3}}$)	ρ_1 ($\mathrm{kg \cdot m^{-3} \cdot K^{-1}}$)	ρ_2 ($\mathrm{kg \cdot m^{-3} \cdot K^{-2}}$)	$\delta\rho^{a}$ ($\mathrm{kg \cdot m^{-3}}$)
2498.451 ± 0.315	-1.7714 ± 0.0010	–	0.02
c_0 ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$)	c_1 ($\mathrm{J \cdot kg^{-1} \cdot K^{-2}}$)	c_2 ($\mathrm{J \cdot kg^{-1} \cdot K^{-3}}$)	$\delta C_p{}^{a}$ ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$)
1013.519 ± 142.898	-1.9300 ± 0.9244	0.004171 ± 0.001493	0.50
1,5-dibromopentane			
u_0 ($\mathrm{m \cdot s^{-1}}$)	u_1 ($\mathrm{m \cdot s^{-1} \cdot K^{-1}}$)	u_2 ($\mathrm{m \cdot s^{-1} \cdot K^{-2}}$)	δu^{a} ($\mathrm{m \cdot s^{-1}}$)
2139.919 ± 8.922	-4.0100 ± 0.0588	0.002129 ± 0.000097	0.01
ρ_0 ($\mathrm{kg \cdot m^{-3}}$)	ρ_1 ($\mathrm{kg \cdot m^{-3} \cdot K^{-1}}$)	ρ_2 ($\mathrm{kg \cdot m^{-3} \cdot K^{-2}}$)	$\delta\rho^{a}$ ($\mathrm{kg \cdot m^{-3}}$)
2105.891 ± 1.084	-1.3891 ± 0.0036	–	0.06
c_0 ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$)	c_1 ($\mathrm{J \cdot kg^{-1} \cdot K^{-2}}$)	c_2 ($\mathrm{J \cdot kg^{-1} \cdot K^{-3}}$)	$\delta C_p{}^{a}$ ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$)
908.447 ± 32.862	-0.6010 ± 0.2168	0.002601 ± 0.000358	0.05

[a] Mean deviations from the regression line δ_i

Table 4 Coefficients of Eq. 7 and mean deviations from the regression line δu

	a_{1j} ($K^{-j}\cdot\mathrm{MPa \cdot s \cdot m^{-1}}$)	a_{2j} ($K^{-j}\cdot\mathrm{MPa \cdot s^{2} \cdot m^{-2}}$)	a_{3j} ($K^{-j}\cdot\mathrm{MPa \cdot s^{3} \cdot m^{-3}}$)	δu^{a} ($\mathrm{m \cdot s^{-1}}$)
1,3-dibromopropane				
j				
0	0.9227726751	$2.83749578 \times 10^{-4}$	$5.00895407 \times 10^{-7}$	0.13
1	$-1.73679378 \times 10^{-3}$	–	–	
2	–	–	–	
1,5-dibromopentane				
j				0.14
0	0.7830615660	$4.01227511 \times 10^{-4}$	–	
1	$-1.43927129 \times 10^{-3}$	–	–	
2	–	–	$2.12918481 \times 10^{-3}$	

[a] Mean deviations from the regression line δu

Table 5 Densities, ρ, of 1,3-dibromopropane and 1,5-dibromopentane at pressures up to 100 MPa and within the temperature range from 293 K to 313 K

Density ($\mathrm{kg \cdot m^{-3}}$)					
Pressure (MPa)	Temperature (K)				
	293.15	298.15	303.15	308.15	313.15
1,3-dibromopropane					
0.1[a]	1979.16	1970.30	1961.44	1952.58	1943.73
10	1990.29	1981.70	1973.12	1964.55	1955.98
20	2000.99	1992.65	1984.33	1976.01	1967.70
30	2011.22	2003.11	1995.00	1986.91	1978.84
40	2021.02	2013.10	2005.21	1997.32	1989.46
50	2030.43	2022.69	2014.98	2007.29	1999.62
60	2039.47	2031.91	2024.38	2016.86	2009.36
70	2048.20	2040.80	2033.42	2026.06	2018.73
80	2056.63	2049.37	2042.14	2034.93	2027.75
90	2064.78	2057.67	2050.57	2043.51	2036.46
100	2072.68	2065.70	2058.74	2051.80	2044.89
1,5-dibromopentane					
0.1[a]	1698.68	1691.74	1684.79	1677.84	1670.90
10	1707.99	1701.26	1694.53	1687.81	1681.09
20	1716.94	1710.40	1703.87	1697.34	1690.83
30	1725.49	1719.13	1712.77	1706.42	1700.09
40	1733.68	1727.47	1721.28	1715.09	1708.92
50	1741.55	1735.49	1729.43	1723.40	1717.38
60	1749.12	1743.19	1737.28	1731.38	1725.49
70	1756.43	1750.62	1744.83	1739.06	1733.30
80	1763.49	1757.79	1752.12	1746.46	1740.82
90	1770.32	1764.73	1759.17	1753.62	1748.09
100	1776.94	1771.46	1765.99	1760.55	1755.12

[a] Calculated from Eq. 6

The second step is to calculate the other thermodynamic quantities, namely, the isentropic compressibility, κ_S, from the Newton–Laplace equation:

$$\kappa_S = \frac{1}{\rho u^2} \tag{4}$$

and the isothermal compressibility, κ_T, from the well-known thermodynamic relationship:

$$\kappa_T = \kappa_S + \frac{T V \alpha_p^2}{C_p}. \tag{5}$$

Table 6 Isobaric molar heat capacities, C_p, of 1,3-dibromopropane and 1,5-dibromopentane at pressures up to 100 MPa and within the temperature range from 293 K to 313 K

Isobaric molar heat capacity (J · mol^{-1} · K^{-1})					
Pressure (MPa)	Temperature (K)				
	293.15	298.15	303.15	308.15	313.15
1,3-dibromopropane					
0.1[a]	162.76	163.30	163.89	164.51	165.18
10	162.33	162.85	163.42	164.04	164.69
20	161.95	162.47	163.03	163.63	164.27
30	161.63	162.14	162.69	163.28	163.92
40	161.36	161.86	162.40	162.99	163.61
50	161.11	161.61	162.15	162.73	163.35
60	160.90	161.39	161.93	162.50	163.12
70	160.71	161.20	161.73	162.30	162.91
80	160.55	161.03	161.56	162.12	162.73
90	160.40	160.88	161.40	161.97	162.57
100	160.26	160.74	161.26	161.82	162.43
1,5-dibromopentane					
0.1[a]	219.77	220.85	221.95	223.09	224.26
10	219.29	220.35	221.44	222.56	223.72
20	218.87	219.92	221.01	222.12	223.26
30	218.52	219.56	220.64	221.74	222.87
40	218.22	219.25	220.32	221.41	222.53
50	217.95	218.98	220.04	221.13	222.25
60	217.72	218.75	219.80	220.88	222.00
70	217.52	218.54	219.59	220.67	221.78
80	217.34	218.36	219.40	220.48	221.58
90	217.18	218.19	219.24	220.31	221.41
100	217.03	218.05	219.09	220.16	221.26

[a] Calculated from Eq. 6

Our computations and numerical procedures are based on Sun's algorithm [8]. We have developed an automation client for Microsoft Excel, the most popular spreadsheet, for calculating and visualizing thermodynamic data. Our program has been written in the C++ programming language. We have also used MFC (Microsoft Foundation Classes) to read and analyze the thermodynamic data, which are stored in a plain text (ASCII) files. Subsequently, we have used COM (Component Object Model) to provide access to the Microsoft Excel automation server. Using this automation server, in the performance calculations, we were able to put the collected data into an Excel sheet, create plots, and finally save it in a native Microsoft Excel file format. The benefit of our approach is that the end user is provided with thermodynamic data in an easy-to-use format (Microsoft Excel sheet).

Table 7 Isentropic compressibilities, κ_S, of 1,3-dibromopropane and 1,5-dibromopentane at pressures up to 100 MPa and within the temperature range from 293 K to 313 K

Isentropic compressibility × 10^{10} (Pa^{-1})					
Pressure (MPa)	Temperature (K)				
	293.15	298.15	303.15	308.15	313.15
1,3-dibromopropane					
0.1	4.352	4.485	4.623	4.766	4.914
10	4.144	4.264	4.388	4.516	4.648
20	3.955	4.064	4.176	4.291	4.409
30	3.785	3.883	3.985	4.089	4.196
40	3.630	3.720	3.813	3.908	4.005
50	3.489	3.572	3.658	3.745	3.834
60	3.360	3.438	3.517	3.597	3.679
70	3.242	3.315	3.388	3.463	3.539
80	3.134	3.202	3.270	3.340	3.411
90	3.034	3.098	3.162	3.228	3.294
100	2.942	3.002	3.063	3.124	3.187
1,5-dibromopentane					
0.1	4.472	4.600	4.732	4.869	5.010
10	4.248	4.363	4.481	4.602	4.727
20	4.049	4.152	4.259	4.368	4.480
30	3.870	3.965	4.062	4.161	4.262
40	3.710	3.797	3.886	3.976	4.068
50	3.565	3.645	3.727	3.810	3.894
60	3.433	3.507	3.583	3.660	3.738
70	3.312	3.381	3.452	3.523	3.595
80	3.201	3.265	3.331	3.397	3.465
90	3.097	3.158	3.220	3.282	3.345
100	3.002	3.059	3.117	3.175	3.234

The program was checked using data from literature sources. The results obtained by our procedure are in very good agreement with those reported originally by Sun et al. [8].

Due to the fact that both terms of Eq. 2 are not independent of each other, the estimation of the uncertainty of calculated values of heat capacities and densities is a non-trivial problem. Sun et al. [8] proposed the introduction of perturbations on the input data and the tracing of their effects on the final values of density. Our calculations confirmed the results of Sun et al. that the systematic error of ±0.1 % in the speed of sound causes a maximum error of ±0.02 % in the calculated densities and ±0.2 % in the calculated thermal expansion coefficient. However, taking into account the *AAD*s between results obtained by the acoustic method and those measured directly by a vibrating-tube densimeter, the overall uncertainties of the density and thermal

Table 8 Isobaric thermal expansions, α_p, of 1,3-dibromopropane and 1,5-dibromopentane at pressures up to 100 MPa and within the temperature range from 293 K to 313 K

Isobaric thermal expansion $\times 10^4$ (K^{-1})					
Pressure (MPa)	Temperature (K)				
	293.15	298.15	303.15	308.15	313.15
1,3-dibromopropane					
0.1	8.95	8.99	9.03	9.07	9.11
10	8.63	8.66	8.69	8.72	8.76
20	8.34	8.37	8.39	8.41	8.44
30	8.08	8.10	8.12	8.13	8.15
40	7.84	7.86	7.87	7.88	7.90
50	7.63	7.63	7.64	7.65	7.66
60	7.42	7.43	7.44	7.44	7.45
70	7.24	7.24	7.25	7.25	7.26
80	7.07	7.07	7.07	7.07	7.08
90	6.90	6.90	6.91	6.91	6.91
100	6.75	6.75	6.75	6.75	6.75
1,5-dibromopentane					
0.1	8.18	8.21	8.24	8.28	8.31
10	7.89	7.91	7.94	7.96	7.99
20	7.62	7.64	7.66	7.68	7.70
30	7.39	7.40	7.42	7.43	7.45
40	7.17	7.18	7.19	7.20	7.21
50	6.97	6.98	6.99	7.00	7.00
60	6.79	6.80	6.80	6.81	6.81
70	6.62	6.63	6.63	6.63	6.63
80	6.46	6.47	6.47	6.47	6.47
90	6.32	6.32	6.32	6.32	6.32
100	6.18	6.18	6.18	6.18	6.17

expansion coefficient calculated for high pressures were found to be of 0.05 % and 1 %, respectively [14]. The heat capacity depends rather weakly on pressure, and the second term on the right-hand side of Eq. 2 is significantly smaller than the first one; hence, the maximum error in the heat capacity would be larger, i.e., at 0.3 % [14]. In addition, taking into account the above-mentioned *AAD*, the overall uncertainty of the isobaric heat capacity calculated for high pressures was found to be 1 % [14]. The overall uncertainties of the compressibility values are estimated to be 0.15 % and 0.5 % for isentropic and isothermal compressibilities, respectively [14].

The validity of the calculation method involves a comparison of the calculated thermodynamic properties from sound-speed data with those obtained by direct *pVT* measurements. These comparisons lead to the conclusion that the acoustic method is very suitable for precise determination of thermodynamic properties of liquid substances under elevated pressures [15,16].

Table 9 Isothermal compressibilities, κ_T, of 1,3-dibromopropane and 1,5-dibromopentane at pressures up to 100 MPa and within the temperature range from 293 K to 313 K

Isothermal compressibility $\times 10^{10}(\mathrm{Pa}^{-1})$

Pressure (MPa)	Temperature (K)				
	293.15	298.15	303.15	308.15	313.15
1,3-dibromopropane					
0.1	5.82	6.00	6.18	6.36	6.55
10	5.51	5.66	5.82	5.99	6.15
20	5.23	5.36	5.51	5.65	5.80
30	4.97	5.10	5.23	5.36	5.49
40	4.75	4.86	4.98	5.10	5.22
50	4.54	4.65	4.75	4.86	4.97
60	4.35	4.45	4.55	4.65	4.75
70	4.18	4.27	4.37	4.46	4.55
80	4.03	4.11	4.20	4.28	4.37
90	3.89	3.96	4.04	4.12	4.21
100	3.75	3.83	3.90	3.98	4.05
1,5-dibromopentane					
0.1	5.68	5.84	6.00	6.17	6.34
10	5.37	5.51	5.65	5.80	5.95
20	5.09	5.22	5.35	5.48	5.61
30	4.85	4.96	5.08	5.19	5.32
40	4.63	4.73	4.84	4.94	5.05
50	4.43	4.52	4.62	4.72	4.82
60	4.25	4.34	4.43	4.52	4.61
70	4.09	4.17	4.25	4.33	4.42
80	3.94	4.01	4.09	4.17	4.25
90	3.80	3.87	3.94	4.01	4.09
100	3.67	3.74	3.80	3.87	3.94

As mentioned above, to calculate $\rho(p, T)$ and $C_p(p, T)$, we required simultaneously the temperature dependencies of $\rho(T)$ and $C_p(T)$ as well as pressure dependencies of $u(p, T)$.

The required speeds of sound, densities, and heat capacities of 1,5-dibromopentane at atmospheric pressure were taken from our earlier study [5]. However, the isobaric heat capacities of 1,3-dibromopropane were taken from the previous study [2].

The dependencies of the molar heat capacities, densities, and speeds of sound on temperature were fitted to the following equation:

$$y = \sum_{i=0}^{2} a_i \, (T/\mathrm{K})^i, \tag{6}$$

where y is the molar heat capacity, density, or speed of sound, T/K is the absolute temperature, and a_i's are the polynomial coefficients ($a_i = c_i$ for the molar heat capacity, $a_i = \rho_i$ for the density, and $a_i = u_i$ for the speed of sound) calculated by the least-squares method. The backward stepwise rejection procedure was used to reduce the number of non-zero coefficients. The values of the coefficients and mean deviations from the regression line are collected in Table 3.

The experimental data of the sound velocity have been fitted by a least-squares method with a double polynomial equation suggested by Sun et al. [8]:

$$p - p_0 = \sum_{i=1}^{m} \sum_{j=0}^{n} a_{ij} \left(u - u_0\right)^i T^j, \tag{7}$$

where a_{ij}'s are the polynomial coefficients, u is the speed of sound at $p > 0.1\,\mathrm{MPa}$, and u_0 is the speed of sound calculated from Eq. 6. The coefficients a_{ij} and the mean deviations from the regression lines are given in Table 4. The stepwise rejection procedure was used to reduce the number of non-zero coefficients.

Results of the calculations, i.e., the values of the density, isobaric heat capacity, isentropic compressibility, isobaric thermal expansion, and the isothermal compressibility are listed in Tables 5, 6, 7, 8, and 9, respectively.

The experimental results of the speed of sound in 1,3-dibromopropane and 1,5-dibromopentane are plotted as function of temperature and pressure in Figs. 1 and 2, respectively. As shown, the isotherms of speed of sound increase monotonically and non-linearly with increasing pressure, and isobars decrease linearly with increasing temperature. The speeds of sound increase with increasing carbon chain length. The values of isentropic compressibilities for 1,3-dibromopropane and 1,5-dibromopentane decrease with increasing pressure, and isobars increase linearly with increasing temperature (Figs. 3 and 4).

Figures 5 and 6 show that the values of the thermal expansion coefficient decrease with increasing pressure, as well as with increasing pressure, the influence of temperature on α_p decreases. It is worth noting that the single crossing point of the thermal expansion coefficient isotherms appears practically at the same pressure for 1,3-dibromopropane and 1,5-dibromopentane, i.e., in the vicinity of 80 MPa. Randzio et al. [17] suggested the correlation between the pressure of the crossing point of isobaric thermal expansion and the nature of liquids. For associated liquids, a shift of the crossing points toward the higher-pressure region was observed, for example, for non-associated liquids such as hexane, the crossing point of α_p appears in the vicinity of 65 MPa [18]; however, for associated 1-hexanol, the crossing point is observed close to 280 MPa [17].

α, ω-Dibromoalkanes are polar non-associated liquids, in which important electrostatic intermolecular interactions occur due to permanent dipole moments of the molecules and/or their possible higher multipoles. The compressibility of a liquid is a result of the combination of various factors: the size and shape of the molecules, the intermolecular interaction energy, and molecular structure (correlation of molecular orientations).

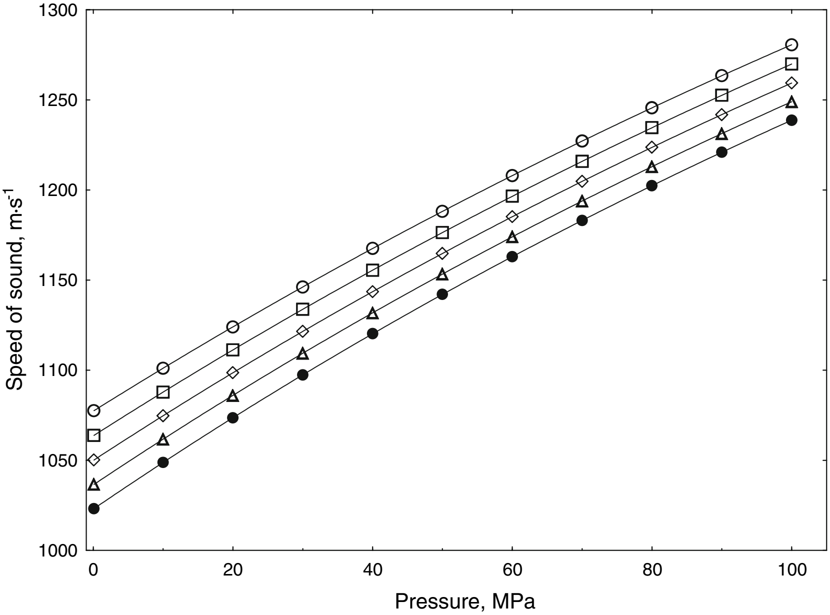

Fig. 1 Speeds of sound in 1,3-dibromopropane as a function of pressure: (○) 293.15 K, (□) 298.15 K, (◇) 303.15 K, (△) 308.15 K, and (●) 313.15 K. Lines calculated from the empirical function: $u = \sum_{i=0}^{3} a_i p^i$

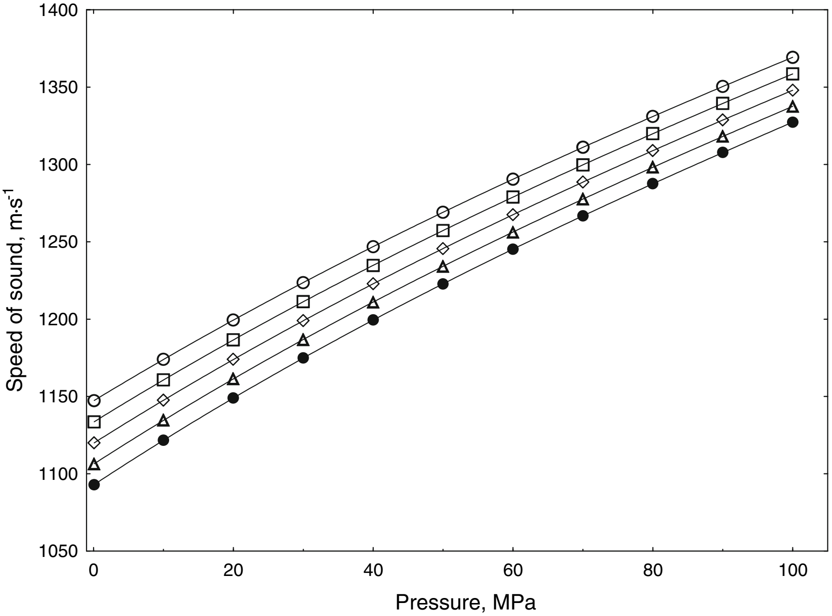

Fig. 2 Speeds of sound in 1,5-dibromopentane as a function of pressure: (○) 293.15 K, (□) 298.15 K, (◇) 303.15 K, (△) 308.15 K, and (●) 313.15 K. Lines calculated from the empirical function: $u = \sum_{i=0}^{3} a_i p^i$

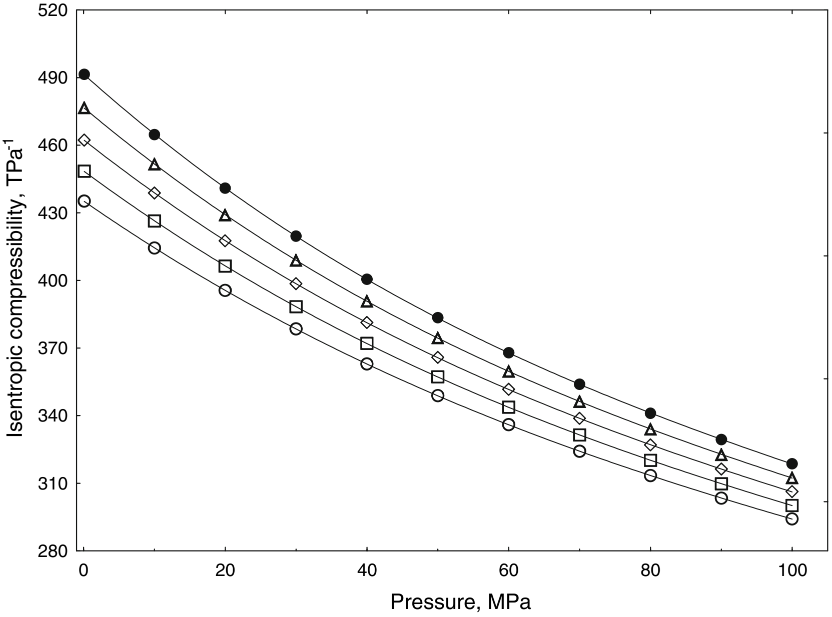

Fig. 3 Isentropic compressibility as a function of pressure for 1,3-dibromopropane at the temperatures: (○) 293.15 K, (□) 298.15 K, (◇) 303.15 K, (△) 308.15 K, and (●) 313.15 K. Lines calculated from the empirical function: $\kappa_S = \sum_{i=0}^{3} a_i p^i$

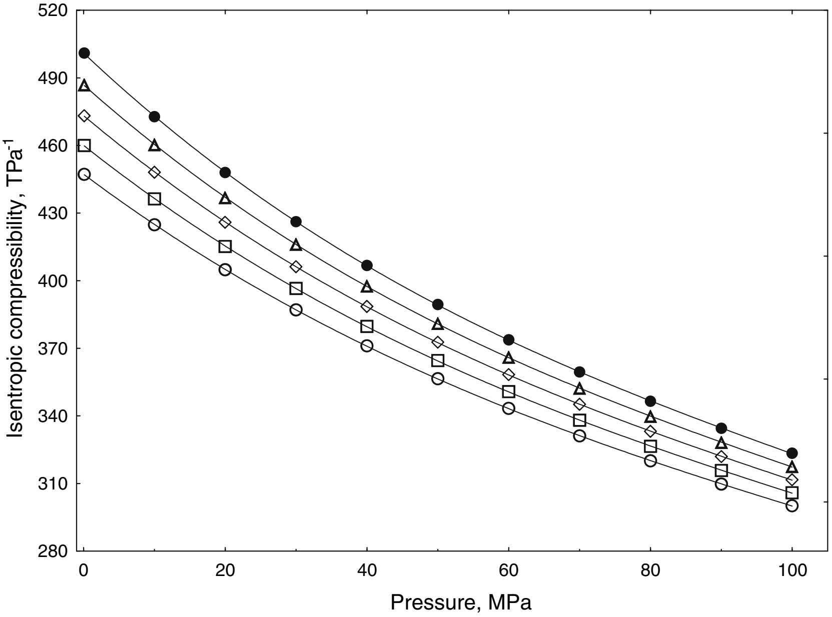

Fig. 4 Isentropic compressibility as a function of pressure for 1,5-dibromopentane at the temperatures: (○) 293.15 K, (□) 298.15 K, (◇) 303.15 K, (△) 308.15 K, and (●) 313.15 K. Lines calculated from the empirical function: $\kappa_S = \sum_{i=0}^{3} a_i p^i$

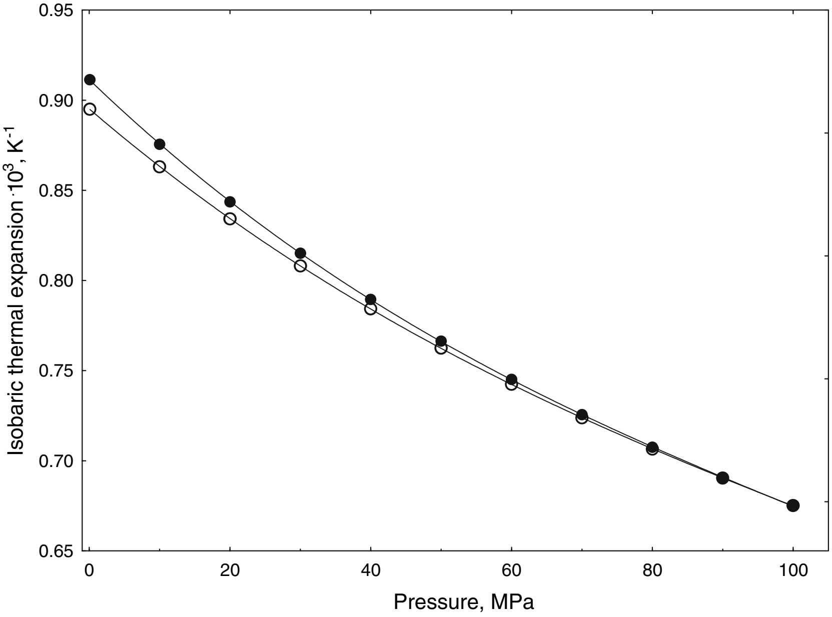

Fig. 5 Isobaric thermal expansion of 1,3-dibromopropane as a function of pressure at the temperatures: (○) 293.15 K and (●) 313.15 K. Lines calculated from the empirical function: $\alpha_p = \sum_{i=0}^{3} a_i\, p^i$

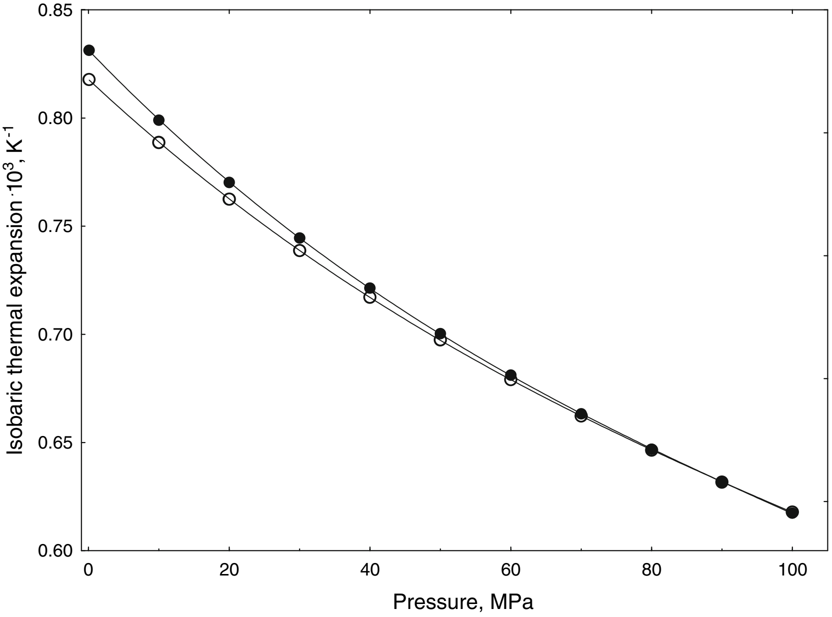

Fig. 6 Isobaric thermal expansion of 1,5-dibromopentane as a function of pressure at the temperatures: (○) 293.15 K and (●) 313.15 K. Lines calculated from the empirical function: $\alpha_p = \sum_{i=0}^{3} a_i\, p^i$

The variation of the compressibility with increasing length of the carbon chain of the α, ω-dibromoalkanes is therefore difficult to explain on the molecular level. However, the variation of the compressibility with increasing length of the chain is undoubtedly related to the space filling effect, which is one of the molecular features that is responsible for the observed compressibility variations. A closer packing of the molecules (higher degree of space-filling) results in a compressibility decrease, while a more bulky structure brings about a compressibility increase. Since no specific interactions are expected in the α, ω-dibromoalkanes (association of molecules can be neglected) [19], the observed variation of the compressibility is evidently the result of van der Waals interactions (of Keesom and/or Debye type) and of the molecular shape and size.

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