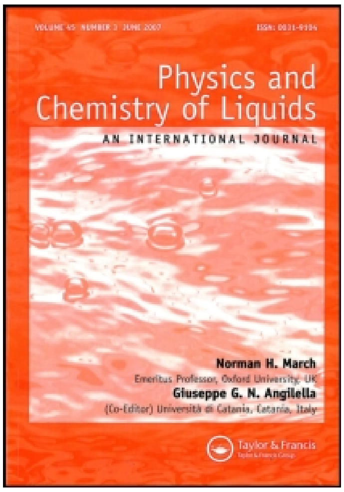

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Acoustic and Thermodynamic Properties of Ethanol from 273.15 to 333.15 K and up to 280 MPa

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The velocity of sound in ethanol has been measured in the temperature range between 273.15 and 333.15 K and at pressures up to 280 MPa using the phase comparison pulse-echo method with two reflectors, which has been described previously. The density, isothermal compressibility, isobaric thermal expansion and the specific heat at constant pressure of ethanol have been evaluated from the measured sound velocity, using an improved method of computation.

Key Words: Sound velocity, pulse-echo, specific heat.

1 INTRODUCTION

We have recently set up a programme of ultrasonic measurements of the sound velocity in liquids at elevated pressures and at temperatures down to the melting line.[1,2] The principal aim of these measurements is to derive the equation of state and several important thermodynamic properties of a liquid at higher pressures from the measured sound velocity data. The precision of the equation of state data determined from ultrasonic measurements is generally higher than those obtained from direct methods, so that such data have been used earlier for precise volume calibrations of high pressure vessels.[3] In the case of thermodynamic properties of a liquid at higher pressures, direct determination is not only tedious but extremely difficult. We have already completed sound velocity measurements on a number of simple organic liquids, namely toluene, *n*-heptane, benzene and cyclohexane,[1,2] over a wide pressure and temperature range and evaluated the density and several thermodynamic properties of these liquids from the measured sound velocity, following a computational method similar to that of Davis and Gordon.[4]

In the present investigation, we have chosen ethanol because the equation of state data and thermodynamic properties of ethanol are of considerable interest both from a fundamental and a technological point of view and because the existing data in literature for this compound are few and scattered. We have also developed an improved computational method to evaluate these properties, which assumes that isobaric densities can be described by appropriate polynomials in temperature. The method is simpler than that of Davis and Gordon and differs from several other computational procedures where a specific empirical equation of state for the liquid was chosen.[5,6] Ethanol is considered to be a very suitable substance for testing the present method of computation since the melting line of ethanol is outside the present experimental range and, consequently, an appreciable number of isotherms covering a large temperature interval can be included in the computation.

2 EXPERIMENTAL METHOD

The materials for the present investigation were purchased from BDH Chemicals Ltd, Poole, U.K. According to the specifications of the supplier, the material was of Anala R grade and the purity of the sample was better than 99.7% by volume, the main impurity being water (<0.2%). The material was used without further purification.

The measurements were performed with an ultrasonic apparatus based on the phase comparison pulse-echo method, which operates at 2 MHz and which is designed for pressures up to 300 MPa and temperatures down to 77 K. Since the details of the apparatus as well as a few modifications are described elsewhere,[1,2] only a short description is given here. In the center of the pressure vessel an ultrasonic cell is located with two reflectors at different distances, d_1 and d_2, from an X-cut quartz transducer serving both as transmitter and receiver. Ultrasonic pulses traverse the acoustic path lengths $2d_1$ and $2d_2$ in transit times t_1 and t_2 respectively. The experimental procedure is such that the difference $t_1 - t_2$ is determined accurately; the sound velocity is then calculated as $2(d_1 - d_2)/(t_1 - t_2)$. The distances d_1 and d_2 are measured directly and corrected for the influence of pressure and temperature.

The pressure on the liquid sample is generated by a mercury gas compressor coupled to a hydraulic oil press and measured with an accuracy better than 1 in 10^4 by means of a Michels pressure balance. The temperature of the ultrasonic cell is stabilized by the use of a vacuum type of cryostat which is provided with a proportional-integral temperature regulation system. The temperature is measured with a calibrated resistance thermometer with an accuracy better than 0.01 K. Details of the high pressure system and the vacuum cryostat can be found elsewhere.[1,2]

3 EXPERIMENTAL RESULTS

The sound velocity in ethanol has been measured isothermally as a function of pressure in the temperature range between 273 and 333 K with intervals of about 10 K. For each isotherm, data are taken from 0.1 MPa up to 280 MPa at intervals of about 20 MPa. In Table 1, the original experimental data of the sound velocity at each isotherm are recorded as a function of the pressure. The accuracy of the sound velocity data is estimated to be better than 0.03 %.

Table 1 The original experimental data of sound velocity in ethanol.

	$T(K)$						
p (MPa)	273.91	283.19	293.11	303.11	313.10	323.02	333.01
	u (m. s^{-1}) in ethanol						
0.10	1229.2	1196.7	1163.0	1126.9	1094.1	1060.9	1027.4
19.99	1333.3	1304.6	1274.6	1243.1	1214.7	1186.6	1158.1
39.93	1421.9	1395.7	1368.3	1339.8	1314.1	1288.5	1263.3
59.77	1499.8	1475.1	1449.7	1423.0	1399.2	1375.8	1352.5
79.96	1570.9	1547.7	1523.6	1498.5	1476.0	1454.1	1432.4
100.09	1635.4	1613.2	1590.2	1566.4	1545.3	1524.3	1503.8
120.13	1694.9	1673.5	1651.6	1628.6	1608.2	1588.3	1568.6
140.04	1749.8	1729.4	1708.1	1685.7	1666.4	1647.1	1628.3
160.17	1802.1	1782.4	1761.7	1740.0	1721.3	1702.7	1684.3
180.39	1851.6	1832.5	1812.5	1791.2	1773.1	1755.0	1737.4
200.55	1898.6	1879.6	1860.4	1839.6	1821.9	1840.3	1787.1
220.30	1942.1	1923.7	1904.8	1884.4	1867.1	1850.2	1833.2
240.24	1984.1	1966.4	1947.8	1927.9	1911.0	1894.2	1877.8
260.39	2025.1	2007.6	1989.3	1970.1	1953.5	1936.7	1920.7
275.93	2055.6	2038.2	2020.1	2001.4	1984.6	1968.6	1952.8

Table 2 Coefficients a_{ij} of Eq. (1) for ethanol in MPa $m^{-i}\,s^{i}\,K^{-j}$

j \ i	1	2	3
0	0.3974031385	$3.366484511 \times 10^{-4}$	$-2.795885068 \times 10^{-8}$
1	$-9.184931297 \times 10^{-4}$	$-8.855611262 \times 10^{-7}$	$4.182224110 \times 10^{-10}$
2	$3.674386464 \times 10^{-7}$	$-9.381016419 \times 10^{-10}$	$-6.781244978 \times 10^{-13}$

The complete experimental data of the sound velocity have been fitted by a least-squares analysis to a double polynomial equation of the form

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

where u_0, the sound velocity (in ms^{-1}) at $p_0 = 0.1$ MPa, is expressed as

$$u_0 = 2344.044 - 4.607374\,T + 1.9621604 \times 10^{-3}\,T^2, \qquad (2)$$

u is the sound velocity at pressure p, T is the temperature and a_{ij} are the coefficients. It turns out from the least-squares analysis that the best fit is achieved with $m = 3$ and $n = 2$. The resulting 9 coefficients for a_{ij} are presented in Table 2. The average deviation for the best fit is found to be 0.3 ms^{-1}, while the maximum deviation is less than 1 ms^{-1}. These figures are higher than those found previously for benzene and cyclohexane.

The agreement between the present sound velocity data at 0.1 MPa and those reported previously by Wilson[7] is very good, the deviation being less than 0.01 % at 273.15 K, 283.15 K and 303.15 K and 0.04 % at 313.15 K. Also at higher pressures the present data are in excellent agreement with those of Wilson, namely within 0.02 % at 293.15 K and up to 100 MPa. However, the agreement of the present data with those of Hawley *et al.*[8] at 303.15 K and up to 300 MPa is less satisfactory, the average deviation being 0.5 %. The present data at 0.1 MPa are found to be in good agreement with those of Aleksandrov and Khasanshin,[9] namely 0.2 %.

4 EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF ETHANOL

The equation of state and thermodynamic properties of ethanol have been computed from the present sound velocity data by using a method which starts from the following relations for density ρ_0 and isobaric specific heat c_{p_0} at 0.1 MPa, obtained by fitting the experimental data found in literature[10,11] by a least-squares analysis:

$$\rho_0 = 1019.529 - 0.71942\,T - 2.244294 \times 10^{-4}\,T^2 \qquad (3)$$

$$C_{p_0} = 2111.617 - 2.016296\,T - 3.858685 \times 10^{-3}\,T^2 + 4.78882 \times 10^{-5}\,T^3 \qquad (4)$$

Subsequently, the density ρ, the volume thermal expansion α and the isobaric specific heat C_p at elevated pressures are determined by using the following well-known thermodynamical relations

$$(\partial\rho/\partial p)_T = 1/u^2 + \alpha^2 T/C_p \qquad (5)$$

$$(\partial C_p/\partial p)_T = -(T/\rho)/(\alpha^2 + (\partial\alpha/\partial T)_p) \qquad (6)$$

and assuming that the isobaric density at these pressures can be represented by the form

$$\rho_{p_1}(T) = b_0(p) + b_1(p)T + b_2(p)T^2, \qquad (7)$$

an assumption based on the fact that the density data at 0.1 MPa can be represented by a second degree polynomial in T of the form (3). By a simultaneous step-by-step integration of Eqs (5) and (6) with respect to pressure, starting from 0.1 MPa and applying Eq. (7) at each step, the values of ρ (in kg m^{-3}), α (in K^{-1}) and C_p (in J kg^{-1} K^{-1}) can be computed at elevated pressures for each isotherm.

The calculations were carried out in the following sequence of operations:

A) Compute the densities $\rho_{p_1}(T)$ at a new (higher) pressure p_1 from those, $\rho_{p_0}(T)$, at the pressure of the last step p_o, by using Eq. (5). The values of $u_{p_1}(T)$ are calculated from Eqs (1) and (2) for several temperatures T and pressure p_1, whereas the values of $\alpha_{p_0}(T)$ and $C_{p_0}(T)$ are taken at the previous pressure p_0.

B) Fit the densities $\rho_{p_1}(T)$ to Eq. (7) and find thus the coefficients $b_i(p_1)$; with the help of this expression calculate $\alpha_{p_1}(T) = -(1/\rho)(\partial\rho/\partial T)$ and $(\partial\alpha/\partial T)_{p_1}(T)$.

C) Compute the values $C_{p_1}(T)$ from the values $C_{p_0}(T)$ by using Eq. (6).

D) Repeat Step A taking, however, the values of $\alpha_{p_1}(T)$ and $C_{p_1}(T)$ just calculated, and thus obtaining new, somewhat different values for $\rho_{p_1}(T)$ which are taken to be the final ones. Repeat Steps B and C taking these new values of $\rho_{p_1}(T)$, thus obtaining new (final) values for $\alpha_{p_1}(T)$, $(\partial\alpha/\partial T)_{p_1}(T)$ and $C_{p_1}(T)$.

E) Now calculate the isothermal compressibility $\beta_T = (1/\rho)(\partial\rho/\partial p)_T$ by using the expression given in (5).

The method of numerical integration followed in the present computation is the same as that described in our previous paper,[2] namely a 'prediction and modification' method. In order to increase the precision of the numerical integration, a small pressure step of 2 MPa is chosen. Since the major contribution to the density increment due to pressure actually comes from the first term of r.h.s. of Eq. (5), i.e. the term $1/u^2$, it is important to evaluate as accurately as possible the integral:

$$\int_{p_0}^{p_1} (1/u^2)dp = I(p_1) - I(p_0) \tag{8}$$

where $I(p)$ is the indefinite integral

$$\int (1/u^2)dp = \int (1/u^2)(\partial p/\partial u)_T \, du. \tag{9}$$

By using Eqs (1) and (2), this integral becomes

$$I = \sum_{i=1}^{m} i \sum_{j=0}^{n} a_{ij} T^j \sum_{k=0}^{i-1} \binom{i-1}{k} f_k(u)(-u_0)^{i-k-1} \tag{10}$$

where $f_k(u) = (k-1)^{-1}u^{k-1}$ if $k \neq 1$; $f_1(u) = \ln u$, which is of the form suitable for computer calculation.

The present method of computation is simpler than the well-known Davis and Gordon[4] method where the pressure dependence of the volume thermal expansion α is determined by using the additional thermodynamic relation $(\partial\alpha/\partial p)_T = -(\partial\beta_T/\partial T)_p$, and which therefore requires an additional assumption that β_T is a polynomial function of T. In the present method, however, the volume thermal expansion coefficient is calculated directly from successive ρ vs. T isobars, which are found to be described precisely by second degree polynomials in T. The present method also differs from those described by Fine and Millero,[12] Kell and Whalley[3] and Takagi and Teranishi,[13] where a specific empirical equation of state (e.g. the Murnaghan equation, the secant modulus equation) appropriate for the liquid under investigation was chosen, instead of the more general expression for the isobaric densities used here, namely the one given in Eq. (7).

The calculated values of ρ, β_T, α and C_p as a function of pressure and temperature are presented in Tables 3-6. The data are given at

Table 3 Density of ethanol as a function of pressure and temperature.

	$T(K)$						
p (MPa)	273.15	283.15	293.15	303.15	313.15	323.15	333.15
	ρ (kg. m^{-3}) of ethanol						
0.1	806.27	797.83	789.34	780.81	772.23	763.61	754.94
20.0	820.71	812.99	805.26	797.53	789.79	782.06	774.33
40.0	833.20	826.00	818.80	811.61	804.44	797.28	790.14
60.0	844.25	837.45	830.65	823.87	817.11	810.36	803.65
80.0	854.23	847.74	841.26	834.80	828.36	821.94	815.55
100.0	863.35	857.13	850.92	844.72	838.54	832.39	826.26
120.0	871.78	865.79	859.80	853.83	847.88	841.94	836.02
140.0	879.64	873.85	868.06	862.28	856.52	850.77	845.04
160.0	887.02	881.40	875.78	870.18	864.58	858.99	853.42
180.0	893.97	888.51	883.05	877.60	872.15	866.71	861.28
200.0	900.56	895.24	889.92	884.61	879.30	873.99	868.68
220.0	906.82	901.64	896.45	891.26	886.07	880.88	875.69
240.0	912.80	907.74	902.67	897.60	892.52	887.44	882.35
260.0	918.52	913.58	908.62	903.65	898.68	893.70	888.71
280.0	924.01	919.17	914.32	909.45	904.58	899.69	894.79

Table 4 Isothermal compressibility of ethanol as a function of pressure and temperature.

	$T(K)$						
p (MPa)	273.15	283.15	293.15	303.15	313.15	323.15	333.15
	$\beta_T \times 10^4$ (MPa^{-1}) of ethanol						
0.1	9.815	10.474	11.184	11.951	12.781	13.681	14.662
20.0	8.172	8.620	9.091	9.586	10.105	10.652	11.226
40.0	7.036	7.368	7.712	8.067	8.434	8.813	9.204
60.0	6.211	6.472	6.740	7.013	7.292	7.577	7.868
80.0	5.580	5.794	6.011	6.231	6.454	6.680	6.908
100.0	5.078	5.258	5.440	5.624	5.808	5.994	6.181
120.0	4.669	4.824	4.980	5.136	5.293	5.450	5.607
140.0	4.327	4.463	4.599	4.735	4.871	5.006	5.141
160.0	4.036	4.157	4.278	4.398	4.517	4.636	4.754
180.0	3.786	3.895	4.003	4.110	4.217	4.322	4.427
200.0	3.568	3.666	3.764	3.861	3.957	4.052	4.146
220.0	3.375	3.465	3.555	3.643	3.731	3.817	3.902
240.0	3.205	3.288	3.370	3.451	3.531	3.610	3.688
260.0	3.052	3.128	3.204	3.280	3.354	3.426	3.498
280.0	2.914	2.985	3.056	3.126	3.195	3.262	3.329

Table 5 Thermal expansion coefficient of ethanol as a function of pressure and temperature.

			$T(K)$				
p (MPa)	273.15	283.15	293.15	303.15	313.15	323.15	323.15
			$\alpha \times 10^4$ (K^{-1}) of ethanol				
0.1	10.44	10.61	10.78	10.96	11.14	11.32	11.51
20.0	9.41	9.51	9.60	9.70	9.79	9.89	9.99
40.0	8.66	8.72	8.78	8.84	8.91	8.97	9.03
60.0	8.08	8.13	8.17	8.22	8.26	8.31	8.35
80.0	7.62	7.65	7.69	7.72	7.76	7.80	7.83
100.0	7.23	7.26	7.29	7.32	7.35	7.38	7.42
120.0	6.89	6.92	6.95	6.98	7.01	7.04	7.07
140.0	6.60	6.63	6.66	6.69	6.72	6.75	6.78
160.0	6.35	6.37	6.40	6.44	6.47	6.50	6.53
180.0	6.12	6.15	6.18	6.21	6.24	6.27	6.31
200.0	5.91	5.94	5.97	6.01	6.04	6.07	6.11
220.0	5.72	5.75	5.79	5.82	5.86	5.89	5.93
240.0	5.54	5.58	5.62	5.65	5.69	5.73	5.77
260.0	5.38	5.42	5.46	5.50	5.54	5.58	5.62
280.0	5.23	5.27	5.31	5.36	5.40	5.44	5.48

Table 6 Isobaric specific heat of ethanol as a function of pressure and temperature.

			$T(K)$				
p (MPa)	273.15	283.15	293.15	303.15	313.15	323.15	333.15
			C_p ($J \cdot kg^{-1} \cdot K^{-1}$) of ethanol				
0.1	2249	2318	2395	2480	2572	2673	2782
20.0	2234	2303	2378	2462	2553	2652	2760
40.0	2224	2292	2367	2450	2540	2639	2746
60.0	2216	2284	2358	2440	2530	2628	2735
80.0	2210	2277	2351	2433	2522	2620	2726
100.0	2204	2271	2345	2426	2516	2613	2719
120.0	2199	2266	2339	2420	2509	2606	2712
140.0	2195	2261	2334	2415	2504	2600	2706
160.0	2190	2256	2329	2410	2498	2595	2700
180.0	2186	2252	2325	2405	2493	2589	2694
200.0	2182	2247	2320	2400	2488	2584	2688
220.0	2178	2243	2316	2395	2483	2579	2683
240.0	2174	2239	2311	2391	2478	2574	2678
260.0	2170	2235	2307	2386	2473	2569	2672
280.0	2166	2230	2302	2382	2468	2563	2667

pressures between 0.1 and 280 MPa in steps of 10 MPa and at temperatures between 273.15 and 333.15 K in steps of 10 K. It should be pointed out here that the number of significant figures for the derived quantities given in Tables 3-6 does not indicate the absolute accuracy but extra figures are retained in order to calculate the pressure and temperature dependence of these quantities. This is justified since the relative accuracy of the calculated values is higher than the absolute accuracy.

The error in the calculated values of the density and thermodynamic properties can, in principle, be estimated by introducing appropriate perturbations on the input data and recording their effects on the final results. The input data consist of the sound velocity data obtained in the present measurement and the density and specific heat data at 0.1 MPa taken from literature. All these quantities have both random and systematic errors. However, the overall accuracy of the derived quantities cannot be estimated easily because the errors in the density and specific heat data at 0.1 MPa are not known exactly. Although a systematic error in the density data at 0.1 MPa only introduces an error of the same magnitude to the density data at higher pressures, a random error may affect the precision of all the quantities at higher pressure considerably. An error in the specific heat data at 0.1 MPa only affects the value of the density at higher pressures. The influence of a systematic error in the sound velocity data on the calculated values of ρ and α is found to be small. For instance, a systematic error of 0.1 % in the sound velocity can introduce a maximum error of 0.02 % in the calculated values for ρ and 0.2 % in the calculated values for α. We may, therefore, conclude that for the construction of an accurate equation of state of a liquid from ultrasonic measurements, the density data at 0.1 MPa should be accurate and be a smooth function of temperature over a wide temperature range and that the precision of the present ultrasonic method is sufficient for this purpose.

It is interesting to compare the present equation of state data obtained in an indirect way with those determined from direct measurements. However, as mentioned in the introduction of this paper, the equation of state data for ethanol available in literature[14–18] are few and do not always cover the experimental range of this work. The density data of Moriyoshi and Inubushi[17] at 298 K and up to 140 MPa are found to be within 0.1 % of the present ones which indicates good agreement. At pressures up to 200 MPa our density data agree very well—within 0.03 %—with those of Ozawa *et al.*[18] at 298 K. However, at 323 K the present density data are up to 0.2 % higher than those of Ozawa *et al.*

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