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Determination of the Thermodynamic Properties of Liquid Ethanol from 193 to 263 K and up to 280 MPa from Speed-of-Sound Measurements

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The sound velocity in liquid ethanol has been measured up to 280 MPa and at temperatures between 193 and 263 K, using a phase-comparison, pulse-echo technique operating at 2 MHz. The density, isothermal compressibility, isobaric thermal expansion coefficient, and specific heat have been evaluated from the measured speed of sound starting from the density and specific heat data at 0.1 MPa and making use of a modified computational method originally developed by Davis and Gordon. The derived density data have been used to examine the validity of several empirical equations of state.

KEY WORDS: sound velocity; ethanol; high pressure.

1. INTRODUCTION

In a continuation of a program of systematic investigations of equations of state and thermodynamic properties of organic liquids using speed-of-sound measurements at high pressures, we have now studied liquid ethanol at temperatures down to 193 K and pressures up to 280 MPa. Apart from general interest in the precise evaluation of several important physical properties of ethanol which have both industrial and fundamental importance, the present work was undertaken for the following reasons. First, until now, the experimental investigation of thermodynamic properties of liquid ethanol at high pressures has been restricted mostly to higher temperatures, i.e., temperatures above the ice point. Our own previous study on ethanol covered temperatures from 273.15 to 333.15 K [1]. It was considered worthwhile to extend our speed-of-sound measurements in ethanol

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to lower temperatures, where there is a lack of accurate experimental data of thermodynamic properties at high pressures. Second, we have recently examined the validity of several empirical equations of state for organic liquids at temperatures above 273.15 K, for which an extensive amount of accurate experimental data is now available [2]. However, it was not possible to extend this analysis to lower temperatures in view of the lack of experimental data in that region. An important purpose of the present work is to examine the validity of several empirical isothermal equations of state for describing the p–ρ relation of ethanol at lower temperatures and at high pressures.

2. EXPERIMENTAL METHOD

The material for the present investigation was obtained from BDH Chemical Ltd., Poole, U.K. According to the specifications of the supplier, the material was of Anala R grade and the purity of all samples was better than 99.7% by volume, the main impurity being water ($<0.2\%$). The amount of water content was established by the well-known Karl Fischer method based on iodimetric determination of water, while the amount of other impurities (methanol, <100 ppm; propanol, <100 ppm; higher alcohols, <200 ppm) was found by gas-liquid chromatographic analysis. The material was used without purification.

The speed-of-sound measurements in ethanol were performed with an ultrasonic apparatus operating at 2 MHz. The design of the ultrasonic cell (diameter, 4 cm; length, 20 cm) is based on a modified phase-comparison pulse-echo method which made use of two reflectors (diameter, 1 cm) placed at distances of, respectively, 4 and 6 cm from a quartz transducer. The complete description of the apparatus as well as the principle of its operation can be found elsewhere [3, 4]. In addition to the previously described measures to reduce unwanted reflections, the back part of each of the two reflectors now has a concave section so that reflections from the corresponding surfaces are delayed in reaching the transducer, and consequently, the pulse length can be increased. Further, appropriate corrections were introduced in the measured data to account for the effects of diffraction on the transit time.

The high-pressure system consists of a steel pressure vessel containing the ultrasonic cell, a mercury gas compressor coupled to a hydraulic oil press for compressing the liquid, and a pressure balance for controlling and measuring the pressure with an accuracy better than 1 in 10^4. The steel pressure vessel is surrounded by a demountable vacuum jacket, and together, they form an adiabatic cryostat. A detailed description of the cryostat is given elsewhere [5]. The temperature is measured with a calibrated Pt resistance thermometer to an estimated accuracy of 10 mK. All temperatures are recorded on the IPTS 68 scale.

3. EXPERIMENTAL RESULTS ON SPEED OF SOUND IN ETHANOL

The speed of sound in ethanol has been measured isothermally as a function of pressure in the temperature range between 193 and 263 K with intervals of about 10 K between the successive isotherms. For each isotherm, the experimental data are recorded at 20-MPa pressure intervals from 0.1 up to 280 MPa. The original experimental data of the sound speed as a function of pressure and temperature are given in Table I. The absolute accuracy of the sound-velocity data is estimated to be better than 0.05%.

To derive the thermodynamic properties of ethanol from the present experimental speed-of-sound data, the latter must be obtained as a function of the pressure (p) and the temperature (T). This can be achieved by choosing a double polynomial equation for the sound speed u, namely, $u(p, T)$, instead of a single polynomial equation for $u(p)$ for each isotherm. However, the function $p(u, T)$ fits the data better than the function $u(p, T)$ and is also very convenient for the calculation of the equation of state data [4]. Accordingly, the present experimental data on the sound velocity in ethanol have been fitted, by a least-squares analysis, to

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

where a_{ij} are the coefficients, and u_0, the sound velocity (in $\mathrm{m \cdot s^{-1}}$) at $p_0 = 0.1$ MPa, is given as a function of the temperature by the expression

$$u_0 = 2516.901 - 5.651946T + 3.616259 \times 10^{-3} T^2 \tag{2}$$

The best fit was achieved with $m = 3$ and $n = 2$. The nine coefficients, a_{ij}, are given in Table II. The average deviation for the best fit is found to be $0.5\ \mathrm{m \cdot s^{-1}}$, while the maximum deviation is less than $1.6\ \mathrm{m \cdot s^{-1}}$, which are equivalent to percentage deviations of 0.03 and 0.1, respectively. These figures are higher than those found previously [1] for the high-temperature (i.e., 273 to 333 K) experimental data of ethanol.

Table I. Measured Sound Velocity, u ($m \cdot s^{-1}$), in Ethanol

	T (K)							
p (MPa)	193.40	203.27	213.13	223.21	233.46	243.27	253.16	263.05
0.10	1558.1	1518.9	1476.7	1435.4	1393.9	1355.8	1317.9	1280.6
19.98	1632.7	1596.7	1558.1	1520.2	1482.0	1447.1	1413.1	1380.2
39.93	1700.6	1665.8	1630.5	1594.9	1559.5	1527.3	1495.5	1465.1
59.77	1761.6	1729.4	1696.1	1662.4	1629.0	1598.5	1568.6	1539.6
79.96	1819.5	1789.0	1756.4	1725.1	1693.4	1664.5	1635.9	1608.7
100.09	1872.9	1844.1	1813.2	1783.1	1752.3	1724.8	1697.6	1671.4
120.13	1922.5	1895.7	1865.6	1836.8	1807.9	1781.0	1754.6	1730.0
140.04	1969.4	1944.0	1915.0	1887.0	1859.1	1833.1	1807.9	1783.5
160.17	2015.9	1990.2	1962.1	1934.2	1907.9	1882.6	1858.5	1834.8
180.39	2058.8	2034.2	2007.0	1980.1	1954.4	1930.0	1906.2	1883.4
200.55	2099.9	2076.3	2049.7	2023.8	1998.6	1974.7	1951.4	1929.5
220.30	2138.7	2115.8	2090.0	2064.2	2039.1	2016.8	1994.1	1972.6
240.24	2176.3	2153.8	2129.0	2103.9	2079.2	2057.5	2035.1	2014.1
260.39	2212.7	2191.3	2166.7	2142.2	2118.4	2096.4	2075.0	2054.4
275.93	2240.2	2218.4	2194.8	2170.8	2147.1	2126.0	2105.0	2084.6

Table II. Coefficients a_{ij} of Eq. (1) for Ethanol in $\mathrm{MPa \cdot m^{-i} \cdot s^{i} \cdot K^{-j}}$

	i		
j	1	2	3
0	$5.37723983 \times 10^{-1}$	$7.03750309 \times 10^{-4}$	$-4.15552543 \times 10^{-7}$
1	$-1.85366620 \times 10^{-3}$	$-4.20147674 \times 10^{-6}$	$4.02863289 \times 10^{-9}$
2	$1.93647937 \times 10^{-6}$	$8.29324241 \times 10^{-9}$	$-8.85041814 \times 10^{-12}$

4. DETERMINATION OF *pVT* AND THERMODYNAMIC PROPERTIES OF ETHANOL

The pVT and thermodynamic properties of ethanol have been derived from the experimental data of the sound velocity following the method initiated by Davis and Gordon [6] and modified by Sun et al. [1, 4]. It is based on the following thermodynamic relations:

$$(\partial\rho/\partial p)_T = 1/u^2 + \alpha^2 T/C_{\mathrm{p}} \tag{3}$$

$$(\partial C_{\mathrm{p}}/\partial p)_T = -(T/\rho)/[\alpha^2 + (\partial\alpha/\partial T)_p] \tag{4}$$

Here ρ is the density, C_{p} is the specific heat at constant pressure, and α is the thermal expansion defined by $\alpha = -(1/\rho)(\partial\rho/\partial T)_p$. Equations (3) and (4) form a set of first-order differential equations with initial values ρ_0 ($\mathrm{kg \cdot m^{-3}}$) and $C_{\mathrm{p}0}$ ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$), both at 0.1 MPa, which are given as a function of temperature by the expressions

$$\rho_0 = 806.594 - 0.84589T - 1.361 \times 10^{-4}T^2 - 5.557 \times 10^{-6}T^3 \tag{5}$$

$$C_{\mathrm{p}0} = 2015.6 - 2.8976 \times 10^{-1}T - 1.2074 \times 10^{-2}T^2 + 5.9629 \times 10^{-5}T^3 \tag{6}$$

Equation (5) was developed from the experimental data for the density of ethanol in the temperature range from 193 to 333 K obtained from recent measurements at this laboratory [7], while expression (6) is derived from the recent experimental data reported in literature [8]. These recent data of $C_{\mathrm{p}0}$ are in very good agreement (within a few tenths of a percent) with the earlier data [9] used in the analysis of our high-temperature experimental results of ethanol.

For each isotherm, the calculation of the density and the heat capacity at high pressures starts from 0.1 MPa, at which the quantities α_0, ρ_0, and $C_{\mathrm{p}0}$ are obtained by using Eqs. (5) and (6). Then Eqs. (3) and (4) are integrated numerically with respect to pressure. The proper choice of the temperature and pressure intervals is found by gradual decrease of these intervals until the calculated values of ρ, α, and C_p become constant. The optimum pressure interval is about 2 MPa and the optimum temperature interval is about 2.5 K.

The integration of the first term of the L.H.S. of Eq. (3), which contains the speed of sound, makes a major contribution to the final results, namely, more than 80%, for this liquid. This was noted previously [1]. In the present calculation, the integration variable is changed from dp to du and use is made of Eq. (1), so that the integral $\int du$ can be evaluated analytically. As for the evaluation of the second term of the L.H.S. of Eq. (3), we used a normal numerical procedure previously described [1].

The calculated values of ρ, α, and C_p as a function of pressure and temperature are given in Tables III–V. The data are tabulated at pressure intervals of 20 MPa and at temperature intervals of 10 K. The number of significant figures for the tabulated values does not indicate the absolute accuracy but extra figures are retained to show the relative pressure and temperature dependence of these quantities. This is justified since the relative accuracy of the calculated values is higher than the absolute accuracy.

Additional thermodynamic properties of liquid ethanol have been derived from present experimental data by using the following thermodynamic identities:

$$(\partial H/\partial \rho)_T = (1/\rho)(1 - T\alpha) \tag{7}$$

$$(\partial S/\partial \rho)_T = -\alpha/\rho \tag{8}$$

$$\beta_T = (1/\rho)(1/u^2 + T\alpha^2/C_p) \tag{9}$$

$$C_v = C_p/(1 + T\alpha^2 u^2/C_p) \tag{10}$$

where H is the enthalpy, S is the entropy, β_T is the isothermal compressibility, and C_v is the specific heat at constant volume. The calculated values of β_T, H, S, and C_v are recorded in Tables VI–IX.

Owing to lack of accurate thermodynamic data at lower temperatures, it is not possible to compare the present data on both the speed of sound and the derived quantities with any previous measurement. However, it was found from detailed comparisons of the equations-of-state data obtained previously from speed-of-sound measurement and those of direct measurements reported in the literature that the accuracy of the derived density data depends mainly on the accuracy of the sound-speed and the initial density data. Considering that the accuracy of the present speed-of-sound data is better than 0.05% and that of initial density is better than 0.02% (cf. Ref. 2), it is found that the estimated accuracy of the density is better than 0.05%.

Table III. Derived Density, ρ ($kg \cdot m^{-3}$), for Ethanol

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	876.24	867.05	858.06	849.24	840.57	832.00	823.50	815.04
20.0	886.06	877.39	868.86	860.53	852.37	844.36	836.45	828.63
40.0	895.26	886.83	878.65	870.70	862.93	855.33	847.86	840.50
60.0	903.66	895.51	887.62	879.95	872.49	865.21	858.08	851.08
80.0	911.49	903.58	895.92	888.49	881.28	874.26	867.40	860.08
100.0	918.84	911.13	903.66	896.44	889.43	882.62	875.99	869.51
120.0	925.78	918.25	910.95	903.89	897.06	890.43	883.98	877.70
140.0	932.37	924.99	917.83	910.92	904.23	897.76	891.47	885.36
160.0	938.64	931.40	924.37	917.58	911.03	904.69	898.54	892.56
180.0	944.64	937.52	930.61	923.93	917.49	911.26	905.23	899.38
200.0	950.38	943.38	936.58	930.00	923.65	917.52	911.60	905.85
220.0	955.91	949.01	942.31	935.82	929.56	923.52	917.68	912.03
240.0	961.23	954.43	947.82	941.41	935.23	929.26	923.51	917.94
260.0	966.36	959.66	953.13	946.80	940.68	934.79	929.10	923.61
280.0	971.32	964.71	958.26	952.00	945.95	940.12	934.50	929.06

Table IV. Thermal Expansion Coefficient, $\alpha = -(10^4/\rho)(\partial\rho/\partial T)_p$, in K^{-1}, of Ethanol

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	10.62	10.48	10.37	10.29	10.25	10.25	10.29	10.36
20.0	10.03	9.85	9.70	9.58	9.48	9.42	9.40	9.41
40.0	9.55	9.36	9.18	9.03	8.90	8.81	8.74	8.71
60.0	9.15	8.96	8.76	8.59	8.44	8.32	8.23	8.16
80.0	8.81	8.62	8.42	8.23	8.07	7.93	7.82	7.73
100.0	8.52	8.33	8.13	7.93	7.76	7.61	7.48	7.38
120.0	8.26	8.08	7.88	7.68	7.50	7.34	7.20	7.08
140.0	8.03	7.86	7.67	7.46	7.27	7.10	6.95	6.82
160.0	7.83	8.66	7.48	7.27	7.08	6.90	6.74	6.60
180.0	7.64	7.48	7.31	7.10	6.90	6.72	6.56	6.41
200.0	7.47	7.31	7.15	6.95	6.75	6.57	6.40	6.25
220.0	7.31	7.16	7.01	6.81	6.61	6.43	6.26	6.10
240.0	7.17	7.02	6.88	6.69	6.49	6.30	6.13	5.97
260.0	7.03	6.89	6.75	6.58	6.38	6.19	6.01	5.85
280.0	6.90	6.77	6.64	6.47	6.28	6.09	5.91	5.75

Table V. Isobaric Specific Heat, C_p ($J \cdot kg^{-1} \cdot K^{-1}$), of Ethanol

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	1938.8	1958.3	1982.7	2012.3	2047.4	2088.5	2135.8	2189.8
20.0	1941.4	1960.4	1983.5	2011.6	2044.9	2083.9	2128.6	2179.9
40.0	1945.2	1964.4	1986.7	2013.5	2045.4	2082.7	2125.6	2174.4
60.0	1949.4	1969.7	1991.3	2017.2	2047.9	2083.9	2125.2	2172.2
80.0	1953.8	1975.3	1996.9	2022.0	2051.8	2086.7	2126.7	2172.4
100.0	1958.4	1981.1	2003.2	2027.8	2056.8	2090.7	2129.8	2174.2
120.0	1962.9	1986.7	2010.0	2034.1	2062.5	2095.7	2133.9	2177.3
140.0	1967.3	1991.9	2016.9	2040.8	2068.8	2101.3	2138.8	2181.3
160.0	1971.8	1996.8	2023.9	2048.0	2075.5	2107.5	2144.3	2186.1
180.0	1976.1	2001.4	2030.7	2055.3	2082.6	2114.1	2150.2	2191.4
200.0	1980.2	2005.8	2037.1	2062.9	2089.8	2121.1	2156.7	2197.3
220.0	1984.2	2010.2	2043.0	2070.4	2097.2	2128.3	2163.4	2203.5
240.0	1988.0	2014.4	2048.5	2077.9	2104.8	2135.6	2170.4	2210.1
260.0	1991.5	2018.5	2053.2	2085.3	2112.5	2143.2	2177.5	2216.8
280.0	1995.1	2022.6	2057.5	2092.3	2120.2	2150.7	2184.8	2223.8

Table VI. Isothermal Compressibility, $\beta_T = (10^4/\rho)(\partial\rho/\partial p)_T$, in MPa^{-1}, of Ethanol

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	5.980	6.328	6.701	7.102	7.537	8.007	8.517	9.072
20.0	5.372	5.643	5.929	6.233	6.555	6.899	7.266	7.659
40.0	4.883	5.102	5.329	5.567	5.817	6.081	6.360	6.657
60.0	4.489	4.671	4.857	5.049	5.251	5.461	5.683	5.918
80.0	4.163	4.319	4.474	4.634	4.800	4.973	5.155	5.345
100.0	3.888	4.024	4.156	4.292	4.432	4.577	4.728	4.887
120.0	3.653	3.772	3.888	4.004	4.124	4.247	4.376	4.510
140.0	3.448	3.555	3.657	3.758	3.862	3.969	4.080	4.195
160.0	3.268	3.364	3.456	3.546	3.636	3.730	3.826	3.926
180.0	3.108	3.196	3.280	3.359	3.440	3.522	3.606	3.694
200.0	2.965	3.046	3.123	3.194	3.266	3.339	3.414	3.494
220.0	2.836	2.911	2.982	3.048	3.112	3.177	3.244	3.312
240.0	2.719	2.788	2.855	2.916	2.974	3.033	3.093	3.153
260.0	2.613	2.677	2.740	2.796	2.849	2.903	2.957	3.011
280.0	2.515	2.576	2.634	2.687	2.737	2.785	2.834	2.883

Table VII. Enthalpy, $0.1H$ ($\mathrm{J \cdot kg^{-1}}$), for Ethanol, Relative to 193.15 K and 0.1 MPa

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	0	1933	3890	5876	7895	9955	12061	14219
20.0	1808	3744	5703	7688	9706	11762	13862	16012
40.0	3629	5569	7531	9520	11539	13595	15692	17838
60.0	5452	7396	9363	11356	13378	15436	17534	19678
80.0	7273	9223	11196	13193	15220	17281	19381	21526
100.0	9093	11048	13027	15030	17062	19128	21232	23379
120.0	10910	12870	14855	26865	18903	20974	23082	25233
140.0	12724	14688	16680	18697	20741	22818	24932	27087
160.0	14535	16503	18501	20525	22576	24660	26779	28940
180.0	16341	18314	20317	22349	24408	26498	28623	30790
200.0	18144	20121	22130	24168	26234	28331	30464	32636
220.0	19943	21924	23937	25983	28056	30161	32300	34479
240.0	21737	23723	25740	27793	29874	31986	34132	36318
260.0	23528	25518	27539	29597	31686	33806	35960	38052
280.0	25315	27308	29333	31397	33494	35621	37782	39982

Table VIII. Entropy, S ($\mathrm{J \cdot kg \cdot K^{-1}}$), for Ethanol, Relative to 193.15 K and 0.1 MPa

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	0.00	97.59	191.61	282.64	371.17	457.66	542.52	626.12
20.0	−23.29	74.43	168.52	259.56	348.02	434.36	518.99	602.26
40.0	−45.25	52.67	146.94	238.09	326.61	412.95	497.49	580.59
60.0	−66.02	32.14	126.65	217.99	306.65	393.06	477.61	560.68
80.0	−85.79	12.61	107.40	198.98	287.83	374.38	459.03	542.12
100.0	−104.72	−6.06	89.02	180.87	269.96	356.70	441.49	524.67
120.0	−122.91	−24.01	71.38	163.54	252.88	339.85	424.82	508.14
140.0	−140.44	−41.30	54.39	146.86	236.49	323.70	408.88	492.38
160.0	−157.39	−58.02	37.95	130.75	220.68	308.17	393.58	477.28
180.0	−173.81	−74.22	22.02	115.15	205.40	293.17	378.84	462.76
200.0	−189.76	−89.95	6.54	100.00	190.57	278.64	364.58	448.74
220.0	−205.27	−105.25	−8.53	85.25	176.15	264.52	350.74	435.16
240.0	−220.37	−120.15	−23.22	70.86	162.10	250.78	337.78	421.97
260.0	−235.10	−134.68	−37.56	56.81	148.38	237.38	324.19	409.13
280.0	−249.48	−148.88	−51.57	43.06	134.96	224.28	311.39	396.60

Table IX. Specific Heat at Constant Volume, C_v ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$), for Ethanol

	T (K)							
p (MPa)	193.15	203.15	213.15	223.15	233.15	243.15	253.15	263.15
0.1	1519.5	1548.8	1581.7	1618.3	1659.0	1703.8	1752.9	1806.8
20.0	1525.8	1554.8	1587.1	1623.0	1662.7	1706.2	1753.9	1805.9
40.0	1535.5	1564.8	1596.9	1632.4	1671.5	1714.5	1761.3	1812.4
60.0	1544.4	1574.2	1606.1	1641.3	1680.0	1722.5	1768.8	1819.2
80.0	1552.7	1582.9	1615.0	1649.9	1688.3	1730.4	1776.3	1826.5
100.0	1560.4	1591.0	1623.4	1658.2	1696.4	1738.2	1784.0	1833.9
120.0	1567.6	1598.4	1631.6	1666.3	1704.3	1746.1	1791.6	1841.3
140.0	1574.5	1605.3	1639.4	1674.1	1712.1	1753.7	1799.2	1848.7
160.0	1580.9	1611.6	1646.9	1681.9	1719.7	1761.3	1806.6	1856.0
180.0	1587.1	1617.6	1653.9	1689.4	1727.2	1768.7	1814.0	1863.3
200.0	1592.9	1623.2	1660.6	1696.7	1734.6	1776.2	1821.2	1870.4
220.0	1598.5	1628.6	1666.6	1703.9	1741.8	1783.4	1828.3	1877.4
240.0	1603.8	1633.9	1672.3	1710.8	1748.9	1790.5	1835.3	1884.2
260.0	1609.0	1639.0	1677.4	1717.4	1755.9	1797.4	1842.1	1890.9
280.0	1613.9	1644.1	1682.1	1723.8	1762.7	1804.3	1848.8	1897.2

Table X. Coefficients C_{ij} ($\mathrm{MPa \cdot kg^{-i} \cdot m^{3i} \cdot K^{-j}}$) of Eq. (11) for Ethanol at Low Temperature

$C_{10} = 3.663164$ $C_{20} = 1.891190 \times 10^{-2}$ $C_{30} = -3.941484 \times 10^{-5}$
$C_{11} = -9.967357 \times 10^{-3}$ $C_{21} = -6.364615 \times 10^{-5}$ $C_{31} = 4.223545 \times 10^{-7}$
$C_{12} = 4.451192 \times 10^{-6}$ $C_{22} = 8.761412 \times 10^{-8}$ $C_{33} = -8.486796 \times 10^{-10}$

5. EQUATION OF STATE OF ETHANOL

The derived densities of liquid ethanol have been used to examine several empirical equations of state which are frequently used for describing the volumetric behavior of liquids at elevated pressures. These equations can be classified into two groups, namely, linear polynomial equations, such as a pressure expansion and a density expansion, and nonlinear equations, such as the Tait equation, the Murnaghan equation, the quadratic secant modulus equation, and the second-order equation of bulk modulus. A review of equations of state for liquids can be found elsewhere [10]. The purpose of the present work is to find the best equation of state for ethanol at lower temperatures. The criteria for selection of the best equation include (i) the standard relative deviation of the density and (ii) the standard relative deviation of the isothermal compressibility. Since in the ultrasonic method, the values of the isothermal compressibility can be determined with a high accuracy, the second criterion is very useful for a proper selection of the best equation of state of a liquid. The following two equations of state give the best results:

$$p - p_0 = \sum_{i=1}^{3} \sum_{j=0}^{2} C_{ij} (\rho - \rho_0)^i \, T^j \tag{11}$$

$$\rho = \rho_0 \Big/ \left[1 - \left(\sum_{i=1}^{2} A_i T^i \right) \ln \left(1 + p \sum_{j=0}^{2} B_j T^j \right) \right] \tag{12}$$

Here the coefficients C_{ij}, A_i, and B_j have been evaluated from the experimental data using a least-squares analysis, and the values of these coefficients are given in Tables X and XI. Of these two equations, the den-

Table XI. Coefficients A_i ($\mathrm{K^{-i}}$) and B_j ($\mathrm{MPa^{-1} \cdot K^{-j}}$) of Eq. (12) for Ethanol at Low Temperature

$A_1 = 1.035409 \times 10^{-1}$ $A_2 = 3.911956 \times 10^{-5}$ $A_3 = -2.507500 \times 10^{-7}$
$B_1 = 8.091073 \times 10^{-3}$ $B_2 = -5.581732 \times 10^{-5}$ $B_3 = 2.270875 \times 10^{-7}$

sity expansion equation of the form given by Eq. (12) is the more accurate one, although the well-known Tait relation given by Eq. (11) is simpler and provides fairly accurate results.

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