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Acoustic and Thermodynamic Properties of Methanol from 273 to 333 K and at Pressures to 280 MPa

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The speed of sound in liquid methanol has been measured at temperatures from 273 to 333 K and at pressures up to 280 MPa, using a phase comparison pulse-echo technique operating at 2 MHz. The density, the isobaric thermal expansivity, the isothermal compressibility, the entropy, the enthalpy, and the specific heat have been evaluated from the measured sound speed following a modified computational method. The derived density data were fitted to a 16-constant equation of state within the accuracy of the measurement. In the region of overlap, the experimental data agree well with those determined by direct measurements.

1. Introduction

The pVT and thermodynamic properties of organic liquids are of considerable interest from both fundamental and technological points of view. In order to determine these properties at elevated pressures with high precision, an ultrasonic apparatus has been developed recently at this laboratory which is suitable at pressures up to 300 MPa. The measured ultrasonic speed of sound in the liquid under investigation together with the available data of the density and specific heat at atmospheric pressure can be used to develop the equation of state and to determine a number of important thermodynamic properties at high pressures. The method has already been used on a number of organic liquids, namely, toluene, n-heptane, benzene, cyclohexane, and, recently, ethanol (*1-3*).

In a continuation of this program of systematic investigation of thermodynamic properties of organic liquids, we have now chosen liquid methanol because of the following reasons. Firstly, liquid methanol is widely used in technology and is a large potential source of energy for the future. Secondly, the chemical structure of methanol is very simple which makes it a very suitable compound for testing theoretical equations of state of liquids. And finally, the existing data of the equation of state and thermodynamic properties of methanol are only few and scattered. The older pVT data (*4-6*) of Amagat and Bridgman are not of sufficient accuracy and were restricted to a narrow temperature range while the pressure range of several later measurements (*7-9*) were restricted to 100 MPa. The purpose of the present work is, therefore, to increase the precision of the equation of state data and to extend the pressure range to much higher pressures.

2. Experimental Section

Reagent grade methanol with a specified purity of 99.8 mol % was purchased from BDH Chemical Ltd, Poole, U.K. The main impurity in the material was water (<0.1 mol %). The material was used without further purification.

The measurement of the speed of sound in methanol was carried out with an ultrasonic apparatus operating at 2 MHz. The design of the apparatus was based on a modified phase comparison pulse-echo method which made use of two reflectors placed at unequal distances from a quartz transducer. The complete description of the apparatus as well as the principle of its operation can be found elsewhere (*1*, *2*). The pressure was generated by a Michels type mercury gas compressor coupled to a hydraulic oil press and measured by a Michels pressure balance with an accuracy better than 1 in 10^4. The temperature was stabilized in a metal cryostat and measured with an accuracy to better than 0.01 K by a calibrated Pt-resistance thermometer. Details of the high-pressure system and of the metal cryostat were given elsewhere (*10*).

Table I. Measured Sound Speed u (m s^{-1}), in Methanol

	T/K						
p/MPa	274.74	283.17	293.15	303.15	313.11	323.05	332.95
0.10	1183.4	1154.1	1121.0	1087.1	1054.6	1022.3	990.3
19.98	1283.1	1257.6	1228.4	1199.1	1171.1	1143.7	1116.8
39.93	1368.6	1345.1	1318.6	1292.1	1267.0	1242.4	1218.5
59.75	1443.5	1421.4	1396.9	1372.1	1349.0	1326.5	1304.6
79.95	1512.1	1491.3	1468.2	1445.0	1423.5	1402.5	1381.9
100.06	1574.5	1554.6	1532.8	1510.9	1490.3	1470.5	1450.2
120.09	1632.0	1612.7	1591.8	1570.9	1551.3	1532.6	1514.3
140.00	1685.2	1666.5	1646.5	1626.4	1607.5	1589.7	1572.0
160.11	1735.7	1717.5	1698.2	1678.8	1660.6	1643.4	1626.4
180.33	1783.7	1765.9	1747.2	1728.5	1710.9	1694.2	1677.7
200.49	1829.0	1811.5	1793.4	1775.0	1758.1	1741.9	1726.0
220.22	1871.3	1853.7	1836.2	1818.4	1802.1	1786.2	1770.7
240.16	1912.2	1895.0	1877.7	1860.5	1844.4	1829.1	1814.0
260.31	1951.8	1934.8	1918.1	1901.1	1885.3	1870.7	1855.7
275.85	1981.3	1964.5	1948.1	1931.4	1915.9	1901.6	1886.8

Table II. Coefficients a_{ij} of Eq 1 for Methanol in MPa m^{-i} s^{i} K^{-j}

	i =		
j	1	2	3
0	0.561 668 1029	$-1.056\,125\,258 \times 10^{-4}$	$3.316\,551\,463 \times 10^{-7}$
1	$-1.895\,861\,861 \times 10^{-3}$	$2.111\,114\,264 \times 10^{-6}$	$-1.898\,329\,232 \times 10^{-9}$
2	$1.866\,939\,187 \times 10^{-6}$	$-4.001\,729\,024 \times 10^{-9}$	$3.073\,335\,858 \times 10^{-12}$

3. Results and Discussion

3.1. Sound Speed in Liquid Methanol. The speed of sound in methanol was measured isothermally as a function of pressure in the temperature range between 273 and 333 K with intervals of about 10 K. At each temperature, the experimental data were taken from 0.1 MPa upwards with a pressure interval of about 20 MPa, the maximum pressure being 280 MPa. The unsmoothed experimental data are presented in Table I. The reproducibility of the sound speed data is found to be within 0.02% while the absolute accuracy is estimated to be better than 0.04%.

The complete experimental data of the sound speed have been fitted to a nine-parameter double polynomial equation of the form

$$p - p_0 = \sum_{i=1}^{3}\sum_{j=0}^{2} a_{ij}(u - u_0)^i T^j \qquad (1)$$

by a least-squares method. Here p is the pressure in MPa, u is the sound speed in m s^{-1}, T is the temperature in K, and u_0 is the sound speed at p_0 = 0.1 MPa which is fitted, by a separate least-squares analysis, to the expression

$$u_0 = a + bT + cT^2 \qquad (2)$$

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Table III. Derived Density ρ (kg m^{-3}) of Methanol

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	809.99	800.70	791.32	781.86	772.32	762.70	753.00
20.0	825.63	817.16	808.67	800.13	791.57	782.98	774.36
40.0	839.13	831.27	823.39	815.49	807.58	799.66	791.74
60.0	851.07	843.67	836.26	828.84	821.41	813.98	806.56
80.0	861.83	854.80	847.76	840.72	833.68	826.63	819.58
100.0	871.66	864.94	858.22	851.49	844.76	838.02	831.28
120.0	880.73	874.28	867.83	861.37	854.90	848.42	841.93
140.0	889.17	882.96	876.74	870.52	864.27	858.02	851.75
160.0	897.08	891.08	885.08	879.05	873.01	866.95	860.87
180.0	904.53	898.73	892.91	887.07	881.21	875.33	869.42
200.0	911.58	905.95	900.30	894.63	888.94	883.21	877.46
220.0	918.28	912.81	907.32	901.81	896.26	890.68	885.06
240.0	924.67	919.35	914.00	908.63	903.22	897.77	892.28
260.0	230.77	925.59	920.38	915.14	909.86	904.54	899.16
280.0	936.63	931.58	926.49	921.37	916.21	911.00	905.74

with a = 2286.37 m s^{-1}, b = −4.59438 m s^{-1} K^{-1}, c = 2.108 33 × 10^{-3} m s^{-1} K^{-2}. The fitted values for the coefficients a_{ij} are given in Table II. The maximum deviation of the measured sound velocity from that calculated with eq 1 is found to be 0.04% which is about the accuracy of the present measurement. The average deviation of the experimental points from the fitted equation turns out to be 0.015%.

In the past, several authors reported sound speed measurements on methanol, some of which overlap the present experimental range of pressure and temperature. However, since accurate high-pressure sound speed data on methanol are not available over a wide temperature range, a detailed comparison of the present results with the previous ones can only be made at atmospheric pressure. Such a comparison shows that the present data at 0.1 MPa and from 273 to 333 K are systematically higher than those of Aleksandrov et al. (*11*) by 0.18% and systematically lower than those of Wilson (*12*) by 0.09%. At elevated pressures, the present sound speed data at 293 K and up to 100 MPa agree with those of Wilson within 0.05%.

3.2. pVT Properties of Liquid Methanol. The pVT properties of liquid methanol have been derived by repeated use of the relations

$$\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{u^2} + \frac{\alpha_p{}^2 T}{C_p} \tag{3}$$

$$\rho(p,T) = \sum_{i=0}^{2} b_i(p) T^i \tag{4}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -\frac{T}{\rho}\left(\alpha_p{}^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p\right) \tag{5}$$

in which ρ is the density, α_p is the volume thermal expansion coefficient, C_p is the isobaric specific heat, and $b_i(p)$ are the coefficients, and use of available experimental data (*13*, *14*) of ρ and C_p at 0.1 MPa expressed as a function of the temperature in the form

$$\rho_0 = 1032.594 - 0.704285T - 4.050949 \times 10^{-4} T^2 \tag{6}$$

$$C_{p_0} = 2438.75 - 1.572755T - 7.027293 \times 10^{-3} T^2 + 4.446968 \times 10^{-5} T^3 \tag{7}$$

the units being kg m^{-3} for ρ_0 and J kg^{-1} K^{-1} for C_{p_0}. It is assumed that the derived densities over the full pressure and temperature range can be represented by the form given in eq 4. The computation of the derived densities starts with the 0.1 MPa values of ρ and C_p determined with eq 6 and 7, respectively, and then continues with a simultaneous step by step integration with respect to pressure of eq 3 and 5 after introducing eq 1 in eq 3 and applying eq 4 at each step to compute $\rho(T)$, $\alpha_p(T)$ and $\partial \alpha_p/\partial T$. In this computation, a small pressure step of 2 MPa is chosen in order to increase the precision of the numerical integration. Further details of the method of computation can be found elsewhere (*3*). The computed values of ρ, α_p and C_p at seven different equally spaced temperatures ranging between 273.15 and 333.15 K and at pressures up to 280 MPa are presented in Tables III–V. Recently, Machado and Streett (*9*) have shown that their high-temperature pVT data of liquid methanol can be fitted to the following 16-constant equation of state

$$p = \sum_{ij} C_{ij} \rho^i (1000/T)^j \tag{8}$$

where C_{ij} are the coefficients. Therefore, it is considered worthwhile to examine whether the present pVT data of methanol which extend to much higher pressures can also be fitted to the same equation. The derived 105 pVT data points were fitted to this equation of state by a least-squares analysis. The average of the absolute deviations of the computed values from the fitted curve is about 0.0006% while the maximum deviation is less than 0.0017%. Thus shows that the equation

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

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	11.43	11.66	11.90	12.15	12.40	12.67	12.94
20.0	10.24	10.38	10.53	10.68	10.83	10.99	11.15
40.0	9.37	9.48	9.58	9.69	9.80	9.91	10.02
60.0	8.70	8.78	8.87	8.95	9.04	9.13	9.22
80.0	8.16	8.23	8.30	8.38	8.45	8.53	8.61
100.0	7.70	7.77	7.84	7.90	7.97	8.04	8.12
120.0	7.31	7.38	7.44	7.51	7.57	7.64	7.71
140.0	6.97	7.03	7.10	7.16	7.23	7.30	7.37
160.0	6.67	6.73	6.80	6.86	6.93	7.00	7.07
180.0	6.40	6.46	6.53	6.60	6.66	6.73	6.80
200.0	6.15	6.22	6.29	6.36	6.43	6.50	6.57
220.0	5.93	6.00	6.07	6.14	6.21	6.28	6.36
240.0	5.72	5.79	5.87	5.94	6.01	6.09	6.16
260.0	5.54	5.61	5.68	5.75	5.83	5.91	5.98
280.0	5.36	5.43	5.51	5.58	5.66	5.74	5.82

Table V. Isobaric Specific Heat, C_p (J kg^{-1} K^{-1}), for Methanol

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	2391.1	2439.5	2494.1	2555.1	2622.7	2697.3	2779.1
20.0	2371.4	2418.2	2471.1	2530.3	2596.1	2668.7	2748.3
40.0	2357.3	2403.1	2454.9	2513.0	2577.6	2648.9	2727.2
60.0	2346.1	2391.2	2442.3	2499.5	2563.2	2633.7	2711.0
80.0	2336.8	2381.3	2431.7	2488.3	2551.3	2621.0	2697.6
100.0	2328.6	2372.5	2422.4	2478.5	2540.9	2610.0	2685.9
120.0	2321.0	2364.6	2414.0	2469.5	2531.4	2599.9	2675.3
140.0	2314.0	2357.1	2406.0	2461.1	2522.5	2590.5	2665.4
160.0	2307.3	2350.0	2398.5	2453.1	2514.1	2581.6	2655.9
180.0	2300.8	2343.1	2391.2	2445.4	2505.9	2572.9	2646.8
200.0	2294.5	2336.4	2384.1	2437.9	2497.9	2564.5	2637.9
220.0	2288.3	2329.9	2377.2	2430.5	2490.1	2556.3	2629.2
240.0	2282.2	2323.4	2370.3	2423.2	2482.5	2548.2	2620.6
260.0	2276.2	2317.0	2363.5	2416.1	2474.9	2540.1	2612.1
280.0	2270.2	2310.7	2356.8	2409.0	2467.3	2532.2	2603.7

Table VI. Constants C_{ij} of Eq 8 in MPa kg^{-i} m^{3i}

$C_{10} = -4.622392383$
$C_{11} = 4.409203362$
$C_{12} = -1.099836469$
$C_{13} = 7.643112953 \times 10^{-2}$
$C_{14} = 1.014231327 \times 10^{-2}$
$C_{20} = 8.881394952 \times 10^{-3}$
$C_{21} = -9.386141702 \times 10^{-3}$
$C_{22} = 2.772964885 \times 10^{-3}$
$C_{23} = -4.348734148 \times 10^{-4}$
$C_{31} = -1.384338115 \times 10^{-6}$
$C_{32} = 8.079787716 \times 10^{-7}$
$C_{33} = 1.945696073 \times 10^{-7}$
$C_{41} = 3.887463117 \times 10^{-9}$
$C_{42} = -2.072418800 \times 10^{-9}$
$C_{51} = -6.048737986 \times 10^{-13}$
$C_{52} = 6.198638433 \times 10^{-13}$

[a] The units used are MPa for p, kg m^{-3} for ρ, and K for T.

Table VII. Isothermal Compressibility, $\beta_T = (1/\rho)(\partial\rho/\partial p)_T \times 10^4$ MPa^{-1}, for Methanol

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	10.579	11.341	12.165	13.058	14.025	15.077	16.221
20.0	8.794	9.312	9.858	10.435	11.043	11.685	12.362
40.0	7.553	7.938	8.337	8.752	9.181	9.627	10.087
60.0	6.652	6.995	7.266	7.586	7.913	8.248	8.590
80.0	5.962	6.211	6.464	6.723	6.985	7.250	7.519
100.0	5.415	5.625	5.838	6.053	6.271	6.489	6.709
120.0	4.968	5.149	5.333	5.517	5.702	5.887	6.071
140.0	4.596	4.755	4.915	5.076	5.236	5.396	5.555
160.0	4.280	4.421	4.564	4.706	4.847	4.988	5.127
180.0	4.008	4.135	4.263	4.390	4.517	4.642	4.736
200.0	3.771	3.887	4.002	4.117	4.232	4.345	4.456
220.0	3.563	3.669	3.774	3.879	3.983	4.086	4.187
240.0	3.378	3.476	3.573	3.669	3.764	3.858	3.951
260.0	3.213	3.303	3.393	3.482	3.570	3.657	3.743
280.0	3.064	3.148	3.232	3.314	3.396	3.477	3.556

Table VIII. Enthalpy, $0.1H$ (J kg^{-1}), for Methanol, Relative to 273.15 K and 0.1 MPa

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	0	2 415	4 881	7 405	9 993	12 653	15 391
20.0	1 715	4 110	6 554	9 054	11 617	14 248	16 956
40.0	3 475	5 855	8 284	10 767	13 312	15 924	18 612
60.0	5 258	7 627	10 043	12 513	15 044	17 642	20 314
80.0	7 056	9 415	11 821	14 280	16 800	19 385	22 044
100.0	8 864	11 214	13 611	16 061	18 570	21 145	23 792
120.0	10 679	13 021	15 410	17 851	20 351	22 916	25 553
140.0	12 498	14 833	17 214	19 647	22 139	24 695	27 322
160.0	14 320	16 649	19 022	21 448	23 931	26 478	29 096
180.0	16 145	18 466	20 833	23 250	25 726	28 264	30 874
200.0	17 970	20 285	22 644	25 055	27 522	30 053	32 654
220.0	19 795	22 103	24 457	26 860	29 320	31 842	34 434
240.0	21 620	23 922	26 269	28 665	31 117	33 632	36 216
260.0	23 444	25 740	28 080	30 469	32 914	35 421	37 997
280.0	25 267	27 557	29 891	32 273	34 711	37 210	39 777

Table IX. Entropy, S (J kg^{-1} K^{-1}), for Methanol, Relative to 273.15 K and 0.1 MPa

	T/K						
p/ MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	0.00	86.82	172.42	257.07	341.07	424.66	508.09
20.0	−26.27	59.81	144.64	228.50	311.66	394.39	476.91
40.0	−49.78	35.78	120.06	203.36	285.94	368.06	449.96
60.0	−71.14	14.01	97.87	180.73	262.86	344.51	425.93
80.0	−90.80	−6.00	77.50	159.99	241.75	323.02	404.04
100.0	−109.09	−24.59	58.60	140.77	222.20	303.13	383.81
120.0	−126.21	−41.99	40.91	122.79	203.92	284.54	364.90
140.0	−142.34	−58.39	24.25	105.86	186.70	267.04	347.11
160.0	−157.61	−73.90	8.48	89.83	170.41	250.48	330.26
180.0	−172.11	−88.64	−6.50	74.59	154.92	234.72	314.24
200.0	−185.92	−102.69	−20.79	60.06	140.13	219.68	298.93
220.0	−199.12	−116.12	−34.46	46.15	125.98	205.27	284.27
240.0	−211.77	−128.99	−47.56	32.81	112.40	191.44	270.18
260.0	−223.90	−141.35	−60.15	19.99	99.34	178.14	256.63
280.0	−235.57	−153.24	−72.26	7.65	86.75	165.31	243.55

Table X. Specific Heat at Constant Volume, C_v (J kg^{-1} K^{-1}), for Methanol

	T/K						
p/MPa	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.1	1974.9	2015.5	2062.8	2116.8	2177.9	2246.4	2322.6
20.0	1969.2	2008.8	2054.6	2106.9	2165.7	2231.4	2304.3
40.0	1972.5	2011.4	2056.2	2107.3	2164.9	2229.1	2300.2
60.0	1975.7	2013.6	2057.5	2107.4	2163.7	2226.6	2296.2
80.0	1978.7	2015.6	2058.5	2107.3	2162.4	2223.9	2292.1
100.0	1981.4	2017.4	2059.2	2107.0	2160.9	2221.2	2288.1
120.0	1983.9	2019.0	2059.8	2106.5	2159.3	2218.4	2284.0
140.0	1986.2	2020.3	2060.2	2105.8	2157.6	2215.5	2280.0
160.0	1988.2	2021.5	2060.3	2105.0	2155.7	2212.6	2275.9
180.0	1989.9	2022.4	2060.3	2104.1	2153.8	2209.6	2271.8
200.0	1991.4	2023.0	2060.2	2103.0	2151.7	2206.6	2267.7
220.0	1992.7	2023.5	2059.8	2101.8	2149.6	2203.5	2263.7
240.0	1993.7	2023.8	2059.3	2100.5	2147.4	2200.4	2259.6
260.0	1994.5	2023.9	2058.7	2099.0	2145.2	2197.3	2255.6
280.0	1995.1	2023.8	2057.9	2097.5	2142.8	2194.1	2251.6

of state (8) is capable of representing the present *pVT* data within the experimental accuracy. The 16 coefficients are given in Table VI.

Figure 1 shows a comparison of the present density data of liquid methanol at several temperatures with those obtained by direct *pVT* measurements. At 298 K and pressures up to 140 MPa, our data are in excellent agreement (<0.02%) with those obtained by Moriyoshi and Inubushi (*8*) using a piezometer method in which the claimed accuracy is better than 0.016%. At temperatures from 298 to 333 K and at pressures up to 100 MPa, the present data are also in very good agreement with those of Machado and Streett (*9*) obtained with a direct-weighing *pVT* apparatus. It is found that, in this region of overlap, the average deviation and the maximum deviation between the two sets of density data are less than, respectively, 0.05% and 0.08%. At a temperature of 353 K which is 20 K higher than our temperature range, the agreement between their measured data and our extrapolated data is still good: the average and the maximum deviations are 0.08% and 0.14%, respectively. Thus, the *pVT* properties of a liquid at elevated pressures derived from ultrasonic data are consistent with those determined by conventional methods.

However, in spite of the good agreement with the two previous measurements mentioned above, the present data for methanol are systematically higher by 0.4–0.8% (see Figure 1) than those obtained by Ledwig and Würflinger (*17*, *18*) using a moving-piston method. These figures are much larger than the inaccuracy claimed by these authors, namely 0.1%. Although the reason for such large discrepancies is not clearly understood, it may presumably be due to the drawbacks of the measuring technique itself. Apart from the possible sources of error arising in the volume calibration, the moving-piston method involves large frictional force and consequently appreciable pressure corrections due to the resulting hysteresis effects. It is doubtful whether these corrections can be determined with high precision as is required for accurate measurement of *pVT* properties of liquids.

3.3. Derived Thermodynamic Properties. A number of important thermodynamic properties of liquid methanol have been derived by using the following thermodynamic relations

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{\rho}(1 - T\alpha) \tag{9}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{\alpha}{\rho} \tag{10}$$

$$\beta_T = \frac{1}{\rho}\left(\frac{1}{u^2} + \frac{T\alpha^2}{C_p}\right) \tag{11}$$

$$C_v = C_p\bigg/\left(1 + \frac{T\alpha^2 u^2}{C_p}\right) \tag{12}$$

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 VII–X. A comparison of these values with those reported by Machado and Streett shows that, in the region of overlap, the agreement is very good for the calculated ΔH and ΔS, and is good in the case of C_p, namely within 0.7%. The observed good agreement for C_p may be due to the fact that the comparison can only be made at pressures up to 100 MPa at which C_p changes by a small amount (3–4%). A detailed

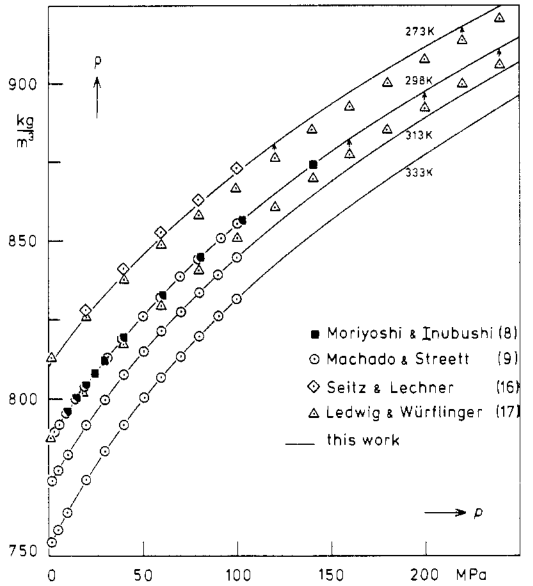

Figure 1. The density of methanol as a function of pressure.

comparison has shown that, qualitatively, the features of $\Delta C_p = C_p(p) - C_p(0.1\text{ MPa})$ are the same in both sets of data, and, quantitatively, the agreement is fair: about 20% in difference up to a pressure of 100 MPa. However, the comparison is less satisfactory for α, and even worse for β_T, the maximum deviations at 100 MPa being 3% and 5%, respectively. A large discrepancy for C_p and α can be understood since the calculations involve first and second derivatives of the equation of state. On the other hand, the discrepancy in β_T may be due to errors inherent in the conventional pVT measurements. In the case of the ultrasonic measurements, the major contribution to the β_T (nearly 80% of its value) comes from the term in sound speed of eq 11 which is directly determined with very high accuracy. Accordingly, one may expect that the value of β_T derived from the ultrasonic measurements is more accurate than that from pVT measurements.

The calculated values of the density and thermodynamic properties of the liquid are based on the $\rho_0(T)$ data of methanol as collected by Brunel and van Bibber (*14*) and expressed in the form given in eq 6. In addition to this set of data, other sets of $\rho_0(T)$ data are also available in literature which can as well be expressed by an analytical function of temperature. However, the set of $\rho_0(T)$ data used in the present calculation appears to be more precise than other sets, although this cannot easily be established on experimental grounds. It is, therefore, worthwhile to examine how far the discrepancies in the $\rho_0(T)$ data of various available sources influence the values of the derived properties at elevated pressures. Accordingly, the calculation for the derived properties are carried out with the same values for $u(p,T)$ and $C_{p_0}(T)$ but with two different sets of previously published $\rho_0(T)$ data (*15*, *19*) which show a maximum discrepancy of 0.1% in the density among themselves and from the previous set. In both cases the calculated values are shifted by an amount which, at 280 MPa, can be as large as 0.2% for ρ, 10% for α, and 5% for C_p. The influence of a particular set of $\rho_0(T)$ data on the calculated values of C_p is so large that it dictates the entire behavior of the calculated C_p vs p isotherms. The $\rho_0(T)$ data reported in ref *19* are obtained by combining experimental data from several sources which may have different systematic errors and which may involve different sample purities. Therefore, it is considered very useful to measure ρ_0 as a function of temperature at 0.1 MPa with a single experimental apparatus and using the same sample. Development of this apparatus, based on the use of a calibrated glass pycnometer, is now in progress in this laboratory.

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