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Thermodynamic Properties of Compressed Liquid Methanol in the Vicinity of the Freezing Line

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We present direct measurements of the isothermal compressibility (κ_T) and thermal expansion coefficient (α_p) of liquid methanol using an expansion technique. The measurements of κ_T were carried out along six isotherms from (208.17 to 298.16) K at pressures up to 101 MPa. For α_p, we have measured four isobars from (0.59 to 80.03) MPa from 195 K up to 300 K. Our experimental results of $\alpha_p(T)$ for the 0.59 MPa isobar exhibit a minimum around 224 K. A clear shift of the minimum to higher temperatures is observed as the pressure increases along the different isobars. Interestingly, the minima for the isobars of $\alpha_p(\rho)$ take place within a narrow range of densities, around 26.5 mol·dm^{-3} (about 3.15 times the critical density).

Introduction

The study of the thermodynamic properties of methanol has attracted great interest over the years because it is a prototypical substance for the study of hydrogen-bonding phenomena. There have been several efforts describing the effect of temperature and pressure on the hydrogen bond strength of methanol. A number of theoretical and experimental studies have been performed to understand the thermodynamic, structural, and dynamic properties of methanol at high densities, among others, correlations of the equation of state;[1−14] measurements of the dielectric constant,[15,16] refractive index,[17] viscosity,[18,19] and elastic properties;[20,21] and computer simulations.[22,23] However, efforts to understand the high-pressure behavior of methanol have been focused at room temperature and above. The limited number of reliable high-pressure measurements available to date at temperatures close to the melting line is somewhat surprising. For the volumetric properties of liquid methanol, there exist density measurements at high pressures between its melting point (175 K) and room temperature: those of Amagat between (273 and 303) K and up to 203 MPa,[1] those of Seitz et al. between (175 and 273) K at a maximum pressure of 101 MPa,[2] those of Ledwig and Würflinger between (223 and 298) K and up to 300 MPa,[16] those of Sun et al. from (203 to 263) K and up to 280 MPa,[9] and those of Hrubý et al. from (205 to 321) K at a maximum pressure of 50 MPa.[13] Unfortunately, some of these data show limited accuracy, and we found important discrepancies with results at higher temperatures. For instance, Sun et al. studied liquid methanol with high accuracy in two different temperature ranges;[8,9] however, the derived properties calculated from both sets of data do not match each other. Therefore, accurate knowledge of the thermophysical properties at low temperatures and high densities of liquid methanol is required to understand the peculiar thermodynamic behavior of methanol in the liquid phase.

Here we are interested in the analysis of the isothermal compressibility (κ_T) and the thermal expansion coefficient (α_p), which represent the first derivatives of the pressure−volume−temperature (pVT) surface of an equation of state (EOS). As a matter of fact, accurate values for these properties at high densities are found with enough accuracy for only a few substances. As we recently described,[24] the behavior of α_p is some peculiar: the isotherms of $\alpha_p(p)$ intersect at high pressures for many liquids, a characteristic feature first described by Bridgman,[25] then by Cutler et al.[26] and Jenner and Millet.[27,28] In that work, we also discussed whether the crossings take place at a single pressure[29] or not[24,30] for different kinds of liquids. From that analysis we could conclude that isothermal measurements of $\alpha_p(p)$ are appropriate to characterize the pressure dependence of α_p. However, if the isotherms of α_p are largely separated in temperature (ca. 50 K or so), the curvature of $\alpha_p(T)$ cannot be well-characterized. In order to characterize the pressure range where the α_p crossings occur, it is more convenient to measure the variation of α_p with temperature at constant pressure instead of measuring this property along isothermal paths. For this purpose, it is necessary to carry out high-pressure density measurements along isobaric paths. Measurements of this kind are somewhat unusual at high pressures and difficult to find in the literature because they require direct techniques and special experimental procedures. For this reason, we have performed measurements with an expansion technique since it allows accurate determination of the curvature of $\alpha_p(T)$ isobars. Needless to say that an accurate knowledge of both κ_T and α_p provides the most direct way to develop a very accurate EOS for liquid methanol by integration of both properties over wide ranges of pressure and temperature. Thus, our goal in this paper is to provide accurate measurements of κ_T and α_p of compressed methanol at thermodynamic conditions close to the melting line, where the effect of hydrogen bonding is expected to be stronger.

Experimental Section

Our experimental technique is based on an expansion principle.[31] This method is based on determining the amount of liquid contained in a sample vessel of known volume, under known pressure and temperature conditions, by expanding the liquid to the vapor phase into a larger vessel of known volume at constant temperature. Using the virial EOS for the gas, the amount of liquid contained in the high-pressure vessel can be determined with great accuracy. Here we use the modification

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introduced by Calado et al.[32] known as the differential expansion method (DEM). At a fixed temperature and at the maximum pressure of the used apparatus, an expansion is made to a slightly lower pressure. A series of successive partial expansions are performed down to a pressure slightly higher that saturation pressure. Thus, if a reference density is known at room pressure, the pressure dependence of the density along the selected isotherm can be easily obtained. The advantage of this method is that a direct determination of κ_T is possible, as one directly measures the change in density due to a decrease of pressure at constant temperature. We later modified the DEM to allow density measurements along an isobar.[33] This procedure consists in setting the expansion apparatus to the desired temperature and pressure. Once thermal equilibrium has been reached, the temperature is raised a few degrees, which causes an increase in the pressure of the system, which is maintained at constant volume. After equilibrium, the over-compressed liquid is expanded to restore the initial reference pressure. The procedure is repeated up to the highest temperature attainable in the apparatus. This procedure allows direct determination of $\alpha_p(T)$ at selected isobars with a high degree of accuracy.

Liquid methanol was purchased from Aldrich Chemical Co. with a minimum purity of 99.9 % and was used without further purification. The liquid was degassed and dehydrated prior to its introduction into the high-pressure apparatus, which has been described in detail elsewhere.[33] Temperatures were measured with accuracies of 0.01 K using a Leeds and Northrup calibrated platinum resistance thermometer. Temperatures were controlled to within ± 0.01 K in both high-pressure and expansion cell baths. High pressures were measured with a calibrated Sensotec TJE1108-20 pressure transducer with an accuracy of 0.02 %. The expansion pressures were measured with a calibrated Druck PDCR110/W low-pressure transducer with an accuracy of 0.06 %.

As noted above, a reference density and the second virial coefficient B of the substance under study are required.[33] We used the following values: $\rho(298.15\ \text{K}, 0.1\ \text{MPa}) = (24.547 \pm 0.005)\ \text{mol}\cdot\text{dm}^{-3}$ and $B(298.15\ \text{K}) = -1.9\ \text{dm}^3\cdot\text{mol}^{-1}$, as given in refs 34 and 35, respectively. The estimated uncertainties of the present results are the following: $0.016\ \text{GPa}^{-1}$ in κ_T, $0.015\ \text{kK}^{-1}$ in α_p, and less than $0.01\ \text{mol}\cdot\text{dm}^{-3}$ in density along both isothermal and isobaric pathways.

Results and Discussion

Isothermal Behavior of the Compressibility in Liquid Methanol. We have measured six isotherms at the following temperatures: 208.17, 223.17, 248.19, 263.17, 273.17, and 298.16 K. Each isotherm consists of about 30 measurements between (0.1 and 100) MPa. The experiments were carried out at small pressure steps (2 to 5 MPa) to obtain accurate values of κ_T. Table 1 summarizes our experimental results of κ_T. Three selected isotherms are compared with available results[1−9,11,12,16] in Figure 1. It must be emphasized that data from other sources are calculated from isothermal $\rho(p)$ measurements. Overall, good agreement is observed, with the exception of the results derived from the equation proposed by Goodwin[6], which is supposed to be accurate between (176 and 673) K and up to 70 MPa. Figure 1 confirms that this equation yields unreliable results of κ_T at low temperatures. We speculate that the reason for such disagreement is that most of the data correlated by Goodwin were at temperatures above room temperature, so extrapolation to low temperatures must be done with caution. Nevertheless, all data sets confirm that $\kappa_T(p, T)$ of liquid methanol follows the typical trend found in most molecular liquids (i.e., a smooth decrease as the pressure increases and an almost linear dependence on the temperature at a given pressure).

Table 1. Experimental Results of the Isothermal Compressibility (κ_T/GPa^{-1}) of Liquid Methanol at Various Temperatures (T) and Pressures (p/MPa)

p	κ_T	p	κ_T	p	κ_T	p	κ_T	p	κ_T
$T = 208.17$ K									
97.91	0.418	70.74	0.470	49.21	0.515	30.16	0.568	10.91	0.637
92.96	0.435	66.30	0.478	45.13	0.526	23.23	0.590	7.97	0.647
88.60	0.441	61.92	0.485	41.12	0.534	20.09	0.602	5.02	0.663
84.30	0.448	57.61	0.495	37.19	0.546	16.98	0.612	2.11	0.678
79.85	0.453	53.37	0.504	33.54	0.557	13.88	0.624	0.39	0.715
75.25	0.460								
$T = 223.17$ K									
98.85	0.451	73.00	0.498	49.40	0.555	29.04	0.620	10.64	0.701
94.20	0.454	69.05	0.506	45.78	0.566	25.93	0.633	8.01	0.714
89.63	0.466	65.06	0.515	42.23	0.574	22.85	0.645	5.54	0.728
85.33	0.472	61.04	0.523	38.77	0.587	19.82	0.659	3.16	0.744
81.11	0.482	56.96	0.530	35.45	0.598	16.66	0.662	1.06	0.759
76.98	0.490	53.08	0.545	32.21	0.608	13.50	0.684		
$T = 248.19$ K									
100.84	0.490	75.07	0.549	51.23	0.619	33.00	0.692	15.47	0.774
96.40	0.500	71.74	0.557	47.88	0.633	30.18	0.707	12.58	0.801
92.54	0.518	68.31	0.566	44.76	0.645	27.31	0.719	9.88	0.818
88.99	0.518	64.80	0.575	41.78	0.656	24.33	0.730	7.25	0.836
85.38	0.525	61.27	0.585	38.60	0.664	21.36	0.748	4.59	0.853
81.89	0.531	57.93	0.599	35.67	0.684	18.45	0.762	1.68	0.860
78.41	0.541	54.64	0.609						
$T = 263.17$ K									
100.06	0.522	73.03	0.588	48.96	0.672	30.60	0.756	13.92	0.862
95.98	0.533	69.34	0.597	45.79	0.684	27.74	0.773	11.36	0.882
92.05	0.552	65.72	0.612	42.67	0.697	24.86	0.788	8.84	0.902
88.07	0.547	62.28	0.621	39.59	0.711	22.00	0.807	6.36	0.920
84.12	0.557	58.83	0.632	36.56	0.726	19.27	0.826	3.92	0.942
80.31	0.568	55.43	0.646	33.55	0.741	16.58	0.842	1.42	0.964
76.64	0.578	52.17	0.658						
$T = 273.17$ K									
98.21	0.544	72.68	0.619	49.18	0.692	24.88	0.826	11.22	0.947
94.00	0.547	69.16	0.624	45.71	0.711	22.14	0.856	9.17	0.962
90.03	0.563	65.79	0.635	42.29	0.721	19.75	0.872	7.10	0.982
86.55	0.573	62.51	0.646	38.72	0.729	17.51	0.890	5.05	1.003
83.15	0.582	59.21	0.657	30.87	0.791	15.43	0.912	3.00	1.021
79.63	0.590	55.98	0.673	27.90	0.810	13.32	0.925	1.01	1.052
76.17	0.602	52.69	0.679						
$T = 298.16$ K									
98.44	0.602	69.96	0.689	47.18	0.796	26.99	0.937	11.95	1.087
94.83	0.605	66.99	0.703	44.45	0.814	24.71	0.959	9.92	1.118
91.29	0.617	63.90	0.714	41.74	0.830	22.49	0.982	7.97	1.137
87.89	0.641	60.87	0.728	39.12	0.847	20.32	1.002	6.09	1.168
84.45	0.637	58.04	0.743	36.55	0.865	18.19	1.018	4.23	1.185
80.99	0.649	55.32	0.757	34.09	0.885	16.08	1.045	2.36	1.217
77.32	0.655	52.59	0.768	31.70	0.899	14.02	1.062	0.74	1.266
73.41	0.665	49.87	0.783	29.29	0.923				

In earlier works we have confirmed that κ_T follows a power law in the pressure along isothermal paths.[36,37] According to this, $\kappa_T(p)$ can be represented by the following phenomenological expression:

$$\kappa_T(p) = \kappa^*[p - p_{\text{sp}}]^{-\beta} \tag{1}$$

where p_{sp} is the divergence pressure at the spinodal curve,[38] and κ^* is the pseudocritical amplitude for κ_T. Both parameters depend on temperature only. β is the pseudo-critical exponent, which is independent of temperature and characterizes the divergence of $\kappa_T(p)$ as the spinodal curve is approached. In the stable liquid range, the pseudo-critical exponent is close to 0.85.[36−40] In Table 2, we record the parameters of eq 1 obtained from fitting the six isotherms of κ_T given in Table 1.

The experimental measurements of $\kappa_T(p)$ also allow us to obtain the pressure dependence of the molar density (ρ) for the

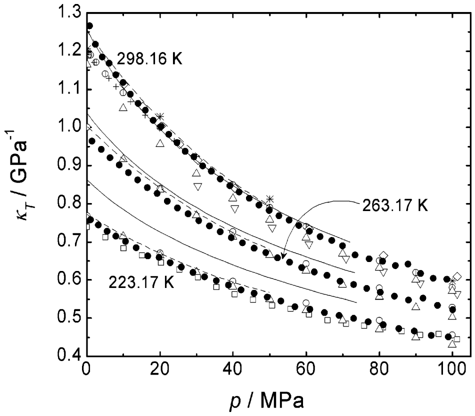

Figure 1. Isothermal compressibility (κ_T) of methanol along the isotherms: 223.17, 263.17, and 298.16 K: ●, experimental results of this work. Literature sources: ▽, Amagat;[1] □, Seitz et al.;[2] ◇, Moriyoshi and Inubushi;[3] ⏀, Machado and Streett;[4] ∗, Easteal and Woolf;[5] ⊗, Kubota et al.;[7] ○, Sun et al.;[8,9] +, Papaioannau and Panayiotou;[14] △, Ledwig and Würflinger.[16] Curves are results calculated for these isotherms from the equations proposed in references: —, Goodwin;[6] – –, Hrubý et al.[13]

Table 2. Parameters of Equation 1 and Standard Deviations (σ) Obtained from the Fit to the Results Recorded in Table 1

	$10^3\kappa^*$	p_{sp}	σ
T/K	MPa$^{-0.15}$	MPa	GPa^{-1}
208.17	41.60 ± 0.47	−125.13 ± 2.15	0.0070
223.17	42.68 ± 0.44	−115.50 ± 1.85	0.0041
248.19	44.78 ± 0.41	−101.91 ± 1.51	0.0036
263.17	45.08 ± 0.38	−91.47 ± 1.28	0.0041
273.17	44.19 ± 0.33	−81.53 ± 1.03	0.0078
298.16	45.88 ± 0.30	−69.57 ± 0.79	0.0076

Table 3. Parameters of Equation 2 and Standard Deviations (σ) for the Isotherms (p, ρ) of Liquid Methanol

T	$10^3\kappa^*$	p_{sp}	ρ_{sp}	σ
K	MPa$^{-0.15}$	MPa	mol·dm^{-3}	mol·dm^{-3}
208.17	42.78 ± 0.67	−131.75 ± 3.18	15.03 ± 0.17	0.0009
223.17	42.89 ± 0.55	−116.82 ± 2.37	14.92 ± 0.14	0.0008
248.19	44.63 ± 0.44	−101.53 ± 1.64	14.34 ± 0.10	0.0006
263.17	44.89 ± 0.38	−91.12 ± 1.30	14.19 ± 0.09	0.0009
273.17	44.87 ± 0.37	−86.50 ± 1.21	14.10 ± 0.08	0.0059
298.16	45.72 ± 0.25	−69.48 ± 0.69	13.80 ± 0.06	0.0013

six measured isotherms. We include such data in tabular form in Table S1 of the Supporting Information. These isothermal molar density values have been fitted with

$$\rho(p) = \rho_{sp} \exp\left\{\frac{\kappa^*}{(1-\beta)}[p - p_{sp}]^{(1-\beta)}\right\} \qquad (2)$$

Equation 2 is obtained from direct integration of eq 1,[39,41] where the parameter ρ_{sp} is the divergence density of the liquid branch of the spinodal curve at the considered temperature. Equation 2 with $\beta = 0.85$ has been used to represent experimental densities of many liquids within their estimated uncertainties, and the results are of a quality comparable to those obtained from other well-known isothermal EOS values.[41,42] Table 3 summarizes the results of the fits of our experiments.

Isobaric Response of the Thermal Expansion Coefficient in Liquid Methanol. We measured α_p along four isobars at the following selected pressures: 0.59, 20.01, 45.10, and 80.03 MPa. Each isobar consists of ca. 40 measurements at temperatures ranging from (195 to 300) K. The 0.59 MPa isobar includes several experimental runs to check the reproducibility of our data. Again, the experiments were performed at relatively small temperature steps (2 to 3 deg) to obtain reliable results for α_p(T). Our results are recorded in Table 2 and compared in Figure 2a with previous results at room pressure (formally 0.1 MPa). The three remaining isobars obtained in this work are plotted in Figure 2b. Good agreement is observed with available results, although significant differences are observed at low temperatures. The differences can be explained as follows. First, the older data from Seitz et al. [2] have limited accuracy. On the other hand, as already mentioned, the results of Sun et al. at low temperatures[9] (203 to 263 K) are not consistent with their own data at higher temperatures[8] (263 to 333 K), the differences being more significant at high pressures. Furthermore, the data from ref 11 appear to be inconsistent with the rest of the experiments below 220 K. Finally, Figure 2b confirms that the 45.10 MPa isobar of α_p as calculated from the EOS of Goodwin[6] predicts higher values than other sources.

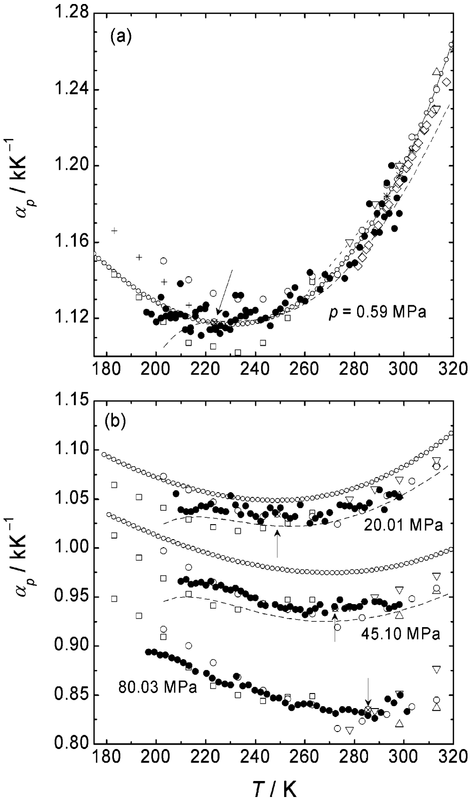

Figure 2. Thermal expansion coefficient (α_p) of liquid methanol as a function of temperature. (a) Experimental results of this work at 0.59 MPa and from literature at 0.1 MPa. (b) Results for the isobars of p = (20.01, 45.10, and 80.03) MPa. ●, this work; □, Seitz et al. (at 20.27, 45.10, and 81.06 MPa);[2] ---, McKinney et al.;[44] ◇, Reisler et al.;[45] ∗, Hales and Ellender;[46] △, Machado and Streett;[4] ▽, Easteal and Woolf;[5] +, Riembauer et al.;[10] ○, Sun et al. [8,9] Curves are results calculated for the isobars of (0.59, 20.01, and 45.10) MPa from the equations proposed in references: —, Goodwin;[6] – –, Hrubý et al.[13] Arrows represent the coordinates where the isobars of $\alpha_p(T)$ have a minimum, in accordance with our experimental results.

In any case, an interesting feature deduced from Figure 2 is that the $\alpha_p(T)$ isobars present minima as a function of temperature. Arrows in Figure 2 indicate the minima coordinates deduced from our experiments. The minimum is found around 224 K at 0.59 MPa. Furthermore, as the pressure increases a shift of the minimum to higher temperatures is observed. To find the minima coordinates, we used a parabolic function for each isobar, that is,

$$\alpha_p(T) = \alpha_m(1 + at^2) \qquad (3)$$

Table 4. Experimental Results of the Thermal Expansion Coefficient (α_p/kK^{-1}) of Liquid Methanol at Various Pressures (p) and Temperatures (T/K)

T	α_p	T	α_p	T	α_p	T	α_p	T	α_p
$p = 0.59$ MPa									
run 1		248.19	1.123	286.15	1.180	209.97	1.122	run 3	
218.19	1.111	250.18	1.125	288.16	1.165	211.93	1.114	202.14	1.131
220.16	1.127	252.18	1.128	290.16	1.165	213.91	1.116	204.09	1.122
222.14	1.114	254.18	1.132	292.16	1.173	215.90	1.123	206.06	1.120
224.15	1.114	256.17	1.136	294.16	1.175	217.87	1.125	208.02	1.122
226.15	1.116	258.17	1.130	296.16	1.167	219.84	1.125	209.97	1.138
228.15	1.122	260.18	1.129	298.17	1.175	221.82	1.114	211.93	1.121
230.17	1.118	262.17	1.144	300.16	1.193	223.82	1.115	213.91	1.113
232.18	1.132	266.17	1.135	run 2		225.86	1.112	215.90	1.121
234.16	1.132	268.17	1.143	196.17	1.123	227.95	1.115	run 4	
236.16	1.124	270.16	1.141	198.11	1.122	230.04	1.114	289.13	1.175
238.17	1.123	276.12	1.141	200.13	1.118	232.14	1.119	291.13	1.180
240.17	1.124	278.16	1.148	202.14	1.120	234.19	1.121	293.12	1.191
242.17	1.119	280.16	1.149	204.09	1.125	236.18	1.121	295.12	1.200
244.18	1.120	282.15	1.157	206.06	1.122			297.12	1.183
246.19	1.116	284.14	1.163	208.02	1.120				
$p = 20.01$ MPa									
208.16	1.055	226.17	1.038	244.19	1.034	264.17	1.030	282.15	1.043
210.16	1.039	228.16	1.037	246.19	1.041	266.17	1.034	284.14	1.041
212.17	1.037	230.16	1.053	248.17	1.036	268.16	1.027	286.15	1.046
214.17	1.037	232.17	1.044	250.17	1.041	270.16	1.036	290.14	1.059
216.17	1.039	234.17	1.034	252.18	1.033	274.15	1.044	292.15	1.039
218.17	1.043	236.17	1.043	254.18	1.030	276.15	1.043	294.14	1.054
220.18	1.042	238.17	1.035	256.17	1.032	278.15	1.043	296.14	1.055
222.17	1.045	240.25	1.032	258.17	1.044	280.15	1.040	298.15	1.052
224.17	1.039	242.25	1.027	262.17	1.025				
$p = 45.10$ MPa									
210.17	0.966	228.16	0.958	248.17	0.942	264.17	0.938	282.13	0.940
212.17	0.968	230.17	0.957	250.17	0.939	266.17	0.942	284.13	0.945
214.17	0.963	232.17	0.959	252.18	0.938	268.17	0.934	288.14	0.945
216.17	0.964	234.17	0.956	254.18	0.940	272.14	0.940	290.13	0.945
218.18	0.965	236.17	0.953	256.18	0.937	274.14	0.947	292.14	0.943
220.18	0.962	238.17	0.949	258.18	0.937	276.14	0.938	294.13	0.938
222.18	0.966	240.17	0.949	260.18	0.932	278.13	0.940	296.13	0.940
224.17	0.960	242.17	0.942	262.17	0.936	280.14	0.940	298.13	0.942
226.16	0.962	244.18	0.941						
$p = 80.03$ MPa									
196.97	0.894	220.38	0.872	242.29	0.853	262.21	0.841	282.88	0.832
199.30	0.894	222.80	0.867	244.74	0.851	264.77	0.839	285.53	0.829
201.61	0.891	225.25	0.863	247.21	0.847	267.34	0.835	288.17	0.826
203.94	0.891	227.72	0.861	249.69	0.847	269.32	0.834	290.79	0.832
206.30	0.888	230.17	0.860	252.20	0.842	272.52	0.831	293.40	0.846
208.68	0.886	232.57	0.869	254.72	0.837	275.11	0.835	296.02	0.842
211.07	0.883	234.98	0.859	257.20	0.840	277.69	0.835	298.65	0.850
213.46	0.880	237.42	0.860	259.68	0.841	280.28	0.833	301.27	0.833
216.00	0.874	239.85	0.855						

Table 5. Coefficients of Equation 3 and Standard Deviations (σ) Obtained from the Fit to the Isobars of Liquid Methanol Recorded in Table 4[a]

p	T_0	α_m		σ	ρ_m
MPa	K	kK^{-1}	a	kK^{-1}	mol·dm^{-3}
0.59	223.6 ± 2.3	1.118 ± 0.001	0.54 ± 0.05	0.007	26.74 ± 0.10
20.01	248.9 ± 2.4	1.034 ± 0.001	0.46 ± 0.09	0.006	26.42 ± 0.07
45.10	272.2 ± 2.5	0.938 ± 0.001	0.69 ± 0.07	0.004	26.31 ± 0.05
80.03	285.4 ± 4.0	0.835 ± 0.001	0.81 ± 0.06	0.005	26.62 ± 0.04

[a] The last column (ρ_m) records the density for the coordinates (p, T_0) of the minima in $\alpha_p(T)$.

where $t = 1 - T/T_0$, and α_m and T_0 are the coordinates (α_p, T) of the minimum. Table 5 records the fitting parameters of eq 3, the standard deviation, and the densities of the coordinates of the minima. As can be observed, an interesting finding is that the minima for the isobars of $\alpha_p(\rho)$ occur within a narrow range of densities (26.7 to 26.3 mol·dm^{-3}, 3.18 to 3.13 times the critical density) between (220 and 290) K.

Properties Correlations. As mentioned above, in a recent publication[24] we analyzed the general behavior of α_p as a function of pressure and temperature for a number of liquids. It was concluded that $\alpha_p(T)$ isobars may present maxima, minima, or both extrema. So the isotherms of α_p as a function of pressure present characteristic crossings at high pressures. Such analysis allowed us derive the following α_p-based EOS:

$$\alpha_p = \alpha^*(p - p_{\mathrm{sp}})^{-1/2} \tag{4}$$

$$p_{\mathrm{sp}}(T) = p_{\mathrm{vap}}(T) + p^*\left[\frac{(1 - T/T_{\mathrm{c}})^{3\epsilon}}{T/T_{\mathrm{c}}}\right]^{1/2} \tag{5}$$

$$\alpha^*(T) = \alpha_0^*\left[1 + A\left(\frac{p_{\mathrm{sp}}(T) - p_{\mathrm{c}}}{p^*}\right)^{\omega}\right] \tag{6}$$

where T_{c} and p_{c} are the critical temperature and pressure of the substance, respectively. $p_{\mathrm{vap}}(T)$ is the vapor pressure (which constitutes a negligible correction, except at temperatures close to the critical point). The complete EOS of a given liquid, methanol in this case, is characterized by five parameters: p^*, ϵ, α^*_0, A, and ω, which with the exception of the scaling pressure p^*, are always positive. For our present purposes, the relevant parameter in such an EOS is the exponent ω that determines the curvature of an isobar of $\alpha_p(T)$. We have correlated the $\alpha_p(p, T)$ of Table 4 to eqs 4 to 6, using $T_{\mathrm{c}} = 512.6$ K, $p_{\mathrm{c}} = 8.0946$ MPa, and $p_{\mathrm{vap}}(T)$ results given in ref 6. We obtained the following characteristic parameters: $p^* = (-140.72 \pm 6.94)$ MPa, $3\epsilon = (2.008 \pm 0.141)$, $\alpha_0^* = (8.847 \pm 0.260)$ MPa$^{0.5}$·kK^{-1}, $A = (0.46451 \pm 0.08)$, and $\omega = (1.90647 \pm 0.186)$. We provide more digits than those statistically significant to minimize round-off errors. With these parameters, the standard deviation of the fit to our $\alpha_p(p, T)$ results was 0.0058 kK^{-1}. Calculated values of $\alpha_p(p, T)$ with these equations at rounded values of pressure and temperature are included in Table S2 of the Supporting Information.

We have recently derived a new correlation scheme for κ_T data using a quite simple but general expression to evaluate the temperature dependence of κ^*. We have not used polynomials since their predictive power out of the experimental range is quite restricted, making them unpractical for most purposes. Such correlation scheme is in the line of others proposed by us in earlier works.[43] The correlation scheme is based on the eq 6 for $\alpha^*(T)$ and the relation between α_p and κ_T by means of the thermal pressure coefficient.[43] Within this scheme an κ_T-based EOS is obtained, which can be written as follows:

$$\kappa_T(p, T) = \kappa^*(T)[p - p_{\mathrm{sp}}(T)]^{-0.85} \tag{7}$$

$$p_{\mathrm{sp}}(T) = p_{\mathrm{vap}}(T) + p^*\left[\frac{(1 - T/T_{\mathrm{c}})^{3\epsilon}}{T/T_{\mathrm{c}}}\right]^{1/2} \tag{8}$$

$$\kappa^*(T) = \kappa_0^*\left[1 + A\left(\frac{p_{\mathrm{sp}}(T) - p_{\mathrm{c}}}{p^*}\right)^{\omega}\right]\left(\frac{\mathrm{d}p_{\mathrm{sp}}}{\mathrm{d}T}\right)^{-1} \tag{9}$$

Within this model the EOS of a given liquid can also be characterized by five characteristic parameters: p^*, ϵ, κ_0^*, A, and ω. We have correlated the $\kappa_T(p, T)$ of Table 1 to eqs 7 to 9, using $T_{\mathrm{c}} = 512.6$ K, $p_{\mathrm{c}} = 8.0946$ MPa, and $p_{\mathrm{vap}}(T)$ results given in ref 6, with the following characteristic parameters: $p^* = (-154.284 \pm 5.4)$ MPa, $3\epsilon = (2.442 \pm 0.097)$, $\kappa_0^* = (15.55 \pm 0.75)$ MPa$^{0.85}$·kK^{-1}, $A = (1.4925 \pm 0.26)$, and $\omega = (1.5355 \pm 0.100)$. With these parameters the standard deviation of the fit to our $\kappa_T(p, T)$ results is 0.0064 GPa^{-1}. Calculated values of

$\kappa_T(p, T)$ at rounded values of pressure and temperature are included in the Supporting Information (Table S3), together with a deviation plot (Figure S1) of eqs 7 to 9 from our data and other results available in the literature at higher temperatures.[4]

Summary and Conclusions

A differential expansion technique has been used to provide accurate measurements of the isothermal compressibility (κ_T) and thermal expansion coefficient (α_p) of liquid methanol in the (p, T) range close to its solidification line. Our results provide an accurate thermodynamic description of this controversial region of the phase diagram of liquid methanol, where serious discrepancies existed due to limited accuracy in existing experiments. We have confirmed that minima are observed in the temperature dependence of the thermal expansion coefficient. Furthermore, we observe that the minimum shifts to higher temperatures with increasing pressure.

Supporting Information Available:

Three additional tables and one figure. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Amagat, E. H. Mémories sur l'élasticité et la dilatation des fluids jusqu'aux très hautes pressions. Troisieme mémoire. *Liq. Ann. Chim. Phys.* **1893**, *29*, 505−574.

(2) (a) Seitz, W.; Alterthum, H.; Lechner, G. Wärmeausdehnung und Kompressibilität von flüssigkeiten bei tiefen temperaturen. Part I. Thermal expansion. *Ann. Physik.* (*Leipzig*) **1916**, *49*, 85−92. (b) Seitz, W.; Lechner, G. Wärmeausdehnung und Kompressibilität von flüssigkeiten bei tiefen temperaturen. Part II. *Ann. Physik.* (*Leipzig*) **1916**, *49*, 93−115.

(3) Moriyoshi, T.; Inubushi, H. Compression of some alcohols and their aqueous binary mixtures at 298.15 K and at pressures up to 1400 atm. *J. Chem. Thermodyn.* **1977**, *9*, 587−592.

(4) Machado, J. R. S.; Streett, W. B. Equation of state and thermodynamic properties of liquid methanol from 298 to 489 K and pressures to 1040 bar. *J. Chem. Eng. Data* **1983**, *28*, 218−223.

(5) Easteal, A. J.; Woolf, L. A. (p, V_m, T, x) measurements for [$(1 - x)H_2O + xCH_3OH$] in the range 278 to 323 K and 0.1 to 280 MPa. I. Experimental results, isothermal compressibilities, thermal expansivities, and partial molar volumes. *J. Chem. Thermodyn.* **1985**, *17*, 49−62.

(6) Goodwin, R. D. Methanol thermodynamic properties from 176 K to 673 K at pressures to 700 bar. *J. Phys. Chem. Ref. Data* **1987**, *16*, 799−892.

(7) Kubota, H.; Tanaka, Y.; Makita, T. Volumetric behavior of pure alcohols and their water mixtures under high pressure. *Int. J. Thermophys.* **1987**, *8*, 47−70.

(8) Sun, T. F.; Biswas, S. N.; Trappeniers, N. J.; Ten Seldam, C. A. Acoustic and thermodynamic properties of methanol from 273 to 333 K and at pressures to 280 MPa. *J. Chem. Eng. Data* **1988**, *33*, 395−398.

(9) Sun, T. F.; Schouten, J. A.; Biswas, S. N. Determination of the thermodynamic properties of liquid methanol from 203 to 263 K and up to 280 MPa from speed of sound measurements. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 528−534.

(10) Riembauer, M.; Schulte, L.; Würflinger, A. *PVT* data of liquid and solid phases of methanol, cyclohexanol, and 2,3-dimethylbutane up to 300 MPa. Z. *Phys. Chem. Neue Folge* **1990**, *166*, 53−61.

(11) Vacek, V.; Hany, A. M. Measurements of *pVT* properties of liquid methanol in the temperature range of 200 K to 300 K and up to 50 MPa. *Fluid Phase Equilib.* **1992**, *76*, 187−198.

(12) Reuck, K. M. de; Craven, R. J. B. *Methanol. International Thermodynamic Tables of the Fluid State*−*12*; IUPAC Chemical Data Series No. 38; Blackwell Scientific Publications: London, 1993.

(13) Hrubý, J.; Klomfar, J.; Sifner, O. (T, p, and σ) relation of liquid methanol at temperatures from 205 to 321 K and pressures up to 50 MPa. *J. Chem. Thermodyn.* **1993**, *25*, 1229−1242.

(14) Papaioannou, D.; Panayiotou, C. Viscosity of binary mixtures of propylamine with alkanols at moderately high pressures. *J. Chem. Eng. Data* **1995**, *40*, 202−209.

(15) Franck, E. U.; Deul, R. Dielectric behaviour of methanol and related polar fluids at high pressures and temperatures. *Faraday Discuss. Chem. Soc.* **1978**, *66*, 191−198.

(16) Ledwig, R.; Würflinger, A. Dielectric measurements at high pressures and low temperatures. IV. Dielectric and *pVT* data of methanol. *Z. Phys. Chem. Neue Folge* **1982**, *132*, 21−27.

(17) Vedam, K.; Limsuwan, P. Piezo- and elasto-optic properties of liquids under high pressure. II. Refractive index vs density. *J. Chem. Phys.* **1982**, *69*, 4772−4778.

(18) Herbst, C. A.; King, H. E., Jr.; Gao, Z.; Ou-Yang, H. D. Dynamic light scattering measurements of high-pressure viscosity utilizing a diamond anvil cell. *J. Appl. Phys.* **1992**, *72*, 838−844.

(19) Grocholski, B.; Jeanloz, R. High-pressure and -temperature viscosity measurements of methanol and 4:1 methanol:ethanol solution. *J. Chem. Phys.* **2005**, *123*, 204503-1−204503-6.

(20) Zaug, J. M.; Slutsky, L. J.; Brown, J. M. Equilibrium properties and structural relaxation in methanol to 30.4 GPa. *J. Phys. Chem.* **1994**, *98*, 6008−6016.

(21) Gromnitskaya, E. L.; Stal'gorova, O. V.; Yagafarov, O. F.; Brazhkin, V. V.; Lyapin, A. G.; Popova, S. V. Ultrasonic study of the phase diagram of methanol. *JETP Lett.* **2004**, *80*, 597−601.

(22) Jorgensen, W. L.; Ibrahim, M. Pressure dependence of hydrogen bonding in liquid methanol. *J. Am. Chem. Soc.* **1982**, *104*, 373−378.

(23) Wick, C. D.; Dang, L. X. Investigating pressure effects on structural and dynamical properties of liquid methanol with many-body interactions. *J. Chem. Phys.* **2005**, *123*, 184503-1−184503-7.

(24) Taravillo, M.; Baonza, V. G.; Cáceres, M.; Núñez, J. Thermodynamic regularities in compressed liquids. I. The termal expansion coefficient. *J. Phys.*: *Condens. Matter* **2003**, *15*, 2979−2989.

(25) Bridgman, P. W. *The Physics of High Pressure*; Dover: New York, 1970.

(26) Cutler, W. G.; McMickle, R. H.; Webb, W.; Schiessler, R. W. Study of the compressions of several high molecular weight hydrocarbons. *J. Chem. Phys.* **1958**, *29*, 727−740.

(27) Jenner, G.; Millet, M. Relations pression−volume−température des bromures d'alcoyle primaries. 4. Dilatation isobare du bromoéthane et du bromo-1-butane. *High Temp.*−*High Pressures* **1970**, *2*, 205−213.

(28) Jenner, G.; Millet, M. Relations pression−volume−température des bromures d'alcoyle primaries. 6. Compression du bromo-1-hexane et du bromo-1-heptane. *High Temp.-High Pressures* **1973**, *5*, 145−153.

(29) Alba, C.; Ter Minassian, L.; Denis, A.; Soulard, A. Reduction into a rational fraction of a thermodynamic property of the liquid state: experimental determinations in the case of CO_2 and *n*-butane. Extension to the other properties. *J. Chem. Phys.* **1985**, *82*, 384−393.

(30) Randzio, S. L. State variables in calorimetric investigations: Experimental results and their theoretical impact. *Thermochim. Acta* **1997**, *300*, 29 - 41.

(31) Streett, W. B.; Sagan, L. S.; Staveley, L. A. K. An experimental study of the equation of state of liquid xenon. *J. Chem. Thermodyn.* **1973**, *5*, 633−650.

(32) Calado, J. C. G.; Clancy, P.; Heintz, A.; Streett, W. B. Experimental and theoretical-study of the equation of state of liquid ethylene. *J. Chem. Eng. Data* **1982**, *27*, 376−385.

(33) Baonza, V. G.; Núñez Delgado, J.; Cáceres Alonso, M. (p, ρ, T) properties of liquid carbon disulfide from 198 to 298 K and pressures up to 104 MPa. *J. Chem. Thermodyn*. **1989**, *21*, 231−236.

(34) Sun, T. F.; Schouten, J. A.; Trappeniers, N. J.; Biswas, S. N. Measurements of the densities of liquid benzene, cyclohexane, methanol, and ethanol as functions of temperature at 0.1 MPa. *J. Chem. Thermodyn.* **1988**, *20*, 1089−1096.

(35) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, 1980.

(36) Baonza, V. G.; Cáceres Alonso, M.; Núñez, Delgado, J. Estimation of the spinodal curve for liquids. Application to 2,3-dimethylbutane. *J. Phys. Chem.* **1994**, *98*, 1993−1998.

(37) (a) Baonza, V. G.; Cáceres, M.; Núñez, J. The spinodal as a reference curve for the high-pressure volumetric behavior of liquids. *Chem. Phys. Lett.* **1993**, *216*, 579−584. (b) Baonza, V. G.; Cáceres, M.; Núñez, J. High-pressure compressibility behavior of liquids referred to a pseudospinodal curve. *Chem. Phys. Lett.* **1994**, *228*, 137−143.

(38) Debenedetti, P. G. *Metastable Liquids: Concepts and Principles*; Princeton University Press: Princeton, NJ, 1996.

(39) Baonza, V. G.; Cáceres Alonso, M.; Núñez, Delgado, J. Universal behavior of compressed liquids. *J. Phys. Chem.* **1994**, *98*, 4955−4958.

(40) Pruzan, P. Pressure-dependence of expansivity in the liquid hexane as a model for liquids. *J. Phys. Lett.* **1984**, *45*, L273−L278.

(41) Baonza, V. G.; Cáceres Alonso, M.; Núñez Delgado, J. Extended analytical equation of state for liquids from expansivity data-analysis. *J. Phys. Chem.* **1993**, *97*, 10813−10817.

(42) Baonza, V. G.; Cáceres, M.; Núñez, J. Application of simple expressions for the high-pressure volumetric behaviour of liquid mesitylene. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 553−557.
(43) Taravillo, M.; Baonza, V. G.; Cáceres, M.; Núñez, J. Equation of state for representing the thermodynamic properties of liquids at high pressure. *J. Phys. Chem.* **1995**, *99*, 8856−8862.
(44) McKinney, W. P.; Skinner, G. F.; Staveley, L. A. K. Solutions of alcohols in non-polar solvents. Part V. Values at 0 °C of the coefficients of expansion, the isothermal compressibility, and the quantity $(\partial S/\partial V)_T$ for the normal primary alcohols from methanol to octanol. *J. Chem. Soc*. **1959**, 2415−2420.
(45) Reisler, E.; Eisenberg, H.; Minton, A. P. Temperature and density dependence of the refractive index of pure liquids. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 1001−1015.
(46) Hales, J. L.; Ellender, J. H. Liquid densities from 293 to 490 K of nine aliphatic alcohols. *J. Chem. Thermodyn.* **1976**, *8*, 1177−1184.

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