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Vapor Pressure Measurements of Dimethyl Ether from (213 to 393) K

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Vapor pressure of dimethyl ether was measured using a modified constant volume apparatus. Measurements were carried out at temperatures from (213 to 393) K and at pressures from (16 to 4706) kPa. A total of 39 experimental points were obtained with uncertainties of ± 5 mK on ITS-90 for temperature and ± 0.7 kPa for pressure. The measurement results were fitted to a Wagner-type equation with an average absolute deviation of 0.033 %. Also, the new vapor pressure equation was compared with the published data.

Introduction

This work is further experimental research of saturated vapor pressure of dimethyl ether (DME) published in the *Journal of Chemical and Engineering Data* in 2004.[1] The experimental apparatus and measurement procedures were improved in this work from our previous, and also the temperature was down to 213 K. Furthermore, the experimental results were compared with the updated literature data.

Experimental Section

Materials. The sample of dimethyl ether was provided by Shandong Jiutai Chemical Co. Ltd. (the largest dimethyl ether supplier in China). The mass purity is better than 99.95 %, as indicated by the analysis of gas chromatography (Agilent 6890N). To eliminate the effect of gaseous impurity, the sample was purified several times by freeze−pump−thaw cycles by using liquid nitrogen and a vacuum (< 0.05 Pa) pump.

Apparatus. The modified experimental apparatus used in this work is illustrated in Figure 1. An optical sample cell, a thermostatic bath, a temperature measurement system, and a pressure measurement system were used in this experiment. Detailed information was described in ref 1. In this work, the optical cylinder cell was rebuilt, and charge and drain fitting were added so that pure sample could be filled into and discharged from the cell online. The temperature and pressure measurement system and data acquisition system were the same as in the previous work. The used quartz pressure sensor (model: Paroscientific 31K-101, 0.01 % accuracy) was recalibrated by a dead weight gauge with an accuracy of 0.005 % (model: DHI PG7601). The overall temperature uncertainty was estimated to be ± 5 mK on ITS-90 scale, while the pressure measurement uncertainty was within ± 0.7 kPa.

Results and Discussion

The experimental vapor pressures of DME at temperatures in the range from (213 to 393) K are given in Table 1, where temperatures are given on the ITS-90 scale. Experimental data were fit to a four-parameter Wagner-type equation

$$\ln(P_r) = (A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^{9.5})T_r^{-1} \qquad (1)$$

where $P_r = P/P_c$; $T_r = T/T_c$; $\tau = (T_c - T)/T_c$; T_c is the critical temperature of DME with a value of 400.378 K;[1] and P_c is the critical pressure. The parameters of A_1, A_2, A_3, and A_4 in eq 1 are $A_1 = -7.067646$, $A_2 = 1.885731$, $A_3 = -2.396113$, and $A_4 = -20.728288$. The critical pressure was fitted to be $P_c = 5335.1$ kPa. The applicable temperature range of the equation is from 213 K to the critical temperature.

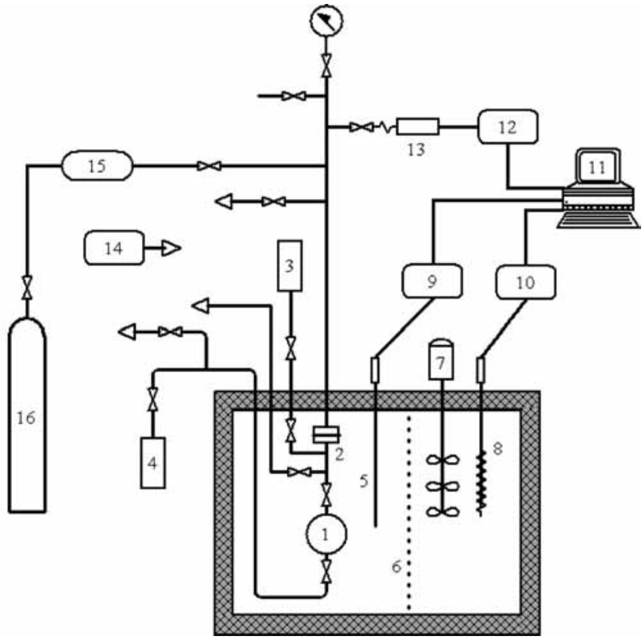

Figure 1. Schematic diagram of the apparatus: 1, optical cylinder cell; 2, differential pressure transducer; 3, sample cell; 4, discharge container; 5, platinum resistance thermometer; 6, shield board; 7, stirrer; 8, heater; 9, thermometric bridge; 10, temperature controller; 11, acquisition computer; 12, pressure acquisition system; 13, quartz pressure transducer; 14, vacuum system; 15, expansion chamber; 16, nitrogen reservoir.

Defining the average absolute deviation in pressure as

$$\mathrm{AAD} = \frac{1}{n}\sum_n \left|\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{cal}}}\right| \qquad (2)$$

where n is the number of experimental points, the AAD values were found to be 0.033 %. The deviations of the experimental results from eq 1 are shown in Figure 2, and it can be found that all the relative deviations are within ± 0.15 %.

The literatures data listed in Table 2 indicate that only three sources have systematically measured the vapor pressure of pure

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Table 1. Experimental Vapor Pressure of Dimethyl Ether

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
213.076	16.46	278.166	316.12	333.165	1449.22
218.110	22.24	283.160	372.90	338.166	1621.53
223.152	29.61	288.134	436.69	343.163	1809.11
228.058	38.64	293.165	509.01	348.160	2012.44
233.092	49.96	298.084	588.17	353.162	2232.34
238.110	63.84	298.784	600.51	358.159	2468.87
243.070	80.36	303.151	679.68	363.157	2723.27
248.123	100.43	303.782	691.56	368.136	2996.38
253.125	124.09	308.127	778.92	373.136	3291.17
258.135	152.40	313.166	889.98	378.151	3608.63
263.132	184.96	318.164	1011.55	383.150	3948.62
268.130	222.70	323.165	1144.73	388.162	4313.91
273.167	266.50	328.161	1290.23	393.163	4706.18

dimethyl ether at temperatures lower than 273 K: 16 points down to 171 K of Kennedy et al.,[3] 8 points down to 233 K of Wu et al.,[1] 25 points down to 219 K of Corvaro et al.[18]

The relative deviations of literature data [1−20] including this work from eq 1 are shown in Figure 3. It can be seen from Figure 3a that there is a positive systematic shift of the previous data reported in ref 1 from this work especially in the temperature range lower than 273 K. Analysis shows the systematic deviation may have been due to a volatile impurity since no effort had been made to remove it by freeze−pump−thaw cycles in the last work. The comparison in Figure 3 also shows that the overall deviation of all the literature data from eq 1 was within ± 2.0 % in the temperature range from (213 to 393) K, except for some data of ref 1 and the data at temperatures lower than 228 K of ref 18 and several others [(273 and 298) K points of Cardoso et al.,[2] 278 K point of Jónasson et al.[5]] which were thought to be bad points as they also have a relatively large deviation from the data in the same work. Generally speaking, there was a good agreement among the most reported data from different authors in the temperature range from about (240 to 393) K, which can be seen in Figure 3b, and the deviation was within ± 0.5 %, except mostly that of Jónasson et al.,[5] some data of Cardoso et al.,[2] and of Florusse et al.,[11] and some points [(288 and 318) K points of Teodorescu et al.,[9] (353 and 363) K points of Im et al.,[17] (313 and 353) K points of Im et al.[20]). The obvious deviation of Jónasson et al.[5] may be caused by the low accuracy of their temperature and pressure measurements. The data of ref 2 at temperatures above 363 K in 1923 have a deviation around −1.0 % which may be caused by the limitation of the experimental instruments in that

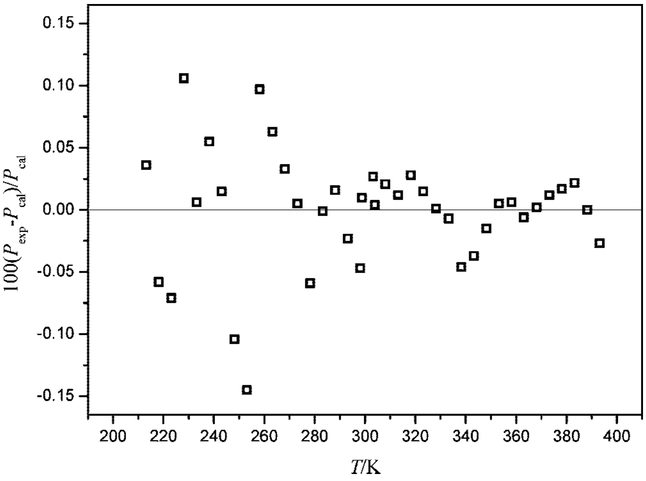

Figure 2. Deviation of the experimental vapor pressure data from eq 1.

Table 2. Reported Experimental Vapor Pressure of Dimethyl Ether

				range	uncertainty	
year	ref	fraction/%	no. pts	T/K	T/mK	P/kPa
1923	2	−	23	273 to 400	50	50.0
1941	3	99.99	16	171 to 248	50	−
1992	4	99.9	6	283 to 395	20	3.0
1995	5	99.2	14	273 to 393	20	10.0
1998	6	−	2	303 to 323	5	0.3
2000	7	99.0	3	283 to 313	20	1.0
2000	8	99.0	4	280 to 320	5	0.3
2001	9	99.8	4	288 to 353	50	10.0
2002	10	99.0	4	258 to 303	20	1.0
2002	11	99.8^{a}	24	288 to 399	20	0.05 % of reading
2003	12	99.9	10	263 to 383	100	5.0/25.0
2004	13	99.0^{a}	3	278 to 308	20	1.0
2004	1	99.95	39	233 to 399	5	0.7
2005	14	99.9^{a}	22	303 to 399	10	0.5
2005	15	99	3	258 to 293	20	1.0
2005	16	99.9^{b}	27	278 to 360	20	0.1
2006	17	99.8	6	313 to 363	50	0.05 %
2006	18	99.8^{a}	71	219 to 361	20	1.0
2007	19	99.9	19	264 to 397	100	0.1 + 0.001P
2007	20	99.9	6	313 to 363	50	0.05 %
2008	this work	99.95	39	213 to 393	5	0.7

[a] Indicates that the purity of DME is in molar fraction. [b] Indicates that the purity of DME is in volume fraction.

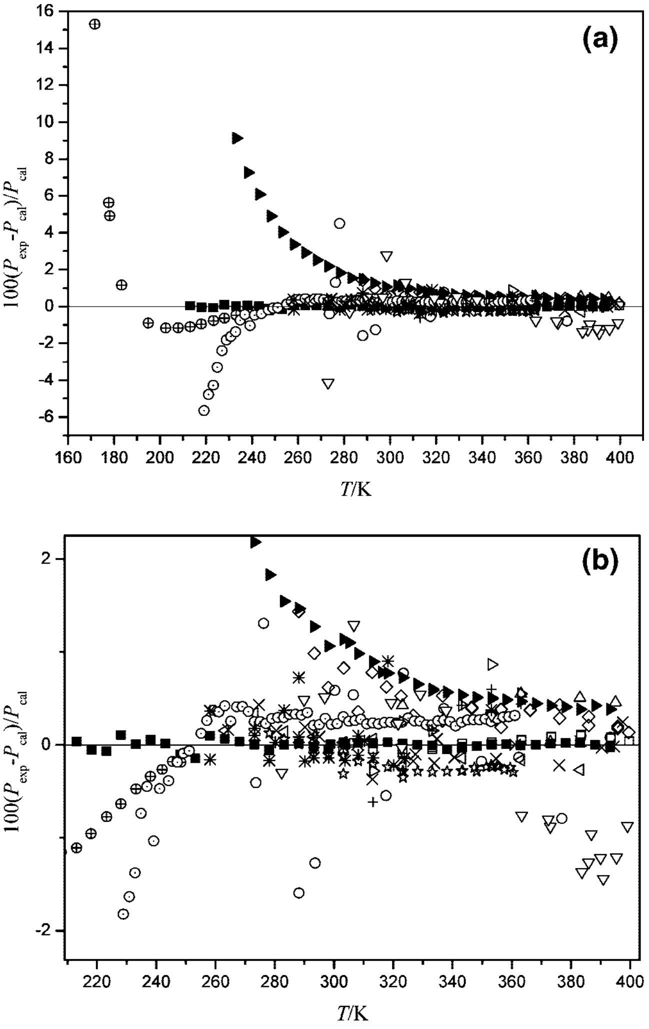

Figure 3. (a) Deviation of the literature vapor pressure data from eq 1. (b) Deviation of partial literature vapor pressure data from eq 1: ■, this work; ▽, ref 2; circle with a plus in it, ref 3; △, ref 4; ○, ref 5; ◇, ref 11; open arrow pointing left, ref 12; solid arrow pointing right, ref 1; □, ref 14; ☆, ref 16; ⊙, ref 18; open arrow pointing right, ref 17; +, ref 20; ×, ref 19; ∗, refs 6−10, 13, 15.

time, and the data lower than 336 K provided by Florusse et al.[11] also exceed ± 0.5 % deviation as the reason might be the limitation of the accuracy of instruments and purity of sample.

On the basis of the above discussion, it can be concluded that there is a good consistency between this work and the literature, and the vapor pressure equation of DME provided by this work was thought to be of high accuracy.

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