Articles

Vapor Pressure Measurements of Dimethyl Ether from (233 to 399) K

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Vapor pressures of dimethyl ether were measured at temperatures from (233 to 399) K and at pressures from (54 to 5146) kPa. The uncertainties of measurements are within ±5 mK on the ITS-90 scale for temperature and are within ±0.7 kPa for pressure, respectively. With the new experimental data, a Wagner type vapor pressure equation of dimethyl ether was fitted. The absolute average deviation between the experimental data and the new Wagner equation is 0.043%, and the maximum deviation is 0.096%. The new vapor pressure equation of dimethyl ether was also compared with the published data.

Introduction

At present, dimethyl ether (DME) is often used as an aerosol propellant, assistant solvent, fuel additive, and liquefied petroleum gas substitute. Also, it can be used as an alternative refrigerant, since it is not harmful to the ozone layer and is easily degraded in the atmosphere. Especially, recent investigations indicate that dimethyl ether and its mixtures have excellent properties as diesel fuels[1] and have a future as a replacement for fuels obtained from fossil reserves.[2] Thus, the thermophysical properties of dimethyl ether are indispensable for these applications. Presently, precise experimental data for dimethyl ether are scarce. A few data are available, such as critical parameters, boiling point, freezing points, vapor pressure, and specific heat capacity in a limited temperature range. Most of these results were obtained before the 1940s. Also, there are large differences among the present experimental data. In this work, the vapor pressure of dimethyl ether was measured at temperatures from (233 to 399) K and compared with the earlier published data.

Experimental Section

Materials. The sample of dimethyl ether was provided by Zhongshan Fine Chemical Co. Ltd. The mass purity is better than 99.95%, as indicated by the analysis of gas chromatography (made by Dongxi Instruments Corp. in China, model GC-4000A). No further purification was done.

Apparatus. The experimental apparatus used in this work is shown in Figure 1. It consists of an optical sample cell, a thermostatic bath, a temperature measurement system, a pressure measurement system, and so forth. The optical sample cell (H) is a cylindrical vessel made of type 304 stainless steel (36 mm long and 20 mm inner diameter) with two quartz glass windows for observation. The cell is set in a thermostatic bath. The thermostatic bath, temperature measurement system, and pressure measurement system are described in detail in ref. 3. Thus, in this work only a brief introduction will be given.

The thermostatic bath has two glass windows (120 mm diameter) with inner dimensions of (550 × 350 × 450) mm^3. The temperature can be varied from (233 to 550) K. Ethanol, pure water, or silicon oil can be used as the bath fluid, depending on the anticipated temperature range. The temperature in the bath is controlled with a computer with two heaters (HL and HS) and a cooler, and it is monitored continuously. To improve the performance of the thermostatic bath, a Fuzzy-PID algorithm was applied in the temperature control system. The stability and uniformity of temperature in the working area of the thermostat bath depend on the temperature range and the selected bath fluid. If pure water is used as the bath fluid, the temperature stability and uniformity are better than ±1 mK from ambient temperature to 363 K. In this paper, the temperature stabilities are better than ±3 mK from ambient temperature to 550 K (silicon oil used) and ±4 mK from 233 K to ambient temperature (ethanol used), respectively.

The temperature measurement system mainly consists of a thermometry bridge and two 25 Ω standard platinum resistance thermometers: one thermometer (No. 92822) is used from (273.15 to 933.473) K, and the other (No. 92825) is used for (83.8058 to 273.16) K. The thermometers are calibrated with an accuracy of ±0.65 mK on the ITS-90 scale at the National Institute of Metrology of China. The model of the thermometry bridge is F18 (Automatic Systems Laboratories Limited), and the temperature uncertainty is ±0.1 mK with a 100 Ω standard resistor.

In pressure measurement, two high precision quartz pressure sensors (A, B, Paroscientific Inc. models 2000A-101 and 31K-101) and one differential pressure transducer (DP, Rosemount, model 3051) were used. The pressure sensor model 2000A-101 was used for the pressures (0 to 1.38) MPa (accuracy 0.01%), and model 31K-101 was used for (1.38 to 6.9) MPa (accuracy 0.01%). The accuracy of pressure transducer model 3051 is 0.075%.

On the basis of the above discussion, the uncertainties of the measurement results are within ±5.0 mK for

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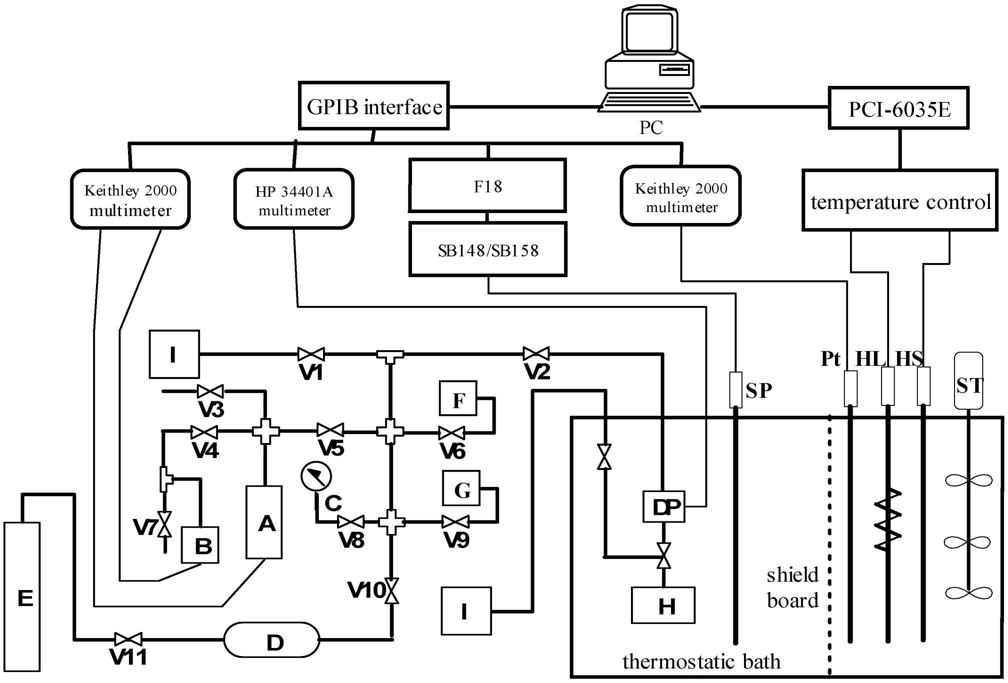

Figure 1. Schematic diagram of experimental apparatus: A, pressure sensor (0 to1.38 MPa); B, pressure sensor (0 to 6.9 MPa); C, pressure gauge (0 to 16 MPa); D, gas reservoir; DP, pressure transducer; E, nitrogen gas; F, piston pressure gauge; G, standard pressure source; H, apparatus; HL, auxiliary heater; HS, controlled heater; I, vacuum pump; Pt, platinum resistance thermometer; SP, 25 Ω SPRT; ST, stirrer motor; V1−V11, valves.

Table 1. Experimental Vapor Pressures of Dimethyl Ether

T/K	P_{exp}/kPa	T/K	P_{exp}/kPa	T/K	P_{exp}/kPa
233.128	54.61	298.172	596.21	348.147	2022.45
238.126	68.49	303.160	687.37	353.146	2242.74
243.157	85.57	305.160	726.26	353.158	2243.07
248.152	105.59	308.158	787.07	358.145	2479.92
253.152	129.42	313.156	897.59	363.148	2735.67
258.160	157.53	316.154	968.55	368.158	3010.81
263.160	190.44	318.158	1018.91	373.154	3305.67
268.161	228.48	323.148	1152.35	378.150	3622.60
273.153	272.17	328.149	1298.23	383.143	3962.25
278.145	321.87	333.157	1457.50	388.155	4331.48
283.160	378.66	333.159	1457.76	393.158	4725.02
288.174	443.57	338.154	1631.01	398.157	5146.82
293.161	515.53	343.147	1818.80	400.378	5355.8

temperature, considering the temperature stability and uniformity of the thermostatic bath, and are ±0.7 kPa for pressure.

Results

The critical temperature is very important to correlate the saturated vapor pressure equation, but from ref 4, it is found that there are large deviations among different researchers' results. Therefore, the critical temperature of dimethyl ether was measured before the experiment.

On the basis of our measurements, the critical temperature was determined in consideration of the meniscus disappearing level as well as the intensity of the critical opalescence.

$$T_c = (400.378 \pm 0.005)\ \mathrm{K} \tag{1}$$

A total of 37 points were measured at temperatures from (233 to 399) K, and the pressures varied from (54 to 5146) kPa. The vapor pressure measurements of dimethyl ether are given in Table 1, and the temperatures are given on the ITS-90 scale.

Table 2. Reported Vapor Pressures of Dimethyl Ether

				range	uncertainty	
year	ref	mass purity/%	no. pts	T/K	T/mK	P/kPa
1923	13		23	273−400	50	50.0
1941	5	99.99	4	171−183	50	
1941	5	99.99	12	194−248	50	
1992	14	99.9	6	283−395	20	3.0
1995	15	99.2	14	273−393	20	10.0
2000	16	99.0	3	283−313	20	1.0
2002	this work	99.95	37	233−399	5	0.7

On the basis of the present vapor pressure measurements, a Wagner type vapor equation of dimethyl ether was fitted.

$$\ln(P_r) = (A_1\tau + A_2\tau^{1.5} + A_3\tau^{3.0} + A_4\tau^{6.0})T_r^{-1} \tag{2}$$

where $P_r = P/P_c$, $T_r = T/T_c$, $\tau = 1 - T_r$, T_c is the critical temperature of dimethyl ether (400.378 K), and P_c is the critical pressure of dimethyl ether, found to be 5355.8 kPa by fitting eq 2 to data. The parameters A_1, A_2, A_3, and A_4 in eq 2 are −7.027 754, 1.638 934, −3.302 604, and 11.935 528, respectively. The applicable range of temperature is from 233 K to the critical temperature.

Comparisons

Only Kennedy[5] had systemically measured the vapor pressure of pure dimethyl ether at temperatures from (171.63 to 248.24) K, and a vapor pressure equation was given, but the form was complicated. Using these experimental data, Boublik et al.[6] correlated an Antoine type vapor pressure equation of dimethyl ether, and McGarry[7] correlated a Wagner type vapor pressure equation. These vapor pressure equations of dimethyl ether are compiled in published monographs[8−10] and chemical handbooks.[11,12] In addition, other researchers have measured some experimental data points, but the studies were not systematically carried out or the accuracy is limited. The details are shown in Table 2.

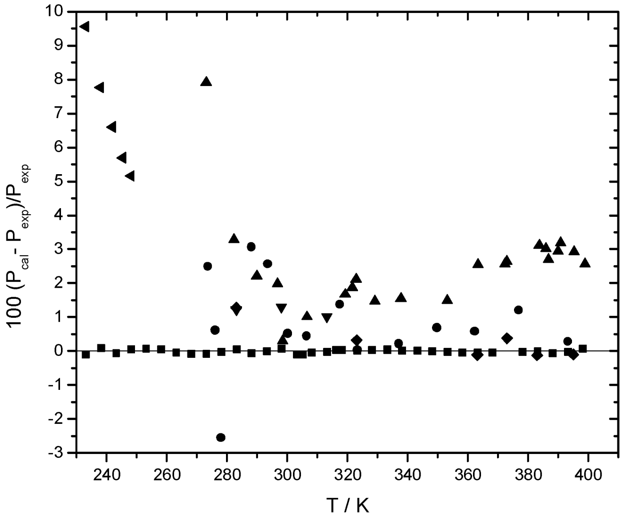

Figure 2. Deviation of the vapor pressure data from eq 2: (■) this work; (●) Jonasson et al.;[15] (▲) Cardoso andBruno;[13] (▼) Bobbo et al.;[16] (◆) Noles and Zollweg;[14](solid triangle pointing left) Kennedy et al.[5]

The relative deviations from eq 2 of all the measured values, including the present measurements, are shown in Figure 2. The maximum deviation and the average deviation of this work are 0.096% and 0.043%, respectively. But there are distinct deviations among the earlier published measurements, and the largest deviation is 9.56% at the temperature 233.13 K. We think that the reason for the deviation of published data is the limited precision and accuracy of their instruments, and the purity of sample is not as good as that for this work.

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