

# Saturated Pressure Measurements of Dimethyl Ether at Temperatures from (219 to 361) K

Francesco Corvaro, Giovanni Di Nicola,\* Fabio Polonara, and Giulio Santori

Dipartimento di Energetica, Università Politecnica delle Marche, Via Brecce Bianche, 60100 Ancona, Italy

The vapor pressure data of dimethyl ether (RE170), an ozone-friendly refrigerant, was measured using a constant-volume apparatus. Measurements were carried out at temperatures from (219 to 361) K and at pressures from (22 to 2622) kPa. A total of 71 experimental points were obtained. The measurements were fitted to a Wagner-type equation and an absolute deviation of 0.26 %. After a literature survey of the saturated pressure experimental findings, our experimental results were compared with the REFPROP 7.0 prediction together with the published data.

## Introduction

Dimethyl ether is an important chemical material and has many engineering applications. It is now developed as a substitute of engine fuel for gasoline, as an assistant solvent, and as an aerosol propellant. It can be made from coal, natural gas, residual oil, oil coke, and other biological materials. Its production cost is very low. In addition, dimethyl ether is nontoxic and noncarcinogenic. Considering that dimethyl ether has zero ozone depletion potential (ODP), zero global warming potential (GWP), and good thermodynamic properties, it was also suggested as an alternative refrigerant (RE170). In particular for air conditioning systems applications, the mixture of 60 % in mass of ammonia and 40 % in mass of dimethyl ether forms an interesting azeotrope (R723). For all these reasons, the study of its thermophysical properties is very important.

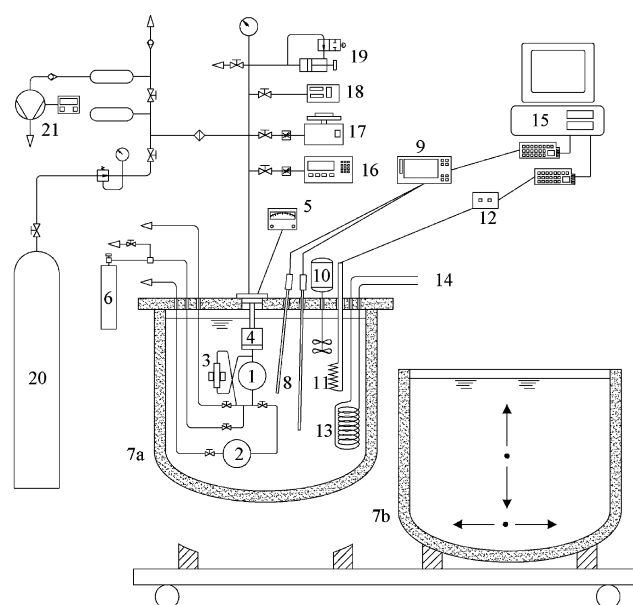
In the saturation region, excluding very old and less precise data,<sup>1,2</sup> accurate experimental data for RE170 are not very numerous. In fact, in the last few years, a limited number of points have been collected by different laboratories while studying the VLE of its binary systems.<sup>3–12</sup> Confirming the rising interest on this fluid, an intensive research was recently carried out in terms of critical parameters,<sup>13</sup> surface tension,<sup>14</sup> viscosity,<sup>15</sup> and thermal conductivity<sup>16</sup> by Wu and co-workers. Inside this research project, quite a large amount of vapor pressure data at temperatures from (233 to 399) K were collected by the same authors.<sup>17</sup> Furthermore, large differences among the published experimental vapor pressure data are evident.

For these reasons, 71 experimental points were collected in the two-phase region in a temperature range from (219 to 361) K. Experimental observations were regressed with a Wagner-type equation. A comparison of all the available data through the REFPROP 7.0<sup>18</sup> prediction in a special version for this specific fluid<sup>19</sup> was also carried out.

## Experimental Section

**Materials.** The sample was provided by Aldrich Inc. (Milwaukee, WI). It was de-aerated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography

\* Corresponding author. Tel: +39-0712204277. Fax: +39-0712204770. E-mail: g.dinicola@univpm.it.



**Figure 1.** Schematic illustration of the apparatus: 1, constant volume spherical cell; 2, auxiliary cell; 3, magnetic pump; 4, differential pressure transducer; 5, electronic null indicator; 6, charging system; 7, thermostatic baths; 8, platinum thermoresistances; 9, thermometric bridge; 10, stirrer; 11, heater; 12, power system; 13, cooling coil; 14, connections to auxiliary thermostatic bath; 15, acquisition system; 16, Bourdon gage; 17, dead weight gage; 18, vibrating cylinder pressure gage; 19, precision pressure controller; 20, nitrogen reservoir; 21, vacuum pump system.

using a thermal conductivity detector and was found to be better than 99.8 % in molar basis by analysis of peak area.

**Apparatus.** The new experimental setup is illustrated in Figure 1. The basic experimental setup has already been described elsewhere,<sup>20</sup> so it is only briefly outlined here. Two twin thermostatic baths were filled with different silicone oils (Baysilone M10 and Baysilone M100, Bayer). After charging with the sample, the setup could be operated over two temperature ranges, approximately from (210 to 290) K and from (290 to 360) K, depending on which bath was used. The two silicone oils have different kinematic viscosity values (10 and 100 cSt at room temperature, respectively). The one with lower kinematic viscosity, due to its higher volatility, was applied only for the low temperature range, while that with a

**Table 1. Experimental Saturation Pressures  $P$  at Temperature  $T$  for RE170**

$T_{90}/\text{K}$	$P/\text{kPa}$	$T_{90}/\text{K}$	$P/\text{kPa}$	$T_{90}/\text{K}$	$P/\text{kPa}$	$T_{90}/\text{K}$	$P/\text{kPa}$
219.15	22.3	259.14	159.0	295.07	540.0	329.02	1319.9
221.13	25.2	261.13	171.8	297.07	573.0	331.11	1385.3
223.11	28.3	263.13	185.6	299.08	606.9	333.11	1450.6
224.88	31.5	265.13	199.8	301.11	643.1	335.11	1518.8
226.88	35.4	267.13	215.5	303.08	680.2	337.10	1588.4
228.85	39.5	269.13	231.8	305.07	718.4	339.10	1660.3
230.86	43.9	271.13	248.9	307.07	758.8	341.08	1733.3
232.86	48.7	273.13	266.8	309.06	800.7	343.09	1811.3
234.85	54.1	275.04	285.1	311.07	844.2	345.09	1891.2
236.85	59.8	277.02	305.0	313.06	889.5	347.08	1972.8
239.14	66.3	279.02	326.4	315.06	936.6	349.08	2057.4
241.14	73.2	281.02	348.8	317.04	985.3	351.07	2144.3
244.14	84.0	283.02	372.3	319.03	1036.0	353.05	2232.7
247.13	96.1	285.01	397.0	321.03	1088.7	355.05	2326.0
249.13	104.9	287.00	422.8	323.02	1143.3	357.05	2421.9
251.14	114.3	288.99	449.8	325.02	1200.6	359.05	2520.3
255.13	135.1	290.99	478.4	327.13	1262.3	361.04	2621.5
257.12	146.6	293.08	508.9				

greater viscosity was applied only at high temperatures. The thermostatic baths were easy to move thanks to the new system configuration. The spherical cells and pressure transducer are immersed in one of the two thermostatic baths. An auxiliary thermostat was used to reach below-ambient temperatures. The cell volume was estimated to be  $(273.5 \pm 0.3) \text{ cm}^3$  at room temperature,<sup>20</sup> and the cell volume change with temperature was taken into account.<sup>21</sup> The pressure and temperature data acquisition systems were identical to those of the previous apparatus.<sup>21,22</sup> A PID device was used to control the temperature, which was measured using a calibrated resistance thermometer; the total uncertainty of the temperature measurements was  $\pm 0.02 \text{ K}$ . The uncertainty in the pressure measurements stems from the uncertainty of the transducer and null indicator system and the pressure gauges. The uncertainty of the digital pressure indicator (Ruska, model 7000) is  $\pm 0.003 \%$  of its full scale. Temperature fluctuations due to bath instability can also affect the total uncertainty in the pressure measurement, which was nonetheless found to be less than  $\pm 1 \text{ kPa}$ . The charging procedure by gravimetric method has been described elsewhere.<sup>23</sup>

## Results and Discussion

**Vapor Pressure.** The experimental vapor pressures at temperatures in the range (219 K to 361) K are given in Table 1. Experimental data were fit to the four-parameter Wagner equation:

$$\ln \frac{P}{P_c} = \frac{T_c}{T} [A_1 \tau + A_2 \tau^{1.5} + A_3 \tau^2 + A_4 \tau^5] \quad (1)$$

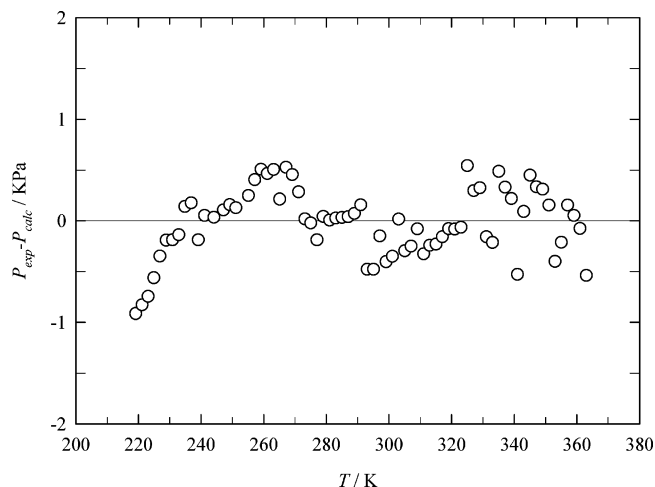
where  $\tau = (T_c - T)/T_c$ ; the critical temperature  $T_c = 400.1 \text{ K}$ .<sup>18</sup> The following values were found for the parameters:  $A_1 = -7.40714$ ,  $A_2 = 3.42409$ ,  $A_3 = -2.97850$ , and  $A_4 = -3.43070$ . From the fitting procedure, the critical pressure was fixed to be  $P_c = 5370.2 \text{ kPa}$ .<sup>18</sup>

Defining the deviations in pressure as

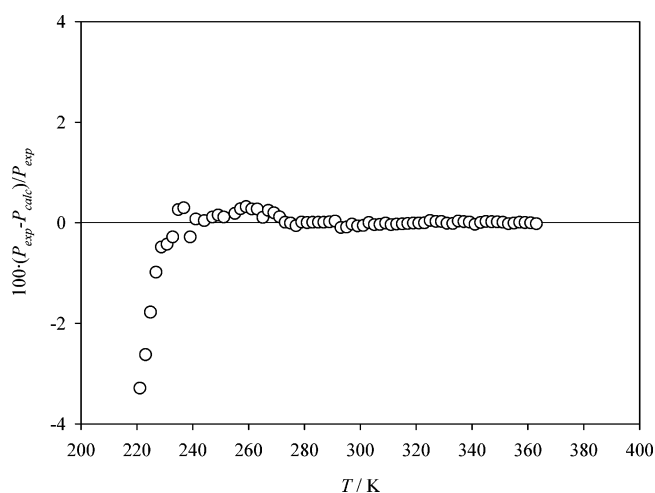
$$dP = \frac{1}{n} \sum_{i=1}^n [(P_{\text{exp}} - P_{\text{calc}})/P_{\text{exp}}] \times 100 \quad (2)$$

$$|dP| = \frac{1}{n} \sum_{i=1}^n [| (P_{\text{exp}} - P_{\text{calc}}) / P_{\text{exp}} |] \times 100 \quad (3)$$

where  $n$  is the number of experimental points, the following



**Figure 2.** Scatter diagram of the saturated pressure absolute deviations from the fit with the Wagner equation (eq 1).



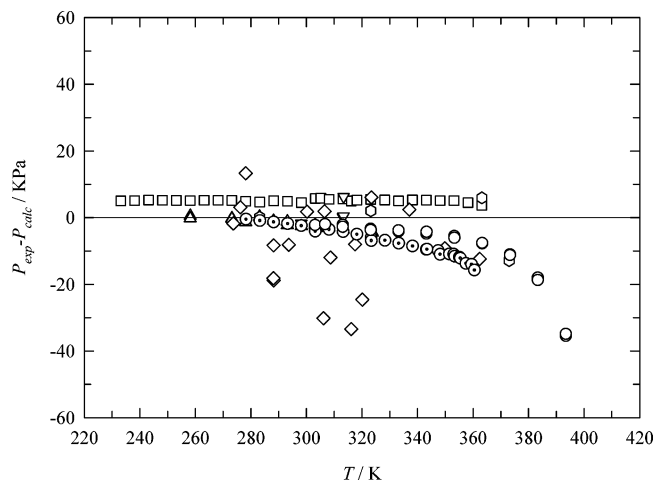
**Figure 3.** Scatter diagram of the saturated pressure relative deviations from the fit with the Wagner equation (eq 1).

values were found:  $dP = 0.16 \%$  and  $\text{abs}(dP) = 0.26 \%$ . The error distribution is shown in Figures 2 and 3. The absolute deviations were found to be well distributed within  $\pm 1 \text{ kPa}$ , while the relative deviations were found to be within  $\pm 1 \%$ , excluding a few points at the lower temperatures that, due to the very low experimental pressures, produced higher deviations in percent.

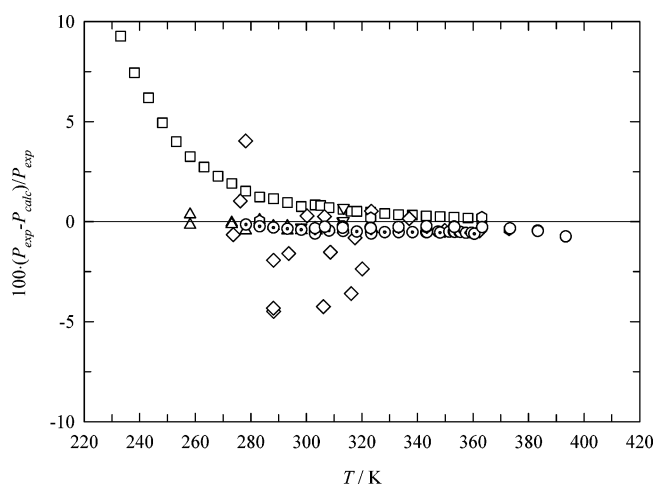
The experimental results were also compared with the published data in the literature. In Figures 4 and 5 are reported absolute and relative deviations for the literature data<sup>3-12,17</sup> from eq 1.

Most of the deviations are well within  $\pm 10 \text{ kPa}$ , showing a general consistency between the sources; a systematic shift of  $5 \text{ kPa}$  was found only for one source,<sup>17</sup> while higher deviations were found at temperatures greater than  $320 \text{ K}$  for two sources.<sup>11,12</sup> The common trend but the systematic shift found with one source<sup>17</sup> could be due to the different sample purity.

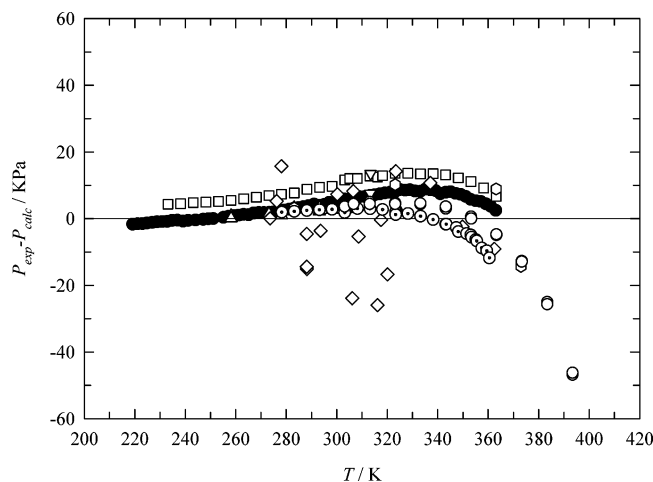
Our experimental results were also compared with REFPROP 7.0 together with the published data in the literature. In Figure 6, the distribution of deviations between the literature sources and REFPROP 7.0 is shown. From Figure 6, it is evident that the same trend (but with slightly shifted results) was obtained by comparing the present work data with the more recent and numerous ones.<sup>11,12,17</sup> Excluding again one source,<sup>17</sup> a very good agreement for temperatures between (250 and 300) K was obtained.<sup>11,12</sup> An excellent agreement was also obtained with



**Figure 4.** Vapor pressure absolute deviations of RE170 from eq 1 and measurements published in the literature:  $\nabla$ , ref 3;  $\circ$ , ref 4;  $\diamond$ , ref 5;  $\Delta$ , refs 6–10;  $\odot$ , ref 11;  $\circ$ , ref 12;  $\square$ , ref 17.

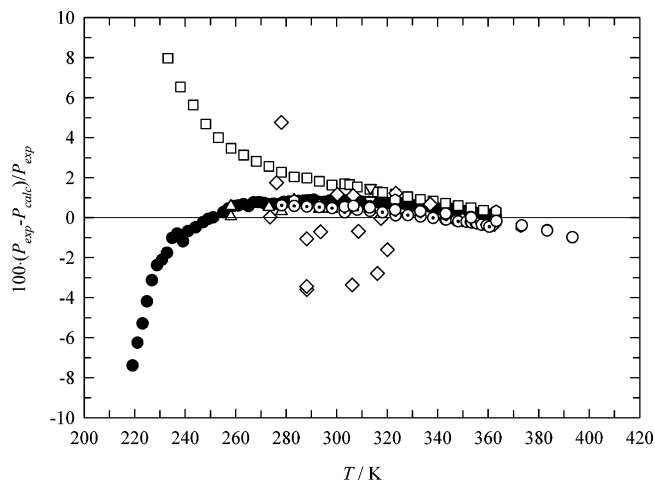


**Figure 5.** Vapor pressure relative deviations of RE170 from eq 1 and measurements published in the literature:  $\nabla$ , ref 3;  $\circ$ , ref 4;  $\diamond$ , ref 5;  $\Delta$ , refs 6–10;  $\odot$ , ref 11;  $\circ$ , ref 12;  $\square$ , ref 17.



**Figure 6.** Vapor pressure absolute deviations of RE170 from REFPROP 7.0 and measurements published in the literature:  $\bullet$ , present work;  $\nabla$ , ref 3;  $\circ$ , ref 4;  $\diamond$ , ref 5;  $\Delta$ , refs 6–10;  $\odot$ , ref 11;  $\circ$ , ref 12;  $\square$ , ref 17.

sources obtained by direct VLE measurements.<sup>6–10</sup> In general, agreement with REFPROP 7.0 was good, even if measurements had lower temperatures (less than 250 K) as shown in Figure 7, again due to the very low experimental pressures, systematic negative relative deviations.



**Figure 7.** Vapor pressure relative deviations of RE170 from REFPROP 7.0 and measurements published in the literature:  $\bullet$ , present work;  $\nabla$ , ref 3;  $\circ$ , ref 4;  $\diamond$ , ref 5;  $\Delta$ , refs 6–10;  $\odot$ , ref 11;  $\circ$ , ref 12;  $\square$ , ref 17.

## Conclusions

The measurements of 71 experimental points for saturated pressure were obtained using a constant-volume apparatus for RE170. The experimental points taken within the VLE boundary were fitted with a Wagner-type equation. The experimental VLE data were compared with the REFPROP 7.0 prediction and with recently published data. A generally good consistency between the different sources was found.

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