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Citation for published version:

Corvaro, F, Di Nicola, G, Polonara, F & Santori, G 2006, 'Saturated pressure measurements of dimethyl ether at temperatures from (219 to 361) K' Journal of Chemical and Engineering Data, vol. 51, no. 4, pp. 1469-1472. DOI: 10.1021/je060148j

Digital Object Identifier (DOI):

[10.1021/je060148j](https://doi.org/10.1021/je060148j)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Journal of Chemical and Engineering Data

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

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Abstract

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.

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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 assistant solvent and aerosol propellant.

It can be made from coal, natural gas, residual oil, oil coke, and other biological materials and its production cost is very low. In addition dimethyl ether has non-toxicity and non-carcinogenity.

Considering that dimethyl ether has zero Ozone Depletion Potential (ODP) and zero Global Warming Potential (GWP), and for its 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,^{1,2} accurate experimental data for RE170 are not very numerous. In fact, since last years a limited number of points was collected by different laboratories while studying the VLE of its binary systems.³⁻¹² Confirming the rising interest on this fluid, an intensive research was recently carried in terms of critical parameters,¹³ surface tension,¹⁴ viscosity,¹⁵ thermal conductivity¹⁶ by Wu and co-workers. Inside this research project, a quite large amount of vapor pressure data at temperatures from (233 to 399) K were collected by the same authors.¹⁷

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 spanning from (219 to 361) K. Experimental observations were regressed with a Wagner-type equation. A comparison of all the available data through the REFPROP 7.0¹⁸ prediction in a special version for this specific fluid¹⁹ was also carried out.

Experimental Section

Materials. The sample was provided by Aldrich Inc., USA. It was de-aereated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography 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 set-up is illustrated in Figure. 1. The basic experimental set-up has already been described elsewhere,²⁰ 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 set-up 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 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 ± 0.3) cm³ at room temperature²⁰ and the cell volume change with temperature was taken into account.²¹ The pressure and temperature data acquisition systems were identical to those of the previous apparatus.^{21,22} 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 ± 0.02 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, mod. 7000) is ± 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 ± 1 kPa. The charging procedure by gravimetric method has been described elsewhere.²³

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 $T_c = 400.1$ K.¹⁸

The following values were found for the parameters: $A_1 = -7.40714$, $A_2 = 3.42409$, $A_3 = -2.97850$, $A_4 = -3.43070$. From the fitting procedure, the critical pressure was fixed to be $P_c = 5370.2$ kPa.¹⁸

Defining the deviations in pressure as

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

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

where n is the number of experimental points, the following 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 ± 1 kPa, while the relative deviations were found to be within $\pm 1\%$, excluding 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^{3-12,17} from equation 1.

Most of the deviations are well within ± 10 KPa, showing a general consistency between the sources; a systematic shift of 5 KPa was found only for one source,¹⁷ while higher deviations were found at temperatures greater than 320 K for two sources.^{11,12} The common trend but the systematic shift found with one source¹⁷ 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 comparing the present work data with the more recent and numerous ones.^{11,12,17} Excluding again one source,¹⁷ a very good agreement for temperatures between 250 and 300 K was obtained.^{11,12} An excellent agreement was also obtained with sources obtained by direct VLE measurements.⁶⁻¹⁰ In general, agreement with REFPROP 7.0 was good, even if measurements with lower temperatures (less than 250 K) showed in Figure 7, again due to the very low experimental pressures, systematic negative relative deviations.

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 and a generally good consistency between the different sources was found.

Acknowledgement

This work was supported by MIUR, the Ministry of Education, University and Research.

Figure captions

Figure 1. Schematic illustration of the apparatus.

- | | |
|-------------------------------------|--|
| 1. Constant volume spherical cell | 12. Power system |
| 2. Auxiliary cell | 13. Cooling coil |
| 3. Magnetic pump | 14. Connections to auxiliary thermostatic bath |
| 4. Differential pressure transducer | 15. Acquisition system |
| 5. Electronic null indicator | 16. Bourdon gage |
| 6. Charging system | 17. Dead weight gage |
| 7. Thermostatic baths | 18. Vibrating cylinder pressure gage |
| 8. Platinum thermo-resistances | 19. Precision pressure controller |
| 9. Thermometric bridge | 20. Nitrogen reservoir |
| 10. Stirrer | 21. Vacuum pump system |
| 11. Heater | |

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.

Figure 4. Vapor pressure absolute deviations of RE170 from eq. 1 and measurements published in the literature:

- | | | | |
|----------|-------------|-----------|-----------|
| ▽ Ref. 3 | ◇ Ref. 5 | ⊙ Ref. 11 | □ Ref. 17 |
| ⊙ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 | |

Figure 5. Vapor pressure relative deviations of RE170 from eq.1 and measurements published in the literature:

- | | | | |
|----------|-------------|-----------|-----------|
| ▽ Ref. 3 | ◇ Ref. 5 | ⊙ Ref. 11 | □ Ref. 17 |
| ⊙ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 | |

Figure 6. Vapor pressure absolute deviations of RE170 from REFPROP 7.0 and measurements published in the literature:

- | | | | |
|----------------|----------|-------------|-----------|
| ● Present work | ◊ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |
| ▽ Ref. 3 | ◇ Ref. 5 | ⊙ Ref. 11 | □ Ref. 17 |

Figure 7. Vapor pressure relative deviations of RE170 from REFPROP 7.0 and measurements published in the literature:

- | | | | |
|----------------|----------|-------------|-----------|
| ● Present work | ◊ Ref. 4 | △ Ref. 6-10 | ○ Ref. 12 |
| ▽ Ref. 3 | ◇ Ref. 5 | ⊙ Ref. 11 | □ Ref. 17 |

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Ta

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

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

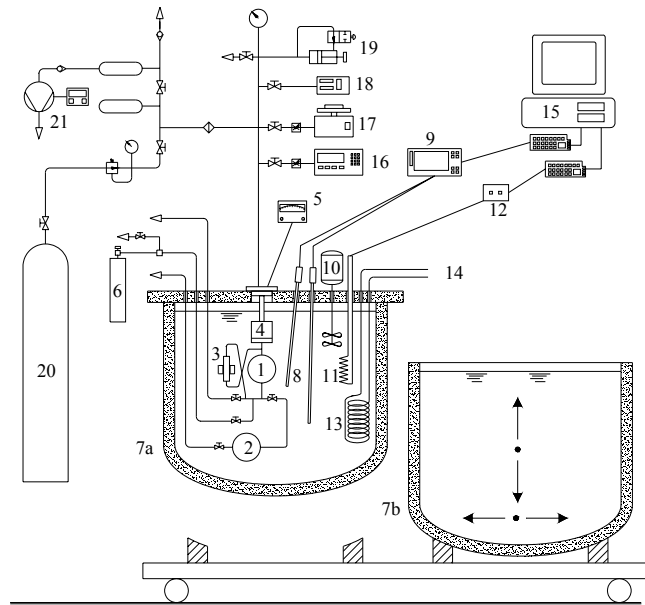


Figure 1

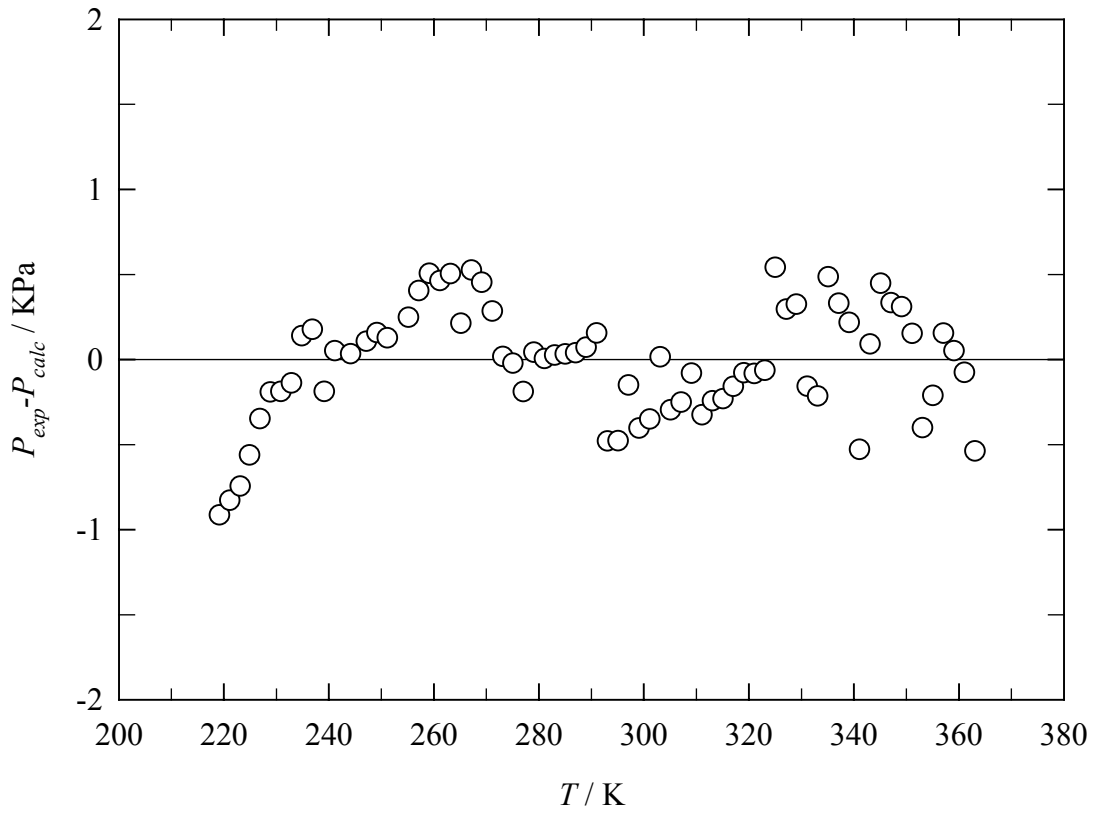


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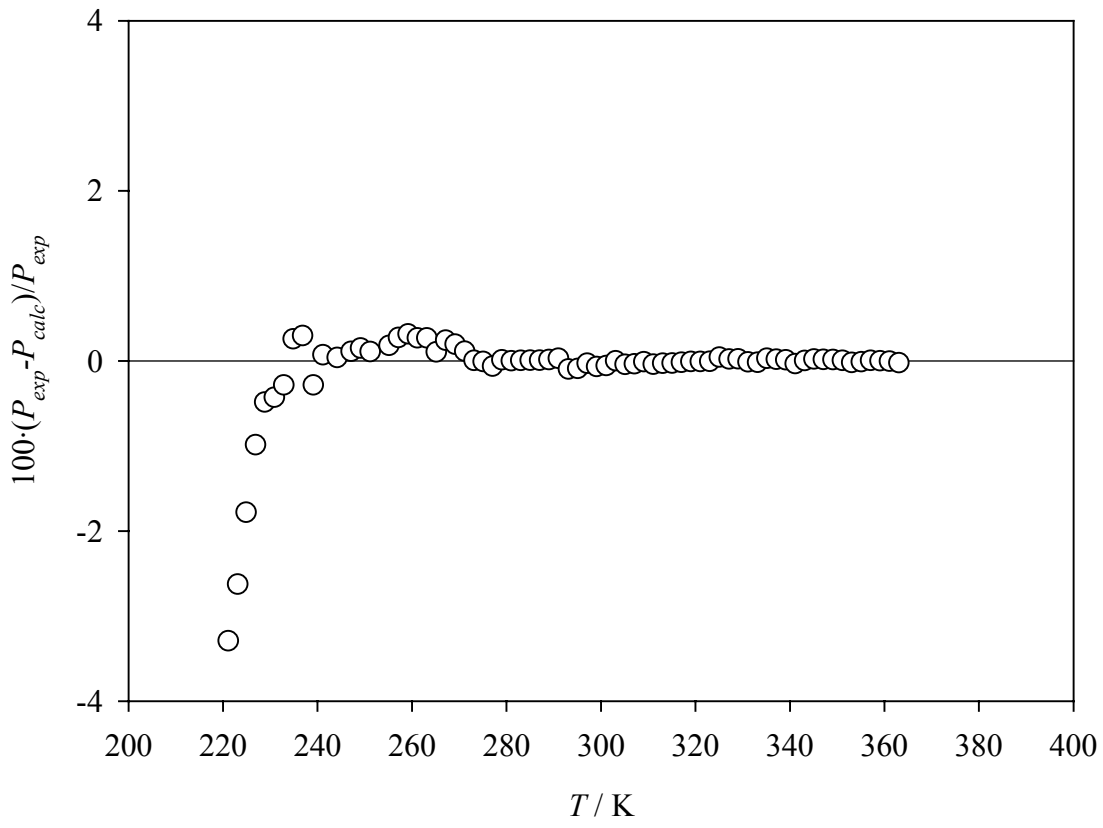


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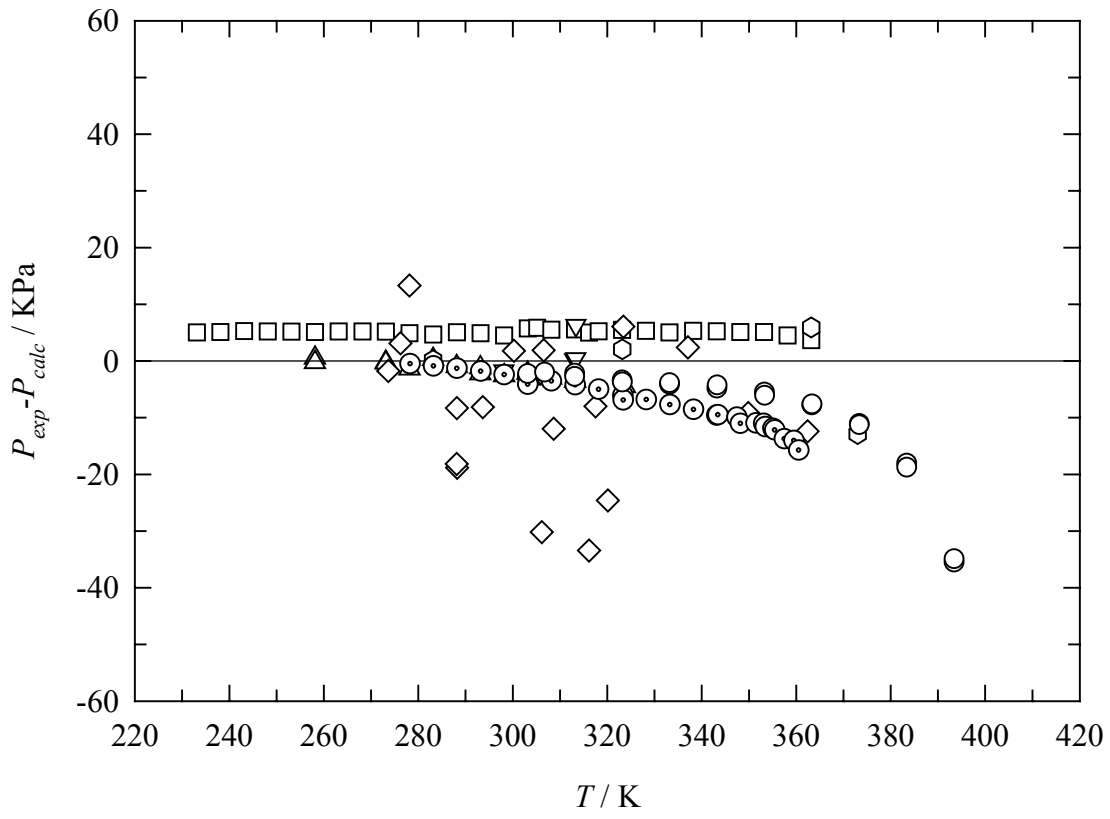


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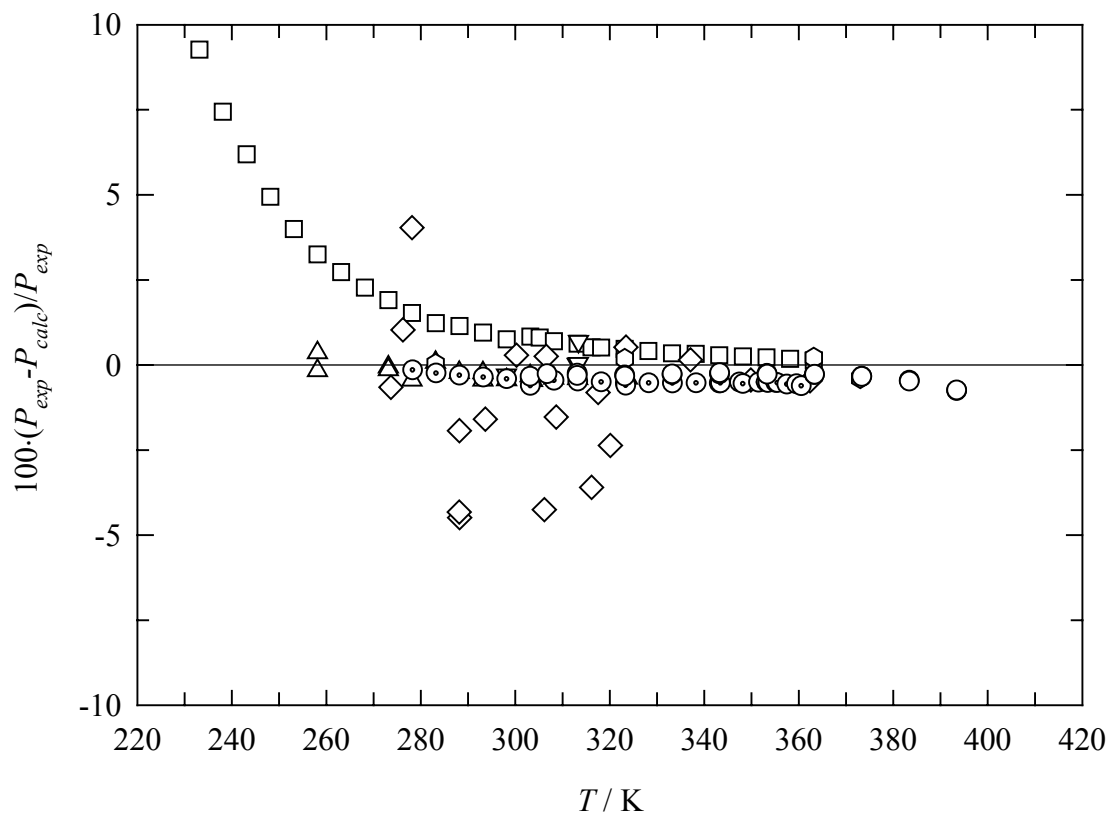


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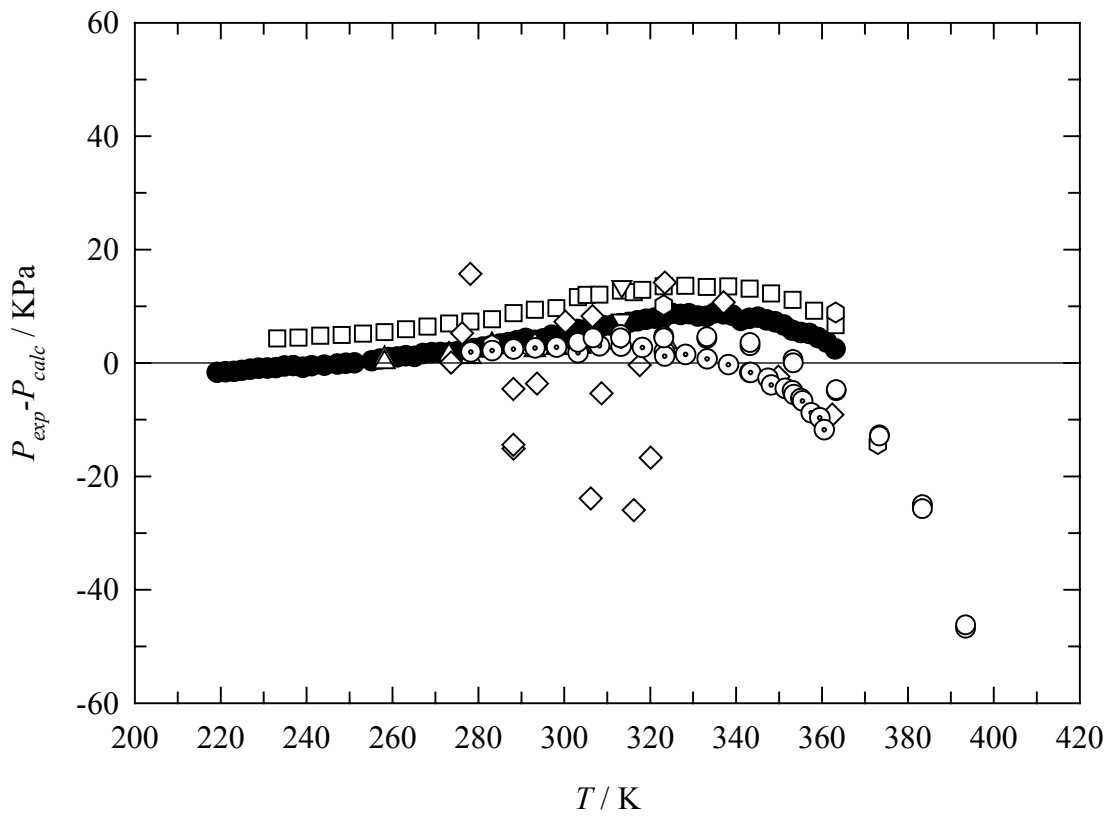


Figure 6.

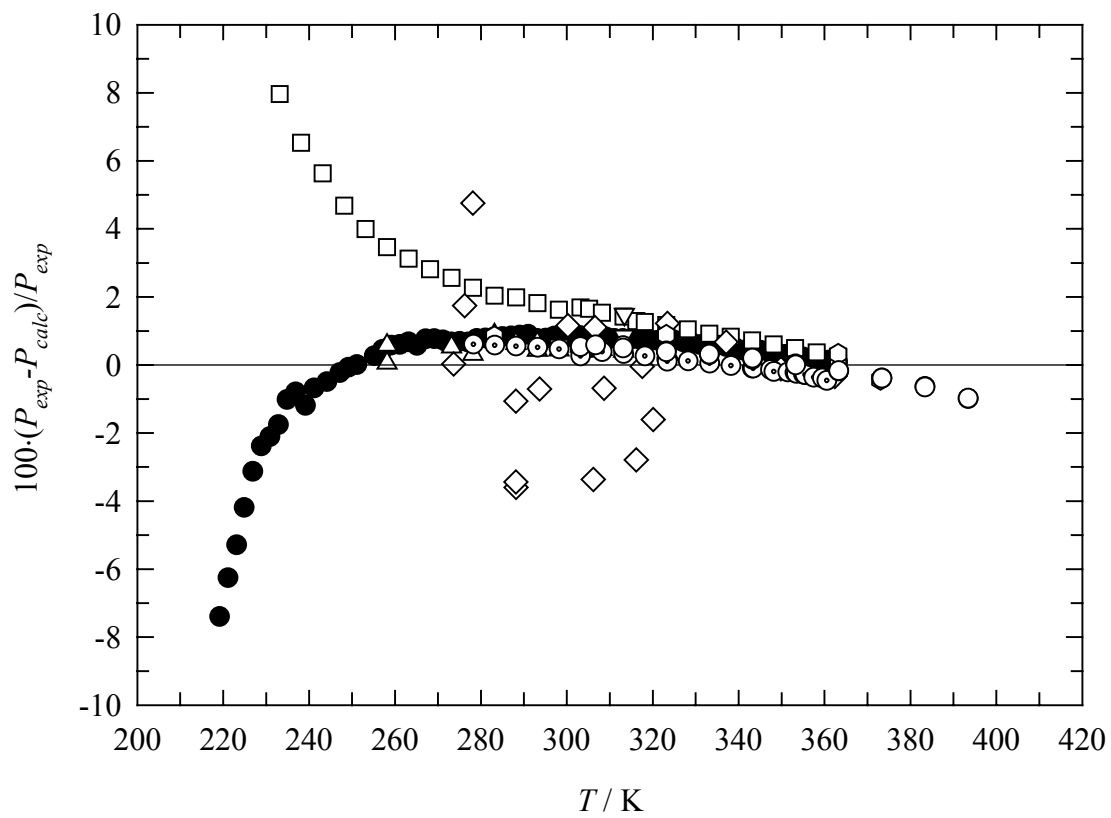


Figure 7.