

PVT properties of an alternative biofuel: dimethyl ether

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Abstract Dimethyl ether is an important chemical material and it has many engineering applications. It is a clean and economical alternative fuel and an ozone-friendly refrigerant. In this work, its *PVT* properties have been object of study. In particular, the experimental work was performed both in the two-phase region and in the superheated vapor region phase by means of the isochoric method. The isochoric measurements were carried out at temperatures from 219 K to 363 K and at pressures from 22 kPa up to 1,740 kPa. A total of 159 points, both in the two phase (71 points) and in the superheated vapor region (88 points) were obtained. The present experimental *PVT* data contribute to the deeper knowledge of the behaviour of the fluid both in the superheated vapour and in the saturation pressure region and to the development of a new equation of state.

Keywords Biofuel · Dimethyl ether · *PVT* · Thermophysical properties

Introduction

Dimethyl Ether (DME— CH_3OCH_3) is the simplest ether. It is a clean and ecological fluid which can be produced from

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various resources as natural gas, coal or biomass through synthesis gas. Its physical and thermophysical properties, compared to the ones of methane, propane, butane, and methanol, are reported in Table 1. From the present table it is evident that its properties are very similar to those of liquefied petroleum gases (i.e., butane or propane). For this reason it can be distributed and stored using the LPG handling technology. It can be used for various fields such as alternative fuel [1] and natural refrigerant (RE 170) [2].

In the case of burning DME, there are no emissions of SO_x or particulate and the emissions of NO_x and CO_2 are extremely small. In addition, its GWP is of 0.3 per 100 years [3]. For all these reasons, its thermophysical properties were recently studied [4] and a fundamental equation of state was also derived [5]. In this work, vapor pressures and *PVT* measurements are presented. Vapor pressures were compared with existing literature sources.

Experimental section

Reagents

DME was supplied by Aldrich Inc., USA., and its purity was checked by gas chromatographic analysis, using a thermal conductivity detector. It was found to be 99.8% on an area-response basis.

Experimental devices

In this paper, the adopted device is the same described elsewhere [6, 7] with no modifications. Here, only a brief description is reported. The constant-volume apparatus with a volume of 273.5 cm^3 was used for the two-phase measurements.

Table 1 Comparison of physical and thermophysical properties of DME and similar fuels

Fuel	DME	Methane	Propane	Butane	Methanol
Chemical formula	CH ₃ OCH ₃	CH ₄	C ₃ H ₈	C ₄ H ₁₀	CH ₃ OH
Boiling point (°C)	−25.1	−161.5	−42.0	−0.5	64.6
Liquid density (g/cm ³ , @20 °C)	0.67	–	0.49	0.57	0.79
Molecular mass (g/mol)	44.068	16.043	44.096	58.122	32.042
Triple point (°C)	−141.5	−182.46	−187.62	−138.26	−97.54
Critical temperature (°C)	127.15	−82.586	96.74	151.98	239.45
Critical pressure (atm)	52.71	45.39	41.96	37.46	79.98
Specific gravity of gas (vs. air)	1.59	0.55	1.52	2.0	–
Saturated vapor pressure (atm, @25 °C)	6.1	–	9.3	2.4	0.17
Ignition point (°C)	235	650	470	430	450
Explosion limit (%)	3.4–1.7	5–15	2.1–9.4	1.9–8.4	5.5–36
Cetane number	55–60	0	5	10	5
Net calorific value (kcal/kg)	6.9	12	11.1	10.93	4.8

An AISI 304 stainless steel spherical cell containing the refrigerant sample is connected to a differential diaphragm pressure transducer coupled to an electronic null indicator. The transducer and sphere were placed vertically, and a magnetic pump for mixing the sample was connected to the sphere. A second spherical cell was also connected and used for volume calibration. Because of the complex volume of the isochoric cell, its total volume (including the piping, the pressure transducer cavity, and magnetic pump volumes) was calibrated according to the classic Burnett calibration procedure, adopting helium as the reference fluid.

The spherical cells and pressure transducer are immersed in two thermostatic baths containing different silicon oils and alternatively used for measurements at different temperature ranges. Both baths are controlled by a Proportional Integrative Derivative (PID) device. An auxiliary bath, also controlled by a PID device, helps the system to keep the temperature constant. A platinum resistance thermometer is immersed near the cell and is connected to a digital indicator.

Mixtures were prepared using the gravimetric method. The sample was first placed in different bottles, degassed to remove noncondensable gases and air, and weighed with an analytical balance. After evacuating the cell, the bottles were discharged into the cell immersed in the bath. At the end of this procedure, the bottles were weighed, and the mass of the charge was calculated from the difference between the two weights. The lost mass inside the duct was estimated and subtracted from the total mass of the charge.

Experimental uncertainties

The uncertainty in the temperature measurements is due to the thermometer and any instability of the bath. The stability of the bath was found to be less than ± 0.015 K and the uncertainty of the thermometer was found to be less than ± 0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than ± 0.03 K. Any uncertainty in the pressure measurements is due to the transducer and null indicator system, and to the pressure gauge. The digital pressure indicator (Ruska, mod. 7000) has an uncertainty of $\pm 0.003\%$ of the full scale. The total uncertainty in the pressure measurement, also influenced by temperature fluctuations due to bath instability, was found to be less than ± 1 kPa.

To check the experimental repeatability, some measurements were repeated under the same experimental conditions. The obtained data were always found to be in agreement with the experimental ones and well within the experimental uncertainty.

Results and discussions

In total, 159 experimental points for dimethyl ether were obtained. By the isochoric method, 71 data points were collected in the two-phase region and reported elsewhere [8], while 88 data were collected along 6 isochores in the superheated vapor region. The experimental points taken

Table 2 Experimental PVT data for DME

<i>T</i> /K	<i>P</i> /kPa	<i>V</i> /dm ³ mol ⁻¹	<i>T</i> /K	<i>P</i> /kPa	<i>V</i> /dm ³ mol ⁻¹
m = 2.91 g			m = 6.14 g		
298.08	535.4	4.332	321.05	1077.8	2.055
301.26	542.9	4.333	325.04	1109.6	2.056
308.03	558.4	4.334	329.03	1129.9	2.056
313.13	568.8	4.335	333.03	1150.4	2.056
318.12	578.2	4.336	337.00	1167.9	2.057
323.01	587.9	4.337	340.99	1186.8	2.057
328.09	597.5	4.338	344.98	1205.4	2.058
332.99	607.1	4.339	348.97	1223.8	2.058
338.16	617.0	4.340	352.96	1242.0	2.058
342.96	626.2	4.341	356.45	1260.1	2.059
348.13	636.1	4.342	360.97	1278.6	2.059
352.92	645.0	4.343	362.98	1287.7	2.059
357.81	654.3	4.344			
m = 3.39 g			m = 7.52 g		
297.08	583.60	3.719	329.05	1316.9	1.679
299.08	593.66	3.719	331.04	1329.4	1.679
301.08	599.95	3.720	333.03	1347.1	1.679
303.07	605.94	3.720	335.03	1360.2	1.679
309.06	622.32	3.721	337.03	1373.2	1.679
310.93	627.89	3.721	339.02	1385.9	1.680
313.05	632.84	3.721	341.01	1398.2	1.680
317.06	643.06	3.722	343.01	1410.4	1.680
321.02	653.13	3.723	345.00	1422.5	1.680
325.07	663.44	3.723	347.02	1434.8	1.680
329.03	673.15	3.724	348.99	1446.7	1.680
333.08	683.23	3.725	351.01	1459.1	1.680
337.03	693.07	3.725	353.00	1470.9	1.681
341.06	702.99	3.726	355.00	1482.8	1.681
345.05	712.79	3.727	356.99	1494.2	1.681
349.02	722.77	3.727	359.00	1506.0	1.681
353.02	732.47	3.728	361.03	1517.9	1.681
357.01	742.16	3.729	363.01	1529.6	1.681
362.93	756.45	3.730			
m = 4.78 g			m = 8.97 g		
308.27	777.4	2.639	337.00	1552.4	1.408
313.15	810.5	2.639	338.98	1563.7	1.408
318.05	828.5	2.640	340.98	1580.5	1.408
323.01	846.5	2.640	342.98	1595.7	1.408
328.17	865.1	2.641	344.98	1610.7	1.408
333.18	883.0	2.642	346.96	1625.2	1.409
337.95	900.0	2.642	348.96	1639.8	1.409
343.26	918.7	2.643	350.95	1654.3	1.409
348.21	936.0	2.643	352.95	1668.8	1.409
353.08	952.9	2.644	354.94	1683.1	1.409
357.99	969.8	2.644	356.93	1697.2	1.409
362.36	984.9	2.645	358.93	1715.5	1.409
			360.91	1730.3	1.409
			362.94	1743.6	1.410

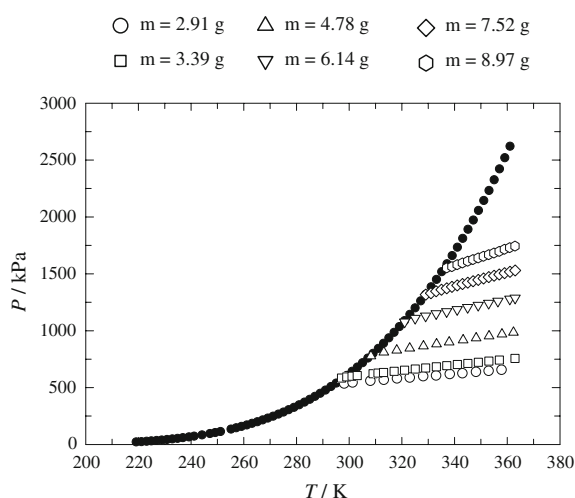


Fig. 1 Summary of the experimental *PVT* data. Black symbol data were reported in Ref. [7]. *open hexagon* $m = 2.91$ g; *open triangle* $m = 4.78$ g; *open diamond* $m = 7.52$ g; *open square* $m = 3.39$ g; *inverted open triangle* $m = 6.14$ g; *open diamond* $m = 8.97$ g

within the VLE boundary were fitted with a Wagner type equation. The experimental VLE data were compared with recently-published data and a generally good consistency between the different sources was found. The vapor phase data are reported in Table 2. A summary of the experimental measurements is showed in Fig. 1.

Vapor pressure data

The 71 vapor pressure points were obtained at temperatures from 219 to 361 K and for pressures from 22 to 2,622 kPa. Experimental data were fit to the four-parameter Wagner equation,

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

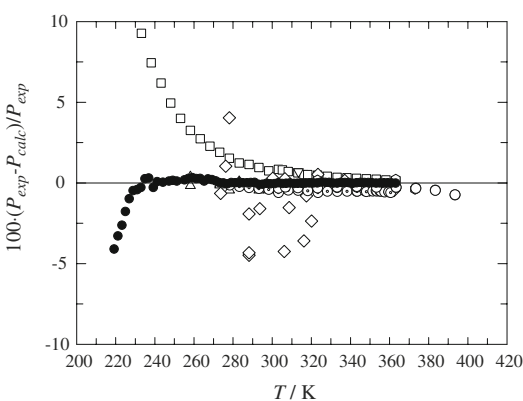
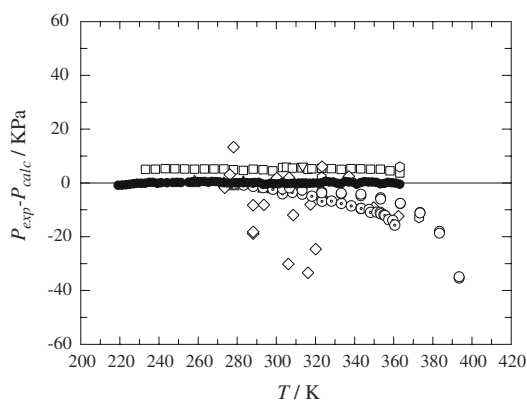


Fig. 2 Vapor pressure absolute (*left*) and relative (*right*) deviations of DME from Eq. 1 and measurements published in the literature (as reported in Ref. [7])

where $\tau = (T_c - T)/T_c$; the critical temperature $T_c = 400.1$ K [9]. The following values were found for the parameters: $A_1 = -7.40714$, $A_2 = 3.42409$, $A_3 = -2.97850$, $A_4 = -3.43070$, reproducing data with $dP = 0.16\%$ and $\text{abs}(dP) = 0.26\%$. In the fitting procedure, the critical pressure was fixed to be $P_c = 5370.2$ kPa [9]. The analysis of the recent literature showed that a total of 11 data sources are available [10–20]. The experimental results were also compared with the published data in the literature. In Fig. 2 are reported absolute and relative deviations for the literature data from Eq. 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 [20], while higher deviations were found at temperatures greater than 320 K for two sources [14, 15].

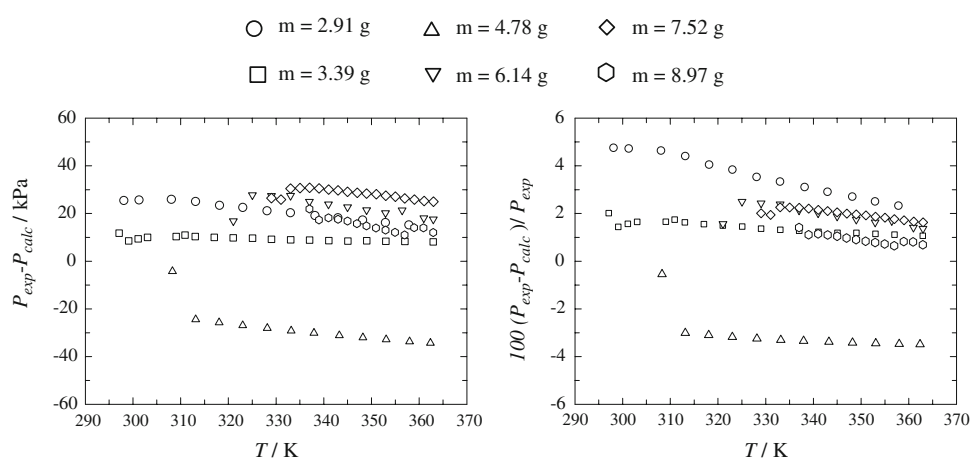
PVT data

The isochoric *PVT* measurements were taken in a temperature range from 219 to 361 K, at pressures from 22 to 2,622 kPa, and for molar volumes from 1.45 to 4.66 $\text{dm}^3 \text{mol}^{-1}$. The experimental *PVT* measurements were compared with the predicted values from the Martin–Hou equation of state in its original expression [21].

$$p = \frac{RT}{(v-b)} + \frac{A_2 + B_2 + C_2 e^{-KT}}{(v-b)^2} + \frac{A_3 + B_3 T + C_3 e^{-KT}}{(v-b)^3} + \frac{A_4}{(v-b)^4} + \frac{B_5 T}{(v-b)^5} \quad (2)$$

Using Eq. 2 with the experimental temperature and volume data, the deviations from the experimental pressure were calculated for each data point. Due to unknown accurate value of T_{Boyle} needed in the original version of the Martin–Hou EoS, we estimated its value to be $1,000 \pm 100$ K (i.e., for many real gases T_{Boyle} is

Fig. 3 Scatter diagram of absolute (*left*) and relative (*right*) pressure deviations from REFPROP 8.0 and present measurements. *open circle* $m = 2.91$ g; *open triangle* $m = 4.78$ g; *open diamond* $m = 7.52$ g; *open square* $m = 3.39$ g; *inverted open triangle* $m = 6.14$ g; *open hexagon* $m = 8.97$ g



approximately $2.5 T_c$). Consequent deviations spanned from $\text{AAD}(P) = 2.48\%$ to $\text{AAD}(P) = 2.81\%$. Since no experimental data were available in the open literature, our experimental results were also compared with REFPROP 8.0 [9]. Absolute and relative deviation between experimental data and REFPROP 8.0 prediction are reported in Fig. 3. Deviations showed an $\text{AAD}(P) = 1.2\%$. The data compared both with the Martin Hou EoS and REFPROP 8.0 showed similar deviation trends. The main source of error could be probably due to the small amount of mass charged.

Conclusions

In this work, the PVT properties of dimethyl ether have been measured, both in the saturation region and in the superheated vapor region. The results in the two phase region were correlated, together with a selection of literature sources, with the Wagner equation. The isochoric PVT data were compared with the Martin–Hou equation of state and REFPROP 8.0 predictions. A generally good agreement with the literature sources was found for the measured saturated pressures, however, a systematic deviation is observed between experimental superheated vapor region data and both predictive models.

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References

1. Semelsberger TA, Borup RL, Greene HL. Dimethyl ether (DME) as an alternative fuel. *J Pow Sour*. 2006;156:497–511.
2. ASHRAE Standard 34-2001. Designation and safety classification of refrigerant. ASHRAE, Atlanta, GA, 2001.
3. Good DA, Francisco JS, Jain AK, Wuebbles DJ. Lifetimes and global warming potentials for dimethyl ethers and for fluorinated

- ethers: CH_3OCF_3 (E143a), $\text{CHF}_2\text{OCHF}_2$ (E134), CHF_2OCF_3 (E125). *J Geophys Res*. 1998;103:28181–6.
4. Liu Z, Wu J. In: Proceedings of the 8th Asian thermophysical properties conference, Paper no. PL2, 21–24 August, 2007, Fukuoka, Japan.
5. Ihmels EC, Lemmon EW. Experimental densities, vapor pressures, and critical point, and a fundamental equation of state for dimethyl ether. *Fluid Phase Equilib*. 2007;260:36–48.
6. Di Nicola G, Giuliani G, Ricci R, Stryjek R. PVTx measurements for the R116 + CO_2 and R41 + CO_2 systems. New isochoric apparatus. *J Chem Eng Data*. 2005;50:312–8.
7. Di Nicola G, Giuliani G, Polonara F, Stryjek R. PVT from the Burnett and isochoric measurements. Nitrous oxide. *J Therm Anal Calorim*. 2005;80:311–6.
8. Corvaro F, Di Nicola G, Polonara F, Santori G. Saturated pressure measurements of dimethyl ether at temperatures from (219 to 361) K. *J Chem Eng Data*. 2006;51:1469–72.
9. Lemmon EW, Huber ML, McLinden MO. NIST Standard Reference Database 23, NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 8.0 (National Institute of Standards and Technology), 2007.
10. Horstmann S, Birke G, Fischer K. Vapor–liquid equilibrium and excess enthalpy data for the binary systems propane + dimethyl ether and propene + dimethyl ether at temperatures from (298 to 323) K. *J Chem Eng Data*. 2004;49:38–42.
11. Noles JR, Zollweg JA. Vapor–liquid equilibrium for chlorodifluoromethane + dimethyl ether from 283 to 395 K at pressures to 5.0 MPa. *J Chem Eng Data*. 1992;37:306–10.
12. Jonasson A, Persson O, Fredenslund A. High pressure solubility of carbon dioxide and carbon monoxide in dimethyl ether. *J Chem Eng Data*. 1995;40:296–300.
13. Bobbo S, Fedele L, Camporese R, Stryjek R. Isothermal vapor–liquid equilibrium for the three binary systems 1,1,1,2,3,3-hexafluoropropane with dimethyl ether or propane, and 1,1,1,3,3,3-hexafluoropropane with dimethyl ether. *Fluid Phase Equilib*. 2000;174:3–12.
14. Bobbo S, Camporese R, Stryjek R. (VapourHliquid)equilibrium measurements and correlations of the refrigerant mixture {dimethyl ether(RE170) H1,1,1,3,3,3-hexafluoropropane(R236fa)} at the temperatures (303.68 and 323.75)K. *J Chem Thermodyn*. 1998;30:1041–6.
15. Bobbo S, Fedele L, Stryjek R, Camporese R. Hydrogen-bonding of HFCs with dimethyl ether: evaluation by isothermal VLE measurements. *Fluid Phase Equilib*. 2002;199:153–60.
16. Bobbo S, Fedele L, Scattolini M, Camporese R, Stryjek R. Isothermal vapour + liquid equilibrium measurements and correlation for the dimethyl ether + 1,1,1,2,3,3,3-heptafluoropropane

- and the propane + 1,1,1,2,3,3,3-heptafluoropropane systems. *Fluid Phase Equilib.* 2004;224:119–23.
17. Fedele L, Bobbo S, De Stefani V, Camporese R, Stryjek R. Isothermal VLE measurements for difluoromethane + dimethyl ether and an evaluation of hydrogen bonding. *J Chem Eng Data.* 2005;50:128–32.
 18. Valtz A, Gicquel L, Coquelet C, Richon D. Isothermal vapour + liquid equilibrium measurements and correlation for the dimethyl ether + 1,1,1,2,3,3,3-heptafluoropropane and the propane + 1,1,1,2,3,3,3-heptafluoropropane systems Vapour–liquid equilibrium data for the 1,1,1,2 tetrafluoroethane (R134a) + dimethyl ether (DME) system at temperatures from 293.18 to 358.15K and pressures up to about 3MPa. *Fluid Phase Equilib.* 2005;230:184–91.
 19. Yasumoto M, Uchida Y, Ochi K, Furuya T, Otake K. Critical properties of three dimethyl ether binary systems: dimethyl ether (RE-170) + propane (HC-290), butane (HC-600), and 2-methyl propane (HC-600A). *J Chem Eng Data.* 2005;50:596–600.
 20. Wu JT, Liu ZG, Pan J, Zhao XM. Vapor pressure measurements of dimethyl ether from (233 to 399) K. *J Chem Eng Data.* 2004;49:32–4.
 21. Martin JJ, Hou YC. Development of an equation of state for gases. *AIChE J.* 1955;6:142–51.