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Alternative biofuels

PVTx measurements for DME + propane

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Abstract This study presents the experimental results for the dimethyl ether (DME) + propane system obtained using the Burnett method. The apparatus was calibrated using helium. *PVTx* measurements were taken for four isotherms (344, 354, 364, and 375 K), performing 16 Burnett expansions in pressures ranging from about 3,000 to 70 kPa. The second and third virial coefficients were derived from experimental results. The experimental uncertainty in the second and third virial coefficients was estimated to be within ±5 cm^3/mol and ±1,000 cm^6/mol^2, respectively.

Keywords Biofuels · Burnett · DME; Propane · Thermophysical properties

Introduction

Dimethyl ether (DME) can be made from coal, natural gas, residual oil, oil coke, and biomass, and its production cost is rather low.

In addition to its use as an assistant solvent and an aerosol propellant, recently DME was shown to be a good alternative fuel [1]. In addition, because of its favorable thermodynamic properties, it has been suggested as an alternative refrigerant (RE170). Recently, a preliminary fundamental equation of state was derived [2].

Its saturation vapor pressure [3], the virial coefficients [4], and the superheated vapor region data [5] were reported in recent articles. Since its physical properties are similar to those of liquefied petroleum gases (i.e., propane and butane), its blends with propane appear to be very interesting [6].

This study presents the experimental results for the dimethyl ether (DME) + propane system obtained using the Burnett method [7]. *PVTx* measurements were taken for four isotherms (344, 354, 364, and 375 K). The second and third virial coefficients were derived from experimental results. In addition, data were compared with REFPROP 8.0 prediction [8].

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. Propane was supplied by Ausimont, Italy, and its purity was found to be 99.95% on an area-response basis.

Experimental devices

In this article, the device adopted is the same as described elsewhere [9] with no modifications. The experimental setup is reported in Fig. 1. It consisted of two pressure vessels, a measurement chamber, V_A, and an expansion

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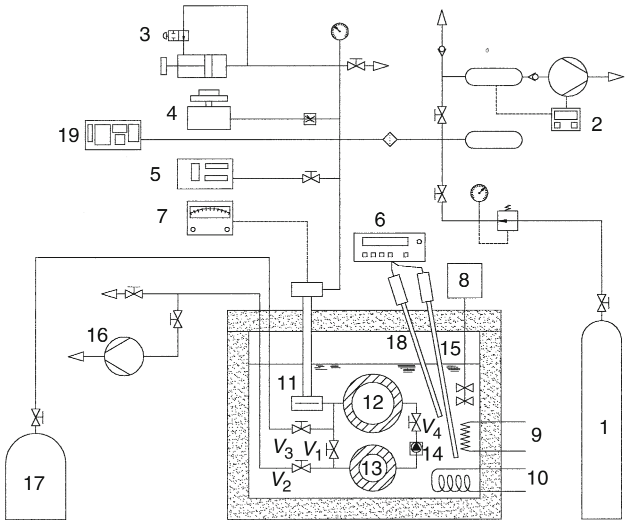

Fig. 1 Schematic view of the experimental apparatus. Legenda: *1* Nitrogen reservoir, *2* Vacuum pump (Vacuubrand, mod. RZ2), *3* Precision pressure controller (Ruska, mod. 3981), *4* Gas lubricated dead weight gage (Ruska, mod. 2465), *5* Vibr. cylinder pressure gage (Ruska, mod. 6220) *6* Digital temperature indicator (Corradi, RP 7000), *7* Electronic null indicator (Ruska, mod. 2416), *8* Stirrer, *9* Heater, *10* Cooling coil connected with an auxiliary bath, *11* Differential press. transducer (Ruska, mod. 2413), *12* Measurement chamber (V_A), *13* Expansion chamber (V_B) 14 Magnetic recirculating pump, *15* Pt resistance thermometer (Tersid, Pt 100), *16* Vacuum pump for V_B (Vacuubrand, mod. RZ2), *17* Charging fluid reservoir, *18* Pt resistance thermometer (Hart Scientific, Pt 25), *19* Digital pressure indicator (Ruska, mod. 7000) V_1,V_2,V_3, and V_4 Constant volume valves

chamber, V_B, with volumes of approximately 70 and 35 cm^3, respectively, and several auxiliary systems for filling and mixing the compounds in the Burnett vessels, and for controlling and measuring the pressure and temperature. The measurement vessel was connected to a diaphragm-type differential pressure transducer (Ruska Model 2413) coupled to an electronic null indicator (Ruska Model 2416). The pressure was regulated by a precision pressure controller (Ruska Model 3981), while a digital pressure indicator (Ruska Model 7000) was used to measure the pressure. Nitrogen is used as the pressure-transmitting fluid, and the nitrogen system consists of a reservoir, expansion vessels, and pressure regulating systems. The vessels were immersed in a thermostatic bath filled with about 45 l of silicon oil. The temperature of the bath was kept constant by means of a system with a PID device, controlled by a computer to which the temperature measurement system is also connected. The control and acquisition system relies on two platinum resistance thermometers calibrated according to ITS 90 at the Istituto Metrologico G. Colonnetti (IMGC) of Turin. In particular, for data acquisition and control measurements, a Hart Scientific Pt 25 resistance thermometer (Hart 5680) and a Tersid Pt 100 resistance thermometer were used, both connected to a digital temperature indicator (Corradi, RP 7000).

The Burnett constant, *N*, defined as the ratio of the volume of cell A and the sum of the volumes of cells A and B at zero pressure, was found to be $N = 1.5184 \pm 0.0001$ for measurements under this study. Measurements were performed using the classical Burnett experimental procedure. Initially, the first vessel was filled with the sample, and its temperature and pressure were measured. Then, after evacuating the second vessel, the expansion valve was opened. Once the pressures between the vessels had equalized, the second vessel was isolated and evacuated again. This procedure was repeated until low pressures were achieved.

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 better than ±0.015 K, and the uncertainty of the thermometer was found to be better than 0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than 0.025 K. The uncertainty in the pressure measurements is due to the transducer and null indicator system, and to the pressure gages. The digital pressure indicator (Ruska Model 7000) has an uncertainty of ±0.003% of full scale. The total uncertainty in the pressure measurement is also influenced by temperature fluctuations due to bath instability and was found to be less than ±1 kPa. The uncertainty of the mixture's composition was found to be constantly lower than 0.5% in mole fraction.

Experimental results

A total of 144 experimental points along four isotherms in a range of temperatures from 343.86 to 374.64 K and pressures between 70 and 3,000 kPa were measured. The data are given in Table 1 along with the regressed compressibility factors of the mixtures.

The *PVTx* measurements obtained by experiment were used to derive the second, *B,* and third, *C,* virial coefficients of the truncated virial equation:

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \tag{1}$$

The virial equation of state has a rigorous theoretical foundation in statistical thermodynamics which provides exact analytic relations between the virial coefficients and the interactions between molecules in isolated clusters. In fact, *B* depends upon interactions between pairs of

Table 1 Pressures measured experimentally during Burnett expansions and regressed compressibility factors (z) for the DME (1) + C_3H_8 (2) system

Series 1		Series 2		Series 3		Series 4	
$T = 343.86$/K		$T = 343.86$/K		$T = 343.86$/K		$T = 343.86$/ K	
$x_1 = 0.1956$		$x_1 = 0.3737$		$x_1 = 0.5710$		$x_1 = 0.7645$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
2486.1	0.65422	2239.5	0.70584	1913.5	0.76046	1684.9	0.78531
1917.1	0.76598	1671.6	0.79997	1388.6	0.83793	1209.2	0.85574
1389.1	0.84273	1189.9	0.86465	973.5	0.89198	840.7	0.90336
971.6	0.89505	825.1	0.91037	667.2	0.92818	573.0	0.93495
665.3	0.93050	561.2	0.94019	450.5	0.95158	386.7	0.95803
449.4	0.95436	377.6	0.96042	301.6	0.96730	258.5	0.97245
301.0	0.97076	252.3	0.97430	200.8	0.97806	172.1	0.98272
200.6	0.98224	167.9	0.98451	133.4	0.98621	114.2	0.99070
133.4	0.99151	111.5	0.99291	88.4	0.99307	75.8	0.99807
Series 5		Series 6		Series 7		Series 8	
$T = 354.09$/K		$T = 354.09$/K		$T = 354.09$/K		$T = 354.09$/K	
$x_1 = 0.2279$		$x_1 = 0.3747$		$x_1 = 0.6125$		$x_1 = 0.7586$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
2715.6	0.67346	2586.9	0.69208	2413.9	0.71407	2073.6	0.76229
2063.1	0.77688	1943.4	0.78942	1795.9	0.80663	1506.0	0.84063
1486.0	0.84961	1390.5	0.85764	1277.1	0.87096	1054.4	0.89366
1036.1	0.89944	966.8	0.90546	882.6	0.91393	721.8	0.92894
707.8	0.93299	658.7	0.93671	599.5	0.94258	488.2	0.95396
477.4	0.95559	443.5	0.95763	402.8	0.96167	326.7	0.96938
319.3	0.97045	296.4	0.97164	268.8	0.97447	217.5	0.97977
212.6	0.98088	197.2	0.98151	178.7	0.98336	144.3	0.98702
141.0	0.98817	130.8	0.98866	118.4	0.98982	95.6	0.99286
Series 9		Series 10		Series 11		Series 12	
$T = 364.36$/K		$T = 364.35$/K		$T = 364.36$/K		$T = 364.35$/K	
$x_1 = 0.2098$		$x_1 = 0.3874$		$x_1 = 0.5817$		$x_1 = 0.8256$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
2844.5	0.70546	2794.7	0.70476	1752.1	0.83390	2254.4	0.76706
2123.5	0.79964	2083.9	0.79790	1230.0	0.88886	1633.5	0.84392
1514.1	0.86571	1485.2	0.86347	843.9	0.92596	1143.1	0.89665
1048.8	0.91054	1029.0	0.90836	570.7	0.95082	782.1	0.93152
713.3	0.94034	700.9	0.93950	382.4	0.96747	527.7	0.95436
479.6	0.95990	471.6	0.95985	254.7	0.97846	353.0	0.96925
320.0	0.97262	315.1	0.97359	169.1	0.98631	234.7	0.97878
212.6	0.98115	209.5	0.98298	112.0	0.99164	155.6	0.98519
140.9	0.98695	138.9	0.98941	74.1	0.99632	103.0	0.99035

Table 1 continued

Series 13		Series 14		Series 15		Series 16	
T = 374.64/K		T = 374.64/K		T = 374.64/K		T = 374.62/K	
$x_1 = 0.1847$		$x_1 = 0.3788$		$x_1 = 0.5817$		$x_1 = 0.7994$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
2976.3	0.72194	2956.3	0.72285	1934.1	0.83367	2409.1	0.77934
2197.7	0.80941	2182.2	0.81018	1357.2	0.88826	1735.0	0.85220
1558.1	0.87132	1546.8	0.87195	931.4	0.92554	1209.4	0.90197
1076.2	0.91385	1068.2	0.91433	629.9	0.95052	825.8	0.93516
731.1	0.94257	725.5	0.94289	422.1	0.96714	556.6	0.95703
491.3	0.96187	487.5	0.96194	281.2	0.97829	371.9	0.97103
327.9	0.97471	325.3	0.97478	186.6	0.98573	247.2	0.97994
217.9	0.98334	216.1	0.98309	123.5	0.99055	163.8	0.98568
144.4	0.98939	143.2	0.98891	81.6	0.99401	108.2	0.98894

Table 2 Second and third virial coefficients for DME (1) + C_3H_8 (2) system

Series	B_{mix}/cm^3 mol^{-1}	C_{mix}/cm^6 mol^{-2}	$\rho(1)$/mol dm^{-3}	dP/kPa	dP/%	B_{11}/cm^3 mol^{-1}	B_{22}/cm^3 mol^{-1}	B_{12}/cm^3 mol^{-1}
1	−282	16,254	1.3292	0.2	0.1	−304	−285	−272
2	−291	23,631	1.1098	0.3	0.0	−304	−285	−293
3	−293	23,631	0.8801	0.3	0.0	−304	−285	−289
4	−304	24,285	0.7504	0.2	0.1	−304	−285	−308
5	−265	19,090	1.3696	0.1	0.0	−294	−268	−254
6	−270	21,599	1.2696	0.2	0.0	−294	−268	−264
7	−268	16,534	1.1482	0.2	0.0	−294	−268	−247
8	−271	15,112	0.9240	0.1	0.0	−294	−268	−236
9	−242	15,593	1.3310	0.4	−0.1	−269	−252	−219
10	−252	20,023	1.3090	0.1	0.0	−269	−252	−246
11	−251	16,547	0.6936	0.0	0.0	−269	−252	−238
12	−251	11,582	0.9702	0.3	−0.1	−269	−252	−210
13	−235	18,865	1.3235	0.1	0.0	−256	−238	−227
14	−236	18,687	1.3130	0.2	0.0	−256	−238	−228
15	−236	17,413	0.7448	0.1	0.0	−256	−238	−222
16	−233	10,464	0.9924	0.3	−0.1	−256	−238	−186

molecules and C upon interactions in a cluster of three molecules. Thus, the virial equation of state forms the connection between experimental results and knowledge of molecular interactions, giving a link between the macroscopic and microscopic points of view.

With the set of data of this study, each run was regressed individually using $(\mathrm{d}P)^2$ as an objective function with the Burnett constant obtained by means of the calibration with helium. The pressure distortion of the Burnett cells was taken into account.

The values of the virial coefficients for the pure compounds (smoothed as a function of reduced temperature) were used to derive the cross virial coefficients, B_{12}, shown in Table 2.

The cross second virial coefficients were calculated from the formula:

$$B_m = \sum_{i=1}^{n}\sum_{j=1}^{n} B_{ij}x_i x_j \tag{2}$$

for each experimental datum point.

The overall AAD in pressure was evaluated at 0.2 kPa.

The second virial coefficients for the system were plotted against the mole fraction in Fig. 2 showing the four different isotherms with four different symbols. The second virial coefficients show a slightly positive deviation from the ideal second virial coefficients, which are defined as

$$B_{12} = (B_{11} + B_{22})/2 \tag{3}$$

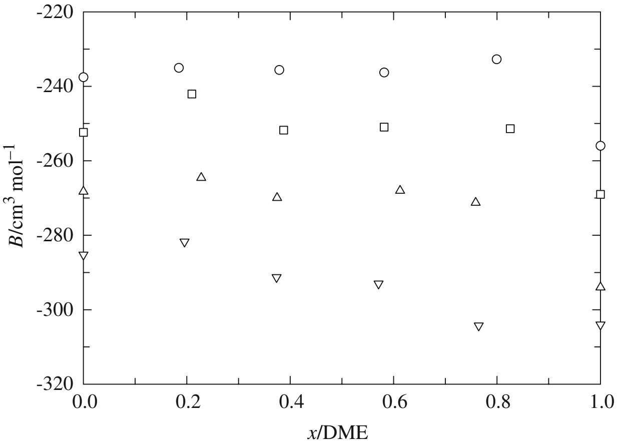

Fig. 2 Second virial coefficients against mole fraction. *open inverted triangle* $T = 343.86$ K, *open square* $T = 364.36$ K, *open triangle* $T = 354.09$ K, *open circle* $T = 374.64$ K

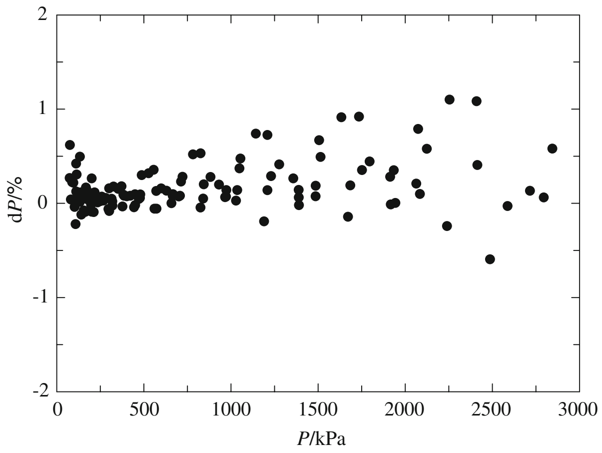

Fig. 3 Deviation within experimental data and values predicted by REFPROP 8.0 software

However, since propane and DME are two homomorphic molecules that differ by the presence of oxygen in DME, the second virial coefficients obtained for the two pure fluids were also found to be of very similar value.

Owing to the lack of other experimental data on the *PVTx* properties of the system, our experimental results were compared with predictions from REFPROP 8.0. The predicted values are reported in Fig. 3. The results are in good agreement (within ± 1%) with the software prediction. In addition, the results obtained for the DME as pure fluid reported as averaged values in Table 2 (B_{11}) were already compared with the literature and discussed elsewhere [4]. The few points obtained for the propane as pure fluid were not published, but the obtained second virial coefficients (B_{22}) showed a good agreement with the ones found in the literature [10].

Conclusions

This study presents an experimental survey for the dimethyl ether (DME) + propane system obtained by the Burnett method. The apparatus was calibrated using helium. *PVTx* measurements were taken for the four isotherms (344, 354, 364, and 375 K), performing 16 Burnett expansions in a range of pressures from about 3,000 to 70 kPa.

The second and third virial coefficients were derived from experimental results. Owing to the lack of other experimental data on the *PVTx* properties of the system, experimental results of this study were compared with predictions from REFPROP 8.0. The results were in good agreement with the software prediction.

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