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Vapor−Liquid Equilibrium for Dimethyl Ether and 2-Methylpropane

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The vapor−liquid equilibrium (P, T, x, y) for dimethyl ether and 2-methylpropane was measured at 280, 290, 300, 310, and 320 K by the dynamic method with recirculation of the vapor through the liquid phase. The composition was measured by a gas chromatograph connected "on-line" to the equilibrium cell. The response of a flame ionization detector was calibrated over a wide composition range using mixtures being prepared by mass. The experimental results were reduced by the Carnahan−Starling−De Santis equation of state assuming that its binary interaction parameter was temperature independent. The system is azeotropic with strong positive deviation from Raoult's law.

Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. In this paper we report part of the experimental measurements that have been made under Project 805(B)/95. The VLE data for the above-mentioned system has not been reported in the literature, and results cannot be predicted with sufficient accuracy neither from pure component property data nor using a known semiempirical method, e.g., based on a group contribution concept such as ASOG[1] or UNIFAC.[2]

Experimental Section

Chemicals. ***Dimethyl ether (CA registry no. 115-10-6)*** was purchased from Aldrich GmBH as 99+% pure. No impurities were detected by GLC using a flame ionization detector (FID). The sample was used with no additional purification.

2-Methylpropane (CA registry no. 75-28-5) was purchased from Aldrich GmBH as 99+% pure. A purity of 99.8% was found by GLC using an FID as evaluated on the basis of the area response ratio. The detected impurity was identified as propane from its retention time. The sample was used with no additional purification.

Apparatus. The apparatus used has been described elsewhere.[3−5] Here, only a brief description will be given. The vapor−liquid equilibrium unit consists of an equilibrium cell of a capacity of about 50 cm^3 equipped with two windows for the observation of phase behavior and a magnetic pump ensuring intensive flow of vapor through the liquid. The equilibrium cell and the magnetic pump were immersed in a glass vessel thermostat, of capacity 100 L, filled with water as the thermostating fluid. Two stirrers forced the fluid circulation.

Temperature and Pressure Measurements. The temperature was measured by a platinum resistance thermometer (PT100 Ω sensor with an HP3458 multimeter) with a precision of ±1.5 mK and continuously recorded by data acquisition software (LABVIEW). The temperature in the bath was stable to ±1 mK using a PID-controlled system governing a 1.5 kW heater immersed in the thermostat. An auxiliary cooler (LAUDA RK8CP) was used to maintain the temperature below or close to ambient. The uncertainty in the temperature measurement was estimated to be within ±5 mK on ITS-90.

The pressure was measured by means of a pressure gauge (RUSKA 6000) with a full scale of 3500 kPa and precision of 0.1 kPa. A differential pressure cell (RUSKA 2413) was installed for the separation of the sample from the pressure gauge. A control box (RUSKA 2416) connected to a null detector was installed to equilibrate the pressure from both sides of the diaphragm. The uncertainty in the pressure measurement was estimated to be within ±0.3 kPa.

Phase Composition Measurement. For the determination of the phase composition, the GLC method was chosen. The gas chromatograph (Hewlett-Packard 6890) with an FID was connected on-line to the VLE cell. A packed, 2 m long column with 1/8 in. o.d. was used with PORAPAK R 100/120 mesh as a packing material. The oven temperature was fixed at 383 K and the carrier flow rate at 30.5 cm^3/min; for these conditions a high resolution and a short retention time (about 4.5 min/analysis) were found.

Considering the molecular weight of these two compounds and their vapor pressure at ambient temperature, the gravitational method of mixture preparation for the gas chromatograph calibration was chosen. For this purpose, stainless steel bottles of capacity about 240 cm^3 and equipped with stainless steel minivalves were used. The weight of the empty bottle was about 170 g; hence, a commercial analytical balance with a capacity of 240 g and a resolution of 0.1 mg was used. The same samples were used for the regular recalibration of the FID response. We evaluate an uncertainty in the preparation of the mixture composition of ±0.0001 mole fraction and the accuracy in the phase composition measurement to be within ±0.001.

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Table 1. Vapor−Liquid Equilibrium for Dimethyl Ether (1) + 2-Methylpropane and Comparison with the CSD EOS

P/kPa	x_1	y_1	$y_{1,\mathrm{calcd}} - y_1$	$P_{\mathrm{calcd}} - P$/kPa	P/kPa	x_1	y_1	$y_{1,\mathrm{calcd}} - y_1$	$P_{\mathrm{calcd}} - P$/kPa
		T = 280.12 K					T = 290.14 K		
201.9	0.0000	0.0000	0.0000	−2.8	277.2	0.0000	0.0000	0.0000	−2.4
217.9	0.0519	0.1179	−0.0016	−2.8	291.3	0.0333	0.0747	−0.0008	−3.0
239.7	0.1268	0.2455	0.0042	−3.6	321.1	0.1075	0.2122	−0.0012	−4.7
270.2	0.2586	0.4136	0.0083	−2.5	346.0	0.1811	0.3173	0.0022	−4.4
293.4	0.3862	0.5312	0.0124	−1.1	384.4	0.3202	0.4703	0.0063	−2.2
314.1	0.5389	0.6461	0.0119	0.8	403.4	0.4064	0.5448	0.0089	−0.2
329.6	0.7059	0.7596	0.0067	2.2	421.8	0.5053	0.6203	0.0100	1.8
330.7	0.7091	0.7620	0.0063	1.4	437.1	0.6051	0.6905	0.0092	3.3
334.3	0.7753	0.8087	0.0026	2.3	451.2	0.7206	0.7697	0.0062	4.1
337.2	0.8323	0.8505	0.0001	2.2	460.2	0.8228	0.8456	0.0000	4.1
338.4	0.8839	0.8915	−0.0020	2.4	464.5	0.9146	0.9193	−0.0024	3.5
339.3	0.9287	0.9300	−0.0027	1.8	465.5	0.9682	0.9678	−0.0015	2.1
339.0	0.9682	0.9673	−0.0021	1.3	465.4	0.9827	0.9824	−0.0012	1.7
337.7	1.0000	1.0000	0.0000	1.1	463.7	1.0000	1.0000	0.0000	2.4
		T = 300.17 K					T = 310.21 K		
373.0	0.0000	0.0000	0.0000	−2.2	493.8	0.0000	0.0000	0.0000	−3.8
398.1	0.0450	0.0970	−0.0032	−4.2	532.6	0.0583	0.1170	−0.0028	−5.2
439.8	0.1305	0.2400	−0.0005	−5.3	578.2	0.1336	0.2356	0.0006	−6.1
479.2	0.2225	0.3615	0.0012	−5.7	643.2	0.2593	0.3932	0.0028	−5.0
509.4	0.3098	0.4532	0.0048	−3.2	701.6	0.4007	0.5276	0.0070	−0.7
529.4	0.3750	0.5137	0.0058	−1.4	763.8	0.5958	0.6791	0.0081	3.6
552.6	0.4613	0.5843	0.0074	0.9	804.4	0.7837	0.8178	0.0014	5.7
571.1	0.5411	0.6438	0.0080	2.8	811.5	0.8300	0.8534	−0.0005	5.6
587.5	0.6244	0.7028	0.0075	4.5	819.7	0.9153	0.9221	−0.0018	5.8
609.1	0.7626	0.8010	0.0033	5.7	822.9	0.9681	0.9692	−0.0013	3.8
617.3	0.8340	0.8545	0.0005	5.5	823.2	0.9848	0.9853	−0.0010	3.4
622.6	0.9053	0.9123	−0.0017	4.9	823.7	1.0000	1.0000	0.0000	2.2
					T = 320.15 K				
638.9	0.0000	0.0000	0.0000	−4.2	1029.2	0.7676	0.8057	0.0016	8.3
752.3	0.1468	0.2486	−0.0014	−7.2	1049.0	0.8635	0.8803	−0.0011	7.7
781.7	0.1921	0.3076	−0.0002	−5.8	1057.2	0.9117	0.9196	−0.0013	5.6
870.7	0.3436	0.4704	0.0037	−2.8	1059.3	0.9416	0.9464	−0.0022	5.6
943.7	0.5020	0.6066	0.0052	2.7	1059.4	0.9443	0.9480	−0.0014	5.9
988.4	0.6230	0.6983	0.0050	5.9	1060.4	1.0000	1.0000	0.0000	5.4

After equilibration with intensive mixing (about 30 min), samples of liquid and vapor phases were analyzed by the gas chromatograph. At least five analyses were made for each phase, and the average value was adopted as corresponding to the equilibrium one. During the measurements we observed a small day by day irreproducibility of the gas chromatograph response; hence, it was continuously rechecked, and the actual values were adopted for the determination of the equilibrium composition.

Results and Discussion

Figure 1 shows all results. Table 1 reports the VLE data for each isotherm.

For reduction of the data the Carnahan−Starling−De Santis[6] (CSD) EOS in the form

$$P = \frac{RT}{V}\left(\frac{1 + Y + Y^2 - Y^3}{(1 - Y)^3}\right) - \frac{a}{V(V + b)} \tag{1}$$

where

$$Y = b/4V \tag{2}$$

with the following expressions for the temperature-dependent a and b parameters

$$a(T) = a_0 \exp(a_1 T + a_2 T^2) \tag{3}$$

$$b(T) = b_0 + b_1 T + b_2 T^2 \tag{4}$$

was used.

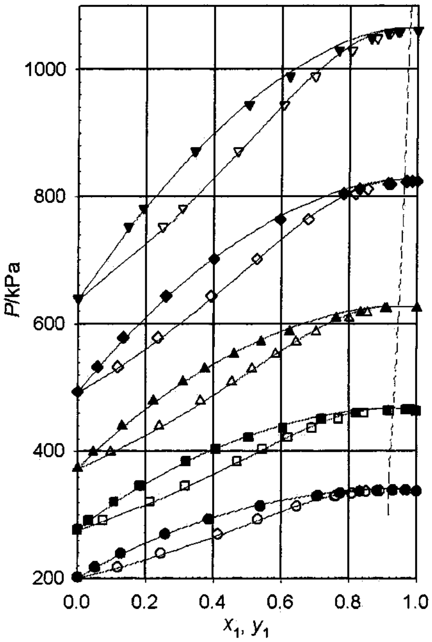

Figure 1. VLE at ●, 280.12 K; ■, 290.14 K; ▲, 300.17 K; ◆, 310.21 K; and ▼, 320.15 K for dimethyl ether (1) + 2-methylpropane (2). The lines represent eq 1 with k_{12} = 0.033 70, the dotted line represents azeotropic composition, solid symbols represent bubble points, and hollow symbols represent dew points.

The coefficients a and b of the CSD EOS for the pure compounds were adopted from Huber et al.[7] They are listed in Table 2.

Table 2. Parameters (Adopted from Huber et al.[7]) of the CSD EOS (Eq 1) Used for the Data Correlation

parameter	dimethyl ether	2-methylpropane	parameter	dimethyl ether	2-methylpropane
a_0/kPa·L^2·mol^{-2}	3208.84	4197.2427	b_0/L·mol^{-1}	0.130775	0.18025412
a_1/K^{-1}	-3.20482×10^{-3}	-2.189385×10^{-3}	b_1/L·mol^{-1}·K^{-1}	-1.97630×10^{-4}	$-1.8719540 \times 10^{-4}$
a_2/K^{-2}	1.50810×10^{-7}	-1.300483×10^{-6}	b_2/L·mol^{-1}·K^{-2}	5.4664×10^{-8}	$-0.8177828 \times 10^{-7}$

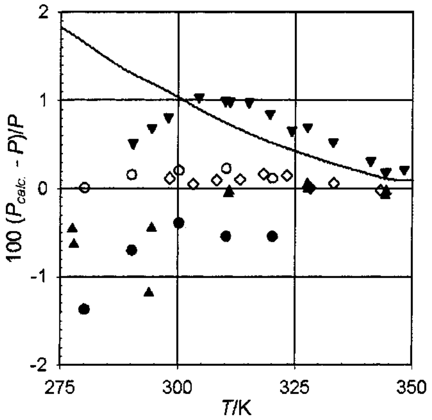

Figure 2. Deviations of the measured vapor pressure of 2-methylpropane from the Younglove and Ely[8] recommendation. Symbols: ▼, Sage and Lacey;[9] ▲, Steele et al;[10] ◇, Waxman and Gallagher;[11] ●, own measurements; ○, own correlation. The line represents the DIPPR correlation.[12]

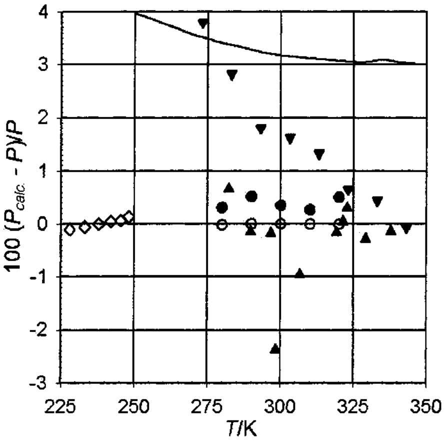

Figure 3. Deviations of the measured vapor pressure of dimethyl ether from the REFPROP Database.[7] Symbols: ▲, Cardoso and Bruno;[13] ◇, Kennedy et al;[14] ▼, *International Critical Tables*;[15] ●, own measurements; ○, own correlation. The line represents the DIPPR correlation.[12]

Comparison of 2-methylpropane vapor pressure data with those recommended by Younglove and Ely[8] is given in Figure 2. For the comparison a typographic error in eq 3 of that paper has been found and corrected to $x = (1 - T_t/T)/(1 - T_t/T_c)$, where T_t is the temperature at the triple point and T_c is the critical temperature. Deviations of our data can be explained by the presence of the detected impurities (propane). Corrections for the influence of the content of propane reduced the observed deviations to below 0.2%. The deviations of the experimental data available in the literature exceed 1% in both directions.[9–11] The deviations of the DIPPR recommendations[12] are systematic, but well within the error of ±3% claimed by the authors of that correlation.

Larger deviations were observed for the vapor pressure of dimethyl ether (Figure 3), probably due to the mediocre accuracy of the vapor pressure data existing in the literature.[13,14] Unfortunately, more recent, comprehensive experimental studies on thermodynamic properties of dimethyl ether cover a temperature range only up to 248.24 K, much below our temperature range. Comparison has been made with the correlation produced by Huber et al.,[7] and the observed deviation of our measurements is within the limits of uncertainty of the data used to derive the correlation. The deviations of the DIPPR recommendation[12] are systematic, but well within the error of ±5% claimed by the authors. Also, systematic of similar course are deviations produced by ITC.[15]

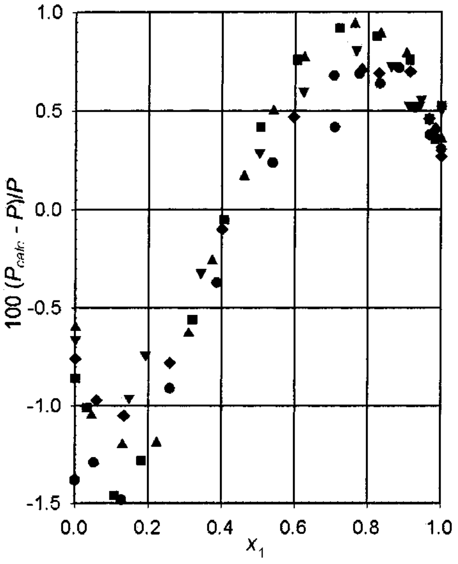

Figure 4. Deviations of the measured vapor pressure of dimethyl ether (1) + 2-methylpropane (2) from eq 1: ○, 280.12 K; ■, 290.14 K; ▲, 300.17 K; ◆, 310.21 K; ▼, 320.15 K.

The combining rules used for the mixtures were

$$a = \sum\sum \xi_i \xi_j a_{ij} \tag{5}$$

$$b = \sum \xi_i b_i \tag{6}$$

where ξ_i is the molar fraction of the ith component and

$$a_{ij} = (a_{ii} a_{jj})^{0.5}(1 - k_{ij}) \tag{7}$$

where k_{ij} is an a-dimensional adjustable parameter when $i \neq j$.

The VLE data have been reduced using the above equations and minimizing the objective function

$$\text{obf} = \sum_{i=1}^{n_p} (\delta P/P_{\text{exptl}})^2 \tag{8}$$

where n_p is the number of experimental points. $\delta P = P_{\text{exptl}} - P_{\text{EOS}}$ and $\delta y = y_{1,\text{exptl}} - y_{1,\text{EOS}}$ are defined throughout the paper.

All experimental data were fitted as a combined set and assuming that the binary interaction parameter was independent of temperature. The results are shown in Figures 4 and 5. In general, reproduction of the experimental pressure is very good, but a small S-shaped deviation in the vapor pressure is observed. Results of the fit of the combined set of all experimental VLE data are reported

Table 3. Azeotropic Data

x_1	P kPa	T K	x_1	P kPa	T K
0.917 ± 0.002	341.1 ± 2	280.12 ± 0.01	0.963 ± 0.001	826.9 ± 4	310.21 ± 0.01
0.933 ± 0.001	468.2 ± 2	290.14 ± 0.01	0.978 ± 0.001	1066.2 ± 5	320.15 ± 0.01
0.949 ± 0.001	628.4 ± 3	300.17 ± 0.01			

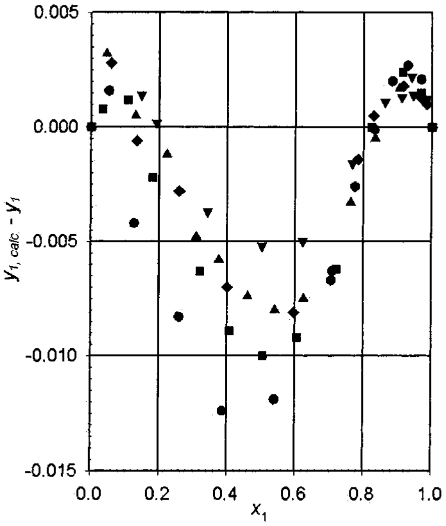

Figure 5. Deviations of the measured vapor composition of dimethyl ether (1) + 2-methylpropane (2) from eq 1: ●, 280.12 K; ■, 290.14 K; ▲, 300.17 K; ◆, 310.21 K; ▼, 320.15 K.

in Table 1. Both the experimentally measured pressure if plotted against composition and the VLE data fit show that the system forms an azeotrope. The azeotropic composition moves in the direction of pure dimethyl ether with an increase in temperature. The azeotropic parameters are given in Table 3 and Figure 1.

Conclusions

Our results showed that the VLE of the system is well represented by the CSD EOS with one adjustable interaction parameter that is practically independent of temperature.

A systematic deviation of the isobutane vapor pressure from literature correlations is clearly present, mostly arising from the influence of the impurity (propane). The average deviation of the dimethyl ether vapor pressure (about −0.5%) is acceptable considering the present deficiency of accurate experimental data published in the literature.

Referring to the reproduction of the VLE experimental data by the CSD EOS, the overall (all isotherms) average deviations of vapor composition and pressure are −0.0024 and −0.01%, respectively; the overall absolute average deviations of vapor composition and pressure are 0.0037 and 0.68%, respectively. The experimental interaction parameter, independent of temperature, is $k_{12} = 0.0337$.

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