Vapor–Liquid Equilibria for the Carbon Dioxide–Cyclopentane System at 37.7, 45.0, and 60.0 °C

Catherine J. Eckert and Stanley I. Sandler*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Vapor–liquid equilibrium data for the CO_2–cyclopentane mixture at 37.7, 45.0, and 60.0 °C are reported. The data sets were correlated to the same degree of accuracy by using the Peng–Robinson and Teja–Patel equations of state, though the shape of the two-phase envelope was not precisely reproduced by either equation. Binary interaction parameters for the CO_2–cyclopentane system are reported for both equations of state, and estimates of the mixture critical points are provided.

Introduction

This study is a continuation of our research program on vapor–liquid equilibrium of binary CO_2–hydrocarbon systems. While much data exist for CO_2 and the *n*-alkanes, there is a scarcity of data for other hydrocarbons. Here vapor–liquid equilibrium data for the CO_2–cyclopentane system at 37.7, 45.0, and 60.0 °C are reported. Also, these data are fitted with two cubic equations of state: one with two properties parameters, and the other with three.

Equipment and Experiment

The apparatus and operating procedure used in this investigation were essentially identical with that of Behrens and Sandler (*1*). A detailed description of both can be found in that reference. The chromatographic analysis of the CO_2–cyclopentane mixtures was done using a 6 ft × 0.125 in. stainless steel column packed with 80/100 mesh silica gel maintained at 150 °C with helium carrier gas flowing at 25 cm^3/min. Cyclopentane, supplied by Aldrich, was purified by distillation under nitrogen and only the middle 50% cut used. The carbon dioxide used was research grade (99.99%) supplied by the Linde Division of Union Carbide.

The only change from our previous procedure was the calibration of the gas chromatograph. In this work, the gas chromatograph system was calibrated by using gas mixtures of known composition prepared in our laboratory. Calibration mixtures were prepared by using a 1-L stainless steel bomb, accurately thermostated at 50 °C, a Heise compound Bourdon tube gauge (Model No. CMM 51065), and a capillary tubing manifold. Gas mixtures were prepared by starting with an evacuated bomb, and then measuring the temperature equilibrated (20 min–1 h) total pressure after the addition of each gas. In these mixtures the partial pressure of each component was kept below its saturation pressure, and the total pressure of the mixture was sufficiently low (below 1 bar) that departures from ideal gas behavior were negligible. The compositions of the prepared gas mixtures were then computed from the partial pressures. The estimated overall error in the gas chromatographic analysis of our samples from calibration and other factors was found to be 0.005 mole fraction. The errors in temperature and pressure measurements were approximately 0.02 °C and 0.25 kPa.

Results and Discussion

In Tables I–III our original, unsmoothed data for the CO_2–cyclopentane system at 37.7, 45.0, and 60.0 °C, respectively, are reported. These data have been correlated by using the two-constant Peng-Robinson (*2*)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (1)$$

and three-constant Teja-Patel (*3*)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)} \quad (2)$$

equations of state. In these equations P is the pressure, R is the gas constant, T is the temperature, and V is the molecular volume. The generalized expressions for the equation of state

Table I. Experimental Data for the CO_2–Cyclopentane System at 37.7 °C

temp, K	press., MPa	x_{CO_2}	y_{CO_2}
310.86	0.1750	0.0067	0.600
310.85	0.8171	0.071	0.915
310.86	1.2999	0.115	0.945
310.86	2.6268	0.250	0.968
310.86	3.0824	0.301	0.970
310.86	3.7160	0.400	0.976
310.85	4.5768	0.515	0.976
310.86	5.3669	0.628	0.976
310.86	5.8338	0.729	0.978
310.85	6.0961	0.781	0.978
310.86	6.3070	0.807	0.978
310.86	6.5490	0.857	0.977

Table II. Experimental Data for the CO_2–Cyclopentane System at 45.0 °C

temp, K	press., MPa	x_{CO_2}	y_{CO_2}
318.17	0.6452	0.048	0.861
318.16	1.2870	0.098	0.926
318.16	1.8040	0.136	0.947
318.17	2.3563	0.195	0.959
318.16	2.9130	0.256	0.969
318.17	3.4092	0.307	0.969
318.17	3.8004	0.356	0.973
318.16	4.2572	0.408	0.976
318.16	4.5027	0.440	0.974
318.17	4.8848	0.476	0.974
318.17	5.3941	0.557	0.974
318.17	5.9639	0.646	0.975
318.16	6.5746	0.738	0.973
318.16	7.1147	0.823	0.973
318.17	7.3569	0.844	0.972

Table III. Experimental Data for the CO_2–Cyclopentane System at 60.0 °C

temp, K	press., MPa	x_{CO_2}	y_{CO_2}
333.17	1.0665	0.058	0.812
333.17	1.7153	0.099	0.889
333.16	2.4949	0.162	0.929
333.16	2.9651	0.187	0.932
333.17	3.5450	0.243	0.941
333.14	4.2215	0.286	0.951
333.16	4.8757	0.349	0.956
333.16	5.4509	0.418	0.957
333.15	6.4564	0.511	0.958
333.17	7.0533	0.586	0.958
333.16	7.5783	0.648	0.949
333.16	8.2634	0.726	0.949

0021-9568/86/1731-0026$01.50/0 © 1986 American Chemical Society

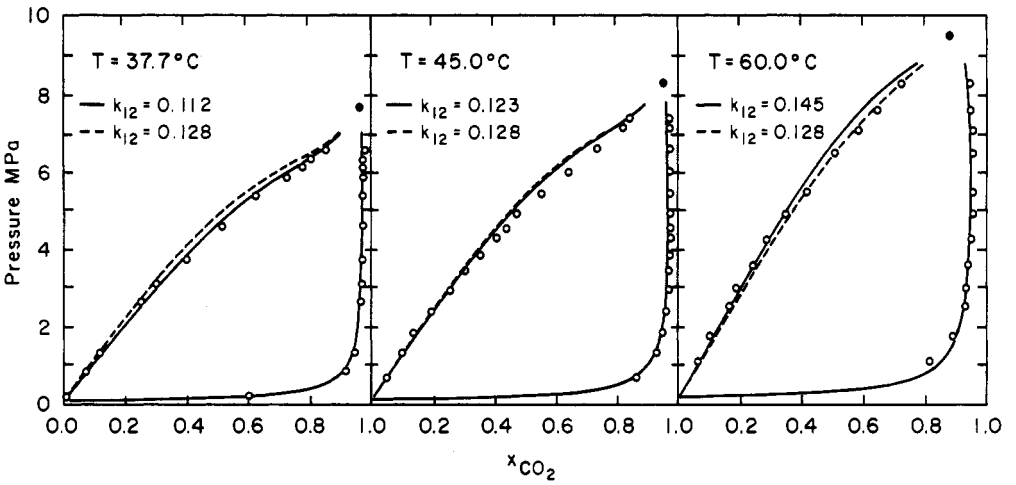

Figure 1. Comparison of experimental data and the Peng–Robinson equation of state predictions for the carbon dioxide–cyclopentane system at each of the three temperatures measured. The Peng–Robinson results were calculated with both a single temperature-independent and temperature-dependent binary interaction parameters. (The predicted vapor curves were indistinguishable, and only one is shown.)

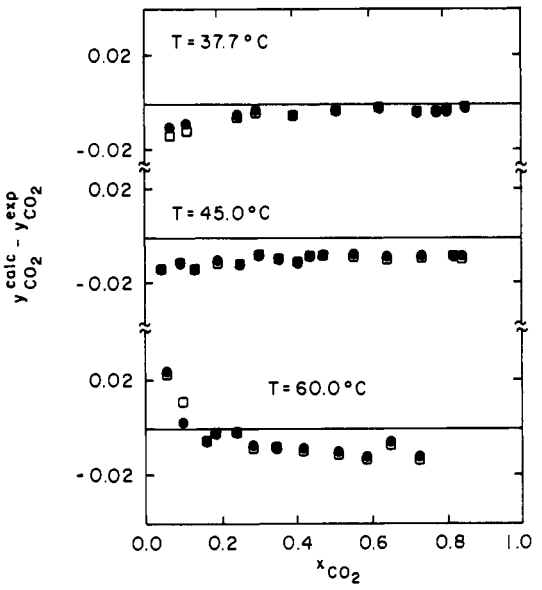

Figure 2. Deviations between the experimental vapor-phase mole fractions and those calculated with the Peng–Robinson equation of state by using a temperature-dependent binary interaction parameter for the carbon dioxide–cyclopentane system.

parameters b and c, and for the temperature-dependent function a for each of these equations were used, together with the van der Waals one-fluid mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

$$b = \sum_i x_i b_i$$

$$c = \sum x_i c_i$$

Also

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \tag{4}$$

where k_{ij} is the binary interaction parameter obtained by fitting the experimental data. The value of the binary interaction parameter was calculated by minimizing the least-squares error in the predicted bubble point pressure by using the experimental temperature, pressures, and liquid-phase compositions. This was done at each temperature and, in the case of the Peng–Robinson equation, for all temperatures simultaneously to obtain a single temperature-independent binary interaction parameter. The values of the k_{12} so calculated appear in Table IV. The fit of both equations of state to our data are comparable, and

Table IV. Binary Interaction Parameters for the CO_2–Cyclopentane System

	equation of state	
T, °C	Peng–Robinson	Teja–Patel
37.7	0.112	0.118
45.0	0.123	0.120
60.0	0.145	0.144
	0.128[a]	

[a] Temperature independent.

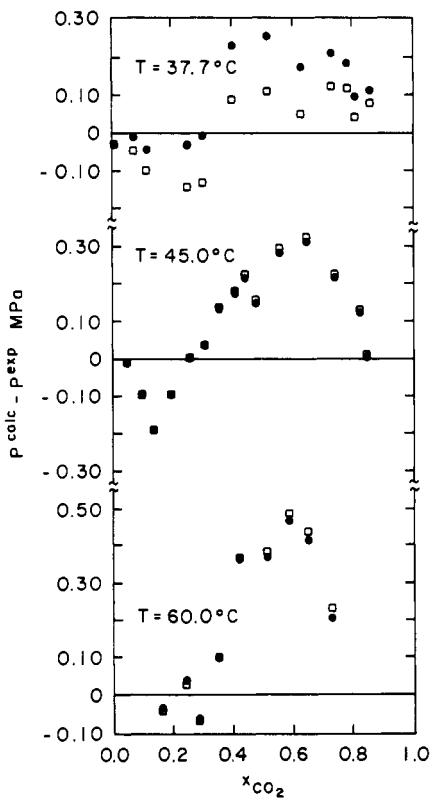

Figure 3. Deviations between the experimental pressure and that calculated with the Peng–Robinson equation of state by using a temperature-dependent binary interaction parameter for the carbon dioxide–cyclopentane system.

the values of k_{12} obtained are similar to those found by Huron et al. (*4*) using the Soave–Redlich–Kwong equation binary mixtures of CO_2 with *n*-butane, *n*-pentane, and *n*-decane. The overall standard deviation of the fit of our data in percent is σ_y

Table V. Estimated Mixture Critical Points Using the Peng-Robinson Equation of State

T_c, K	P_c, MPa	x_{CO_2}
310.87	7.765	0.976
318.17	8.249	0.949
333.18	9.482	0.884

= 0.84 and σ_p = 6.91 which are also comparable to that found by Huron et al.

Figure 1 shows our data at all three temperatures, together with the best bubble point fit with the Peng-Robinson equation of state, with both temperature-dependent and temperature-independent binary interaction parameters. On the scale of this graph, the results obtained by using the Teja-Patel equation would be indistinguishable from those with the Peng-Robinson equation.

Also included in the figure and Table V are the mixture critical points estimated by using the Peng-Robinson equation of state, the binary interaction parameters appropriate to each temperature, and the computational technique described by Heidemann and Khalil (*5*), the Michelsen and Heidemann (*6*).

Finally, Figure 2 shows the departure of the predicted and experimental vapor-phase mole fractions of carbon dioxide. There we see that the compositional deviations are small, and that the Peng-Robinson predictions are generally lower than the measured vapor-phase mole fractions. Similarly, Figure 3 shows the departure of the predicted and experimental bubble point pressures. There we see that the predicted pressures are too low at low carbon dioxide mole fractions, and too high at the higher mole fractions, suggesting that the shape of the predicted phase envelope is not in complete agreement with experimental data. This is also evident from Figure 1.

Glossary

a, b, c	equation of state constants
k_{ij}	binary interaction coefficient
P	pressure
R	gas constant
T	temperature
V	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Registry No. CO_2, 124-38-9; cyclopentane, 287-92-3.

Literature Cited

(1) Behrens, P. K.; Sandler, S. I. *J. Chem. Eng. Data* **1983**, *28*, 52.
(2) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1978**, *15*, 59.
(3) Patel, N. C.; Teja, A. S. *Chem. Eng. Sci.* **1982**, *27*, 463.
(4) Huron, M.-J.; Durou, G.-N., and Vidal, J. *Fluid Phase Equilib.* **1977**, *1*, 247.
(5) Heidemann, R. A.; Khalil, A. M. *AIChE J.* **1980**, *26*, 769.
(6) Michelsen, M. L.; Heidemann, R. A. *AIChE J.* **1981**, *27*, 521.

Received for review November 26, 1984. Accepted June 21, 1985. We are pleased to acknowledge the financial support of the Chevron Oil Field Research Co., the Mobil Foundation, and the Department of Chemcial Engineering at the University of Delaware for this work.

Phase Equilibria for Water–Decane–Propan-1-ol and Water–Butan-1-ol at 20 °C, Including Density and Refractive Index

Eric G. Mahers[†] and Richard A. Dawe*

Mineral Resources Engineering Department, Imperial College, London SW7 2AZ, U.K.

Compositions along the binodal curve of the system water–decane–propan-1-ol at 20 °C have been determined gravimetrically, and characterized by measuring the refractive index and density along the binodal curve. Tie lines were determined from these measurements. The refractive index and density of the miscible system decane–propan-1-ol and the partially miscible system water–butan-1-ol are also reported.

Introduction

Density and refractive index measurements are commonly used for analysis of binary and ternary mixtures. In studies of displacements in porous media modelling oil reservoir behavior, a miscible binary system, decane–propan-1-ol, and a partially miscible ternary system, water–decane–propan-1-ol, have been used (*1*, *2*).

Experimental Section and Results

Components were purchased in their highest commercial purity and used without further purification. The decane was supplied by Koch-Light Ltd., the propan-1-ol and butan-1-ol by British Drug Houses (AnalaR grade), and the water was singly distilled.

Fluid densities were measured to ±0.1 kg m^{-3} with a 4$^1/_2$-digit Anton Parr Model DMA 46 digital density meter, calibrated with water and air according to the maker's instructions. The refractive indices were measured to a precision of ±4 × 10^{-5} by a Bellingham and Stanley Abbè "60" refractometer, Model "high accuracy 60/ED". The refractive indices were measured at the sodium doublet line 589.3 nm and the instrument calibrated with a silica standard. Both instruments were thermostatically controlled at 20 ± 0.05 °C.

Water–Decane–Propan-1-ol System. The phase diagram of the water–decane–propan-1-ol system was determined as follows. The compositions along the binodal curve were determined gravimetrically. For the water-rich side of the system, 10 mL of water were placed in a flask held on an electronic balance measuring to 0.01 g and the mass noted. A drop of decane was added, thus forming a two-phase mixture and the mass noted again. Sufficient propan-1-ol was added to dissolve the decane into the aqueous phase, the mass added noted, and the composition calculated. More decane was added to the system, followed by propan-1-ol to again reach miscibility. The decane-rich compositions were determined similarly but starting with 10 mL of decane and adding water and then propan-1-ol.

[†] Now with Unilever Research, Merseyside, U.K.

0021-9568/86/1731-0028$01.50/0 © 1986 American Chemical Society