Phase Equilibrium for Carbon Dioxide–Benzene at 313.2, 353.2, and 393.2 K

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Bubble-point pressures have been measured for the carbon dioxide–benzene system at 313.2, 353.2, and 393.2 K and pressures from 0.1 to 13.3 MPa (15 to 1930 psia). Vapor-phase compositions were also measured at 313.2 K. The results differ substantially from previous results by Wan and Dodge and by Ohgaki and Katayama. The present data are represented well by the Soave equation of state when two optimum interaction parameters, C_{12} = 0.066 and D_{12} = 0.043, are used; root-mean-square errors in calculated bubble-point pressures are 0.06 MPa (9 psia).

Introduction

A systematic study (1, 2) of phase behavior in systems containing carbon dioxide and hydrocarbons revealed certain systems for which published data appeared to be of questionable accuracy. As a result, new measurements were made and published on carbon dioxide–n-hexane (2). The present work presents data on carbon dioxide–benzene, a system for which two previous studies (3, 4) have been published.

Experimental Method

The experimental measurements were done in a piston-cylinder-type, windowed phase equilibrium cell. The apparatus and the procedures were identical with those described elsewhere (2). Using these procedures, we measured equilibrium vapor and liquid compositions at 313.2 K over the complete composition range.

The data at 313.2 K differed substantially from those of previous studies (3, 4). As a result, a series of bubble-point pressure measurements were undertaken in an attempt to resolve this discrepancy. The bubble points were measured as follows. First, a known amount of degassed benzene (50–70 cm³) was injected volumetrically into the cell from a precision screw pump (Ruska Model 2250). Next, a quantity of carbon dioxide was injected in a similar manner to give a mixture of the desired composition. The cell was then rocked until equilibrium was established at a fixed system volume; the equilibrium pressure was recorded. The system volume was then changed (by adjustment of the piston), equilibrium reestablished, and pressure recorded. This process was repeated to give pressure readings in both the single-phase (liquid) and two-phase (vapor–liquid) regions. The bubble-point pressure was determined by locating the breakpoint on a plot of pressure as a function of system volume. Figure 1 presents typical results. These bubble-point studies required volumetric measurements only (no chromatographic analyses, as for the P–T–x–y data) and are believed to offer an essentially independent check of the P–T–x–y data. The estimated uncertainties in our measurements are ±3 psia in bubble-point pressures, ±0.1 K in temperature, and ±0.002 in x.

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Table I. Phase Equilibrium Data for CO₂-Benzene

press., MPa (psia)	mole fraction CO₂ liquid	vapor
Temperature = 313.2 K (40 °C, 104 °F)		
0.740 (107)	0.056	0.967
1.390 (202)	0.115	0.981
2.135 (310)	0.183	0.986
2.790 (405)	0.253	0.988
3.430 (498)	0.318	0.989
4.025 (584)	0.380	0.989
4.510 (654)	0.439	0.990
4.990 (724)	0.504	0.990
5.400 (783)	0.575	0.990
5.800 (841)	0.643	0.991
6.260 (908)	0.727	0.990
6.710 (973)	0.808	0.990
7.025 (1019)	0.873	0.989
7.280 (1056)	0.904	0.989
7.720 (1120)	0.948	0.989
0.615 (89)	0.049	*a*
1.230 (178)	0.101	
2.315 (336)	0.198	
3.305 (479)	0.297	
4.200 (609)	0.400	
4.990 (724)	0.504	
5.555 (806)	0.595	
6.170 (895)	0.705	
6.535 (948)	0.775	
3.360 (487)	0.301	*b*
4.550 (660)	0.444	
Temperature = 353.2 K (80 °C, 176 °F)		
0.105 (15)*c*	0.000	*a*
1.005 (146)	0.047	
2.075 (301)	0.104	
3.730 (541)	0.199	
5.470 (793)	0.303	
6.950 (1008)	0.402	
8.410 (1220)	0.509	
9.510 (1379)	0.601	
10.655 (1545)	0.706	
10.775 (1563)	0.715	
11.500 (1668)	0.799	
11.665 (1692)	0.817	
Temperature = 393.2 K (120 °C, 248 °F)		
0.305 (44)*c*	0.000	
1.815 (263)	0.064	
2.780 (403)	0.106	
4.935 (716)	0.202	
7.345 (1065)	0.308	
7.475 (1084)	0.315	
9.685 (1405)	0.417	
11.395 (1653)	0.505	
13.295 (1928)	0.616	

a Bubble-point pressures only, this work. *b* Bubble-point pressures, ref 5. *c* Benzene vapor pressure.

Materials

The carbon dioxide used in the studies was 99.99 mol % pure, supplied by Air Products, and the benzene was 99.0 mol % minimum purity from Phillips Petroleum Co. Both were used without further purification.
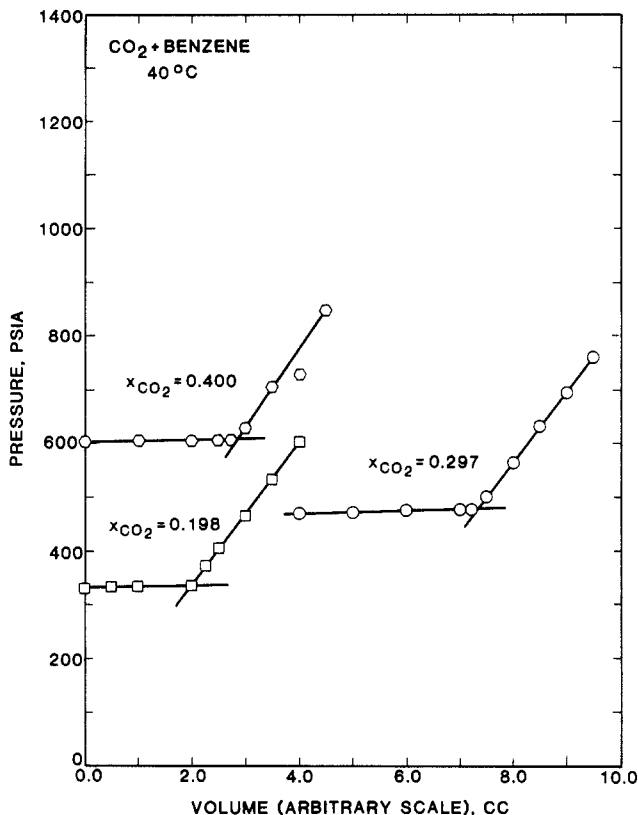
Figure 1. Typical pressure–volume data for determination of bubble-point pressures for carbon dioxide–benzene.
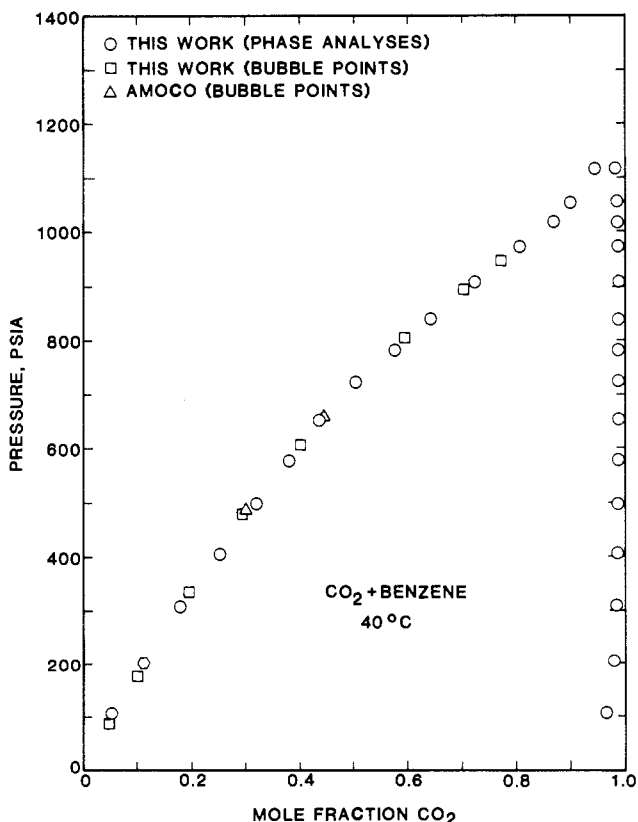

Figure 2. Isothermal pressure–composition data for carbon dioxide–benzene.

Results

The experimental data from this study are presented in Table I. The data at 313.2 K, both $P-T-x-y$ and bubble-point pressures, are shown in Figure 2. Figure 3 presents a com-
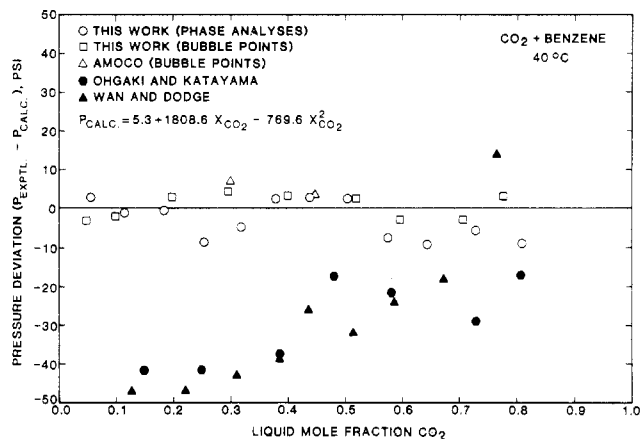

Figure 3. Comparison of bubble-point pressure data for carbon dioxide–benzene.

parison of the present data with those of Wan and Dodge (3) and Ohgaki and Katayama (4) at 313.2 K. Also shown in Table I and Figures 2 and 3 are two bubble-point pressure measurements by Metcalfe and Turek (5) at Amoco Production Co. These two measurements were made at our request in an effort to resolve discrepancies in other data sets.

Figure 3 shows deviations of the bubble-point data sets from an arbitrary polynomial fit to the present bubble-point data. The figure shows excellent agreement of the present $P-T-x-y$ and bubble-point data with the bubble points measured by Metcalfe and Turek, while the other data sets (3, 4) are lower by as much as 0.31 MPa (45 psi).

The data of Wan and Dodge (3) were presented in graphical form only, so precise comparisons cannot be made with the present results. The data of Ohgaki and Katayama (4) at 313.2 K are lower in benzene by as much as 0.03 mole fraction in the liquid phase at low pressures (<4.1 MPa or 600 psia) while their vapor mole fractions are higher in benzene by ∼0.004 mole fraction throughout most of the pressure range studied.

Correlation

The data have been correlated by the Soave equation of state (6), with the following mixing rules:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij}$$

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j b_{ij}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - C_{ij})$$

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 + D_{ij})$$

where C_{ij} and D_{ij} are empirical interaction parameters. The values of C_{12} and D_{12} were evaluated from $P-T-x-y$ data by minimizing the sum of squares, SS, in the predicted phase compositions at constant temperature and pressure:

$$SS = \sum_{i=1}^{M} \{(\Delta x)^2 + (\Delta y)^2\}_i$$

Similar treatment of the present bubble-point pressure data was done by minimizing the sum of squares of errors in predicted bubble-point pressures:

$$SS = \sum_{i=1}^{M} (\Delta P)_i^2$$

Table II presents values of the optimum interaction parameters. The results reveal that the usual procedure of using C_{ij}

Table II. Soave Correlation of Carbon Dioxide–Benzene Data

temp, K	optimum parameters		rms errors in		
	C_{12}	D_{12}	x	y	P, MPa (psi)
Present Work (P-T-x-y)					
313.2	0.083		0.024	0.001	
313.2	0.065	0.041	0.006	0.002	
Ohgaki and Katayama (P-T-x-y)					
313.2	0.069		0.024	0.004	
313.2	0.055	0.035	0.014	0.003	
Present Work (Bubble Points)					
313.2	0.088				0.19 (27)
353.2	0.079				0.40 (58)
393.2	0.088				0.24 (35)
all T	0.084				0.31 (46)
313.2	0.065	0.039			0.03 (5)
353.2	0.065	0.049			0.03 (4)
393.2	0.071	0.036			0.03 (5)
all T	0.066	0.043			0.06 (9)

only ($D_{ij} = 0$) does not lead to satisfactory fit of the data by the Soave equation. However, use of both C_{ij} and D_{ij} (as in ref 1) produces an excellent representation of the data. Individual isotherms can be fitted to root-mean-square errors of 0.03 MPa (5 psi) while all isotherms can be fitted simultaneously with errors of 0.06 MPa (9 psi).

Glossary

a, b	parameters in Soave equation of state
C_{ij}, D_{ij}	interaction parameters between components i and j in mixing rules for Soave equation
M	number of data points
N	number of components in mixture
P	system pressure
T	system temperature
x	liquid mole fraction of CO_2
y	vapor mole fraction of CO_2
Δ	difference between calculated and experimental values

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Excess Volumes of Ternary Mixtures Containing Methyl Ethyl Ketone, 1-Alkanols, and n-Octane

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The excess volumes, V^E_{123}, for ternary mixtures of methyl ethyl ketone + 1-alkanols + n-octane have been measured at 303.15 K, by using a new dilatometer. The alkanols include 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. Experimental results for the ternary mixtures are positive over the whole range of composition in all of the systems. excess volumes for binary system of methyl ethyl ketone + n-octane have also been measured at 303.15 K by using a two-limbed dilatometer.

In continuation of earlier work on excess volumes of ternary mixtures containing methyl ethyl ketone and n-heptane as common components and a homologous series of n-alkanols as noncommon components (1), we report here new excess-volume data for four ternary systems. The mixtures include methyl ethyl ketone and n-octane as common components. The alkanols, used as noncommon components, include 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. The measurements were made to understand the effect of chain length of 1-alkane on excess volumes.

Purification of Materials. The alcohols (BDH) were purified by the method described by Rao and Naidu (2). Methyl ethyl ketone (BDH) was purified by the method described by Reddy and Naidu (3). The sample was dried over anhydrous potassium carbonate and fractionally distilled. n-Octane (Riedel) was purified by drying it over sodium for 1 day. It was then refluxed

Table I. Densities of Pure Substances at 303.15 K

	ρ, g cm^{-3}	
	present work	lit.
methyl ethyl ketone	0.79449	0.79452
1-propanol	0.79562	0.79567
1-butanol	0.80202	0.80206
1-pentanol	0.80762	0.80764
1-hexanol	0.81198	0.81201
n-octane	0.69445	0.69450

for 4 h and finally fractionally distilled. The purities of the liquids were checked by comparing the measured densities with those reported in the literature (4). The data are given in Table I. Densities were measured by using a bicapillary pycnometer described by Rao (5). Excess volumes for ternary systems were measured with the dilatometer described earlier (1).

The mixing cell contains three limbs of different capacities. Mercury was taken at the bottom of the dilatometer to separate the three components. One of the bulbs was fitted with a capillary (i.d. 1.0 mm), and the other two bulbs were fixed with ground-glass stoppers. Four dilatometers with different capacities were used to cover the mole-fraction range 0.1–0.8. The V^E values were accurate to ±0.003 cm^3 mol^{-1}.

The experimental results for the binary systems n-octane with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol, reported in the literature (6), have been used to obtain excess volume–