# Vapor−Liquid Equilibria for the Carbon Dioxide + Pentane and Carbon Dioxide + Toluene Systems

**Katsumi Tochigi,\* Kunihisa Hasegawa, Norihiro Asano, and Kazuo Kojima**

Department of Industrial Chemistry, College of Science and Technology, Nihon University, 1-8 Surugadai, Kanda, Chiyoda-ku, Tokyo 101, Japan

Vapor−liquid equilibrium data have been measured for the systems carbon dioxide + pentane at (310.15, 333.15, and 363.15) K and carbon dioxide + toluene at 323.15 K and 333.15 K. The experimental data have been correlated by the Peng−Robinson equation of state with one interaction parameter. In addition, the group pair parameters relating to $CH_2 + CO_2$ and $ArCH + CO_2$ in the PRASOG group contribution model are determined.

## Introduction

Carbon dioxide is frequently found in naturally occurring hydrocarbon reservoirs and has been widely used as the solvent in supercritical fluid extraction. To predict the phase equilibria in such systems, a group contribution method called PRASOG has been proposed by the authors (Tochigi et al., 1998). The high-pressure vapor−liquid equilibria (VLE) data are required to determine the group pair parameters relating to the $CO_2$ group.

This paper reports the measurement of vapor−liquid equilibria for the systems carbon dioxide + pentane at (310.15, 333.15, and 363.15) K and carbon dioxide + toluene at 323.15 K and 333.15 K. The VLE data were correlated using the Peng−Robinson (1976) equation of state, and the group pair parameters relating to $CH_2 + CO_2$ and $CO_2 + ArCH$ in the PRASOG group contribution method are reported.

## Experimental Section

*Apparatus.* A schematic diagram of experimental apparatus is shown in Figure 1. The apparatus is similar to that used by Sako et al. (1991) and Tsuji and Hongo (1994) and is a static-type apparatus composed of three parts, the equilibrium cell, the vapor−liquid sampling system, and the analyzing system.

The experimental equipment was designed to permit the determination of equilibrium phase compositions in a temperature range from about room temperature to 393 K at pressures to 14.7 MPa. In the equilibrium system, the cell has an internal capacity of about 500 cm$^3$ and is equipped with a Pyrex glass bull's-eye window to observe the interface between phases. The equilibrium cell and sampling system are in a thermostated air bath.

Composition analyses of vapor and liquid samples were done with a Shimadzu gas chromatograph type GC-8APT equipped with a thermal conductivity cell. Porapak QS was used as the column packing, and helium as the carrier gas. The composition was determined using the relative area method with an accuracy within ±0.005 mole fraction.

*Procedure.* Pentane or toluene was placed in the equilibrium cell, and $CO_2$ was added to the desired pressure. After confirmation that the pressure in the equilibrium cell was constant, the temperature and pressure were measured. At that time, small samples in the vapor and liquid phases were removed using the sampling valves and introduced into the sampling system. In the sampling system, each sample was vaporized at decreasing pressure by the use of a vapor−liquid circulating pumps. After all the samples were evaporated, a constant volume sample was sampled through a six-direction valve and introduced into the gas chromatograph, and the composition of each sample was determined.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer (Pt100O) with an accuracy of ±0.03 K. A standard resistance thermometer (Chino Co., model R 800-2, Japan), which is based on ITS-90, was used for this calibration. The equilibrium pressure was measured using a calibrated Bourdon tube pressure gauge with an accuracy within ±0.15% F. S. (full scale) (about 37 kPa).

*Materials.* Special-grade pentane and toluene of 99.6 mol % purity were supplied by Wako Pure Chem. Co. Ltd.
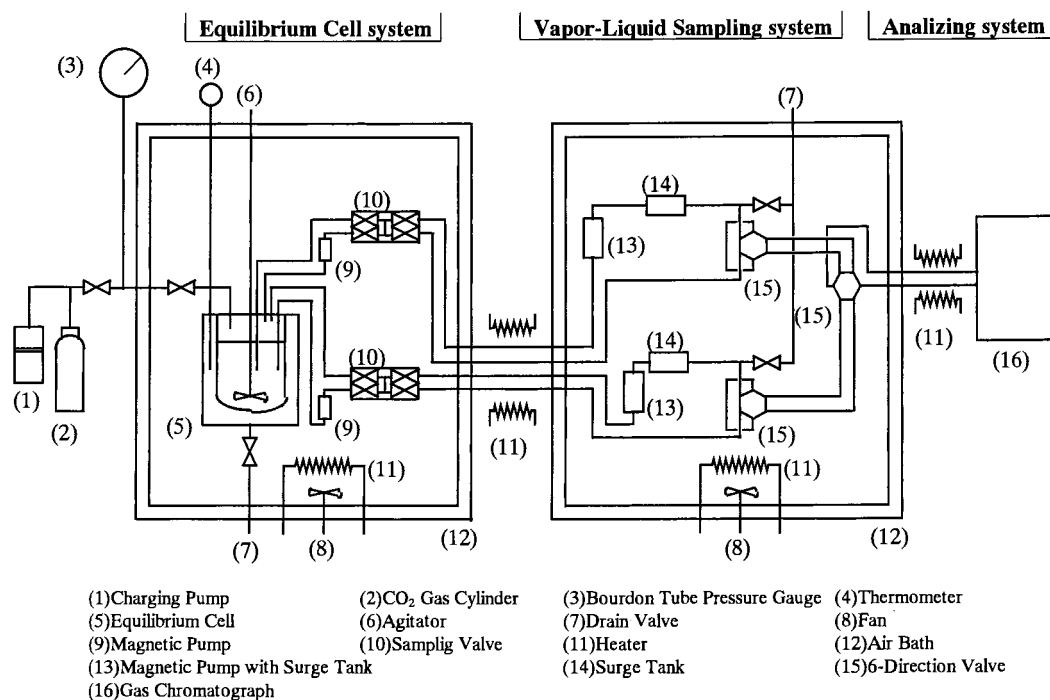
**Table 1. Vapor−Liquid Equilibrium Data, Total Pressure, $P$, Liquid Phase, $x_1$, and Vapor Phase, $y_1$, Mole Fractions for Carbon Dioxide (1) + Pentane (2)**

| $P$/MPa | $x_1$ | $y_1$ | $P$/MPa | $x_1$ | $y_1$ |
|---|---|---|---|---|---|
| 310.15 K | | | | | |
| 0.566 | 0.037 | 0.786 | 5.075 | 0.621 | 0.953 |
| 0.808 | 0.064 | 0.845 | 6.022 | 0.781 | 0.962 |
| 1.088 | 0.101 | 0.874 | 6.516 | 0.846 | 0.963 |
| 2.059 | 0.208 | 0.928 | 6.960 | 0.897 | 0.967 |
| 3.085 | 0.328 | 0.942 | 7.089 | 0.910 | 0.968 |
| 3.863 | 0.444 | 0.951 | 7.310 | 0.925 | 0.968 |
| 333.15 K | | | | | |
| 0.596 | 0.029 | 0.632 | 6.989 | 0.636 | 0.922 |
| 1.291 | 0.086 | 0.802 | 8.054 | 0.751 | 0.915 |
| 2.011 | 0.150 | 0.860 | 8.340 | 0.778 | 0.910 |
| 3.026 | 0.242 | 0.895 | 8.438 | 0.788 | 0.907 |
| 3.992 | 0.332 | 0.908 | 8.665 | 0.815 | 0.899 |
| 5.165 | 0.445 | 0.919 | 8.754 | 0.829 | 0.892 |
| 5.944 | 0.527 | 0.922 | | | |
| 363.15 K | | | | | |
| 0.947 | 0.031 | 0.451 | 7.058 | 0.467 | 0.849 |
| 1.173 | 0.041 | 0.543 | 7.985 | 0.540 | 0.847 |
| 1.459 | 0.062 | 0.611 | 9.136 | 0.636 | 0.826 |
| 2.257 | 0.119 | 0.734 | 9.227 | 0.646 | 0.824 |
| 3.095 | 0.177 | 0.787 | 9.454 | 0.678 | 0.813 |
| 4.071 | 0.251 | 0.821 | 9.532 | 0.688 | 0.807 |
| 5.000 | 0.317 | 0.839 | 9.651 | 0.707 | 0.795 |
| 5.816 | 0.372 | 0.848 | 9.671 | 0.710 | 0.789 |

**Figure 1.** Schematic diagram of experimental apparatus.

(1)Charging Pump
(5)Equilibrium Cell
(9)Magnetic Pump
(13)Magnetic Pump with Surge Tank
(16)Gas Chromatograph

(2)CO₂ Gas Cylinder
(6)Agitator
(10)Samplig Valve

(3)Bourdon Tube Pressure Gauge
(7)Drain Valve
(11)Heater
(14)Surge Tank

(4)Thermometer
(8)Fan
(12)Air Bath
(15)6-Direction Valve
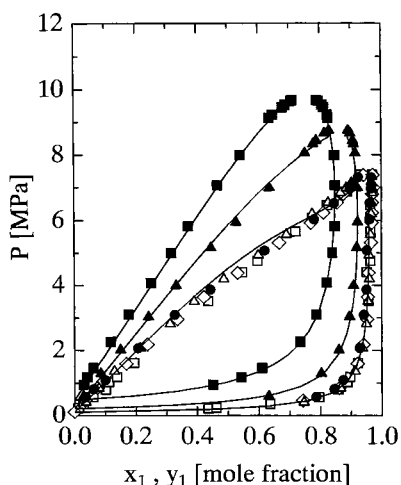


**Figure 2.** Experimental vapor−liquid equilibria for the carbon dioxide (1) + pentane (2) system: △, Cheng et al. (1989); □, Sako et al. (1986); ◇, Besserer and Robinson (1973); ●, this work (310.15 K); ▲, this work (333.15 K); ■, this work (363.15 K); −, PR EOS + $k_{12}$.

Carbon dioxide gas having a purity of 99.99+ mol % was supplied from Showa Tansan Co. Ltd. All reagents were used without further purification.

## Experimental Results

*Carbon Dioxide + Pentane.* The measurements were made at 310.15 K, for which literature values have been reported, and at 333.15 K and 363.15 K. The experimental VLE data are given in Table 1 and are represented graphically in Figure 2. Figure 2 shows the agreement between the experimental data and the literature values at 310.9, 310.5, and 311.59 K by Besserer and Robinson (1973), Sako et al. (1986), and Cheng et al. (1989). The average absolute deviations of total pressure are 3.4, 10.1, and 4.7%.

*Carbon Dioxide + Toluene.* Measurement were made at 323.15 K, where literature values have been reported,
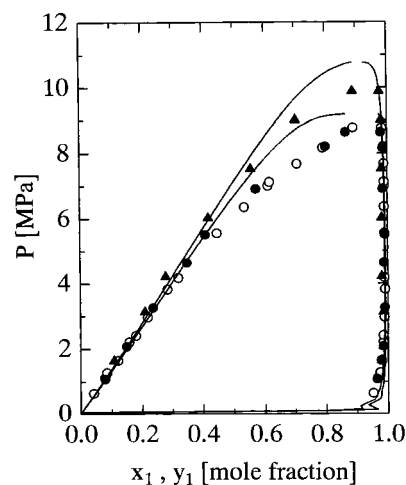


**Figure 3.** Experimental vapor−liquid equilibria for the carbon dioxide (1) + toluene (2) system: ○, Fink et al. (1990); ●, this work (323.15 K); ▲, this work (333.15 K); −, PR EOS + $k_{12}$.

**Table 2. Vapor−Liquid Equilibrium Data, Total Pressure, *P*, Liquid Phase, $x_1$, and Vapor Phase, $y_1$, Mole Fractions for Carbon Dioxide (1) + Toluene (2)**

| *P*/MPa | $x_1$ | $y_1$ | *P*/MPa | $x_1$ | $y_1$ |
|---|---|---|---|---|---|
| | | 323.15 K | | | |
| 1.080 | 0.080 | 0.965 | 5.501 | 0.408 | 0.992 |
| 2.073 | 0.150 | 0.986 | 6.906 | 0.573 | 0.986 |
| 3.261 | 0.237 | 0.991 | 8.200 | 0.800 | 0.988 |
| 4.634 | 0.349 | 0.988 | 8.630 | 0.866 | 0.981 |
| | | 333.15 K | | | |
| 1.634 | 0.109 | 0.979 | 7.533 | 0.556 | 0.982 |
| 3.129 | 0.210 | 0.986 | 9.018 | 0.702 | 0.982 |
| 4.215 | 0.278 | 0.981 | 9.885 | 0.889 | 0.976 |
| 6.019 | 0.418 | 0.982 | | | |

and at 333.15 K. The experimental data are given in Table 2 and shown in Figure 3. Figure 3 shows also the agreement between the experimental and literature values by Fink and Hershey (1990). The average absolute deviation of total pressure is 3.2%.

## Discussion

The Peng−Robinson equation of state (1976) given by eq 1 was used to correlate the VLE results.

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

with the following mixing rule

$$a = \sum_i^n \sum_j^n x_i x_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \quad (2)$$

$$b = \sum_i^n x_i b_i \quad (3)$$

where $a_{ii}$ and $b_i$ are the parameters of pure component $i$ and were calculated using the generalized correlation of Stryjek and Vera (1986). The $k_{ij}$ is the binary interaction parameter and was determined by minimizing the relative deviation between the experimental and calculated total pressures. The optimized values of $k_{ij}$ and the average deviations of total pressure and vapor composition are given in Table 3. The correlated VLE employing these values are shown in Figures 2 and 3. The agreements near critical points are not good for carbon dioxide + toluene.

To predict VLE for carbon dioxide + pentane and carbon dioxide + toluene mixtures, PRASOG (Tochigi et al. 1998) needs the group pair parameters relating to three groups, $CH_2$, ArCH, and $CO_2$. Using the experimental data together with literature values for carbon dioxide + *n*-paraffins ($C_4$−$C_{10}$) systems, the following PRASOG group pair parameters have been determined for the group pairs relating to $CH_2 + CO_2$ and ArCH + $CO_2$.

$$\ln a_{CH_2/CO_2} = -2.2588 + 611.5/(T/K) \quad (4a)$$

$$\ln a_{CO_2/CH_2} = 2.3231 - 692.3/(T/K) \quad (4b)$$

$$\ln a_{ArCH/CO_2} = 2.1209 - 696.1/(T/K) \quad (5a)$$

$$\ln a_{CO_2/ArCO} = -2.1588 + 653.8/(T/K) \quad (5b)$$

Average absolute deviations between the experimental and predicted vapor composition and total pressure results using PRASOG are also shown, respectively, in Table 3.

**Table 3. Calculated Results of Vapor−Liquid Equilibria Using PR EOS and PRASOG**

| system | $T$/K | PR EOS | | | PRASOG | |
|---|---|---|---|---|---|---|
| | | $k_{ij}$ | $\Delta y_1{}^a$ | $\Delta P^b$ | $\Delta y_1{}^a$ | $\Delta P^b$ |
| carbon dioxide (1) + pentane (2) | 310.15 | 0.142 | 1.1 | 4.6 | 2.2 | 8.9 |
| | 333.15 | 0.139 | 0.8 | 2.7 | 6.4 | 8.5 |
| | 363.15 | 0.139 | 0.5 | 2.6 | 11.6 | 14.5 |
| carbon dioxide (1) + toluene (2) | 323.15 | 0.118 | 0.5 | 5.0 | 0.5 | 1.9 |
| | 333.15 | 0.103 | 1.3 | 6.0 | 0.6 | 3.8 |

$^a \Delta y_1$ (%) = $\{|y_{1exp} - y_{1cal}| \times 100\}_{avg}$. $^b \Delta P$ (%) = $\{|P_{exp} - P_{cal}|/P_{exp} \times 100\}_{avg}$.

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