Vapor−Liquid Equilibrium for Carbon Dioxide + 1-Butanol at High Pressure

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Vapor−liquid equilibria and saturated densities for carbon dioxide + 1-butanol at high pressures were measured at 313.15 K including in the vicinity of the critical region with the static-circulation apparatus. The present experimental vapor−liquid equilibrium results significantly differ from the values reported by King et al., but agree with those of Jennings et al. The results were correlated with various equations of state.

Introduction

Phase equilibrium properties of mixtures at high pressures are required for practical use such as in the design and operation of separation equipment in the petroleum, natural gas, and related industries. Supercritical fluid extraction is now attractive as a separation technology.

Vapor−liquid equilibrium relations for the carbon dioxide + 1-butanol system were reported by King et al. (*3*) at 313.15 K and Jennings et al. (*1*) at 314.8 K. King et al. (*3*) used a recirculation apparatus and suggested the existence of vapor−liquid−liquid equilibria in the vicinity of the critical region. Jennings et al. (*1*) used a flow apparatus and reported no three-phase separation. There are considerable differences between the results of King et al. (*3*) and those of Jennings et al. (*1*).

A static-circulation apparatus equipped with three density meters for measuring vapor−liquid−liquid phase equilibrium at high pressures was previously developed (*6*). With this apparatus, the coexisting phase compositions and their saturated densities for the carbon dioxide + 1-butanol mixture at high pressures were measured at 313.15 K including in the vicinity of the critical regions.

Results

The apparatus and experimental procedures are the same as described previously (*6*). The apparatus is a static-circulation type with a maximum temperature and pressure of 400 K and 20 MPa and has three Anton Paar DMA 512S density meters. The equilibrium phase compositions were determined by using a Shimadzu GC-14A gas chromatograph equipped with a 2 m Porapak Q column. Helium was used as a carrier gas at a flow rate of 90 $cm^3 \cdot min^{-1}$. The injection temperature and column temperature were about 413.15 K. The current as measured by a thermal conductivity detector (TCD) was 100 mA.

Carbon dioxide was supplied by Nihon Sanso Co. Ltd. with the guarantee of 99.99% purity. 1-Butanol was the special-grade reagent of Wako Pure Chemicals Co. Ltd. The purity of 1-butanol was 99.9% by gas chromatography.

Table 1. Equilibrium Pressure *P*, Liquid Mole Fraction *x*, Vapor Mole Fraction *y*, Liquid Density ρ_L, and Vapor Density ρ_V for Carbon Dioxide (1) + 1-Butanol (2) at 313.15 K

P/MPa	x_1	y_1	$\rho_L/(kg \cdot m^{-3})$	$\rho_V/(kg \cdot m^{-3})$
6.702	0.489	0.995	828.8	187.5
7.012	0.525	0.997	830.2	205.6
7.405	0.594	0.997	831.0	234.9
7.740	0.681	0.996	827.1	269.3
7.869	0.731	0.995	821.1	286.3
8.003	0.839	0.994	791.1	312.3
8.183	0.955	0.991	670.5	368.3
8.23 ± 0.02[a]	0.987 ± 0.003[a]		510 ± 3[a]	

[a] Estimated critical point.

Table 1 gives the experimental results of coexisting phase compositions and their densities for the carbon dioxide + 1-butanol system at 313.15 K. The critical point was estimated from the experimental vapor−liquid equilibrium values in the vicinity of the critical region, as shown at the bottom of Table 1. The precision and uncertainty of the equilibrium compositions appear to be ±0.0001 and ±0.001 in mole fraction, respectively. The uncertainties of density, temperature, and pressure, respectively, are $\pm 0.1\ kg \cdot m^{-3}$, ±0.1 K, and ±1 kPa.

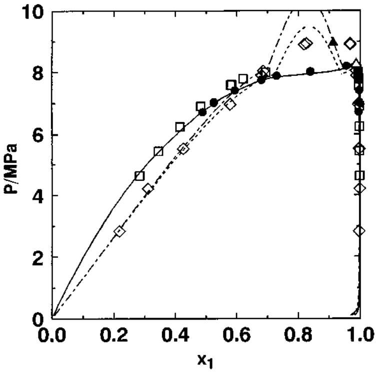

Figure 1. Phase equilibria for carbon dioxide (1) + 1-butanol (2) at 313.15 K: (●) experimental data; (▲) homogeneous data; (◇) King et al. (*3*); (□) Jennings et al. (*1*) at 314.8 K; (△) estimated critical point; (—) pseudocubic EOS; (- - -) Soave−Redlich−Kwong EOS; (— - —) Redlich−Kwong EOS, King et al. (*3*).

Figure 1 gives the experimental pressure−composition diagram, including values reported by King et al. (*3*) at 313.15 K and Jennings et al. (*1*) at 314.8 K. There is considerable discrepancy between the present results and those of King et al. (*3*). King et al. (*3*) estimated the three-phase separation at about 8 MPa with their own values of parameters for the Redlich−Kwong equation of state, as

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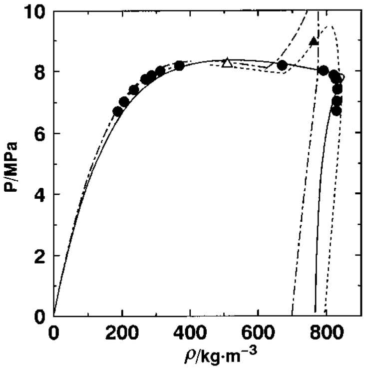

Figure 2. Densities ρ for carbon dioxide (1) + 1-butanol (2) at 313.15 K: (●) experimental data; (▲) homogeneous data; (△) estimated critical point; (—) pseudocubic EOS; (- - -) Soave−Redlich−Kwong EOS; (− − −) Redlich−Kwong EOS, King et al. (*3*).

shown in Figure 1. King et al. (*3*) suggest their results near 9 MPa in Figure 1 correspond to liquid−liquid equilibria. In the present study, no phase separation was observed at 8.944 MPa, 0.9129 mole fraction of carbon dioxide, and a density of 762.4 kg·m^{-3}, as indicated by the point ▲ in Figures 1 and 2. The results reported by King et al. (*3*) seem doubtful. Jennings et al. (*1*) reported no three-phase separation at 314.8 K, similar to the present study. The results of Jennings et al. (*1*) at 314.8 K are relatively close to the present data obtained at 313.15 K. Figure 2 shows the pressure−density data. King et al. (*3*) and Jennings et al. (*1*) did not measure density.

The vapor−liquid equilibrium results were correlated with the conventional Soave−Redlich−Kwong equation of state (*5*) and the following pseudocubic equation of state previously proposed by the authors (*2*):

$$P = \frac{RT}{V^* - b} - \frac{a}{V^{*2}} \qquad V^* = \frac{(V - \epsilon b)(V + \sigma b)}{V} \tag{1}$$

$$\epsilon = (1 - \theta)(\xi - 2) \qquad \sigma = (1 - \theta)(\xi + 2) \tag{2}$$

$$\xi = \left[\frac{4 - \theta}{1 - \theta}\right]^{1/2} \qquad \theta = \frac{8Z_c}{3} \qquad Z_c = \frac{P_c V_c}{RT_c} \tag{3}$$

$$a = Kaa_c \qquad a_c = \frac{27(RT_c)^2}{64P_c} \qquad b_c = \frac{RT_c}{8P_c} \tag{4}$$

$$\ln Ka = S(1 - T_r^{1/2}) \qquad S = 1.1746 + 3.4539\omega \tag{5}$$

where P, R, T, V, Z, and ω, respectively, denote the pressure, gas constant, temperature, molar volume, compressibility factor, and acentric factor. Ka, S, a, b, ϵ, θ, σ, and ξ represent the parameters. The subscripts c and r denote the critical property and reduced property, respectively. The asterisk indicates the apparent value.

The following mixing rules were used in the present correlations with the pseudocubic equation of state, introducing two binary interaction parameters, k and l:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \tag{6}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \qquad b_{ij} = (1 - l_{ij})\frac{(b_i + b_j)}{2} \tag{7}$$

Table 2. Parameters in Equations of State (EOS) k_{12} and l_{12} and Mean Absolute Deviations in Liquid Composition $|\Delta x_1|_{av}$, Vapor Composition $|\Delta y_1|_{av}$, Saturated Liquid Density $|\Delta\rho_L|_{av}$, and Saturated Vapor Density $|\Delta\rho_V|_{av}$ for Carbon Dioxide (1) + 1-Butanol (2) at 313.15 K[a]

EOS	k_{12}	l_{12}	$\|\Delta x_1\|_{av}$	$\|\Delta\rho_L\|_{av}$/(kg·m^{-3})	$\|\Delta y_1\|_{av}$	$\|\Delta\rho_V\|_{av}$/(kg·m^{-3})
PS[b]	0.1251	−0.0909	0.003	20.6	0.001	12.5
SRK[c]	0.0958		0.027	61.4	0.001	9.3

[a] $|\Delta x|_{av} = \sum|x_{1,calcd} - x_{1,exptl}|/I$, $|\Delta\rho_L|_{av} = \sum|\rho_{L,calcd} - \rho_{L,exptl}|/I$, $|\Delta y|_{av} = \sum|y_{1,calcd} - y_{1,exptl}|/I$, and $|\Delta\rho_V|_{av} = \sum|\rho_{V,calcd} - \rho_{V,exptl}|/I$ (I is the number of experimental points). [b] Pseudocubic equation of state. [c] Soave−Redlich−Kwong equation of state.

$$\theta = \sum_i x_i \theta_i \tag{8}$$

x represents the mole fraction. The subscripts i and j denote the components.

The binary interaction parameters k_{ij} and l_{ij} were evaluated to minimize the sum of squares of differences in liquid mole fractions, as shown in Table 2. In the correlations, the critical values and acentric factors were obtained from Reid et al. (*4*). Saturated densities were further evaluated from equations of state. Correlation results are given in Table 2 and Figures 1 and 2. As shown in Figures 1 and 2, the Soave−Redlich−Kwong equation of state gave false vapor−liquid−liquid separation behavior. Satisfactory correlation results were obtained with the pseudocubic equation of states, as shown in Figures 1 and 2.

Conclusions

Phase equilibrium compositions and saturated densities for the carbon dioxide + 1-butanol system at high pressures were measured at 313.15 K with the static-circulation apparatus. The previous data reported by King et al. (*3*) seem doubtful because of the unreasonable large differences from the present data and those of Jennings et al. (*1*).

The results were correlated with the Soave−Redlich−Kwong equation of state and the pseudocubic equation of state. The pseudocubic equation of state gave satisfactory correlation results. The conventional Soave−Redlich−Kwong equation of state however gave a poor correlation of the results.

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