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# High-Pressure Phase Equilibrium for Carbon Dioxide + Ethanol at 291.15 K

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Phase equilibria and saturated densities were measured at 291.15 K and at high pressures with a static-circulation apparatus for carbon dioxide + ethanol. An experimental apparatus, equipped with Anton Paar DMA 512S vibrating tube density meters, was used in the experiments for phase-separation properties at high pressures. Coexisting phase compositions and the saturated density of each phase were measured up to a maximum temperature of 400 K and a maximum pressure of 20 MPa. The experimental data obtained were correlated with the conventional Soave−Redlich−Kwong (SRK) equation.

## Introduction

Phase equilibrium properties of mixtures at high pressures are required for practical uses such as the design and operation of separation equipment in petroleum, natural gas, and related industries. Supercritical fluid extraction is now attractive as a separation technology. The technique of supercritical fluid extraction may be applied to the separations of ethanol from the dilute aqueous solutions produced in biochemical processes. Thus, the literature[1−10] reports phase equilibrium properties for carbon dioxide + ethanol at high pressures above the critical temperature of carbon dioxide.

Previously, the present authors[7] reported high-pressure vapor−liquid equilibria (VLE) and their saturated densities for carbon dioxide + ethanol at 308.15 K. Day et al.[8] have also reported high-pressure phase equilibrium data for carbon dioxide + ethanol at various temperatures including density data. Furthermore, they[9,10] corrected the phase equilibrium data. The reasons for the correction are not written in the papers.[9,10]

A static-circulation apparatus equipped with three density meters for measuring vapor−liquid−liquid equilibria (VLLE) at high pressures was described previously.[7] With this apparatus, VLE and their saturated densities were measured for carbon dioxide + ethanol,[7] carbon dioxide + 1-butanol,[11] and ethane + 2-propanol[12] at high pressures. Phase equilibrium properties of ethane + methanol,[13] ethane + ethanol,[14] ethane + 1-propanol,[15] and ethane + 1-butanol[16] have recently been measured, including VLLE.

In the present study, the VLE compositions and their saturated densities for carbon dioxide + ethanol mixture at high pressures are measured at 291.15 K.

The phase equilibrium relations obtained in the present study are correlated with the conventional Soave−Redlich−Kwong[17] (SRK) equation of state.

## Experimental Section

***Materials.*** Carbon dioxide was supplied by Showa Tansan Co. Ltd. with a guarantee of 99.999% purity. Ethanol was a special-grade reagent of Wako Pure Chemical Industries Ltd. and was used without further purification. The purity of ethanol was more than 99.9 mol % by gas chromatographic area analysis.

***Apparatus and Procedures.*** The apparatus and experimental procedures[7] are the same as described previously. The apparatus is a static-circulation type, which can operate to a maximum temperature and pressure of 400 K and 20 MPa, respectively, and has three Anton Paar DMA 512S vibrating tube density meters. The apparatus is immersed in a constant-temperature liquid bath controlled to within ±0.01 K. The cell volume is approximately 320 $\mathrm{cm}^3$. The coexisting phases were continuously recirculated through the sampling valves and density meters with three magnetic circulation pumps. Temperatures were measured with a Hewlett-Packard 2804A quartz thermometer. Pressures were measured with a Ruska 2480-700 oil dead weight gauge and a Ruska 2439-702 pressure transducer. The equilibrium phase compositions were determined by using a Shimadzu GC-14A gas chromatography equipped with a 3-m Porapak Q column. Helium was used as a carrier gas at a flow rate of 50 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$. The column temperature was about 403 K. The injector and detector temperatures were about 423 K. The current value of a thermal conductivity detector (TCD) was 100 mA.

The cell was evacuated and charged with the samples, carbon dioxide and ethanol. The fluid in the cell was mixed with a magnetic-driven agitator. Each phase was circulated with its circulation pump. After establishing a steady state for 2 or 3 h, the agitator and circulation pumps were stopped. After 1 h, the densities and the pressure were measured with density meters and a dead weight gauge, respectively. A sample of each phase was taken with a sampling valve and analyzed by gas chromatography after a circulation of 2 h in the sampling room.

## Results and Discussion

Table 1 presents the experimental results of coexisting phase compositions and their saturated densities for the carbon dioxide + ethanol system at 291.15 K. The uncertainties of the experimental equilibrium composition, density, temperature, and pressure are ±0.001 mole fraction, $\pm 0.1\ \mathrm{kg\cdot m^{-3}}$, ±0.1 K, and ±1 kPa, respectively.

Figures 1 and 2 give the experimental pressure−composition and their saturated density diagrams, respec-

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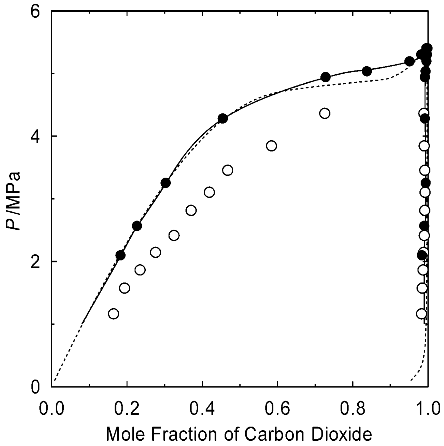

**Figure 1.** Phase equilibria for the carbon dioxide (1) + ethanol (2) system at 291.15 K: –●–, this work; ○, Day et al.;[10] - - -, SRK EOS ($k_{12}$ = 0.0820).

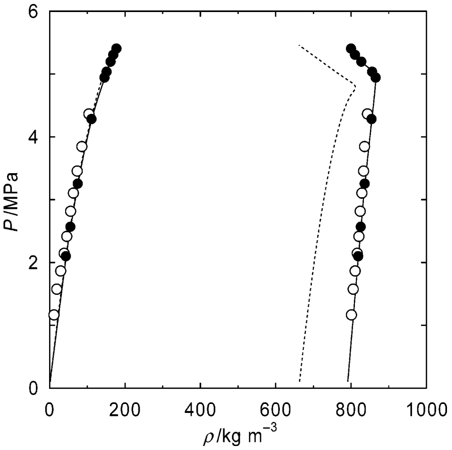

**Figure 2.** Saturated densities for carbon dioxide (1) + ethanol (2) system at 291.15 K: –●–, this work; ○, Day et al.;[10] - - -, SRK EOS ($k_{12}$ = 0.0820).

**Table 1. Saturation Pressure $P$, Liquid Mole Fraction $x$, Vapor Mole Fraction $y$, Liquid Density $\rho_L$, and Vapor Density $\rho_V$ for Carbon Dioxide (1) + Ethanol (2) at 291.15 K**

| $P$/MPa | $x_1$ | $y_1$ | $\rho_L$/kg·m$^{-3}$ | $\rho_V$/kg·m$^{-3}$ |
|---|---|---|---|---|
| 2.094 | 0.184 | 0.985 | 819.5 | 44.1 |
| 2.563 | 0.227 | 0.990 | 826.4 | 56.0 |
| 3.250 | 0.304 | 0.994 | 836.8 | 75.4 |
| 4.278 | 0.455 | 0.992 | 855.1 | 112.0 |
| 4.938 | 0.728 | 0.992 | 865.9 | 146.4 |
| 5.032 | 0.838 | 0.994 | 856.5 | 152.2 |
| 5.191 | 0.951 | 0.997 | 828.0 | 162.6 |
| 5.300 | 0.983 | 0.998 | 811.3 | 169.8 |
| 5.400 | 0.996 | 0.999 | 800.6 | 178.2 |

tively. In Figures 1 and 2, the solid lines denote the smoothed experimental curves drawn by considering the uncertainties of the experimental data. Day et al.[9,10] have measured the VLE, but their data are not consistent with the present measurements, as shown in Figures 1 and 2.

## Correlation

The experimental data obtained were correlated with the conventional SRK[17] equation of state. The binary interaction parameter $k_{12}$ was evaluated as 0.0820 from the present experimental bubble-point–pressure data in the lower pressure regions for the SRK equation. In the correlations, the critical values and acentric factors of ethane and ethanol were obtained from the work of Poling et al.[18] Calculation results with the equation of state are shown in Figures 1 and 2. In Figures 1 and 2, the solid and dotted lines, respectively, denote the experimental smoothed curve and the calculation results by the conventional SRK equation.

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