Volumetric Properties of Carbon Dioxide + Ethanol at 313.15 K

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Volumetric properties of carbon dioxide + ethanol mixtures at 313.15 K were measured, using the vibrating-tube Anton Paar DMA 512P density meter. In the present experiments, no analytical instrument was required. The saturated pressures of carbon dioxide + ethanol mixtures at 313.15 K were measured by the synthetic method. The experimental data obtained were correlated with the density equation, the Soave−Redlich−Kwong (SRK) equation of state, and the pseudocubic equation of state.

Introduction

The phase equilibrium properties of mixtures containing supercritical fluid (SCF) at elevated pressures continue to be of importance in process development and research. The growing motivation for studying the equilibrium of several coexisting phases arises from the need to describe such phase behavior for fluid mixtures of interest in SCF extraction. A large number of applications of SCF technology have been proposed covering the food, pharmaceutical, chemical reaction, coal and oil processing, waste treatment, plastic recycling, and producing industries.

Carbon dioxide is widely used in SCF applications because it has moderate critical temperature, is nontoxic, is nonflammable, is safe, and has a small impact on the earth's environment. Supercritical carbon dioxide and alcohol are excellent candidates for industrial use because of their unique and suitable solvent properties. Ethanol is an important alcohol as the cosolvent of supercritical fluids for the separation of biomaterials. Moreover, ethanol is attracted to the alternative fuel for the car.

The volumetric properties and vapor−liquid equilibria (VLE) are required for the design and operation of the separation equipment with SCF. For carbon dioxide + ethanol mixtures, VLE were reported by some researchers[1−5] without the volumetric property data. On the other hand, Chang et al.[6,7] and Stievano and Elvassore[8] had reported VLE data with saturated density behavior; however, there were not any volumetric property data at constant composition. Pöhler and Kiran[9] had reported volumetric properties from (323 to 423) K and pressures up to 70 MPa, but the data near the critical temperature of carbon dioxide such as 313.15 K were not included. Zúñiga-Moreno and Galicia-Luna[10] had reported saturated liquid densities and excess molar volumes at four compositions up to 25 MPa, but the data of the low pressure region are hardly included.

In the present study, the volumetric properties were measured in the homogeneous region of carbon dioxide + ethanol mixtures at 313.15 K. The saturated pressure was also measured by the synthetic method. The experimental saturated pressures obtained were correlated with the Soave−Redlich−Kwong (SRK) equation of state[11] and the pseudocubic equation of state.[12] Furthermore, the density behaviors of fluid mixtures at high pressures were correlated by almost the same density equation.[13−16]

Experimental Section

Materials. The carbon dioxide was supplied by Showa Tansan Co., Ltd. with a mole fraction purity stated by them of 0.99999. Ethanol was supplied by Wako Pure Chemicals Industries, Ltd. It was used without further purification. Gas chromatographic analysis of ethanol gave a mole fraction purity > 0.999.

Apparatus and Procedure. The apparatus and experimental procedure are almost the same as that described previously.[13,14,16−20] The experimental density data at high pressures were obtained with the variable-volume apparatus equipped with the vibrating-tube density meters. The maximum operating temperature and pressure of the apparatus are 400 K and 20 MPa, respectively. The main parts of the apparatus are a variable-volume cell, piston, Ruska 2465-752 and Ruska 2470-703 air lubricated dead weight gauge, Ruska 2480-700 oil dead weight gauge, hand pump syringe, Anton Paar DMA 512P density meters, circulation pumps, gas reservoir, and Ruska 2439-702 pressure transducers. The density meters were calibrated by dry air and pure water at the experimental temperature.

The apparatus is housed in a constant-temperature liquid bath controlled to a temperature to about ± 0.01 K. Temperatures were measured with the Hewlett-Packard 2804A quartz thermometer calibrated by the triple point of water. The volume of the lower portion of the cell could be varied between (234 and 299) cm^3 by moving a piston, which gave a volume uncertainty of ± 0.01 cm^3. The accuracy of the total volume is known to about ± 1 cm^3.

First, the cell was evacuated and then filled with carbon dioxide. The pressure difference between the upper and lower spaces was kept close to zero, to minimize the leakage between the upper and lower rooms in the cell. The volume was determined by the motion of the piston. The amount of carbon dioxide was determined from the volume and experimental density at the experimental pressure and temperature. The volume of ethanol was then charged into the cell with the syringe pump with an uncertainty ± 0.01 cm^3 after pressurizing the syringe pump as quickly as possible, to eliminate the dissolution effect of carbon dioxide into ethanol in the syringe pump. The amount of ethanol can be determined by the volume and density.

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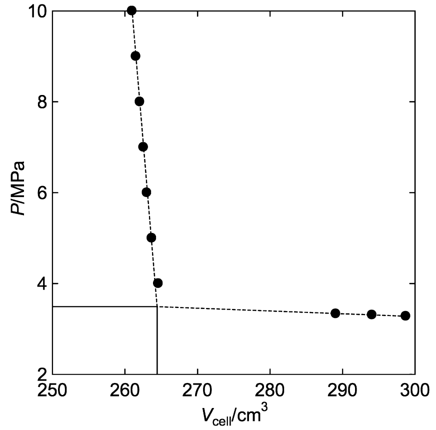

Figure 1. Typical example of experimental results by the synthetic method: ●, 0.200 CO_2 mole fraction.

Table 1. Experimental Densities ρ, Mole Fraction x, and Pressure P of Carbon Dioxide (1) + Ethanol (2) Mixtures at 313.15 K

	ρ/kg·m^{-3} at P/MPa									
x_1	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0.000	773.1	773.9	774.8	775.5	776.4	777.2	778.0	778.8	779.6	780.4
0.100	—	787.2	788.2	789.2	790.2	791.1	792.1	793.1	794.0	795.0
0.200	—	—	—	799.4	800.6	801.9	803.1	804.2	805.3	806.6
0.300	—	—	—	—	—	811.2	812.7	814.3	815.7	817.2
0.400	—	—	—	—	—	816.6	818.7	820.8	822.8	824.7
0.500	—	—	—	—	—	—	821.1	824.0	826.8	829.4
0.600	—	—	—	—	—	—	—	818.8	823.0	827.0
0.700	—	—	—	—	—	—	—	804.5	811.5	817.8
0.800	—	—	—	—	—	—	—	771.1	784.8	795.8
0.899	—	—	—	—	—	—	—	—	729.1	752.3
0.950	—	—	—	—	—	—	—	—	667.0	709.8
1.000	17.9	37.1	58.7	83.5	112.7	148.8	197.3	276.7	483.4	627.4

Table 2. Liquid Mole Fraction x_1 and Saturation Pressure P of Carbon Dioxide (1) + Ethanol (2) Mixtures at 313.15 K

x_1	P/MPa
0.100	1.970
0.200	3.491
0.300	4.802
0.400	5.913
0.500	6.763
0.600	7.291
0.700	7.595
0.800	7.769
0.899	7.960
0.950	8.175

The composition of the mixture was evaluated by the amount of carbon dioxide and the one of ethanol injected into the cell. As the volume of the cell was changed, the volumetric properties of the mixture could be measured at a fixed and known composition. The discontinuity of the pressure as a function of cell volume shown in Figure 1 was used as the determinant of the saturated pressure. The saturated densities of the vapor and liquid were measured at the fixed pressure, while maintaining the vapor−liquid equilibrium separation in the cell. The experimental uncertainties of the pressure, density, temperature, and composition, respectively, are 0.001 MPa, 0.1 kg·m^{-3}, 0.01 K, and 0.001 mole fraction.

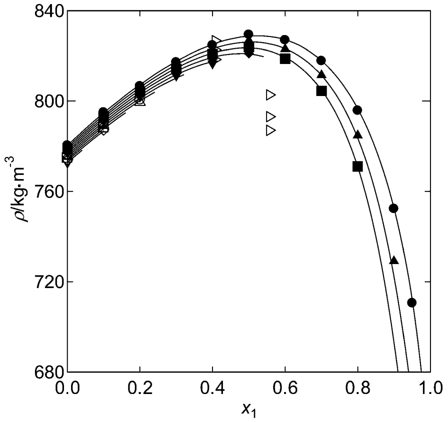

Figure 2. Densities of carbon dioxide (1) + ethanol (2) at 313.15 K: ●, 10 MPa; ▲, 9 MPa; ■, 8 MPa; ♦, 7 MPa; ▼, 6 MPa; ○, 5 MPa; Δ, 4 MPa; □, 3 MPa; ◇, 2 MPa; ∇, 1 MPa; open triangle pointing right, Zúñiga-Moreno and Galicia-Luna[10] at 313.16 K. —, eq 1.

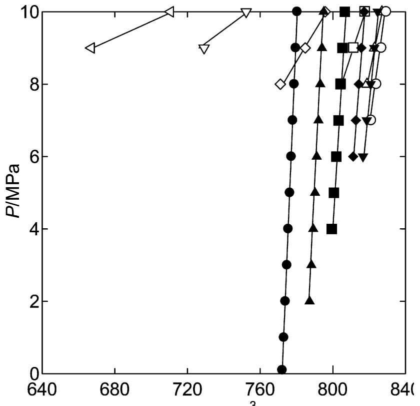

Figure 3. Volumetric properties of carbon dioxide (1) + ethanol (2) at 313.15 K: ●, $x_1 = 0.0$; ▲, 0.1; ■, 0.2; ♦, 0.3; ▼, 0.4; ○, 0.5; Δ, 0.6; □, 0.7; ◇, 0.8; ∇, 0.9; open triangle pointing left, 0.95. —, eq 1.

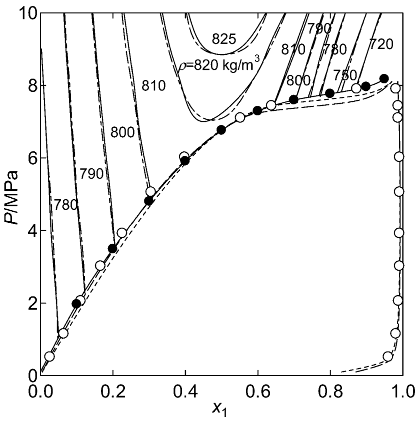

Figure 4. VLE and density curves of carbon dioxide (1) + ethanol (2) at 313.15 K: −●−, —, this work; ○, Suzuki et al.[2] at 313.4 K; - - -, SRK EOS ($k_{ij} = 0.0865$); — — —, pseudocubic EOS ($k_{ij} = 0.1322$, $l_{ij} = -0.0701$); — - — -, eq 1.

Correlation

The experimental saturated pressure data obtained were correlated with the conventional SRK equation of state[11] and the pseudocubic equation of state[12] as shown in the Supporting Information. The binary interaction parameters k_{ij} and l_{ij} were found from our experimental bubble point pressure data in the lower pressure regions. k_{ij} was 0.0865 for the SRK equation of state, and k_{ij} and l_{ij} were 0.1322 and −0.0701 for the pseudocubic equation of state by using the Marquardt method. In the correlations, the critical values and acentric factors of carbon dioxide and ethanol were obtained from the reference.[21]

Table 3. Parameters in Density Equation 1 of Carbon Dioxide (1) + Ethanol (2) at 313.15 K[a]

N	ρ_2^{0*}	P^*	a	b	c	m	n	k	A	B	C	σ
53	780.4	10.000	153.03	−2.089	1.072	−1.626	0.643	21.836	9.772	3.107	1.443	0.64

[a] σ: standard deviation, $\sigma = [(\Sigma(\rho_{\text{calc}} - \rho_{\text{expl}})^2)/(N - 1)]^{1/2}$ (kg·m^{-3}). N: Number of data points. ρ_2^{0*}: density of ethanol at reference pressure (kg·m^{-3}). P^*: reference pressure (MPa).

The experimental density data were also correlated by the following equation, almost similar to the former research.[13−16]

$$\rho = \frac{\rho_2^{0*} + ax_1 \dfrac{1 + bx_1 + cx_1^2}{1 + mx_1 + nx_1^2}}{1 - k\ln\left\{1 - \dfrac{1 - (P/P^*)}{1 + \exp[A - B/(C - x_1)]}\right\}} \qquad (1)$$

where ρ, x, and P, respectively, are density, mole fraction, and pressure. The superscripts, 0 and *, denote pure and reference, respectively. P^* means the reference pressure at high pressure. The subscripts, 1 and 2, denote carbon dioxide and ethanol, respectively. Equation 1 has nine parameters, a, b, c, m, n, A, B, C, and k. Those parameters are independent of composition.

In the previous study,[13,14] the density equation was completely the same as eq 1; however, the parameter was estimated by a fixed point without using the Marquardt method. In the other study,[15,16] the density equation does not include the parameter c, and all the parameters were estimated by using the Marquardt method. In the previous studies,[13−16] the composition range that can be applied was between 0.0 and 0.8. On the other hand, the effective composition range was expanded to 0.95 in the present study.

The density data of carbon dioxide + ethanol mixtures at 313.15 K have been correlated by the present density eq 1. The five parameters in eq 1, a, b, c, m, and n, were first obtained by the optimization of the Marquardt method to minimize the sum of the square of the difference between the calculated density and experimental density at the highest reference pressure P^*, giving the essential restriction to satisfy the experimental density of pure carbon dioxide. Equation 1 becomes therefore applicable in the full composition range at the reference pressure P^*. Next, the remaining four parameters in eq 1, A, B, C, and k, were obtained by the optimization of the Marquardt method to minimize the sum of the square of the difference between the calculated density and the experimental one in the composition range of the mole fraction of carbon dioxide from 0.0 to 0.95.

Results and Discussion

The experimental densities of fixed compositions of carbon dioxide + ethanol mixtures at 313.15 K and pressures to 10 MPa are shown in Table 1. Table 2 shows the experimental saturation pressure of vapor and liquid phases at equilibria.

Figure 2 shows the density−composition diagram for carbon dioxide + ethanol at 313.15 K, showing excellent performance of eq 1 for density. The points and continuing lines denote the experimental values and calculated ones, respectively. As shown in Figure 2, the convex curves were observed with the maximum points near 0.5 mol fraction of carbon dioxide. The present experimental data agreed fairly well with Zúñiga-Moreno and Galicia-Luna[10] around 0.4 mol fraction of carbon dioxide. On the other hand, the present experimental data were shifted from Zúñiga-Moreno and Galicia-Luna[10] around 0.5569 mole fraction of carbon dioxide.

Figure 3 gives the density−pressure diagrams for carbon dioxide + ethanol at 313.15 K, with the high performance of eq 1 for the density calculation. The points and continuing lines denote the experimental values and calculated ones, respectively.

Figure 4 shows the pressure−composition diagram of carbon dioxide + ethanol at 313.15 K. The VLE data given by Suzuki et al.[2] agree with the present experimental ones as shown in Figure 4. The experimental saturated density has been displaced in the solid line in Figure 4. The calculation results with eq 1 are listed in Table 3 and had a standard deviation of 0.64 kg·m^{-3} in density. The performance of eq 1 is satisfactory in the full range of composition, as shown in Figures 2 to 4.

Conclusions

Volumetric properties of carbon dioxide + ethanol mixtures at 313.15 K were measured, using the vibrating-tube Anton Paar DMA 512P density meter. The saturated pressures of carbon dioxide + ethanol mixtures at 313.15 K were measured by the synthetic method. The experimental saturated pressures were correlated with the SRK equation of state and the pseudocubic equation of state. Furthermore, the experimental density behaviors were correlated with high accuracy by the density equation.

Supporting Information Available:

Pseudo-cubic equations of state. This material is available free of charge via the Internet at http://pubs.acs.org.

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