

High-Pressure Vapor-Liquid Equilibria for Carbon Dioxide + Methanol, Carbon Dioxide + Ethanol, and Carbon Dioxide + Methanol + Ethanol

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Vapor-liquid equilibria were measured for carbon dioxide + methanol and carbon dioxide + ethanol at 313.2 K. For carbon dioxide + methanol + ethanol, the equilibrium data were measured at 313.2 K and pressures of 20, 40, 60, and 80 bar. The experimental data for these systems were correlated with the Patel-Teja equation of state and mixing rule of Wilson.

Introduction

The addition of cosolvents to a supercritical fluid solvent such as carbon dioxide can increase significantly solubilities of heavy organic solutes. The use of cosolvents such as methanol and ethanol has often improved both solubility and selectivity as a more powerful separation technique. In this study, vapor-liquid equilibrium data for carbon dioxide + methanol and carbon dioxide + ethanol were measured at 313.2 K. Isothermal vapor-liquid equilibrium data for carbon dioxide + methanol + ethanol were measured at 313.2 K and pressures of 20, 40, 60, and 80 bar.

Experimental Section

Apparatus. The vapor-liquid equilibrium apparatus used in this work is shown in Figure 1. It is a circulation-type apparatus in which the coexisting phases are recirculated, sampled, and analyzed. The equilibrium cell (Jerguson liquid level gauge, 18-T-51) has an internal volume of about 50 cm³ and two sight glass windows at both sides. The windows allow visual observation of phase transitions. The pressure in the equilibrium cell can be measured by a Heise gauge (CMM 104957, 0-600-bar range). The maximum error of this gauge is ± 0.1 bar. The temperature in the equilibrium cell can be measured by a K-type thermocouple with a digital thermometer (Cole-Parmer, 8535-26) of which the resolution is ± 0.1 K. The vapor and liquid phases of the cell are recirculated to obtain a rapid equilibration by using a duplex metering pump (Milton Roy, 2396-31). The pressure is finely adjusted by operating a pressure generator (HIP, 62-6-10). The vapor sampling valve (Rheodyne, 7410) has a loop volume of about 20 μ L, and the liquid sampling valve (Rheodyne, 7413) has a loop volume of about 0.5 μ L. A gas chromatograph (Hewlett-Packard, 5890A) is connected to these sampling valves on-line. The gas chromatograph uses a thermal conductivity detector (TCD) and a 6 ft by 1/8 in. diameter column packed with Porapak Q for analysis of the samples. The conditions of gas chromatography for sample analysis are a carrier gas flow rate of 30 mL/min, a column temperature at 150 $^{\circ}$ C, an injection temperature of 160 $^{\circ}$ C, and a detector temperature of 170 $^{\circ}$ C. The equilibrium cell, sampling valves, pressure generator, and most of the connection valves are contained in an air bath controlled to ± 0.1 K by a PID controller.

Procedure. As a first step for calibration the loop volume of each sampling valve must be accurately measured in the following manner. The vapor sampling loop maintained at a constant temperature of 298.2 K was filled with distilled water. The water in the sampling loop was transported to a

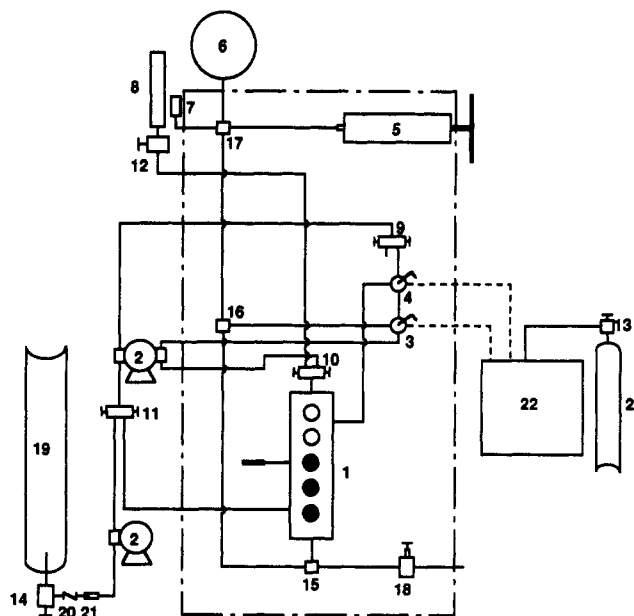


Figure 1. Schematic diagram of experimental apparatus: 1, equilibrium cell; 2, metering pump; 3, vapor sampling valve; 4, liquid sampling valve; 5, pressure generator; 6, pressure gauge; 7, rupture disk; 8, liquid reservoir; 9-11, three-way valve; 12-14, two-way valve; 15, 16, three-way connection; 17, four-way connection; 18, metering valve; 19, CO₂ cylinder; 20, check valve; 21, line filter; 22, gas chromatography; 23, helium gas.

Karl-Fisher titrimer (Fisher, 9-313-448) by a μ LC pump (ISCO, 1240-018) of which the carrier solvent is anhydrous ethanol. The Karl-Fisher titrimer with a resolution of 1 μ g titrates and calculates the amount of water rinsed out of the loop. The volume of water in the loop was determined by the amount of water titrated and the molar volume of water at 298.2 K. The measured loop volume of the vapor sampling valve was determined to be 24.36 μ L. From the calculation curves for the carbon dioxide constructed with the vapor and liquid sampling valves, the loop volume of the liquid sampling valve was determined to be 0.4654 μ L. This technique is quite simple and more accurate than that suggested by Park et al. (1). Calibration for carbon dioxide was performed by using the vapor and liquid sampling valves. After the equilibrium cell was pressurized with pure carbon dioxide at 320 K and various pressures, the carbon dioxide in the sampling loop was transported to the gas chromatograph in order to show the response factors for moles vs peak areas. The constructed calibration curve was fitted to a third-order

Table I. Total Pressure P , Liquid Mole Fraction x_1 , and Vapor Mole Fraction y_1 for Carbon Dioxide + Methanol and Carbon Dioxide + Ethanol at 313.2 K

P/bar	x_1	y_1	P/bar	x_1	y_1
Carbon Dioxide (1) + Methanol (2)					
7.0	0.038	0.945	74.8	0.591	0.985
11.0	0.064	0.964	77.9	0.698	0.982
21.0	0.123	0.979	78.9	0.752	0.980
32.0	0.186	0.983	79.8	0.810	0.979
44.5	0.268	0.984	80.7	0.867	0.976
57.0	0.370	0.986	82.1 ^c	0.968	0.968
68.1	0.480	0.986			
Carbon Dioxide (1) + Ethanol (2)					
6.0	0.033	0.972	77.5	0.799	0.986
12.7	0.076	0.988	78.2	0.838	0.986
22.7	0.139	0.990	79.2	0.904	0.985
39.0	0.242	0.992	80.7	0.948	0.983
56.5	0.404	0.992	81.5 ^c	0.970	0.970
75.5	0.719	0.988			

^c Measured critical point.

polynomial since the response for carbon dioxide in the region of high pressures exhibited an aspect of concavity. Calibration curves for the liquid components were constructed by injecting known amounts of the pure component with the liquid sampling valve and a calibrated microsyringe. These curves were fitted to a linear polynomial for the methanol and a third-order polynomial for the ethanol, which deviated a little from linearity.

The experiment begins by charging the equilibrium cell in a condition of evacuation with a mixture of liquid. After the cell is slightly pressurized by carbon dioxide through the metering pump, it is slowly heated to the experimental temperature. When the experimental temperature reaches a steady state, the cell is pressurized to the pressure of interest with carbon dioxide. In order to obtain a rapid equilibrium, the vapor and liquid phases are recirculated by the recirculating pump at the flow rate of about 320 cm³/h. The equilibrium between two phases is generally attained within about 1 h. Fine control of pressure can be obtained by using a pressure generator. In order to diminish the dead volume effect, whenever the equilibrium pressure was changed by the pressure generator, each phase was rigorously recirculated. During sampling, the recirculating pump should be maintained to the minimum flow rate to prevent pressurizing of the samples. Particularly, the vapor samples are very sensitive to the flow rate change. The equilibrium composition is determined by injecting the high-pressure samples into the gas chromatograph. Each sample is analyzed four times for each equilibrium point. The average of the individual compositions is reported as the equilibrium composition. For the binary systems, the repeatability of the vapor and liquid mole fraction is generally within ± 0.001 and ± 0.002 , respectively. The vapor- and liquid-phase mole fractions for the ternary system are reproducible to within ± 0.002 and ± 0.003 , respectively.

Materials. The carbon dioxide with a minimum purity of 99.9 mol % used in this study was supplied by World Gas Co. in Korea. The methanol supplied by Aldrich Chemical Co. had a purity of 99.97 vol %. The ethanol having a purity of 99.5 vol % was supplied by Merk. These chemicals were used without further purification.

Results and Discussion

The equilibrium data for two binary systems and a ternary system are listed in Tables I and II, respectively. The vapor-liquid equilibrium data of carbon dioxide + methanol of this study were found to compare well with those of Suzuki et al. (2) as shown in Figure 2. Detailed experiments near the

Table II. Total Pressure P , Liquid Mole Fraction x_1 , and Vapor Mole Fraction y_1 for Carbon Dioxide (1) + Methanol (2) + Ethanol (3) at 313.2 K

P/bar	x_1	y_1	x_1	y_1
20	0.123	0.671	0.983	0.013
	0.125	0.500	0.985	0.009
	0.126	0.319	0.986	0.006
	0.125	0.223	0.986	0.004
40	0.248	0.577	0.988	0.009
	0.254	0.426	0.990	0.006
	0.258	0.276	0.991	0.004
	0.257	0.193	0.991	0.003
60	0.403	0.460	0.987	0.010
	0.418	0.333	0.988	0.007
	0.430	0.207	0.989	0.004
	0.433	0.152	0.990	0.003
80	0.876	0.088	0.981	0.014
	0.906	0.050	0.983	0.010
	0.921	0.026	0.984	0.006
	0.921	0.020	0.984	0.005

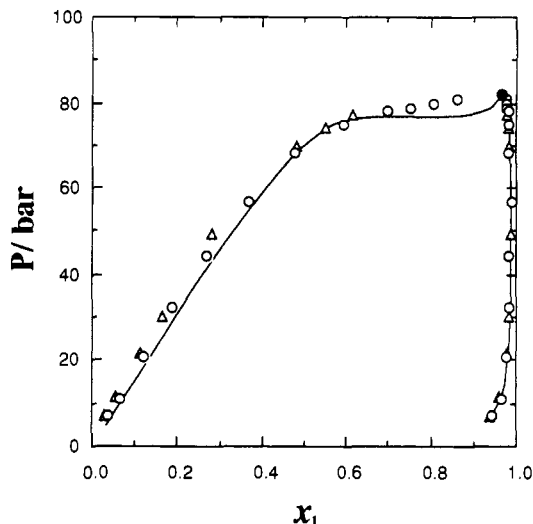


Figure 2. Vapor-liquid equilibria for carbon dioxide (1) + methanol (2): O, this work at 313.2 K; ●, measured critical point at 313.2 K; Δ, Suzuki et al. at 313.4 K; —, calculated values.

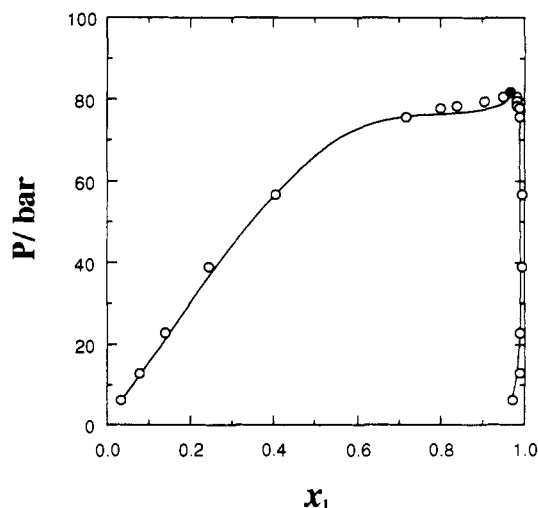


Figure 3. Vapor-liquid equilibria for carbon dioxide (1) + ethanol (2) at 313.2 K: O, this work; ●, measured critical point; —, calculated values.

critical point showed that the critical pressures for carbon dioxide + methanol and carbon dioxide + ethanol at 313.2 K are 82.1 and 81.5 bar, respectively, as shown in Figures 2 and 3. These critical pressures were determined by visual

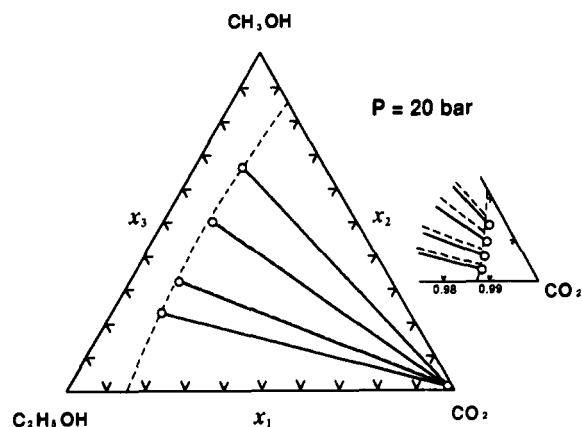


Figure 4. Vapor-liquid equilibria for carbon dioxide (1) + methanol (2) + ethanol (3) at 313.2 K and 20 bar: O, —, measured tie lines; ---, calculated tie lines.

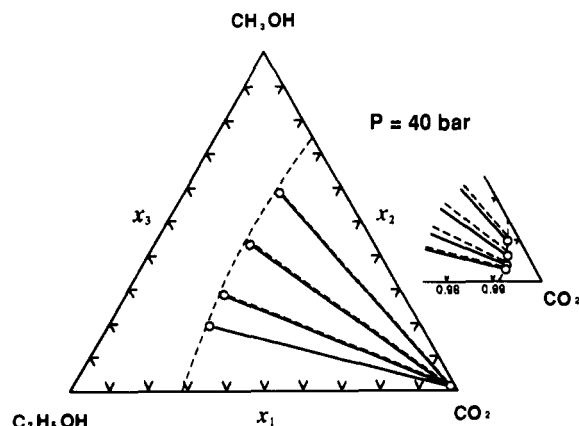


Figure 5. Vapor-liquid equilibria for carbon dioxide (1) + methanol (2) + ethanol (3) at 313.2 K and 40 bar: O, —, measured tie lines; ---, calculated tie lines.

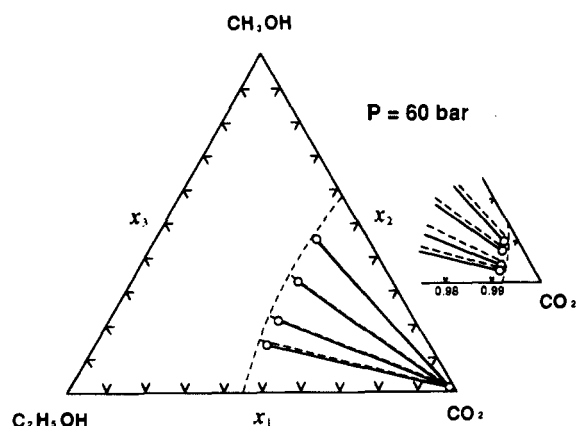


Figure 6. Vapor-liquid equilibria for carbon dioxide (1) + methanol (2) + ethanol (3) at 313.2 K and 60 bar: O, —, measured tie lines; ---, calculated tie lines.

observation, and the overall range of the critical opalescence was less than 0.1 bar. Furthermore, the critical mole fractions repeatedly measured by the liquid sampling valve were reproducible to within ± 0.002 . Baker et al. (3) also measured the critical pressures and compositions at temperatures from 304.0 to 320.8 K for carbon dioxide + ethanol. The interpolated critical pressure and mole fraction of carbon dioxide at 313.2 K were 81.8 bar and 0.970, respectively. The agreement is excellent. For carbon dioxide + methanol + ethanol, the equilibrium data at 20, 40, 60, and 80 bar are presented in Figures 4–7.

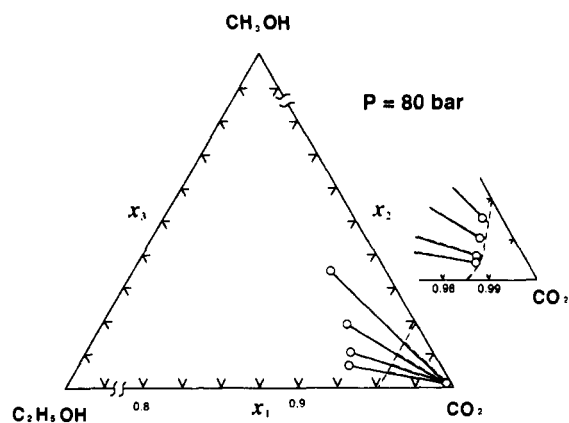


Figure 7. Vapor-liquid equilibria for carbon dioxide (1) + methanol (2) + ethanol (3) at 313.2 K and 80 bar: O, —, measured tie lines; ---, calculated tie lines.

Table III. Binary Interaction Parameters

binary system	T/K	k_{12}	k_{21}
CO ₂ (1) + methanol (2)	313.2	0.9645	0.7860
CO ₂ (1) + ethanol (2)	313.2	1.0770	0.7299
methanol (1) + ethanol (2)	313.2	0.6700	1.2230

The Patel–Teja (4) equation of state with the mixing rule of Wilson (5) was used to correlate these equilibrium data. The mixing rule involves two binary interaction parameters, k_{12} and k_{21} . These binary interaction parameters presented in Table III were determined by a fitting procedure to minimize the average absolute deviation between the experimental data and calculated values. Takishima et al. (6) also used the Patel–Teja equation with the mixing rule of Wilson to remarkably improve correlation over the Peng–Robinson equation of state for carbon dioxide + ethanol. For methanol + ethanol, the vapor-liquid equilibrium data at low pressure from the literature (7) were used for calculation of the binary interaction parameters. As shown in Figures 2–7, the model was quite successful in correlating the experimental data, but gave a slight deviation near the critical region.

Conclusion

Vapor-liquid equilibria have been measured for carbon dioxide + methanol and carbon dioxide + ethanol at 313.2 K. For carbon dioxide + methanol + ethanol, vapor-liquid equilibrium compositions have been measured at 313.2 K and pressures of 20, 40, 60, and 80 bar. The binary and ternary experimental data were both well correlated by using the Patel–Teja equation of state with the mixing rule of Wilson except the region approaching the critical point.

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