High-Pressure Phase Equilibria for the Carbon Dioxide + 3-Pentanol and Carbon Dioxide + 3-Pentanol + Water Systems

Hyun-Song Lee, Sung Yong Mun, and Huen Lee*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong, Yusong-gu, Taejon, 305-701, Korea

High-pressure vapor−liquid equilibria for the binary carbon dioxide + 3-petanol system were measured at 313.2 K. The phase equilibrium apparatus used in this work was of the circulation type in which the coexisting phases were recirculated, on-line sampled, and analyzed. The critical pressure and corresponding mole fraction of carbon dioxide at 313.2 K were found to be 8.22 MPa and 0.974, respectively, for this binary system. The phase equilibria for the ternary carbon dioxide + 3-pentanol + water system were also measured at 313.2 K and pressures of 2.00, 4.00, 6.00, 8.00, and 8.25 MPa. This ternary system showed the liquid−liquid−vapor (LLV) phase behavior over the range of pressure up to the critical pressure of 8.25 MPa. The binary equilibrium data were all reasonably well-correlated with the Redlich−Kwong, Soave−Redlich−Kwong, Peng−Robinson, and Patel−Teja equations of state incorporated with the eight different mixing rules: the van der Waals, Panagiotopoulos−Reid, and six modified Huron−Vidal mixing rules with UNIQUAC parameters. For the prediction of high-pressure phase equilibria for the systems containing carbon dioxide and alcohols, the SRK-MHV2 might reproduce many features of the measured behavior although further tests are needed with other systems.

Introduction

Alcohols are typically synthesized in aqueous solutions and then separated from water by distillation or evaporation. Water−alcohol separation is one of the most energy intensive processes in the chemical industry. Preliminary evaluations reveal that supercritical fluid extraction is a potential separation technology, which requires lower energy and has other advantages over traditional separation processes. This process avoids the current environmental and health concerns associated with many organic solvents. In connection with these concerns, many researchers have investigated the phase equilibria of a variety of carbon dioxide-containing systems. Studies of mixtures containing both carbon dioxide and alcohol are abundant up to the four-carbon alcohols. The phase equilibrium data for the higher-carbon alcohol systems are limited to the normal alcohols. Several review articles concern the experimental techniques and high-pressure phase equilibrium data (Tsiklis, 1968; Schneider, 1975; Eubank et al., 1980; Deiters and Schneider, 1986; Fornari et al., 1990). Hicks (1978) and Knapp et al. (1982) published review papers covering the period from 1900 to 1980, Fornari et al. (1990) from 1978 to 1987, and Dohrn and Brunner (1995) from 1988 to 1993.

The high-pressure phase equilibria of the binary carbon dioxide + 2-pentanol and ternary carbon dioxide + 2-pentanol + water systems were measured at 313.2 K in a previous paper (Lee and Lee, 1998). In this work, the high-pressure phase equilibria of the binary carbon dioxide + 3-pentanol and ternary carbon dioxide + 3-pentanol + water systems were measured at 313.2 K and pressures up to the critical point. The experimental equilibrium data were correlated with the four cubic equations of state incorporated with several different types of mixing rules.

Experimental Section

Chemicals. Kosok Gas Co. supplied carbon dioxide whose purity was at least 99.9 mol % as determined by gas chromatography. Aldrich supplied 3-pentanol with better than 98% purity and HPLC-grade distilled water. These chemicals were all used without any further purification.

Apparatus and Procedure. The phase equilibrium apparatus used in this work is shown in Figure 1. It is a circulation type in which the coexisting phases are recirculated, sampled, and analyzed. The apparatus and experimental procedures are almost the same as those used in previous work (Lee and Lee, 1998; Yoon et al., 1993a,b). The on-line sampling parts were slightly revised in this apparatus so that the light liquid phase (middle phase) was recirculated through an extended tube over a liquid sampling valve. The three-way valve was installed between the middle and bottom liquid phases in order to switch two phases. A liquid sampling valve was used to collect the liquid-phase samples. The pressure in the equilibrium cell was measured by a Heise gauge (CMM 104957, 0−60 MPa range). The maximum error of the gauge is ±0.1 bar. The temperature in the equilibrium cell was measured with a K-type thermocouple connected to a digital thermometer (Cole-Parmer, 8535-26) whose resolution was ±0.1 K. The temperature was carefully recalibrated with a liquid-in-glass thermometer (Ever Ready Thermometer Co. Inc.; marked, ERTCO ASTM 64C−FC S/N-4550; range, +25 to +55 °C in 0.1 °C). The experiment began by evacuating the equilibrium cell with a vacuum pump (KNF Neuberger, N726.3 TTP). After the cell was charged with a mixture of liquid, it was slightly pressurized by carbon dioxide. The cell was then heated to the experimental temperature. When the desired temperature was reached, and a steady state was achieved, the cell was pressurized to the experimental pressure with carbon dioxide using a Simplex

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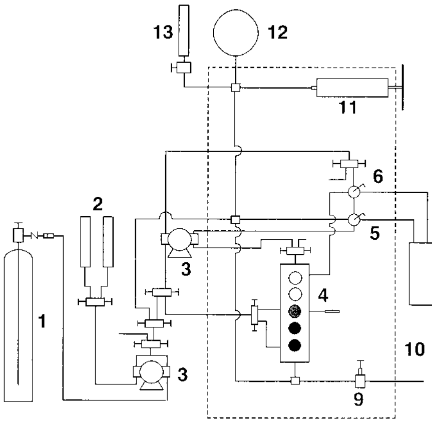

Figure 1. Schematic diagram of high-pressure vapor−liquid equilibrium experimental apparatus: (1) CO_2 cylinder, (2) liquid reservoir, (3) high-pressure pump, (4) equilibrium cell, (5) vapor sampling valve, (6) liquid sampling valve, (7) gas chromatograph, (8) He cylinder, (9) metering valve, (10) air bath, (11) pressure generator, (12) pressure gauge, and (13) liquid reservoir.

Table 1. Physical Properties of Chemicals Used in This Work

name	MW	T_m/K	T_b/K	T_c/K	P_c/MPa	ω
CO_2	44.01	194.7	216.6	304.1	7.38	0.239
water	18.02	273.2	373.2	647.3	22.12	0.344
3-pentanol	88.15		389.3	559.6	3.99	0.547

Table 2. Equilibrium Compositions and Critical Point for the Carbon Dioxide (1) + 3-Pentanol (2) System at 313.2 K

P/MPa	x_1	y_1	P/MPa	x_1	y_1
2.00	0.096	0.996	8.00	0.933	0.990
4.00	0.251	0.997	8.22[a]	0.974	0.974
6.00	0.459	0.996			

[a] Measured critical point.

minipump (Milton Roy, 396-31). To supply carbon dioxide in the liquid state, a bomb with a deep-tube siphon was used. Fine control of the system pressure could be obtained by using a pressure generator (HIP, 62-6-10). A duplex recirculating pump (Milton Roy, 2396-31) was used to rapidly attain equilibrium, and each phase was recirculated through each sampling valve under equilibrium conditions. The equilibrium compositions of each phase were determined by injecting the high-pressure sample into the gas chromatograph for an on-line composition analysis. Each sample was analyzed at least 10 times, and the vapor- and liquid-phase compositions were found to be reproducible within a mole fraction of ±0.002 and ±0.003, respectively.

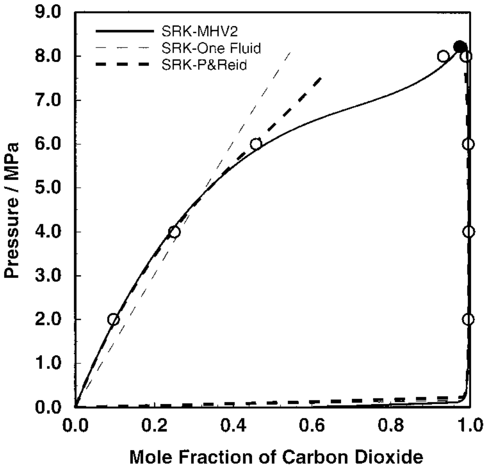

Figure 2. Vapor−liquid equilibria and critical point for the carbon dioxide + 3-pentanol system at 313.2 K: (○) experimental data; (●) measured critical point.

Table 3. Binary Interaction Parameters and Average Absolute Deviations for the Carbon Dioxide + 3-Pentanol System at 313.2 K

model	k_{12}	k_{21}	AAD$_x$	AAD$_y$
RK + van der Waals	0.2319	0.2319	27.23	3.50
SRK + van der Waals	0.1439	0.1439	28.52	0.38
PR + van der Waals	0.1424	0.1424	28.88	0.30
PT + van der Waals	0.1263	0.1263	28.67	0.20
RK + PR	0.3014	0.1546	9.01	8.73
SRK + PR	0.2151	0.0719	5.82	4.96
PR + P&R	0.2114	0.0716	5.51	4.69
PT + P&R	0.1955	0.0578	5.73	4.94
SRK + PSRK (Fischer and Gmehling, 1995; 1996)[a]	−107.8	413.7	3.93	0.09
SRK + MHV1 (Michelson, 1990)[a]	−116.2	399.2	3.95	0.09
SRK + HVOS (Orbey and Sandler, 1995)[a]	−100.0	425.8	3.89	0.09
SRK + MHV2 (Dahl and Michelsen, 1990)[a]	−113.8	555.0	3.24	0.09
SRK + LCVM (Boukouvalas et al., 1994)[a]	−78.9	405.1	4.00	0.09
SRK + CHV (Orbey and Sandler, 1997)[a]	−63.9	423.6	3.91	0.09

[a] The unit of k_{ij} is in kelvin (K) for these values.

Results and Discussion

The physical properties of 3-pentanol are not available in the literature. They were estimated with methods found in the references (Ambrose, 1979, 1980; Lee and Kesler, 1975) and are presented in Table 1. The equilibrium compositions and critical point of the binary carbon dioxide + 3-pentanol system were measured at 313.2 K and are listed in Table 2. The corresponding isothermal pressure−composition diagram is shown in Figure 2. The vapor-phase composition of carbon dioxide was higher than 97.4 mol % over the entire pressure range. A maximum vapor composition of carbon dioxide appeared to be at a pressure of about 4 MPa, while the liquid composition of carbon dioxide increased with pressure. The critical pressure was determined by visual observation. The overall range where critical opalescence was observed was less than 0.01 MPa. Furthermore, the critical mole fractions repeatedly measured by the liquid sampling valve were reproducible within ±0.002. The measured critical pressure and composition at 313.2 K were 8.22 MPa and 0.974 mole fraction of carbon dioxide, respectively. The vapor−liquid equilibrium (VLE) data were correlated with the four conventional cubic equations of state, Redlich−Kwong (RK) (Redlich and Kwong, 1948), Soave−Redlich−Kwong (SRK) (Soave, 1972), Peng−Robinson (PR) (Peng and Robinson, 1976), and Patel−Teja (PT) (Patel and Teja, 1982). The following mixing rules were incorporated with the specific equation of state, van der Waals, Panagiotopoulos−Reid (Panagiotopoulos and Reid, 1986), and six modified Huron−Vidal mixing rules. The calculated equilibrium compositions of the binary carbon dioxide + 3-pentanol system are shown in Figure 2 along with the experimental data. The resulting binary interaction parameters and average absolute deviations between the experimental data and calculated values are listed in Table 3. The objective function, which was minimized, is the sum of the absolute difference of fugacity of each component in each phase. As shown in Figure 2, there is quite good agreement between the experimental and calculated results over the entire pressure range considered. Takishima et al. (1986) used the Patel−Teja

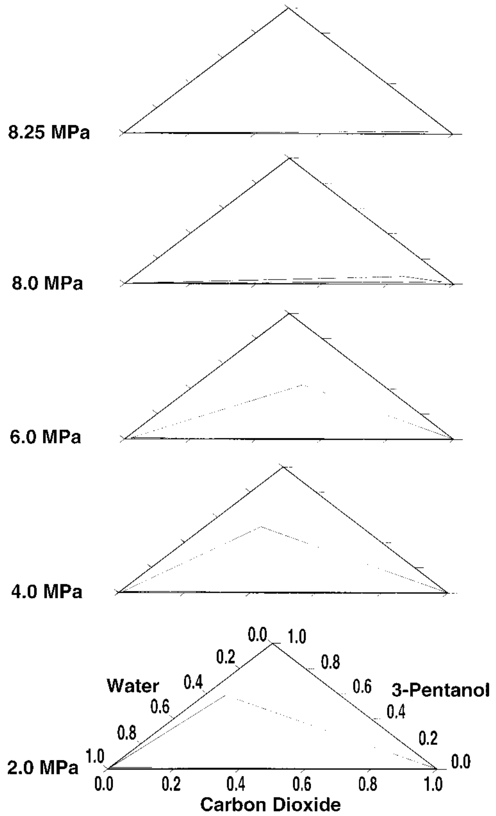

Figure 3. Ternary phase equilibria for the carbon dioxide + 3-pentanol + water system at 313.2 K and pressures of 2.0, 4.0, 6.0, 8.0, and 8.25 MPa.

equation of state with the Panagiotopoulos−Reid mixing rule to improve predictions, compared to those from the Peng−Robinson equation of state for the carbon dioxide + ethanol system. However, the Patel−Teja equation does not show remarkable improvement over other conventional equations used in this study. The Redlich−Kwong equation of state poorly predicts the equilibrium behavior of both liquid and gas phases compared with the other three equations of state. The equilibrium values calculated with the Soave−Redlich−Kwong, Peng−Robinson, and Patel−Teja equations of state incorporating any specified mixing rule were almost the same, as shown in Figure 2. It should also be noted that the van der Waals one-fluid mixing rule badly underestimates the equilibrium liquid carbon dioxide concentrations above 5.0 MPa, while the Panagiotopolous and Reid mixing rule predicts them reasonably well. However, both mixing rules completely fail to predict the equilibrium behavior near the critical point, while the six modified Huron−Vidal mixing rules slightly underestimate the critical pressure. Although the predictive results obtained by using these six mixing rules showed no great differences among them, the MHV2 mixing rule was found to be a little better than the others. The measured equilibrium compositions and pressures of the ternary carbon dioxide + 3-pentanol + water system at 313.2 K and several different pressures are presented in Table 4 and Figure 3. In this figure, the three apexes of each thinly lined triangle undoubtedly indicate the experimental compositions of three phases at equilibrium. This ternary system showed the liquid−liquid−vapor three-phase behavior over the range of pressure up to the critical pressure of 8.25 MPa. Since all binary mixtures containing two of the three components, carbon dioxide + 3-pentanol, carbon dioxide + water, and 3-pentanol + water, become immiscible below the critical pressure of the carbon dioxide + 3-pentanol binary system, the three phases are expected to appear in the ternary mixture under this condition. The equilibrium compositions of the water-rich liquid and carbon dioxide-rich vapor phases changed slightly with pressure. The compositions of the 3-pentanol-rich middle phase changed rapidly with pressure, particularly near the critical point of the binary carbon dioxide + 3-pentanol system. The 3-pentanol-rich middle phase merged into the vapor phase and finally disappeared at 8.25 MPa, which was slightly higher than the critical pressure of the binary system. The color of the middle phase was dark brown just below 8.25 MPa but became clear just above 8.25 MPa.

Table 4. Equilibrium Compositions for the Carbon Dioxide (1) + 3-Pentanol (2) + Water (3) System at 313.2 K

	vapor			liquid$_1$			liquid$_2$ (middle)		
P/MPa	y_1	y_2	y_3	x_1	x_2	x_3	x_1	x_2	x_3
2.00	0.998	0.002	0.000	0.002	0.011	0.987	0.064	0.587	0.349
4.00	0.998	0.002	0.000	0.009	0.010	0.981	0.170	0.525	0.305
6.00	0.997	0.003	0.000	0.015	0.009	0.976	0.327	0.431	0.242
8.00	0.955	0.019	0.026	0.023	0.005	0.972	0.820	0.060	0.120
8.25	0.916	0.019	0.065	0.027	0.004	0.969			

Glossary

AAD	average absolute deviation
CHV	corrected Huron−Vidal
HVOS	Huron−Vidal−Orbey−Sandler
k_{ij}	binary interaction parameter
LCVM	linear combination of the Vidal and Michelsen
MW	molecular weight
MHV1	modified Huron−Vidal first order
MHV2	modified Huron−Vidal second order
P	pressure, MPa
P_c	critical pressure, MPa
PSRK	predictive Soave−Redlich−Kwong
T	temperature, K
T_b	boiling point, K
T_c	critical temperature, K
T_m	melting point, K
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
ω	acentric factor

Literature Cited

Ambrose, D. *Correlation and Estimation of Vapor-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds*; NPL Report Chem 92; National Physical Laboratory, Teddington, U.K., September 1978; Corrected March 1980.

Ambrose, D. *Correlation and Estimation of Vapor-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds*; NPL Report Chem 98; National Physical Laboratory: Teddington, U.K., 1979.

Boukouvalas, C.; Spiliotis, N.; Coutsikos, P.; Tzouvaras, N.; Tassios, D. Prediction of Vapor-Liquid Equilibrium with the LCVM Model: A Linear Combination of the Vidal and Michelsen Mixing Rule Couple with the Original UNIFAC and t-mPR Equation of State. *Fluid Phase Equilib.* **1994**, *92*, 75−100.

Dahl, S.; Michelsen, M. L. High-Pressure Vapor-Liquid Equilibrium with a UNIFAC−Based Equation of State. *AIChE J.* **1990**, *36*, 1829−1836.

Deiters, U. K.; Schneider, G. M. High-Pressure Phase Equilibria: Experimental Methods. *Fluid Phase Equilib.* **1986**, *29*, 145−160.

Dohrn, R.; Brunner, G. High-Pressure Fluid-Phase Equilibria: Experimental Methods and Systems Investigated (1988−1993). *Fluid Phase Equilib.* **1995**, *106*, 213−282.

Eubank, P. T.; Hall, K. R.; Holste, J. C. A Review of Experimental Technique for Vapor-Liquid Equilibria at High Pressures. In *Second International Conference on Phase Equilibria and Fluid Properties in the Chemical Industry*; Knapp, H., Sandler, S. J., Eds.; DECHEMA: Frankfurt, 1980.

Fischer, K.; Gmehling, J. Further Development, Status and Results of the PSRK Method for the Prediction of Vapor-Liquid Equilibria and Gas Solubilities. *Fluid Phase Equilib.* **1995**, *112*, 1−22.

Fischer, K.; Gmehling, J. Further Development, Status and Results of the PSRK Method for the Prediction of Vapor-liquid Equilibria and Gas Solubilities. *Fluid Phase Equilib.* **1996**, *121*, 185−206.

Fornari, R.; Alessi, P.; Kikic, I. High-Pressure Fluid Phase Equilibria: Experimental Methods and Systems Investigated (1978−1987). *Fluid Phase Equilib.* **1990**, *57*, 1−33.

Hicks, C. P. A Bibliography of Thermodynamic Quantities for Binary Fluid Mixtures. *Chemical Thermodynamics*; The Chemical Society: London, 1978.

Kehiaian, H. V. Group Contribution Methods for Liquid Mixtures: A Critical Review. *Fluid Phase Equilib.* **1983**, *13*, 243−252.

Kehiaian, H. V. Thermodynamics of Binary Liquid Organic Mixtures. *Fluid Phase Equilib.* **1985**, *57*, 15−30.

Knapp, H.; Döring, R.; Oellrich, L.; Plöcker, U.; Prausnitz, J. M. *Vapor-Liquid Equilibria for Mixtures of Low-Boiling Substances*; Chemical Data Series VI; DECHEMA: Frankfurt/Main, 1982.

Lee, B. I.; Kesler, M. G. A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States. *AIChE J.* **1975**, *21*, 510.

Lee, H. S.; Lee, H. High-pressure phase equilibria for the carbon dioxide-2-pentanol and carbon dioxide-water-2-pentanol systems. *Fluid Phase Equilib.* **1998**, *151*, 695−701.

Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1995.

Michelson, M. L. Modified Huron-Vidal Mixing Rule for Cubic Equation of State. *Fluid Phase Equilib.* **1990**, *60*, 213.

Orbey, H.; Sandler, S. I. On the Combination of Equation of State and Excess Free Energy Models. *Fluid Phase Equilib.* **1995**, *111*, 53−70.

Orbey, H.: Sandler, S. I. A Comparison of Huron-Vidal Type Mixing Rules of Mixtures of Compounds with Large Size Differences, and a New Mixing Rule. *Fluid Phase Equilib.* **1997**, *132*, 1−14.

Panagiotopoulos, A. Z.; Reid, R. C. New Mixing Rule for Cubic Equation of State for Highly Polar, Asymmetric Systems. *ACS Symp. Ser.* **1986**, *300*, 571.

Patel, N. C.; Teja, A. S. A New Cubic Equation of State for Fluids and Fluid Mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463−473.

Peng, D.; Robinson, D. B. A New Two-Constant Equation of State. *J. Chem. Phys.* **1976**, *15*, 59−64.

Redlich, O.; Kwong, N. S. On the Thermodynamics of Solutions. V: An Equation of State. Fugacities of Gaseous Solutions. *Chem. Rev.* **1948**, *44*, 233.

Schneider, G. M. Phase Equilibria of Liquid and Gaseous Mixtures at High Pressures. In *Experimental Thermodynamics*; Le Neindre, B., Vodar, B., Eds.; Butterworth: London, 1975; Vol. II, Chapter 16, Part 2, pp 787−801.

Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 197−1203.

Takishima, S.; Saik, K.; Arai, K.; Saito, S. Phase Equilibria of CO_2−C_2H_5OH−H_2O System. *J. Chem. Eng. Jpn.* **1986**, *19*, 48−56.

Tsiklis, D. S. *Handbook of Technique in High-Pressure Research and Engineering*; Plenum: New York, 1968.

Yoon, J. H.; Chun, M. K.; Hong, W. H.; Lee, H. High-Pressure Phase Equilibria for Carbon Dioxide−Methanol−Water System: Experimental Data and Critical Evaluation of Mixing Rules. *Ind. Eng. Chem. Res.* **1993a**, *32*, 2882−2887.

Yoon, J.-H.; Lee, H.-S.; Lee, H. High-Pressure Vapor−Liquid Equilibria for Carbon Dioxide + Methanol, Carbon Dioxide + Ethanol, and Carbon Dioxide + Methanol + Ethanol. *J. Chem. Eng. Data* **1993b**, *38*, 53−55.

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