J. Chem. Eng. Data 1995, 40, 459–461

Vapor–Liquid Equilibria in the Carbon Dioxide + 1-Propanol System

Vishnu Vandana and Amyn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Vapor–liquid equilibria for CO_2 + 1-propanol mixtures have been measured at 315.0, 326.5, and 337.2 K using a high-pressure flow apparatus. The pressure in the experiments varied from 26.38 to 89.79 MPa. Data at 315.0 K were found to be significantly different from the data reported by Suzuki et al. and Yao et al. However, the results at 337.2 K are in good agreement with the results of Suzuki et al., and the data appear to be more consistent with the trends exhibited by other CO_2 + 1-alkanol mixtures. The data were correlated with Patel–Teja and Peng–Robinson equations of state using classical van der Waals one-fluid mixing rules and with the Peng–Robinson–Stryjek–Vera equation of state using the Wong–Sandler mixing rules.

Introduction

High-pressure vapor–liquid equilibrium measurements of CO_2 + alkanol systems are of interest due to their importance in the supercritical extraction of thermally labile compounds, dehydration of alcohols using supercritical carbon dioxide, and extraction of natural products using near critical solvents (Kuk and Montagna, 1983; Inomata et al., 1989; Di Giacomo et al., 1989; De la Ossa et al., 1990; King and Bott, 1993). Thermodynamic modeling of these separation processes requires a knowledge of vapor–liquid equilibria of the binary systems. In spite of these interests, however, only the CO_2 + methanol and CO_2 + ethanol systems have been studied extensively, whereas the CO_2 + 1-propanol, CO_2 + 2-propanol, CO_2 + 1-butanol, and CO_2 + 1-pentanol systems have recieved limited attention, and systems with higher alcohols have not been studied at all (Jennings et al., 1992). As part of a continuing effort on the measurement and correlation of phase equilibria of CO_2 + 1-alkanol systems in our laboratory, we have measured high-pressure vapor–liquid equilibria of CO_2 + 1-propanol mixtures using a flow apparatus and correlated the results using several models.

Experimental Section

A flow apparatus was used in this study for the measurement of vapor–liquid equilibria and is briefly described below. Additional details are available elsewhere (Jennings et al., 1991; Jennings, 1991).

Liquid carbon dioxide from a cylinder and 1-propanol from a reservoir were compressed to the desired pressure and pumped through a series of coil and static mixers into an equilibrium cell. The coiled and static mixers were placed in a constant-temperature bath to ensure equilibrium during the pumping process. The two phases were separated in the equilibrium view cell. Each phase exiting the view cell was depressurized across a micrometering valve and yielded a condensed liquid phase (essentially pure 1-propanol) and a vapor phase (essentially pure carbon dioxide). Liquid 1-propanol was collected in a collection vessel placed in an ice bath, while the carbon dioxide was sent through a wet test meter. Equilibrium phase compositions were determined from the weight of the condensed 1-propanol and the gas volume of carbon dioxide measured by the wet test meter. Typically, four liquid samples and three or four vapor samples were collected at a particular temperature and pressure. An average value was then reported for the liquid and vapor compositions at the given conditions. Corrections were made for the carbon dioxide dissolved in the liquid phase and for 1-propanol present in the noncondensible portion of each phase. The errors in liquid and vapor phase compositions were estimated to be within ±0.003 on the basis of the accuracy and precision of the instruments used to measure the compositions and the reproducibility of the measurements.

The pressure was measured by a digital Heise pressure gauge (Model 710A), calibrated against a Budenberg dead weight tester. The accuracy of the pressure measurements was within ±0.014 MPa. The temperature was measured using a thermistor inserted in the view cell and was calibrated against a Leeds and Northrup platinum resistance thermometer (Model 2180 A). The accuracy of the temperature measurements was estimated to be ±0.1 K. The pressure and temperature measurements were taken at regular intervals throughout the experiment to ensure that equilibrium conditions were maintained. The fluctuations in pressure were generally less than ±0.051 MPa during an experiment. The temperature changes were less than ±0.15 K.

Precision wet test meters (Models 63115 and 63111) used to measure the gas volumes were factory calibrated with a stated accuracy of 0.5%. A Sartorius balance (Model 1872) was used to measure the weight of 1-propanol collected. The accuracy of the weight measurements was within ±0.0010 g, and the reproducibility was within ±0.0001 g.

Sources and Purity of Materials. Carbon dioxide (Coleman grade) with a minimum purity of 99.99% was obtained from Matheson Gas Products Co. HPLC grade 1-propanol with a stated purity of 99.5% was obtained from Aldrich Chemical Corp. Both substances were used without further purification in the experiments.

Results and Discussion

Vapor–liquid equilibrium data of CO_2 + 1-propanol mixtures were measured at 315.0, 326.6, and 337.2 K over a range of pressures varying from 2.64 to 8.98 MPa. The experimental data are summarized in Table 1. The measurements at 315.0 K are compared with the data of Suzuki et al. (1990) and Yao et al. (1988) in Figure 1, and the results at 337.2 K are compared with the measure-

0021-9568/95/1740-0459$09.00/0

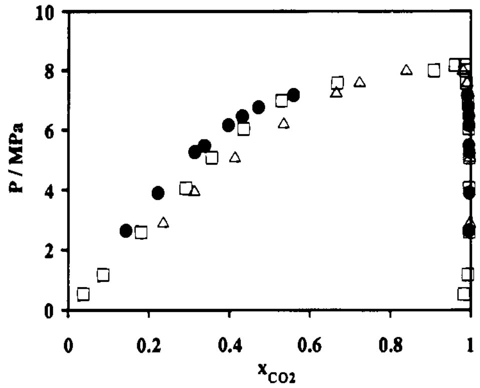

Figure 1. CO_2 + 1-propanol vapor–liquid equilibria: ●, this work (315.0 K); □, Suzuki et al. (313.4 K); △, Yao et al. (313.1 K).

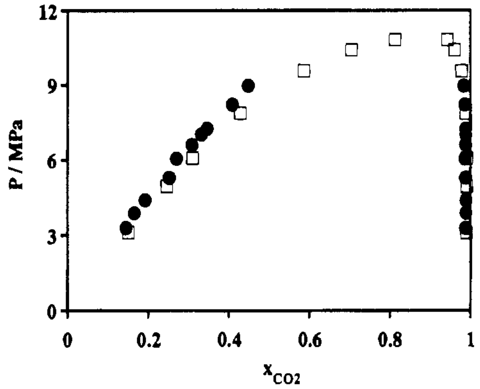

Figure 2. CO_2 + 1-propanol vapor–liquid equilibria: ●, this work (337.2 K); □, Suzuki et al. (334.4 K).

Table 1. Vapor–Liquid Equilibrium Data in the Carbon Dioxide + 1-Propanol System

T/K	P/MPa	x_{CO_2}	y_{CO_2}
315.0	2.64	0.144	0.995
315.2	3.90	0.223	0.996
315.2	5.27	0.315	0.996
315.2	5.48	0.338	0.996
314.9	6.15	0.398	0.996
314.8	6.46	0.432	0.995
314.8	6.76	0.472	0.994
314.7	7.17	0.560	0.992
av 315.0			
326.5	3.48	0.157	0.993
326.8	4.65	0.228	0.993
326.7	5.10	0.250	0.993
326.7	5.22	0.261	0.992
326.8	5.71	0.291	0.992
326.8	6.04	0.320	0.993
326.8	6.66	0.361	0.993
326.8	7.42	0.423	0.992
325.9	8.19	0.511	0.989
326.2	8.88	0.562	0.984
av 326.6			
337.1	3.30	0.145	0.988
337.4	3.97	0.166	0.989
337.1	4.41	0.192	0.989
337.2	5.30	0.252	0.988
337.2	6.07	0.269	0.987
337.2	6.61	0.308	0.988
337.1	7.03	0.332	0.988
337.2	7.25	0.346	0.988
337.1	8.22	0.408	0.986
337.1	8.98	0.448	0.984
av 337.2			

ments of Suzuki et al. in Figure 2. No literature data are available for this system at 326.6 K. Figure 1 shows some disagreement between our data at 315.0 K and the data reported by Suzuki et al. at 313.4 K and by Yao et al. at 313.1 K. Examination of CO_2 + ethanol, CO_2 + 1-propanol, CO_2 + 1-butanol, and CO_2 + 1-pentanol systems (Jennings, 1991) showed that our data are more consistent with the trends observed for the series of CO_2 + 1-alkanol systems (Figure 3). Our data at 337.2 K are also in good agreement with the data of Suzuki et al. at 334.4 K.

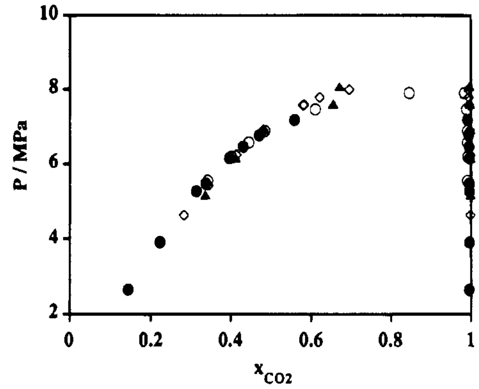

Figure 3. CO_2 + 1-alkanol vapor–liquid equilibria: ●, this work (315.0 K); data of Jennings (1992) (○) CO_2 + ethanol (314.5 K), (◇) CO_2 + 1-butanol (314.8 K); and (△) CO_2 + 1-pentanol (314.6 K).

The experimental data were correlated with the Patel–Teja (PT), Peng–Robinson (PR), and Peng–Robinson–Stryjek–Vera (PRSV) equations of state (Patel and Teja, 1982; Peng and Robinson, 1976; Stryjek and Vera, 1986). The PT and PR equations of state were used with the van der Waals one-fluid mixing rules incorporating a binary interaction parameter k_{ij}, whereas the PRSV equation of state was used with the mixing rule proposed by Wong and Sandler (1992). The Van Laar and Wilson free energy models were used in the PRSV calculations. The critical properties and acentric factors of the two components required for the calculations were obtained from Reid et al. (1987), and the equation of state parameters for the PT equation of state were those recommended by Patel and Teja (1982). The binary interaction parameters k_{ij} in the PT and PR equation of state calculations were optimized using the objective function shown below which minimized deviations from experimental x,y data.

objective function =

$$\sum_{k=1}^{\text{points}} \sum_{i=1}^{\text{components}} \left(\left| \frac{x_i^{\text{calcd}} - x_i^{\text{exptl}}}{x_i^{\text{exptl}}} \right| 100 + \left| \frac{y_i^{calcd} - y_i^{\text{exptl}}}{y_i^{exptl}} \right| 100 \right)$$

The κ parameter in the PRSV equation of state for each pure component was obtained by regressing vapor pressure data. The vapor pressure data for carbon dioxide were taken from the *IUPAC International Thermodynamic Tables of the Fluid State* (Angus et al., 1976) and for 1-propanol were obtained from Ambrose and Ghiassee (1987). Three parameters (A_{12}, A_{21}, k_{ij}) were optimized in the PRSV equation of state calculations for each of the free energy models chosen, using the following objective function:

objective function =

$$\sum_{k=1}^{Npoints} \left(\left| \frac{P_i^{\text{calcd}} - P_i^{\text{exptl}}}{P_i^{\text{exptl}}} \right| 100 + \left| \frac{y_i^{calcd} - y_i^{\text{exptl}}}{y_i^{\text{exptl}}} \right| 100 \right)$$

The results of the correlations are presented in Figures 4 and 5 and summarized in Table 2. The PRSV equation of state with the Wong–Sandler mixing rules gave better

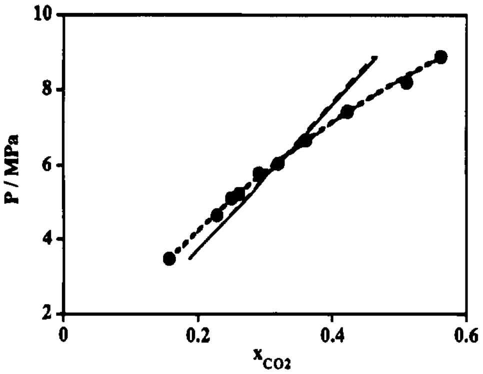

Figure 4. Correlation of CO_2 + 1-propanol vapor–liquid equilibria at 326.6 K (liquid phase) using PT and PR EOS with classical van der Waals one-fluid mixing rules and PRSV EOS with Wong–Sandler mixing rules: ●, experimental; - - -, PT EOS; —, PR EOS; — • —, PRSV EOS–Van Laar; heavy broken line, PRSV EOS–Wilson.

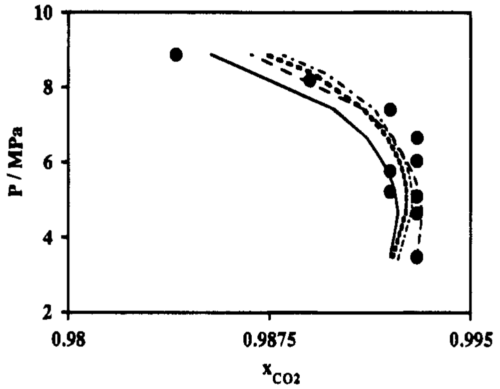

Figure 5. Correlation of CO_2 + 1-propanol vapor–liquid equilibria at 326.6 K (vapor phase) using PT and PR EOS with classical van der Waals one-fluid mixing rules and PRSV EOS with Wong–Sandler mixing rules: ●, experimental; - - -, PT EOS; —, PR EOS; — • —, PRSV EOS–Van Laar; heavy broken line, PRSV EOS–Wilson.

Table 2. Correlation of Vapor–Liquid Equilibrium Data Using Equations of State

	CO_2 + 1-propanol system		
EOS	315.0 K	326.6 K	337.2 K
Patel–Teja			
k_{ij}	0.1501	0.1618	0.1680
AAD % (x_{CO_2})	8.55	8.48	5.80
AAD % (y_{CO_2})	0.06	0.08	0.12
Peng–Robinson			
k_{ij}	0.1519	0.1618	0.1855
AAD % (x_{CO_2})	8.58	8.45	5.74
AAD % (y_{CO_2})	0.09	0.11	0.07
Peng–Robinson–Stryjek–Vera (Van Laar)			
k_{ij}	0.4999	0.5099	0.4999
A_{12}	1.0799	1.1669	1.0304
A_{21}	1.3706	1.2134	1.3006
AAD % (P)	1.30	0.66	0.83
AAD % (y_{CO_2})	0.06	0.09	0.06
Peng–Robinson–Stryjek–Vera (Wilson)			
k_{ij}	0.4940	0.5000	0.5000
A_{12}	0.6223	0.5422	0.7078
A_{21}	0.3220	0.4028	0.3170
AAD % (P)	1.67	0.64	0.93
AAD % (y_{CO_2})	0.06	0.09	0.06

results than the PT and PR equations of state with classical van der Waals mixing rules. However, only one adjustable parameter was used in the PT and PR equation of state calculations, whereas three binary interaction parameters were used in the PRSV calculations. The PRSV equation of state gave similar results with both the Wilson and Van Laar free energy models. The PRSV equation of state was also able to correlate the data within the accuracy of the experiment, even though the system is highly nonideal and contains an associating component (1-propanol).

Conclusions

Vapor–liquid equilibrium data for the CO_2 + 1-propanol system have been measured at three different temperatures. Some disagreement with literature values at one temperature was found. However, our data appear to be more consistent with the trends observed for other CO_2 + alcohol systems. The data have been correlated using PT, PR, and PRSV equations of state. The PRSV equation of state with the Wong–Sandler mixing rules performed better than PT and PR equations of state with classical van der Waals one-fluid mixing rules. However, this is not surprising, since only one adjustable binary interaction parameter was used in the PT and PR equation of state calculations, whereas three binary interaction parameters were used in the PRSV calculations. Nevertheless, it is interesting to note that the PRSV equation yields the correct behavior for this highly nonideal system.

Acknowledgment

We thank Dr. S. I. Sandler for providing the programs to perform the equation of state calculations involving the Wong–Sandler mixing rules.

Literature Cited

Ambrose, D.; Ghiassee, N. B. *J. Chem. Thermodyn.* **1987**, *19*, 505.

Angus, S.; Armstrong, B.; de Reuck, K. M. *International thermodynamic tables of the fluid state: carbon dioxide*; International Union of Pure and Applied Chemistry: Division of Physical Chemistry Commission on Thermodynamics and Thermochemistry Tables Project; IUPAC: Oxford, U.K., 1976.

de la Ossa, E. M.; Brandani, V.; Del Re, G.; Di Giacomo, G.; Ferri, E. *Fluid Phase Equilib.* **1989**, *56*, 325.

Di Giacomo, G.; Brandani, V.; Del Re, G.; Mucciante, V. *Fluid Phase Equilib.* **1989**, *53*, 405.

Inomata, H.; Arai, K.; Saito, S.; Ohba, S.; Takeuchi, K. *Fluid Phase Equilib.* **1989**, *53*, 23.

Jennings, D. W. Ph.D. Thesis, Georgia Institute of Technology, 1991.

Jennings, D. W.; Gude, M. T.; Teja, A. S. *Supercritical Fluid Engineering Science: Fundamentals and Applications*; ACS Symposium Series 514; American Chemical Society: Washington, DC, 1992; Chapter 2.

King, M. B.; Bott, T. R. *Extraction of Natural Products Using Near-Critical Solvents*; Blackie Academic and Professional, Chapman and Hall: Bishopbriggs, Glasgow, 1993.

Kuk, M. S.; Montagna, J. C. In *Chemical Engineering at Supercritical Fluids Conditions*; Paulaitis, M. E., Peninger, J. M. L., Gray, R. D., Davidson, P., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Chapter 4.

Lee, R. J.; Jennings, D. W.; Teja, A. S. *J. Chem. Eng. Data* **1991**, *36*, 303.

Patel, N. C.; Teja, A. S. *Chem. Eng. Sci.* **1982**, *37*, 463.

Peng, D. Y.; Robinson, D. F. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

Prausnitz, J. M.; Reid, R. C.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Stryjek, R.; Vera, J. H. *Can. J. Chem. Eng.* **1986**, *64*, 323.

Suzuki, K.; Sue, H.; Itou, M.; Smith, R. L.; Inomata, H.; Arai, K.; Saito, S. *J. Chem. Eng. Data* **1990**, *35*, 63.

Wong, D. S. H.; Sandler, S. I. *AIChE J.* **1992**, *38*, 671.

Yao, S.; Liu, F.; Han, Z.; Zhu, Z. *Proc. Int. Symp. Thermodyn. Chem. Eng. Ind.* **1988**, *1*, 688.

Received for review September 13, 1994. Revised November 16, 1994. Accepted November 22, 1994.[⊗]

JE9401934

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.