2444 *J. Chem. Eng. Data* **2008,** *53,* 2444–2448

High-Pressure Phase Equilibria for the Carbon Dioxide + 1-Propanol System

Catinca Secuianu,* Viorel Feroiu, and Dan Geană

Department of Applied Physical Chemistry and Electrochemistry, Politehnica University of Bucharest, 1-7 Gh. Polizu Str., S1, 011061 Bucharest, Romania

Isothermal (P, T, x, y) data have been measured for the binary system carbon dioxide + 1-propanol at temperatures from (293.15 to 353.15) K. The pressure range under investigation was between (0.61 and 12.64) MPa. The new experimental results are discussed and compared with available literature data. Measured vapor−liquid equilibria (VLE) data and literature data for the carbon dioxide + 1-propanol system were modeled with a general cubic equation of state (GEOS) using classical van der Waals (two-parameters conventional mixing rule, 2PCMR) mixing rules. A single set of interaction parameters, representing well the critical pressure maximum (CPM) and the temperature of the upper critical end point (UCEP), was used to calculate the global phase behavior in the binary mixture carbon dioxide + 1-propanol in a wide range of temperatures [(293.15 to 426.68) K]. The VLE data are satisfactorily predicted for engineering purposes.

Introduction

Knowledge of phase equilibria at high pressures is very important and required for the design, simulation, and optimization of processes related to supercritical fluid extraction (SFE). The data generated from phase equilibrium studies at high pressure must be reliable and accurate because of the severity of conditions of the possible applications.[1]

This work is a part of a continuing study of carbon dioxide + alkanols[2] of interest in SFE and supercritical fluid chromatography (SFC), in the oil and natural gas industry and in the cosmetic, pharmaceutical, surfactant, and food industries.[1] Previously, we have published vapor−liquid equlibria (VLE) data[3−7] for carbon dioxide + methanol, + ethanol, + 2-propanol, and + 1-butanol. Though in the literature there are some VLE data for the carbon dioxide + 1-propanol system, there is no agreement between the different sources of experimental data.[8]

The goals of this work were to add new experimental data and to represent the global phase behavior of this system with a simple model, using a single set of interaction parameters. Therefore, in this work, we made new measurements using a static-analytical method, in a high-pressure visual cell, for the carbon dioxide + 1-propanol system at (293.15, 303.15, 313.15, 333.15, and 353.15) K up to 11.22 MPa.

The global phase behavior of the system was modeled with a general cubic equation of state (GEOS)[9−12] coupled with classical van der Waals mixing rules (2PCMR). This cubic equation is a generalized form with four parameters for all cubic equations of state with two, three, and four parameters.[11]

A single set of interaction parameters, representing well the critical pressure maximum (CPM) and the temperature of the upper critical end point (UCEP), was used to model the global phase behavior of the carbon dioxide + 1-propanol system.[8,13] The prediction of the critical line and subcritical phase behavior in this binary mixture was done for all available data. The calculation results were compared to the new data reported in this work and to all available literature data. The results show a satisfactory agreement between the model and the experimental data.

Experimental Section

Materials. Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, Bucharest, Romania, and 1-propanol (mass fraction purity > 0.98) was a Fluka product. The chemicals were used as supplied.

Apparatus and Procedure. A detailed description of the experimental apparatus is presented in an earlier paper.[3] The apparatus used in this work is based on the static-analytical method with liquid and vapor phase sampling. The procedure is the same as in our previous papers.[3−7,14,15] The entire internal loop of the apparatus including the equilibrium cell was rinsed several times with carbon dioxide. Then, the equilibrium cell was evacuated with a vacuum pump. The cell was charged with alcohol, and then it was slightly pressurized with carbon dioxide to the experimental pressure and was heated to the experimental temperature. To facilitate the approach to an equilibrium state, the mixture in the cell was stirred for a few hours. Then, the stirrer was switched off, and about 1 h was allowed to pass until the coexisting phases were completely separated. Samples of the liquid and vapor phase were collected by depressurization and expansion into glass traps, by using manually operated valves. The valves were operated in such a way as to keep almost constant the pressure in the visual cell. The total amount of the organic substance in the glass trap was about (0.05 and 0.2) g for the vapor phase and liquid phase, respectively. The amount of carbon dioxide in each phase was obtained by expansion in a glass bottle of calibrated volume. In a typical experiment, the measured volumes of carbon dioxide were about 100 cm^3 from the vapor phase and 50 cm^3 from the liquid phase. The liquid samples of both phases were weighed with a precision balance (A&D Instruments Ltd., type HM-200, Tokyo, Japan) with an accuracy of ± 0.0001 g.

Results and Discussion

The equilibrium compositions for the carbon dioxide + 1-propanol binary system were measured at (293.15, 303.15,

---

* Corresponding author. Tel.: +4021 4023988. Fax: +4021 3154193. E-mail address: tina@catedra.chfiz.pub.ro.

10.1021/je8004485 CCC: $40.75

Table 1. Mole Fraction of Component 1 in the Liquid Phase, x_1, and Mole Fraction of Component 1 in the Vapor Phase, y_1, at the Pressure, *P*, and Temperature, *T*, for the Binary System Carbon Dioxide (1) + 1-Propanol (2)

P/MPa	x_1	y_1	*P*/MPa	x_1	y_1
		T/K = 293.15 ± 0.1			
0.74	0.0492	0.9895	4.52	0.4181	0.9975
1.49	0.1045	0.9950	5.16	0.6120	0.9967
2.55	0.1881	0.9974	5.21	0.6559	0.9959
3.60	0.2882	0.9978	5.26	0.8089	0.9943
		T/K = 303.15 ± 0.1			
0.64	0.0361	0.9873	5.47	0.4389	0.9950
1.41	0.0817	0.9949	6.18	0.5670	0.9931
2.64	0.1729	0.9966	6.49	0.7631	0.9921
3.97	0.2732	0.9970	6.52	0.7913	0.9912
		T/K = 313.15 ± 0.1			
0.61	0.0337	0.9837	5.87	0.3744	0.9952
1.55	0.0890	0.9941	7.16	0.5420	0.9915
2.54	0.1442	0.9958	7.86	0.7423	0.9882
3.65	0.2204	0.9961	8.19	0.9785[a]	
4.79	0.2867	0.9958			
		T/K = 333.15 ± 0.1			
0.94	0.0402	0.9775	7.22	0.3703	0.9885
1.98	0.0858	0.9856	8.29	0.4509	0.9862
3.05	0.1291	0.9893	9.35	0.5285	0.9826
4.44	0.1974	0.9903	9.97	0.6070	0.9786
5.76	0.2758	0.9908	11.15	0.9176[a]	
6.95	0.3517	0.9889			
		T/K = 353.15 ± 0.1			
0.75	0.0263	0.9533	9.62	0.4159	0.9720
2.02	0.0664	0.9691	9.93	0.4335	0.9700
3.01	0.1079	0.9749	10.97	0.5017	0.9641
4.12	0.1559	0.9784	12.01	0.5685	0.9479
5.82	0.2270	0.9807	12.64	0.6286	0.9211
7.72	0.3157	0.9771	13.4	0.8676[a]	
8.56	0.3619	0.9753			

[a] Critical points.

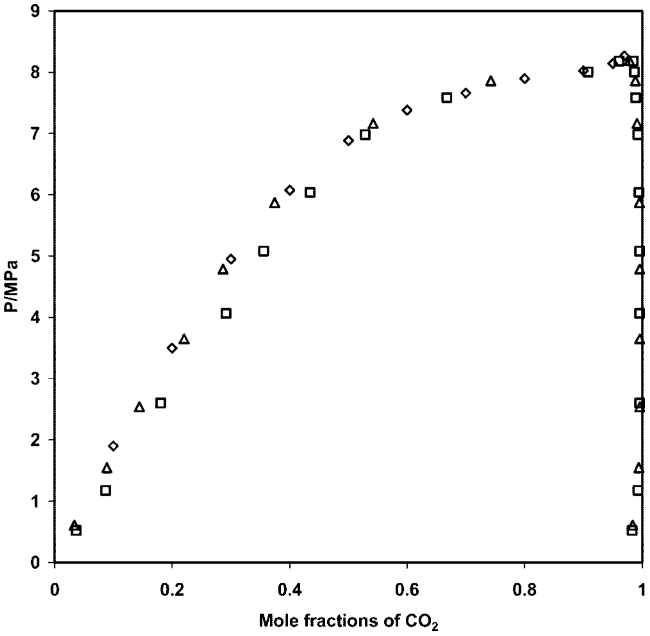

Figure 1. Comparison of measured and literature VLE data for the carbon dioxide (1) + 1-propanol (2) system: Δ, 313.15 K, this work; ◇, 313.15 K, Yaginuma et al.;[16] □, 313.4 K, Suzuki et al.[17]

313.15, 333.15, and 353.15) K, and the results are given in Table 1. The values are typically averages of two or three measurements. For the vapor−liquid equilibria (VLE) measurements, the uncertainty of the mole fraction is typically 0.001 and always < 0.003. As usual in the literature, we calculated the mole fractions with four decimal places. The critical points for our measured isotherms were estimated based on the measurements made near the critical opalescence.

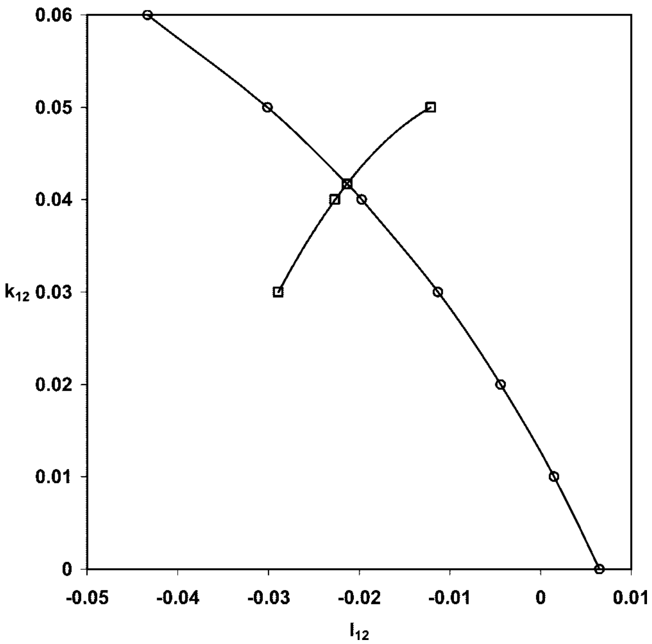

Figure 2. $k_{12}-l_{12}$ global phase diagram for the carbon dioxide (1) + 1-propanol (2) system calculated using the GEOS equation: ○−○, the curve of the critical pressure maximum at constant experimental value; □−□, the curve of the UCEP temperature at constant experimental value.

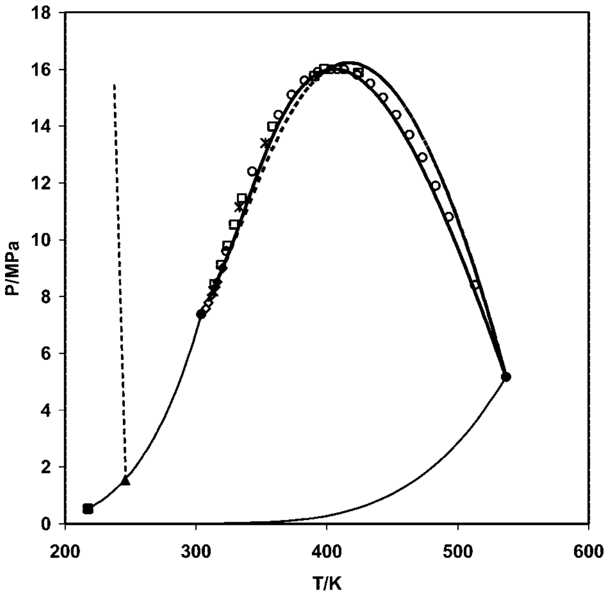

Figure 3. $P-T$ fluid phase diagram of the carbon dioxide (1) + 1-propanol (2) system: *, this work; □, Yeo et al.;[23] ◇, Gurdial et al.;[24] ○, Ziegler et al.;[25] ●, critical points of pure components, Reid et al.;[26] ▲, experimental UCEP, Lam et al.;[22] ---, LL line (sketch); −, vapor pressure curves of pure components; —, critical line predicted with the GEOS/2PCMR EOS (k_{12} = 0.042, l_{12} = −0.021); ····, critical line predicted with the PR/2PCMR EOS (k_{12} = 0.030, l_{12} = −0.105).

Figure 1 shows a detailed comparison of our data at 313.15 K with the existing data of Yaginuma et al.[16] and of Suzuki et al.[17] for the same temperature. The results of the Yaginuma et al.[16] agree with our experimental data to nearly within the experimental uncertainty. The data reported by Suzuki et al.[17] are in acceptable agreement with those of this work and Yaginuma et al.[16] The modeling of phase behavior of this system

Table 2. Average Absolute Deviations in Bubble Point Pressure (AADP, %) and Average Absolute Deviations in the Vapor Phase Compositions (AADY, %) for the Carbon Dioxide (1) + 1-Propanol (2) System Calculated by the GEOS Equation with a Single Set of Interaction Parameters

T/K	AADP %	AADY %	NEXP[a]	*P* range[b]/MPa	ref
293.15	10.3	0.2	8	0.740 to 5.260	this work
303.15	9.6	0.2	3	0.640 to 6.520	this work
303.15	6.1	-	8	6.271 to 6.760	23
313.15	10.3	0.2	8	0.610 to 7.860	this work
313.15	10.2	-	11	1.900 to 8.260	16
313.40	14.2	0.2	10	0.518 to 8.179	17
315.0	12.9	0.2	8	2.640 to 7.170	27
326.60	14.4	0.3	10	3.480 to 8.880	27
333.15	12.1	0.4	10	0.940 to 9.970	this work
333.40	8.1	0.8	9	0.668 to 10.822	17
334.61	8.1	0.6	9	1.620 to 11.050	28
337.20	13.6	0.4	10	3.300 to 8.980	27
344.82	8.8	3.9	4	11.547 to 12.321	29
352.83	6.1	0.7	12	1.500 to 13.330	28
353.15	12.6	0.8	12	0.750 to 12.640	this work
373.16	3.2	0.5	7	12.063 to 14.978	29
397.48	4.7	0.8	5	12.348 to 15.769	29
426.68	22.1	4.2	6	10.602 to 15.335	29

[a] Number of experimental points. [b] Experimental pressure range.

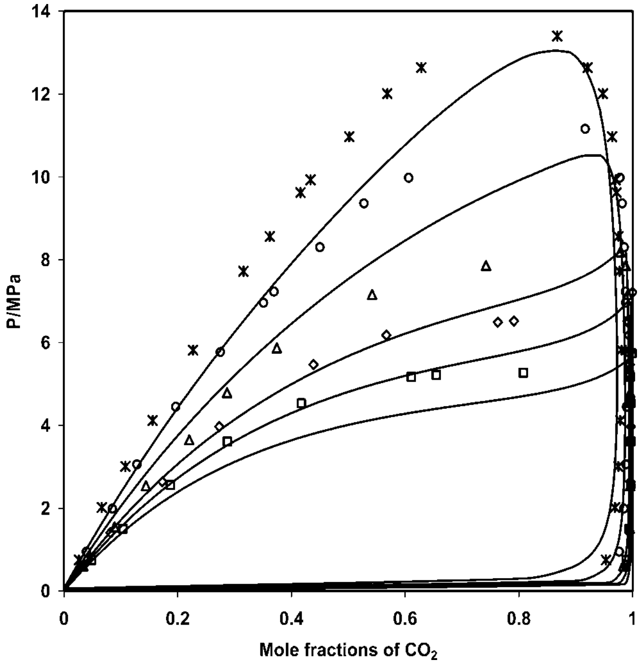

Figure 4. Comparison of our measured data for the carbon dioxide + 1-propanol system and predictions with GEOS/2PCMR ($k_{12} = 0.04$, $l_{12} = -0.02$): □, 293.15 K; ◇, 303.15 K; Δ, 313.15 K; ○, 333.15 K; *, 353.15 K; −, GEOS/2PCMR equation.

was made with the GEOS equation[9−12] coupled with classical van der Waals mixing rules (2PCMR). The GEOS[9] equation of state is

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \tag{1}$$

with the classical van der Waals mixing rules

$$a = \sum_i \sum_j X_i X_j a_{ij} \qquad b = \sum_i X_i b_i \tag{2}$$

$$c = \sum_i \sum_j X_i X_j c_{ij} \qquad d = \sum_i X_i d_i \tag{3}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \qquad b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \qquad c_{ij} = \pm (c_i c_j)^{1/2} \tag{4}$$

with "+" for c_i, $c_j > 0$ and "−" for c_i, $c_j < 0$. Generally, negative values are common for the *c* parameter of pure components.

The four parameters *a*, *b*, *c*, and *d* for a pure component are expressed by

$$a(T) = \frac{R^2 T_c^2}{P_c}\beta(T_r)\Omega_a \qquad b = \frac{RT_c}{P_c}\Omega_b \tag{5}$$

$$c = \frac{R^2 T_c^2}{P_c^2}\Omega_c \qquad d = \frac{RT_c}{P_c}\Omega_d \tag{6}$$

Setting four critical conditions, with α_c as the Riedel criterion

$$P_r = 1 \qquad \left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = 0 \qquad \left(\frac{\partial^2 P_r}{\partial V_r^2}\right)_{T_r} = 0 \qquad \alpha_c = \left(\frac{\partial P_r}{\partial T_r}\right)_{V_r} \tag{7}$$

at $T_r = 1$ and $V_r = 1$, the expressions of the parameters Ω_a, Ω_b, Ω_c, and Ω_d are obtained

$$\Omega_a = (1 - B)^3 \qquad \Omega_b = Z_c - B \qquad \Omega_c = (1 - B)^2(B - 0.25) \tag{8}$$

$$\Omega_d = Z_c - \frac{(1 - B)}{2} \qquad B = \frac{1 + m}{\alpha_c + m} \tag{9}$$

where P_r, T_r, and V_r are the reduced variables and Z_c is the critical compressibility factor.

The temperature function used is

$$\beta(T_r) = T_r^{-m} \tag{10}$$

The GEOS parameters *m* and α_c were estimated by constraining the EOS to reproduce the experimental vapor pressure and liquid

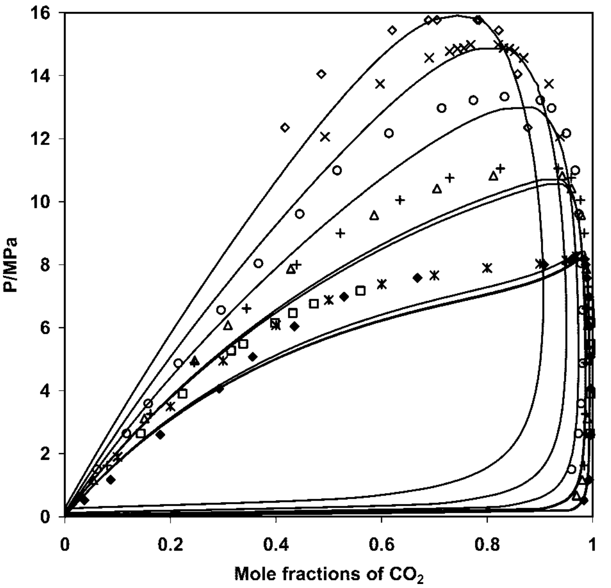

Figure 5. Comparison of selected literature data for the carbon dioxide + 1-propanol system and predictions with GEOS/2PCMR ($k_{12} = 0.04$, $l_{12} = -0.02$): *, 313.15 K, Yaginuma et al.;[16] ♦, 313.4 K, Suzuki et al.;[17] □, 315.0 K, Vandana and Teja;[27] Δ, 333.4 K, Suzuki et al.;[17] +, 334.61 K, Mendoza de la Cruz and Galicia-Luna;[28] ○, 352.83 K, Mendoza de la Cruz and Galicia-Luna;[28] ×, 373.16 K, Elizalde-Solis et al.;[29] ◇, 397.48 K, Elizalde-Solis et al.;[29] −, GEOS/2PCMR equation.

Table 3. Average Absolute Deviations in Bubble Point Pressure (AADP, %) and Average Absolute Deviations in the Vapor Phase Compositions (AADY, %) for Carbon Dioxide (1) + 1-Propanol (2)

		GEOS/2PCMR		PR/2PCMR	
T/K	NEXP	AADP %	AADY %	AADP %	AADY %
293.15	8	1.2	0.2	0.9	0.2
303.15	8	2.6	0.2	2.1	0.5
313.15	8	1.8	0.1	1.6	0.1
333.15	10	1.7	0.6	1.6	0.3
353.15	12	1.6	0.8	1.5	0.5

volume on the saturation curve between the triple point and the critical point.[9]

The calculations were made using the software package PHEQ, developed in our laboratory.[18] The critical curves were calculated using the method proposed by Heidemann and Khalil,[19] with numerical derivatives given by Stockfleth and Dohrn.[20]

In this study, the GEOS equation is used in a semipredictive approach to obtain a set of binary parameters yielding good results in the binary system carbon dioxide + 1-propanol (including VLE in the entire temperature range, critical points, global phase behavior). The set of binary parameters was calculated using the $k_{12}-l_{12}$ method[8] to obtain the experimental value of the vapor−liquid critical pressure maximum (CPM) simultaneously with the temperature of UCEP. The binary system carbon dioxide + 1-propanol is a type II phase diagram, according to the classification of van Konynenburg and Scott.[21] Lam et al.[22] have provided experimental evidence that the system carbon dioxide + 1-propanol exhibits liquid−liquid immiscibility. The experimental temperatures of UCEP (245.89 K[22]) and CPM (160.0 bar;[25] 160.01 bar[23]) have been traced by paths in the $k_{12}-l_{12}$ diagram, and their intersection has given the values of the adjustable parameters, as can be seen in Figure 2. The values of the interaction binary parameters (k_{12} and l_{12}) fulfilling these requirements are 0.042 ± 0.001 and −0.021 ± 0.001. This set of interaction parameters was used to predict the topology of phase behavior and the critical and the bubble- and dew-point lines. The *P*−*T* fluid phase diagram is presented in Figure 3. The average deviation in pressure on the critical curve is 0.5 % for GEOS. In Figure 3 is also illustrated the prediction of the critical curve with the Peng−Robinson (PR) equation of state coupled with classical mixing rules. The set of interaction parameters used with PR/2PCMR is $k_{12} = 0.030$ and $l_{12} = -0.105$. These interaction parameters are those proposed by Polishuk et al.[8] The average deviations in pressure on the critical curve are in this case 3.9 %; however, the UCEP is significantly overestimated,[8] and the bubble-point curves are not accurate.[8] It should be remarked that GEOS leads to better results (critical curve, UCEP, VLE) with a set of interaction parameters smaller in absolute values than those of Polishuk et al.[8]

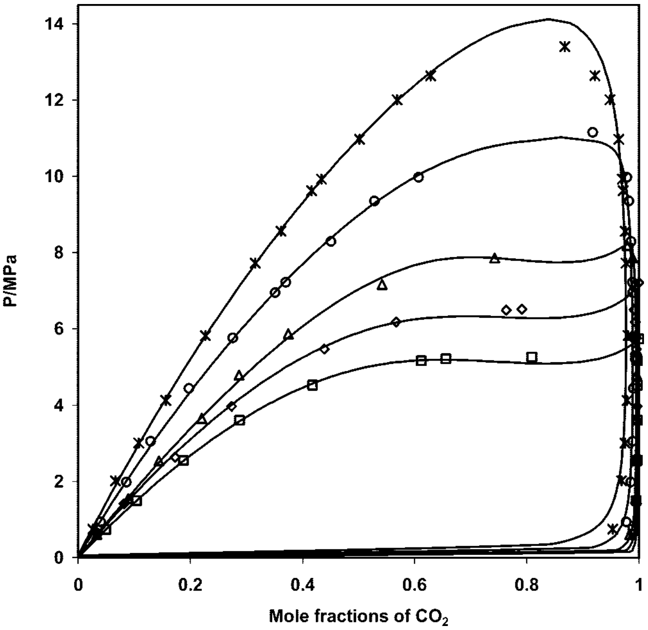

Figure 6. Comparison of our measured data for the carbon dioxide + 1-propanol system and correlations with PR/2PCMR: □, 293.15 K; ◇, 303.15 K; Δ, 313.15 K; ○, 333.15 K; *, 353.15 K; −, PR/2PCMR equation.

GEOS calculations with this set of parameters ($k_{12} = 0.042$, $l_{12} = -0.021$) were done for the new experimental data of this work and for 13 data sets from the literature at temperatures between (293.15 and 426.68) K. Table 2 presents the average absolute deviations in bubble point pressure (AADP, %) and vapor phase compositions (AADY, %) of the experimental data, comparing the prediction results ($k_{12} = 0.042$, $l_{12} = -0.021$). As can be seen, the predictions with the single set of parameters are mostly reasonable. A higher deviation appears at 426.68 K where the data were measured near the critical point of the mixture[29] (see Table 2). The AADP (%) and AADY (%) are calculated by the equations

$$\text{AADP}\ (\%) = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| \cdot 100 \qquad (11)$$

$$\text{AADY}\ (\%) = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \left| Y_i^{\text{exp}} - Y_i^{\text{calc}} \right| \cdot 100 \qquad (12)$$

Several isotherms comparing the prediction results with experimental data are illustrated in Figure 4 (measured data of this work) and Figure 5 (selective literature data). As can be seen, the single set of interaction parameters leads to satisfactory prediction of VLE for the carbon dioxide + 1-propanol system. In Figures 4 and 5, it can be observed that the critical pressure of the mixture is slightly underestimated at lower temperatures but is accurately predicted as temperature increases. As known from a previous work,[8] it is not enough to reproduce well the CPM and the UCEP, but also the liquid−liquid critical line for accurately predicting the bubble-point curves. The liquid−liquid critical line for the carbon dioxide + 1-propanol system was not experimentally measured, and therefore no restrictions were imposed to the single set of interaction parameters used. This fact could be the reason for less accurate bubble-point curves, as can be seen in Figures 4 and 5. However, GEOS is very accurate in predicting the dew-point curves.

Significantly smaller errors can be obtained by correlating the experimental data (Table 3), but at temperatures near the critical point of carbon dioxide, the calculation leads to a false liquid−liquid splitting (a maximum and a minimum in the bubble-point curves). As an example, we illustrated in Figure 6 the correlations with the Peng−Robinson (PR) equation of state coupled with classical van der Waals mixing rules for the new data measured in this work, but this behavior can be observed with other models too (different equation of state coupled with classical and G^E mixing rules). This is a known problem in correlating such systems.[30] Therefore, the proposed approach in this work is justified to avoid the false liquid−liquid splitting and to represent correctly the phase behavior.

Conclusions

New VLE experimental data for the binary system carbon dioxide + 1-propanol were measured at (293.15, 303.15, 313.15, 333.15, and 353.15) K and pressures between (0.61 and 12.64) MPa, with a high-pressure static apparatus. Measured and literature VLE data for the carbon dioxide + 1-propanol system were modeled with cubic equations of state (GEOS) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. One set of interaction parameters was used in a semipredictive approach to predict the critical and subcritical phase behavior in the binary mixture carbon dioxide + 1-propanol in a wide range of temperatures. The predicted results were compared both with our experimental data and the available literature data for carbon dioxide + 1-propanol binary systems. The predictions of the global phase behavior were satisfactorily good.

Literature Cited

(1) Perrut, M. Supercritical fluid applications: Industrial developments and economic issues. *Ind. Eng. Chem. Res.* **2000**, *39*, 4531–4535.

(2) Secuianu, C. High-pressure vapor−liquid equilibria in the binary systems carbon dioxide + monohydroxilic alcohols. Ph.D. Thesis, Politehnica University of Bucharest, Bucharest, 2004 (in Romanian).

(3) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor−Liquid Equilibria in the System Carbon Dioxide and 2-Propanol at Temperatures from 293.25 to 323.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1384–1386.

(4) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Phase Equilibria for the Carbon Dioxide + Methanol and Carbon Dioxide + Isopropanol Systems. *Rev. Chim. (Bucuresti)* **2003**, *54*, 874–879.

(5) Secuianu, C.; Feroiu, V.; and Geană, D. High-Pressure Vapor-Liquid Equilibria in the System Carbon Dioxide and Methanol at Temperatures from 298.15 to 323.15 K. *Ann. West Univ. Timisoara* **2003**, *Series Chemistry 12*, 393–400.

(6) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor-Liquid Equilibria in the System Carbon Dioxide + 1-Butanol at Temperatures from 293.15 to 324.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1635–1638.

(7) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor-Liquid Equilibria in the System Carbon Dioxide + Ethanol. Experimental Data and Calculations with an Equation of State. *U.P.B. Sci. Bull.* **2004**, *Series B 66*, 9–18.

(8) Polishuk, I.; Wisniak, J.; Segura, H. Simultaneous prediction of the critical and sub-critical phase behavior in mixtures using equation of state I. Carbon dioxide-alkanols. *Chem. Eng. Sci.* **2001**, *56*, 6485–6510.

(9) Geană, D. A new equation of state for fluids.Applications to PVT calculations for pure fluids. I. *Rev. Chim. (Bucharest)* **1986**, *3* (7), 303–309 (in Romanian).

(10) Geană, D. A new equation of state for fluids. II. Applications to phase equilibria. *Rev. Chim. (Bucharest)* **1986**, *37*, 951–959 (in Romanian).

(11) Geană, D.; Feroiu, V. Thermodynamic properties of pure fluids using the GEOS3C equation of state. *Fluid Phase Equilib.* **2000**, *174*, 51–68.

(12) Feroiu, V.; Geană, D. Volumetric and thermodynamic properties for pure refrigerants and refrigerant mixtures from cubic equations of state. *Fluid Phase Equilib.* **2003**, *207*, 283–300.

(13) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor-Liquid and Vapor-Liquid-Liquid Equilibria in the Carbon Dioxide + 1-Hexanol System. In *Proceedings of the 23rd European Symposium on Applied Thermodynamics (ESAT 2008)*, Cannes, France, May 29th−June 1st 2008; pp 79−86.

(14) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor-Liquid Equilibria of Carbon Dioxide + 1-Pentanol System: Experimental Measurements and Modeling. *Rev. Chim. (Bucharest)* **2007**, *58*, 1176–1181.

(15) Secuianu, C.; Feroiu, V.; Geană, D. Investigation of phase equilibria in the ternary system carbon dioxide + 1-heptanol + pentadecane. *Fluid Phase Equilib.* **2007**, *261*, 337–342.

(16) Yaginuma, R.; Nakajima, T.; Tanaka, H.; Kato, M. Volumetric properties and vapor-liquid equilibria for carbon dioxide + 1-propanol system at 313.15 K. *Fluid Phase Equilib.* **1998**, *144*, 203–210.

(17) Suzuki, K.; Sue, H.; Itou, M.; Smith, R. L.; Inomata, H.; Arai, K.; Saito, S. Isothermal vapor-liquid equilibrium data for binary systems at high pressures: carbon dioxide-methanol, carbon dioxide-ethanol, carbon dioxide-1-propanol, methane-ethanol, methane-1-propanol, ethane-ethanol, and ethane-1-propanol systems. *J. Chem. Eng. Data* **1990**, *35*, 63–66.

(18) Geană, D.; Rus, L. Phase Equilibria Database and Calculation Program for Pure Components Systems and Mixtures. In *Proc. Romanian Int. Conference on Chemistry and Chemical Eng. (RICCCE XIV)*, Bucharest, Romania, 2005; Vol. 2, pp 170−178.

(19) Heidemann, R. A.; Khalil, A. M. The calculation of critical points. *AIChE J.* **1980**, *26*, 769–779.

(20) Stockfleth, R.; Dohrn, R. An algorithm for calculating critical points in multicomponent mixtures which can easily be implemented in existing programs to calculate phase equilibria. *Fluid Phase Equilib.* **1998**, *145*, 43–52.

(21) van Konynenburg, P. H.; Scott, R. L. Critical lines and phase equilibria in binary van der Waals mixtures. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *298*, 495–540.

(22) Lam, D. H.; Jangkamolkulchai, A.; Luks, K. D. Liquid-liquid-vapor phase equilibrium behavior of certain binary carbon dioxide + n-alkanol mixtures. *Fluid Phase Equilib.* **1990**, *60*, 131–141.

(23) Yeo, S.-D.; Park, S.-J.; Kim, J.-W.; Kim, J.-C. Critical properties of carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol. *J. Chem. Eng. Data* **2000**, *45*, 932–935.

(24) Gurdial, G. S.; Foster, N. R.; Yun, S. L. J.; Tilly, K. D. *Phase behavior of supercritical fluid - entrainer systems*. Kiran, E., Brennecke, J., Eds., Sup. Fluid Eng. Sci., ACS Symp. Series 514: Washington D.C., 1993, Chapter 3, pp 34−45.

(25) Ziegler, J. W.; Chester, T. L.; Innis, D. P.; Page, S. B.; Dorsey, J. G. *Supercritical Fluid Flow Injection Method for Mapping Liquid-Vapor Critical Loci of Binary Mixtures Containing CO2*; Hutchenson, E. K. H., Foster, N. R., Eds.; Innovations in supercritical fluids, science and technology: WA, 1995; pp 93−110.

(26) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill Book Company: Singapore, 1988.

(27) Vandana, V.; Teja, A. S. Vapor-Liquid Equilibria in the Carbon Dioxide + 1-Propanol System. *J. Chem. Eng. Data* **1995**, *40*, 459–461.

(28) Mendoza de la Cruz, J. L.; Galicia-Luna, L. A. High-pressure vapor-liquid equilibria for the carbon dioxide + ethanol and carbon dioxide + propan-1-ol systems at temperatures from 322.36 to 391.96 K. *Int. Electro. J. Phys.-Chem. Data* **1999**, *5*, 157–164.

(29) Elizalde-Solis, O.; Galicia-Luna, L. A.; Camacho-Camacho, L. E. High-pressure vapor-liquid equilibria for CO2 + alkanol systems and densities of *n*-dodecane and *n*-tridecane. *Fluid Phase Equilib.* **2007**, *259*, 23–32.

(30) Polishuk, I.; Wisniak, J.; Segura, H.; Yelash, L. V.; Kraska, T. Prediction of the critical locus in binary mixtures using equations of state. II. Generalized cubic and Carnahan-Starling equations of state. *Fluid Phase Equilib.* **2000**, *172*, 1–26.

Received for review June 20, 2008. Accepted August 4, 2008. The authors are grateful to the National Council for Scientific Research of Romania (CNCSIS), for financial support.

JE8004485