JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Measurements and Modeling of High-Pressure Phase Behavior of the Carbon Dioxide + Pentan-1-ol Binary System

Catinca Secuianu,*,† Viorel Feroiu, and Dan Geană

Department of Applied Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Materials Science,
"Politehnica" University of Bucharest, 1-7 Gh. Polizu Street, S1, 011061 Bucharest, Romania

ABSTRACT: Vapor−liquid (VLE) and vapor−liquid−liquid equilibria (VLLE) data for the carbon dioxide + pentan-1-ol (*n*-pentanol) system at (293.15, 303.15, 316.65, and 333.15) K up to 10.67 MPa are reported. The experimental method used in this work was a static−analytical method with liquid and vapor phase sampling. The new experimental results are discussed and compared with available literature data. Measured data and literature data for the carbon dioxide + *n*-pentanol system were modeled with the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equation of state (EoS) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. A single set of interaction parameters was used to predict the complex phase behavior of the binary mixture carbon dioxide + *n*-pentanol. Both models predict correctly the phase behavior and a good account of the majority of the data available in the literature.

INTRODUCTION

The knowledge of high-pressure phase behavior of carbon dioxide comprising mixtures is of interest in a variety of processes, such as supercritical fluid (SCF) extraction, reaction, fractionation, nanoparticle formation, separation of nonvolatile mixtures, supercritical fluid chromatography, hydrothermal crystal growing, hydrothermal destruction of hazardous waste, polymer processing, and so forth, as well as in the simulation of petroleum reservoirs, enhanced oil recovery, carbon capture and storage, the transportation and storage of natural gas, refrigeration and heat−pump cycles, and the study of geological processes.[1−7]

The carbon dioxide + alcohols mixtures at high pressures is of particular importance in the design, simulation, and optimization of extraction processes, where the alcohols are used as cosolvents.

In the continuation of our previous studies[8−26] on the carbon dioxide + alcohols systems at high pressures, this work presents the results for the carbon dioxide + *n*-pentanol binary mixture. Our goals were to report new complementary experimental data and to represent the complex phase behavior of this system with simple models, using a single set of interaction parameters.

The carbon dioxide + *n*-pentanol system is class[27] $2^P\ l$ (or type IV fluid phase behavior,[28] according to the classification of van Konynenburg and Scott[29]). Type IV fluid phase behavior is characterized by having two separate three-phase loci (gl_1l_2[27] or liquid−liquid−vapor,[29] LLV). The low temperature branch shows an upper critical end point (UCE $g(l_1 = l_2)$[27] or UCEP[29]), and the high-temperature branch shows a lower critical end point (LCE $g(l_1 = l_2)$[27] or LCEP[29]) and a UCE[27] $(g = l_1)l_2$ or UCEP.[29] The critical end point (CE[27] or CEP[29]) of the low-temperature three-phase locus and the lower CE of the three-phase locus situated at higher temperature both have the nature $l_1 = l_2 - g$ (L = L − V), whereas the higher CE of the high temperature three-phase equilibrium has the nature $l_1 - l_2 = g$ (L − L = V).

Among the medium-chained carbon dioxide + alcohols systems, the carbon dioxide + *n*-pentanol system has not been widely studied. Lam et al.[30] have reported the UCEP and the quadruple point (Q-point) solid−liquid−liquid−vapor for this system. Raeissi et al.[28] proved experimentally that the carbon dioxide + *n*-pentanol system is type IV phase behavior by measuring the upper temperature branch of the three-phase line together with its LCEP and UCEP. They also reported experimental data on the lower temperature three-phase curve and its UCEP. Several groups reported isothermal vapor−liquid equilibria (VLE) data for the carbon dioxide + *n*-pentanol system. Thus, Jennings et al.[31] reported data at (314.6, 325.9, and 337.4) K, Staby and Mollerup[32] at (283.2, 313.2, 343.2, and 373.2) K, Silva-Oliver et al.[33] at (333.08, 343.69, 374.93, 414.23, and 426.86) K, Secuianu et al.[17] at (313.15 and 353.15) K, and Gutiérrez et al.[34] at (313, 323, and 333) K. Laursen et al.[35] report solubilities of carbon dioxide in *n*-pentanol at (313, 325.9, and 343) K to test the reliability of a new equipment, and Ghaziaskar et al.[36] present the composition of *n*-pentanol in the gas phase of the carbon dioxide + *n*-pentanol system at 333 K.

In this work we report new measurements using a static−analytical method, in a high-pressure visual cell, for carbon dioxide + *n*-pentanol at (293.15, 303.15, 316.65, and 333.15) K and pressures between (0.51 and 10.67) MPa. We also measured the upper-temperature three-phase line and its LCEP and UCEP.

Measured and literature data for the carbon dioxide + *n*-pentanol system were modeled with two cubic equations of state (Soave−Redlich−Kwong,[37] SRK, and Peng−Robinson,[38] PR) coupled with classical van der Waals mixing rules. A single set of binary parameters was used to predict the global phase behavior of the system for a large range of pressure and temperature. Although the models are simple, they are able

Special Issue: Kenneth N. Marsh Festschrift

Received: August 5, 2011
Accepted: September 8, 2011
Published: September 19, 2011

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 Pressure, P, and Temperature, T, for the Binary System Carbon Dioxide (1) + n-Pentanol (2)[a]

x_1	y_1	P/MPa	x_1	y_1	P/MPa
		T/K = 293.15 ± 0.1			
0.0358	0.9924	0.52	0.4583	0.9988	4.74
0.0738	0.9960	0.98	0.5960	0.9986	5.23
0.1572	0.9986	1.97	0.7457	0.9980	5.42
0.2486	0.9989	2.92	0.7641	0.9980	5.45
0.3832	0.9988	4.20			
		T/K = 303.15 ± 0.1			
0.0394	0.9928	0.60	0.3668	0.9986	4.70
0.0668	0.9962	1.00	0.4843	0.9982	5.78
0.1504	0.9980	2.03	0.5509	0.9968	6.27
0.2293	0.9986	3.00	0.8463	0.9945	6.74
0.2990	0.9988	4.09	0.8471	0.9946	6.75
		T/K = 316.65 ± 0.1			
0.0278	0.9883	0.51	0.2654	0.9975	4.30
0.0782	0.9937	1.25	0.3328	0.9975	5.31
0.1301	0.9969	2.29	0.4089	0.9969	6.28
0.2008	0.9975	3.23	0.4823	0.9959	7.32
		T/K = 333.15 ± 0.1			
0.0383	0.9889	0.59	0.3144	0.9932	5.88
0.0725	0.9905	1.41	0.3927	0.9919	7.34
0.1388	0.9926	2.65	0.4638	0.9903	8.48
0.1820	0.9935	3.38	0.5507	0.9875	9.75
0.2365	0.9931	4.55	0.6208	0.9836	10.67

[a] $u(T) = 0.1$ K, $u(p) = 0.01$ MPa, and $u(x_1) = u(y_1) = 0.001$.

to represent correctly the complex phase equilibria of the system studied in this work.

EXPERIMENTAL SECTION

Materials. Carbon dioxide ($w > 0.997$) was provided by Linde Gaz Romania, and n-pentanol ($w > 0.990$) was a Fluka product. The chemicals were used without further purification, except for careful degassing and drying of the n-pentanol.

Apparatus and Procedure. A detailed description of the experimental apparatus is presented in earlier papers.[23,24] 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.[8−26,39] The entire internal loop of the apparatus including the equilibrium cell was rinsed several times with carbon dioxide. Then, the equilibrium cell, which has a maximum volume of 60 cm^3, was evacuated with a vacuum pump. The temperature in the cell is measured with a Ni−Cr−Ni thermocouple (accuracy ± 0.1 K). The pressure is measured with two pressure gauges (type S 10, WIKA, Germany; accuracy 0.25 % of span; model 2089QG, Precision Digital Test Gauges, Ashcroft, USA, ± 0.05 % of span). The cell was charged with n-pentanol, 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 phases 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 the pressure in the visual cell almost constant ($\Delta P < 0.05$ MPa). The total amounts of the organic substance in the glass trap were about (0.05 and 0.2) g for the vapor and liquid phases, respectively. The amount of carbon dioxide in each phase was obtained by expansion in a glass bottle of calibrated volume (150 ± 0.01 cm^3). 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 experimental uncertainty of the measured volumes is smaller than ± 0.02 %. The liquid samples of both phases were weighed with a precision balance (model: HM-200, A&D Instruments Ltd., Tokyo, Japan) with an accuracy of ± 0.0001 g. We estimate the uncertainties in our measurements to be within ± 0.1 K for temperature and to be better than ± 10 kPa for pressure from calibration with a precision hydraulic dead-weight tester (model 580C, DH-Budenberg SA, Aubervilliers, France).

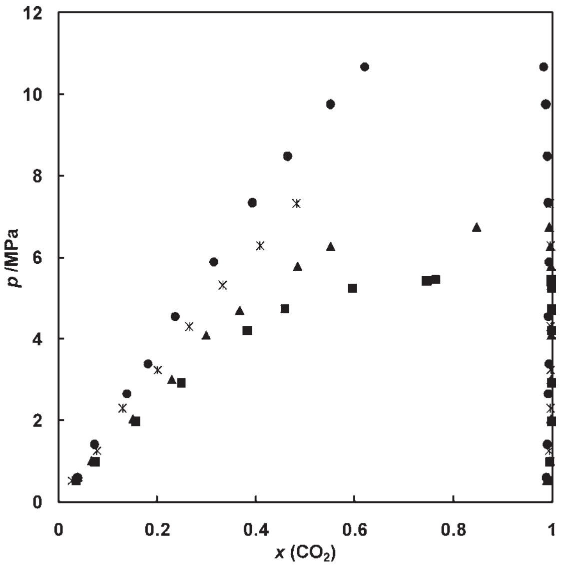

Figure 1. Pressure composition data for the carbon dioxide (1) + n-pentanol (2) system: ■, 293.15 K; ▲, 303.15 K; ∗, 316.65 K; ●, 333.15 K.

MODELING

The phase behavior (critical curves, LLV lines, isothermal VLE, liquid−liquid equilibria (LLE), and vapor−liquid−liquid equilibria (VLLE)) of the carbon dioxide + n-pentanol binary system was modeled using the Soave−Redlich−Kwong (SRK)[37] and Peng−Robinson (PR)[38] equations of state (EoS's) coupled with classical van der Waals mixing rules.

The SRK[37] EoS is:

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

where the two constants, a and b, are:

$$a = 0.42748 \frac{R^2 T_c^{\,2}}{P_c} \alpha(T) \tag{2}$$

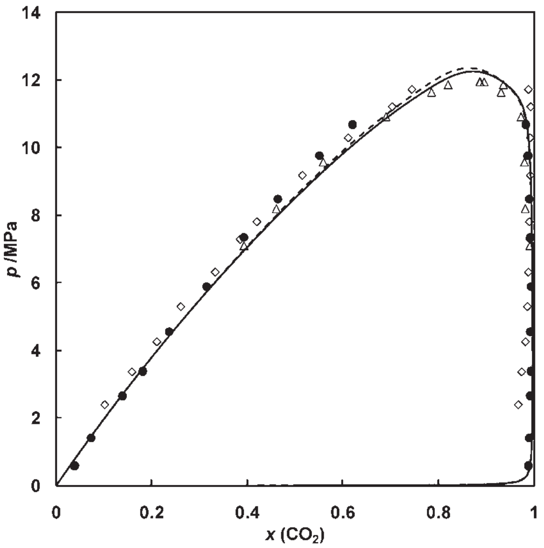

Figure 2. Comparison of measured and literature data for the carbon dioxide (1) + *n*-pentanol (2) system at T = 333.15 K: ●, this work; △, Silva-Oliver et al.;[33] ◇, Gutiérrez et al.[34]

$$b = 0.08664\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T_R, \omega) = [1 + m_{SRK}(1 - T_R{}^{0.5})]^2 \tag{4}$$

$$m_{SRK} = 0.480 - 1.574\omega - 0.176\omega^2 \tag{5}$$

The Peng–Robinson[38] is described by the following equation:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{6}$$

where the two constants, a and b, are:

$$a = 0.45724\frac{R^2 T_c{}^2}{P_c}\alpha(T) \tag{7}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{8}$$

$$\alpha(T_R, \omega) = [1 + m_{PR}(1 - T_R{}^{0.5})]^2 \tag{9}$$

$$m_{PR} = 0.37464 - 1.54226\omega - 0.26992\omega^2 \tag{10}$$

The two-parameter conventional mixing rules are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{11}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{12}$$

where

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{13}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{14}$$

Table 2. Pressure and Temperature of the Three-Phase Curve Liquid–Liquid–Vapor for the Binary System Carbon Dioxide (1) + *n*-Pentanol (2)[a]

P/MPa	T/K	P/MPa	T/K
8.74	315.95[b]	8.86	316.55
8.75	316.00	8.87	316.60
8.76	316.05	8.88	316.65
8.78	316.15	8.89	316.70
8.79	316.20	8.90	316.75
8.80	316.25	8.91	316.80
8.81	316.30	8.92	316.85
8.82	316.35	8.93	316.90
8.83	316.40	8.94	316.95
8.84	316.45	8.95	317.00
8.85	316.50	8.96	317.05[c]

[a] $u(T)$ = 0.1 K, $u(p)$ = 0.01 MPa. [b] Lower critical end point (LCEP). [c] Upper critical end point (UCEP).

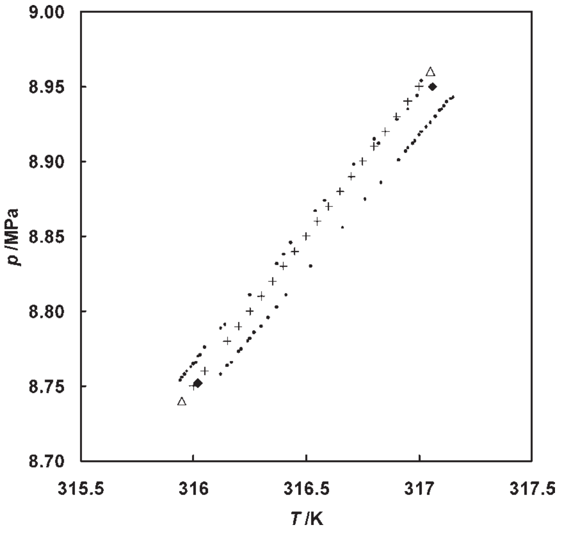

Figure 3. P–T projection of the higher temperature three-phase curve for the carbon dioxide (1) + *n*-pentanol (2) system, comparing experimental results and literature data: +, LLV line, this work; △, LCEP, UCEP, this work; ●, LLV line, Raeissi et al.;[28] ◆, LCEP, UCEP, Raeissi et al.[28]

The models were used in a semipredictive approach[8] to represent the complex phase behavior of the investigated system.

■ RESULTS AND DISCUSSION

The VLE compositions for the carbon dioxide + *n*-pentanol binary system were measured at (293.15, 303.15, 316.65, and 333.15) K, and the results are given in Table 1 and plotted in Figure 1. The values are typically averages of two or three measurements. For the phase equilibria measurements, the uncertainty of the mole fraction is typically 1 % and always < 3 %. As usual in the literature,[40] we calculated the mole fractions with four decimal places.

Three isotherms at (293.15, 303.15, and 333.15) K were measured below and above the higher temperature three-phase line. The 316.65 K isotherm is located on this second three-phase line. Our data measured at 333.15 K were compared

Table 3. Values of Binary Interaction Parameters and Critical End Points of the Carbon Dioxide (1) + *n*-Pentanol (2) Binary System

			UCEP (L = L − V)		LCEP		UCEP (L − L = V)	
EoS	k_{12}	l_{12}	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K
SRK	0.079	−0.039	3.264	273.5749	8.37933	315.5832	9.56897	322.1859
PR	0.079	−0.039	3.203	273.3908	8.32060	315.5105	9.59747	322.5026
C4EOS[49]	0.082	−0.042	5.176	296.2000	10.8114	331.8396	10.8115	331.8400
exp	this work				8.74	315.95	8.96	317.05
exp	27		3.424	273.60				
exp	25		3.413	273.45	8.752	316.02	8.950	317.06

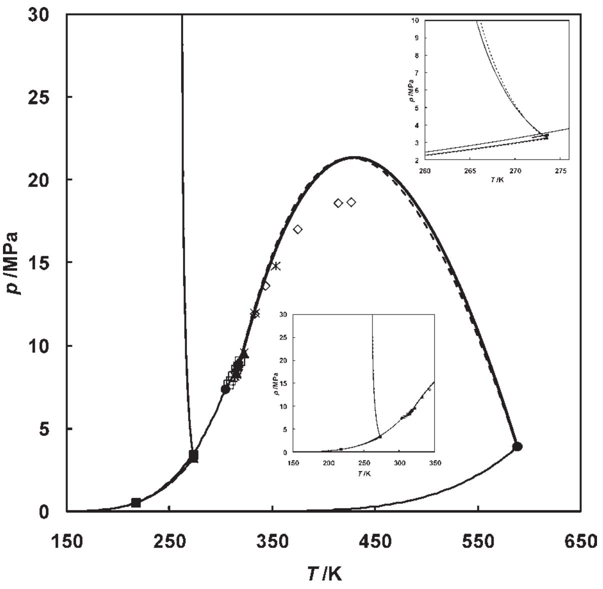

Figure 4. *P*−*T* fluid phase diagram of carbon dioxide (1) + *n*-pentanol (2) system: ◇, Silva-Oliver et al.;[33] □, Gurdial et al.;[52] ∗, Secuianu;[53] ●, critical points of pure components; thin line, vapor pressure curves of pure components; △, experimental LCEP, UCEP, this work; +, LLV line, this work; ◆, UCEP, LCEP, UCEP, Raeissi et al.;[28] ●, LLV line, Raeissi et al.;[28] ■, Q-point, UCEP, Lam et al.;[30] thick line, critical lines predicted by SRK/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); ▲, predicted end points by SRK/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); dashed line, critical lines predicted by PR/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); ×, predicted end points by PR/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039).

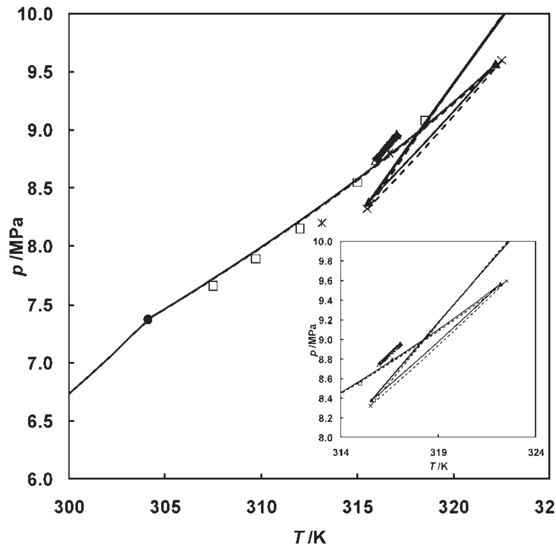

Figure 5. *P*−*T* fluid phase diagram of carbon dioxide (1) + *n*-pentanol (2) system, detailing the higher temperature three phase line and critical curves: □, Gurdial et al.;[52] ∗, Secuianu;[53] ●, critical points of carbon dioxide; thin line, vapor pressure curves of carbon dioxide; △, experimental LCEP, UCEP, this work; +, LLV line, this work; ◆, UCEP, LCEP, UCEP, Raeissi et al.;[28] ●, LLV line, Raeissi et al.;[28] thick line, critical lines predicted by SRK/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); ▲, predicted end points by SRK/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); dashed line, critical lines predicted by PR/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039); ×, predicted end points by PR/2PCMR EoS (k_{12} = 0.079, l_{12} = −0.039).

with the existing literature data at about the same temperature in Figure 2. As can be seen, the new data of this work are in good agreement with both those of Silva-Oliver et al.[33] and Gutiérrez et al.[34]

The higher temperature three-phase liquid−liquid−vapor (LLV) equilibrium curve was experimentally measured at temperatures from (315.95 to 317.05) K and pressures from (8.74 to 8.96) MPa (Table 2). The LCEP and the UCEP were found at 315.95 K and 8.74 MPa and 317.05 K and 8.96 MPa, respectively, in agreement with the values reported by Raeissi et al.[28] Our *P* − *T* LLV data for carbon dioxide + *n*-pentanol binary mixtures agree with those published by Raeissi et al.,[28] as shown in Figure 3, and confirm that this system shows type IV fluid phase behavior, according to the classification of van Konynenburg and Scott.[29] Phase compositions of the two liquid phases and the vapor phase as a function of temperature along the LLV line were not able to be measured with our apparatus, as this LLV line stretches on less than 2 °C. Also, liquid−liquid equilibria data measurements for the 316.65 K isotherm located on the higher temperature three-phase line were not possible using our experimental setup.

Measured and literature data were modeled with the SRK[37] and PR[38] EoS's coupled with classical van der Waals mixing rules. In a previous study[17] we showed that correlations for the carbon dioxide + *n*-pentanol system with a general equation of state (GEoS),[41−44] SRK, and PR coupled with classical van der Waals mixing rules and G^E−EoS (Huron−Vidal (HV)-residual UNIQUAC,[45,46] MHV1,[47] and MHV2[48]) lead to reasonable small average absolute deviations in bubble-point pressure (AADP, %), but also to class[27] 1^P *l* or type II phase behavior, according to the classification of van Konynenburg and Scott.[29] It should be pointed out that in the mentioned study[17] the interaction parameters for the SRK coupled with HV-residual UNIQUAC

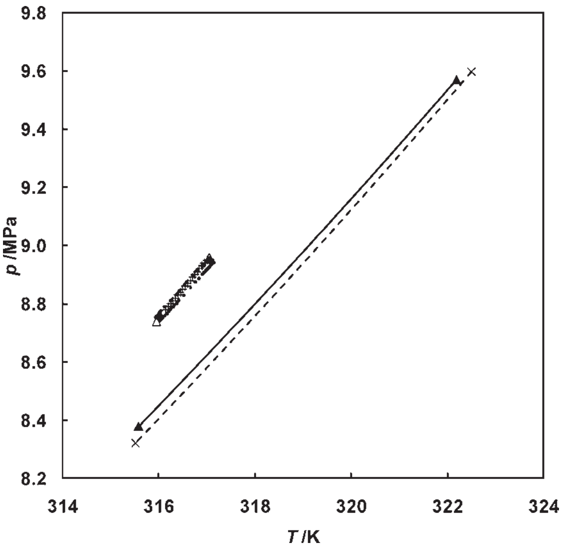

Figure 6. $P-T$ projection of the higher temperature three-phase curve for the carbon dioxide (1) + *n*-pentanol (2) system, comparing experimental results and predictions with SRK/2PCMR and PR/2PCMR ($k_{12} = 0.079, l_{12} = -0.039$): +, LLV line, this work; △, LCEP, UCEP, this work; ●, LLV line, Raeissi et al.;[28] ◆, LCEP, UCEP, Raeissi et al.;[28] ▲, SRK predicted end points (LCEP, UCEP); thick line, SRK predicted LLV line; ×, PR predicted end points (LCEP, UCEP); dashed line, PR predicted LLV line.

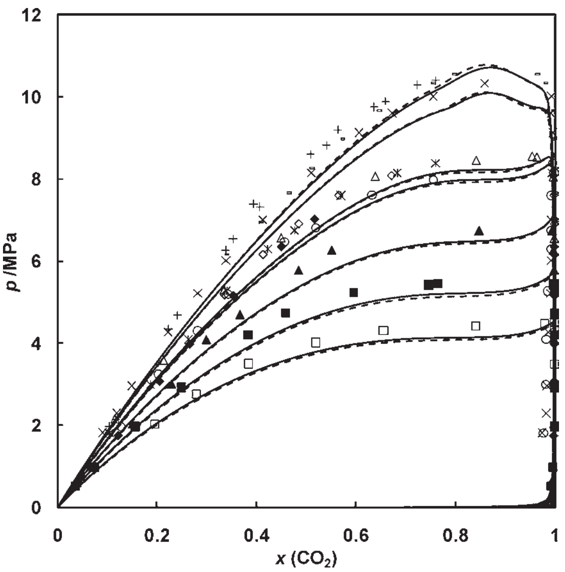

Figure 7. Comparison of measured and literature data for carbon dioxide (1) + *n*-pentanol (2) system and prediction results with EoS: large □, 283.2 K, Staby and Mollerup;[32] ■, 293.15 K, this work; ▲, 303.15 K, this work; ∗, 313.0 K, Gutiérrez et al.;[34] ○, 313.0 K, Laursen et al.;[35] ◆, 313.15 K, Secuianu et al.;[17] △, 313.2 K, Staby and Mollerup;[32] ◇, 314.6 K, Jennings et al.;[31] ×, 323.0 K, Gutiérrez et al.;[34] small □, 325.9 K, Laursen et al.;[35] +, 325.9 K, Jennings et al.;[31] solid line, SRK/2PCMR; dashed line, PR/2PCMR.

mixing rules are temperature-dependent, but this did not improve the correlation results regarding the type phase behavior. Also, Gutiérrez et al.[34] correlated all of their experimental data using PR coupled with van der Waals mixing rules and obtained a

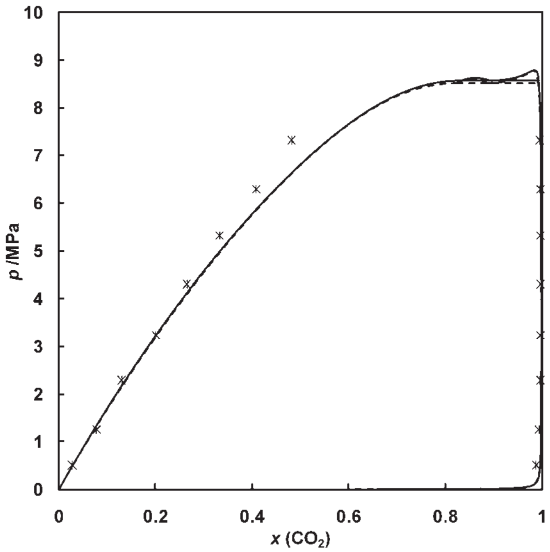

Figure 8. Comparison of our measured data at 316.65 K for the carbon dioxide + *n*-pentanol system and prediction results with SRK and PR equations ($k_{12} = 0.079$, $l_{12} = -0.039$): ∗, 316.65 K; solid line, SRK/2PCMR; dashed line, PR/2PCMR.

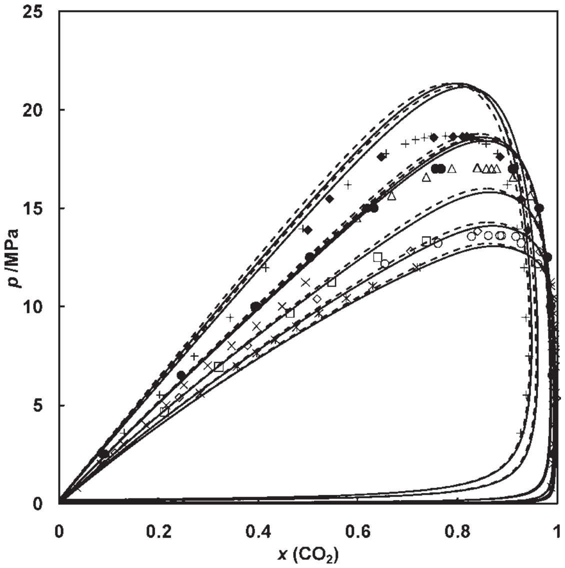

Figure 9. Comparison of literature data for the carbon dioxide + *n*-pentanol system and prediction results with SRK/2PCMR and PR/2PCMR ($k_{12} = 0.079$, $l_{12} = -0.039$): ∗, 337.4 K, Jennings et al.;[31] □, 343.0 K, Laursen et al.;[35] ◇, 343.2 K, Staby and Mollerup;[32] ○, 343.69 K, Silva-Oliver et al.;[33] ×, 353.15 K, Secuianu et al.;[17] ●, 373.2 K, Staby and Mollerup;[32] △, 374.93 K, ◆, 414.23 K, +, 426.86 K, Silva-Oliver et al.;[33] solid line, SRK/2PCMR; dashed line, PR/2PCMR.

set of interaction parameters ($k_{12} = 0.0829$; $l_{12} = -0.0469$), with moderate errors in bubble-point pressures. We calculated the phase diagram using their set of interaction parameters, which predicts class[27] 1^C1^Z or type III phase behavior.[29] Polishuk et al.[49] used a remarkable single set of interaction parameters in their approach combined with three different EoS's (PR, Trebble–Bishnoi–Salim (TBS), and C4EoS) for mixtures of carbon dioxide + alcohols up to 1-hexanol. They showed that both PR ($k_{12} = 0.030$; $l_{12} = -0.105$) and TBS ($k_{12} = 0.054$; $l_{12} = -0.053$)

Table 4. Average Absolute Deviations in Bubble-Point Pressure (AADP, %) and Average Absolute Deviations in the Vapor-Phase Compositions (AADY, %) for the Carbon Dioxide (1) + *n*-Pentanol (2) System Predicted by SRK and PR Equations

T	p range		SRK		PR		
K	MPa	NEXP[a]	AADP %	AADY %	AADP %	AADY %	ref
283.20	2.03 to 4.48	7	4.3		5.6		32
293.15	0.52 to 5.45	9	4.1	0.2	5.2	0.2	this work
303.15	0.6 to 6.75	10	4.4	0.2	4.3	0.2	this work
313.00	1.81 to 8.39	9	6.2	1.9	6.8	2.0	34
313.00	1.96 to 7.98	8	3.2		6.4	0.1	35
313.15	0.59 to 7.02	7	6.9	0.1	6.4	0.1	17
313.20	2.15 to 8.55	7	7.0		7.5		32
314.60	5.178 to 8.074	5	4.3	0.0	4.6	0.1	31
316.65	0.51 to 7.32	8	4.7	0.3	4.9	0.2	this work
323.00	1.82 to 10.32	12	6.7	1.0	7.0	1.2	34
325.90	6.164 to 10.556	8	3.2	0.3	3.2	0.4	31
325.90	1.97 to 10.39	15	5.7		5.6		35
333.00	2.4 to 11.72	11	4.8	1.2	4.8	1.3	34
333.08	7.09 to 11.936	8	2.5	0.7	2.8	0.6	33
333.15	0.59 to 10.67	10	6.5	0.5	6.0	0.4	this work
337.40	5.585 to 11.983	9	1.8	0.1	1.5	0.3	31
343.00	2.24 to 13.31	7	5.3		5.1		35
343.20	2.55 to 13.81	6	4.2		4.3		32
343.69	12.18 to 13.609	5	4.4	1.6	5.7	1.3	33
353.15	0.83 to 11.22	11	3.3	0.2	2.8	0.1	17
373.20	2.5 to 17.0	11	2.8	0.5	3.8	0.8	32
374.93	14.512 to 17.034	6	6.5	2.3	8.6	1.3	33
414.23	13.873 to 18.61	6	9.8	3.3	11.4	2.3	33
426.86	3.563 to 18.665	13	13.2	2.0	15.1	1.1	33

[a] Number of experimental points.

predict falsely type II phase behavior while C4EOS ($k_{12} = 0.082$; $l_{12} = -0.042$) predicts type IV phase behavior, but with high errors in bubble-point pressures. Also the C4EOS leads to a significant overestimation of the maximum of the critical curve and of both temperatures and pressures of the end points. Therefore, in the present work we followed the approach presented in our last papers,[8,9,39] where a single set of temperature-independent interaction parameters was used to predict the critical and subcritical phase behavior in a large range of pressures and temperatures and the correct type of phase behavior. The same set of interaction parameters ($k_{12} = 0.079$, $l_{12} = -0.039$) was used to predict the VLE and VLLE critical curves and LLV line for both SRK and PR EoS. The interaction parameter set was obtained by a trial and error method to reproduce type IV phase behavior and reasonably well the critical end points. In Table 3 the predicted values of critical end points with SRK and PR EoS using this set of interaction parameters are presented, together with the values calculated by Polishuk et al.[49] with C4EOS and the experimental values. It can be seen that the predicted values of the critical end points by SRK and PR are very close to the experimental ones, except for the higher temperature UCEP, which is slightly overestimated. The calculations were made using the GPEC[50,51] software. The topology of global phase behavior is reasonably predicted by both equations, as well as the LLV lines and the critical end points. In Figure 4 we plot the calculated phase diagram by SRK and PR and available experimental data.[28,30,33,52] It can be remarked that the differences between the experimental and predicted lower temperature three-phase line is less than 0.15 MPa, while the temperatures are almost identical. Also, very good agreement between the experimental critical points of the critical curve which connects

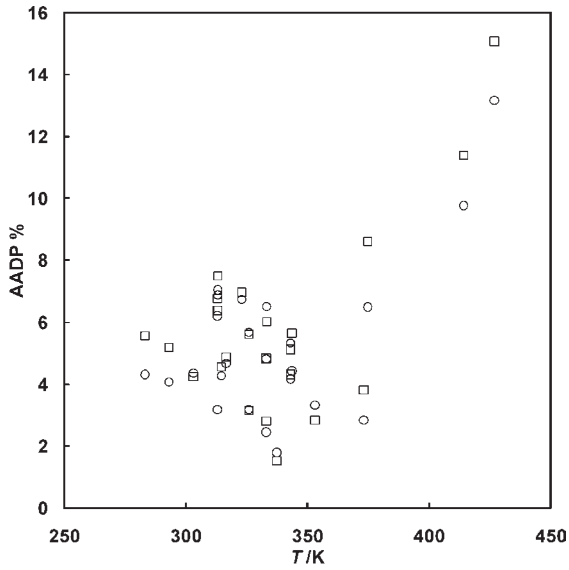

Figure 10. Average absolute deviations in bubble-point pressures as a function of temperature: ○, SRK; □, PR.

the carbon dioxide critical point with the higher temperature UCEP (Figure 5) and the predicted critical curve is observed. Despite this, it can be seen that this critical curve is located below the experimental three-phase line, but the difference is very small, within the experimental uncertainty.[28,52] The maximum pressure of a second critical curve emerging from the critical point of *n*-pentanol and ending in the LCEP is instead overestimated. The narrow high temperature LLV line is predicted similarly by both EoS's, as can be seen in Figure 6. While the pressure difference is between (0.4 and 0.6) MPa, the temperature range is 5 degrees larger than the experimental one. The new measured data and all available literature data were compared with SRK and PR predictions in Figures 7 to 9. The deviations of prediction results with SRK/2PCMR and PR/2PCMR ($k_{12} = 0.079$, $l_{12} = -0.039$) are given in Table 4. The quality of predictions was estimated from the values of average absolute deviations in bubble-point pressures (AADP, %), and the average absolute deviations in the vapor-phase compositions (AADY, %). The AADP and AADY are calculated by the equations:

$$\mathrm{AADP}(\%) = \frac{1}{N_{\mathrm{exp}}}\sum_{i=1}^{N_{\mathrm{exp}}}\left|\frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exp}}}\right| \cdot 100 \qquad (15)$$

$$\mathrm{AADY}(\%) = \frac{1}{N_{\mathrm{exp}}}\sum_{i=1}^{N_{\mathrm{exp}}}|Y_i^{\mathrm{exp}} - Y_i^{\mathrm{calc}}| \cdot 100 \qquad (16)$$

The prediction results are mostly reasonable; the AADP for all data sets in Table 4 is 5.2 % for SRK EoS and 5.8 % for PR EoS (Figure 10). The agreement is generally good, but the errors are higher with increasing temperatures. As expected, the highest errors occur at temperatures for which the critical pressure was overestimated, located near to the critical pressure maximum in the global diagram.

The modeling approach used in this work has advantages to represent the complex phase behavior of the studied system correctly.

CONCLUSIONS

New VLE and LLV experimental data for the binary system carbon dioxide + *n*-pentanol were measured at (293.15, 303.15, 316.65, and 333.15) K and pressures up to 10.67 MPa, with a high-pressure static apparatus. Measured and literature data for carbon dioxide + *n*-pentanol system were modeled with cubic EoS's (SRK, PR) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. The same set of interaction parameters was used to predict the critical and subcritical phase behavior in the binary mixture carbon dioxide + *n*-pentanol with both EoS's. The predicted results were compared both with our experimental data and the available literature data for carbon dioxide + *n*-pentanol binary systems.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tina@catedra.chfiz.pub.ro; c.secuianu@imperial.ac.uk. Tel.: +4021 4023988; +44 20 7594 1341. Fax: +4021 3154193; +44 20 7594 5700.

Present Addresses

[†] Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ, London, United Kingdom.

Funding Sources

The authors are grateful to the National Council for Scientific Research of Romania (CNCS) for financial support.

REFERENCES

(1) Fonseca, J. M. S.; Dohrn, R.; Peper, S. Review. High-pressure fluid-phase equilibria: Experimental methods and systems investigated (2005−2008). *Fluid Phase Equilib.* **2011**, *300*, 1–69.

(2) Dohrn, R.; Peper, S.; Fonseca, J. M. S. High-pressure fluid-phase equilibria: Experimental methods and systems investigated (2000−2004). *Fluid Phase Equilib.* **2010**, *288*, 1–54.

(3) Jaubert, J.-N.; Mutelet, F. VLE predictions with the Peng−Robinson equation of state and temperature dependent k_{ij} calculated through a group contribution method. *Fluid Phase Equilib.* **2004**, *224*, 285–304.

(4) Jaubert, J.-N.; Privat, R. Relationship between the binary interaction parameters (k_{ij}) of the Peng−Robinson and those of the Soave−Redlich−Kwong equations of state: Application to the definition of the PR2SRK model. *Fluid Phase Equilib.* **2010**, *295*, 26–37.

(5) Jaubert, J.-N.; Privat, R.; Mutelet, F. Predicting the phase equilibria of synthetic petroleum fluids with the PPR78 approach. *AIChE J.* **2010**, *56*, 3225–3235.

(6) Vitu, S.; Privat, R.; Jaubert, J.-N.; Mutelet, F. Predicting the phase equilibria of CO_2 + hydrocarbon systems with the PPR78 model (PR EOS and k_{ij} calculated through a group contribution method). *J. Supercrit. Fluids* **2008**, *45*, 1–26.

(7) Mutelet, F.; Vitu, S.; Privat, R.; Jaubert, J. N. Solubility of CO_2 in branched alkanes in order to extend the PPR78 model (Predictive 1978, Peng-Robinson EOS with temperature-dependent k_{ij} calculated through a group contribution method) to such systems. *Fluid Phase Equilib.* **2005**, *238*, 157–168.

(8) Secuianu, C.; Feroiu, V.; Geană, D. Phase equilibria of carbon dioxide + 1-nonanol system at high pressures. *J. Supercrit. Fluids* **2010**, *55*, 653–661.

(9) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure phase equilibria in the (carbon dioxide + 1-hexanol) system. *J. Chem. Thermodyn.* **2010**, *42*, 1286–1291.

(10) Secuianu, C.; Feroiu, V.; Geană, D. Phase behavior for carbon dioxide + methanol system: experimental measurements and modeling with a cubic equation of state. *Int. J. Liq. State Sci.* **2010**, *2*, 1–14.

(11) Secuianu, C.; Feroiu, V.; Geană, D. Phase equilibria calculations for carbon dioxide + methanol binary mixture with the Huron−Vidal infinite dilution (HVID) mixing rules. *Rev. Chim. (Bucharest)* **2009**, *60*, 472–475.

(12) Secuianu, C.; Feroiu, V.; Geană, D. Phase behavior for carbon dioxide + 2-butanol system: experimental measurements and modeling with cubic equations of state. *J. Chem. Eng. Data* **2009**, *54*, 1493–1499.

(13) Secuianu, C.; Feroiu, V.; Geană, D. Phase equilibria experiments and calculations for carbon dioxide + methanol binary system. *Cent. Eur. J. Chem.* **2009**, *7*, 1–7.

(14) Secuianu, C.; Feroiu, V.; Geană, D. Phase behavior for carbon dioxide + ethanol system: experimental measurements and modeling with a cubic equation of state. *J. Supercrit. Fluids* **2008**, *47*, 109–116.

(15) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure phase equilibria for the carbon dioxide + 1-propanol system. *J. Chem. Eng. Data* **2008**, *53*, 2444–2448.

(16) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure vapor−liquid and vapor−liquid−liquid equilibria in the carbon dioxide + 1-heptanol system. *Fluid Phase Equilib.* **2008**, *270*, 109–115.

(17) 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.

(18) 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.

(19) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure phase equilibrium for carbon dioxide + ethanol at 333.15 K. *Sci. Technol. Environ. Prot. J.* **2005**, *12*, 77–86.

(20) 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.

(21) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure vapor—liquid equilibria in the system carbon dioxide + 2-butanol and calculations with EOS methods. *Sci. Technol. Environ. Prot. J.* **2004**, *11*, 48–60.

(22) 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., Ser. B* **2004**, *66*, 9–18.

(23) 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.

(24) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure phase equilibria for the carbon dioxide + methanol and carbon dioxide + isopropanol systems. *Rev. Chim. (Bucharest)* **2003**, *54*, 874–879.

(25) Secuianu, C.; Feroiu, V.; Geană, D. High-pressure phase equilibrium in binary mixtures of carbon dioxide + 1-butanol. *Sci. Technol. Environ. Prot. J.* **2003**, *10*, 62–70.

(26) Secuianu, C.; Feroiu, V.; 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 Ser. Chem.* **2003**, *12*, 393–400.

(27) Bolz, A.; Deiters, U. K.; Peters, C. J.; de Loos, Th. Nomenclature for phase diagram with particular reference to vapour-liquid and liquid-liquid equilibria. *Pure Appl. Chem.* **1998**, *70*, 2233–2257.

(28) Raeissi, S.; Gauter, K.; Peters, C. J. Fluid multiphase behavior in quasi-binary mixtures of carbon dioxide and certain 1-alkanols. *Fluid Phase Equilib.* **1998**, *147*, 239–249.

(29) 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.

(30) 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.

(31) Jennings, D. W.; Chang, F.; Bazaan, V.; Teja, A. S. Vapor—liquid equilibria for carbon dioxide + *n*-pentanol. *J. Chem. Eng. Data* **1992**, *37*, 337–338.

(32) Staby, A.; Mollerup, J. Measurement of mutual solubilities of *n*-pentanol and supercritical carbon dioxide. *J. Supercrit. Fluids* **1993**, *6*, 15–19.

(33) Silva-Oliver, G.; Galicia-Luna, L. A.; Sandler, S. I. Vapor—liquid equilibria and critical points for the carbon dioxide + *n*-pentanol and carbon dioxide + 2-pentanol systems at temperatures from 332 to 432 K. *Fluid Phase Equilib.* **2002**, *200*, 161–172.

(34) Gutiérrez, J. E.; Bejarano, A.; de la Fuente, J. C. Measurement and modeling of high-pressure (vapour + liquid) equilibria of (CO_2 + alcohol) binary systems. *J. Chem. Thermodyn.* **2010**, *42*, 591–596.

(35) Laursen, T.; Andersen, S. I.; Dahl, S.; Henriksen, O. Measurement and modeling of the solubility of CO_2 and N_2 in a model resin system based on resin from spruce wood (*Picea abies* (L.)). *J. Supercrit. Fluids* **2001**, *19*, 239–250.

(36) Ghaziaskar, H. S.; Daneshfar, A.; Rezayat, M. The co-solubility of 2-ethylhexanoic acid and some liquid alcohols in supercritical carbon dioxide. *Fluid Phase Equilib.* **2005**, *238*, 106–111.

(37) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.

(38) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(39) Secuianu, C.; Feroiu, V.; Geană, D. Phase behavior for carbon dioxide + *n*-pentadecane binary system. *J. Chem. Eng. Data* **2010**, *55*, 4255–4259.

(40) Bamberger, A.; Maurer, G. High-pressure (vapour + liquid) equilibria in (carbon dioxide + acetone or 2-propanol) at temperatures from 293 to 333 K. *J. Chem. Thermodyn.* **2000**, *32*, 685–700.

(41) Geană, D. A new equation of state for fluids. I. Applications to PVT calculations for pure fluids. *Rev. Chim. (Bucharest)* **1986**, *37*, 303–309.

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

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

(44) 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.

(45) Feroiu, V.; Geană, D. Prediction of vapor—liquid equilibria at high pressures using activity coefficients at infinite dilution. *Fluid Phase Equilib.* **1996**, *120*, 1–10.

(46) Geană, D.; Feroiu, V. Prediction of vapor—liquid equilibria at low and high pressures from UNIFAC activity coefficients at infinite dilution. *Ind. Eng. Chem. Res.* **1998**, *37*, 1173–1180.

(47) Michelsen, M. L. A modified Huron-Vidal mixing rule for cubic equations of state. *Fluid Phase Equilib.* **1990**, *60*, 213–219.

(48) Dahl, S.; Fredenslund, A.; Rasmussen, P. The MHV2 model: a UNIFAC-based equation of state model for prediction of gas solubility and vapor-liquid equilibria at low and high pressures. *Ind. Eng. Chem. Res.* **1991**, *30*, 1936–1945.

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

(50) Cismondi, M.; Nunez, D. N.; Zabaloy, M. S.; Brignole, E. A.; Michelsen, M. L; Mollerup, J. M. GPEC: a program for global phase equilibrium calculations in binary systems. In *EQUIFASE 2006: VII Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design*, Morelia, Michoacán, México, 2006.

(51) Cismondi, M.; Nunez, D. N. In *GPEC (Global Phase Equilibrium Calculations)*; Zabaloy, M. S., Brignole, E. A., Eds.; Bahía Blanca and Córdoba, 2005—2009; http://www.gpec.efn.uncor.edu.

(52) Gurdial, G. S.; Foster, N. R.; Yun, S. L. J.; Tilly, K. D. Phase Behavior of Supercritical Fluid Entrainer Systems. *ACS Symp. Ser.* **1993**, *514*, 34–45.

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