Phase Behavior for the Carbon Dioxide + 2-Butanol System: Experimental Measurements and Modeling with Cubic Equations of State†

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Vapor−liquid equilibria (VLE) data for the carbon dioxide + 2-butanol system at (298.15, 303.15, 308.15, 313.15, and 318.15) K up to 81.5 bar 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 VLE data and literature data for the carbon dioxide + 2-butanol system were modeled with a general cubic equation of state (GEOS), Peng−Robinson (PR) equation of state (EoS), and Soave−Redlich−Kwong (SRK) EoS using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. A single set of interaction parameters for each equation of state, representing exactly the experimental critical pressure maximum (CPM) and the experimental temperature of the upper critical end point (UCEP), was used to calculate the phase behavior in the binary mixture carbon dioxide + 2-butanol in a wide range of temperatures [(278.21 to 512.3) K]. The GEOS equation is more reliable for predicting the critical curve and the bubble-point lines, and it is less exact for predicting the gas phase composition at higher temperatures.

Introduction

Research on the physicochemical properties of fluid mixtures at high pressures predominantly on their phase behavior and critical phenomena has been a focus of the scientific activities of many laboratories for decades.[1]

Carbon dioxide + alcohol systems are of interest because of their importance as supercritical fluid/cosolvent pairs in the separation of biomaterials, in the extraction of alcohols from aqueous solution with carbon dioxide, in the production of alcohols from syngas, in the supercritical extraction of different pollutants from soils, as pesticides, and so forth.[2−5] Butyl alcohols can be solvents, entrainers, modifiers, and simulators for supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC), and biomaterials and can be used in synthesizing high-porosity materials via sol−gel processes and in supercritical drying processes.[6]

Previously, we have published vapor−liquid equlibria (VLE) data[7−11] for carbon dioxide + methanol, + ethanol, + 1-propanol, + 2-propanol, and + 1-butanol. In the literature, the high-pressure phase equilibrium of the carbon dioxide + 2-butanol systems was studied by few groups.[6,12−15] The goals of this work were to add new experimental data and to represent the phase behavior of this system with simple models, using a single set of binary interaction parameters. Therefore, in this work, we made new measurements using a static-analytical method, in a high-pressure visual cell, for carbon dioxide + 2-butanol at (298.15, 303.15, 308.15, 313.15, and 318.15) K and pressures between (4.6 and 81.5) bar.

In a recent paper,[8] we have used a general equation of state (GEOS)[16−19] coupled with classical van der Waals mixing rules (2PCMR), in a semipredictive approach, to model the phase behavior for the carbon dioxide + 1-propanol system. A single set of interaction parameters, representing well the experimental critical pressure maximum (CPM) and the experimental temperature of the upper critical end point (UCEP), was used to model the carbon dioxide + 1-propanol system. We have shown that the results obtained using this semipredictive approach correctly described the phase behavior of the system, even if the errors in bubble-point pressure are higher compared with the correlation of the experimetal data. It is known[8] that correlating the experimental data leads to smaller errors but also to a false liquid−liquid splitting. In this study, we use the same method to model the phase equilibria data of the carbon dioxide + 2-butanol system. In addition, we show the results obtained with the Soave−Redlich−Kwong (SRK)[20] and the Peng−Robinson (PR)[21] equations of state (EoS), coupled with classical van der Waals mixing rules (2PCMR). SRK and PR equations of state are particular cases of the general cubic equation of state (GEOS).[16−19] This cubic equation is a generalized form with four parameters for all cubic equations of state with two, three, and four parameters.[18] The prediction of the critical line and subcritical phase behavior in this binary mixture was done in a wide range of temperatures. 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 predictions and the experimental data. The GEOS equation leads to better results compared with the PR and SRK EoS.

Experimental Section

Materials. Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, and 2-butanol (mass fraction purity > 0.998) was a Sigma product. The chemicals were used without further purification.

Apparatus and Procedure. A detailed description of the experimental apparatus is presented in earlier papers.[7,10] The apparatus used in this work is based on the static analytical

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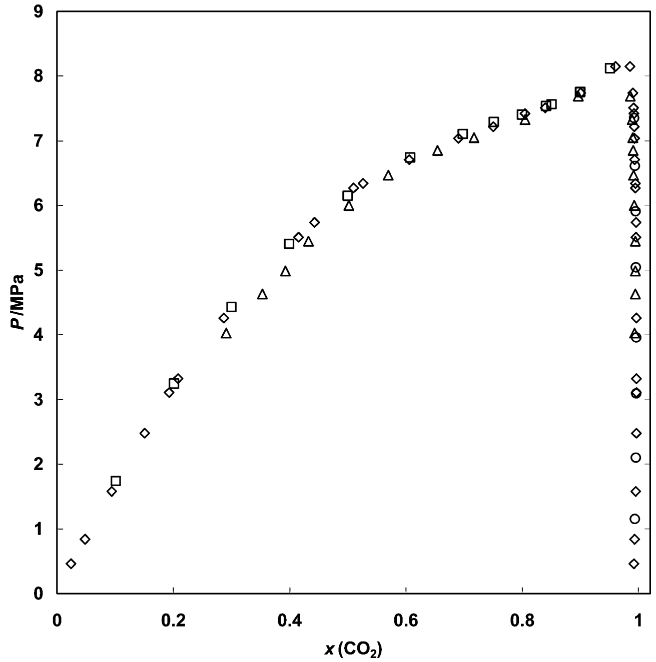

Figure 1. Comparison of measured and literature VLE data for the carbon dioxide (1) + 2-butanol (2) system at $T = 313.15$ K: ◇, this work; Δ, Hiaki et al.;[12] □, Stevens et al.;[13] ○, Stevens et al.[14]

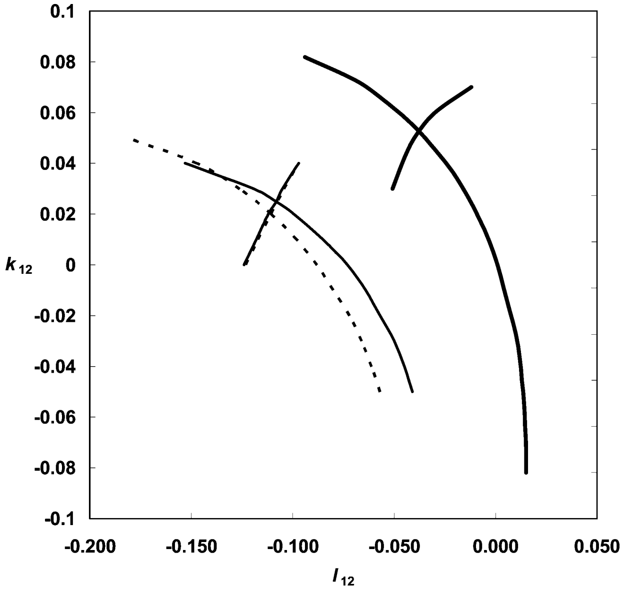

Figure 2. $k_{12}-l_{12}$ global phase diagram for the carbon dioxide (1) + 2-butanol (2) system calculated using the GEOS, PR, and SRK equations by intersecting the curve of critical pressure maximum at experimental value with the curve of the UCEP temperature at experimental value: bold −, GEOS; −, PR; - - - -, SRK.

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) + 2-Butanol (2)

P/MPa	x_1	y_1	*P*/MPa	x_1	y_1
		$T/\text{K} = 298.15 \pm 0.1$			
0.74	0.0412	0.9962	5.51	0.5965	0.9977
1.62	0.1021	0.9975	5.65	0.6572	0.9975
2.66	0.1942	0.9979	5.79	0.7171	0.9978
3.73	0.3121	0.9986	6.01	0.8724	0.9982
4.68	0.4269	0.9982	6.28	0.9641	0.9988
5.04	0.4857	0.9980			
		$T/\text{K} = 303.15 \pm 0.1$			
0.5	0.0245	0.9941	5.04	0.4465	0.9970
1.03	0.0546	0.9963	5.46	0.5367	0.9967
2.05	0.1269	0.9974	5.93	0.6753	0.9964
3.19	0.2282	0.9977	6.11	0.7847	0.9965
3.74	0.2775	0.9977	6.53	0.9175	0.9971
4.28	0.3384	0.9976	6.73	0.9468	0.9979
		$T/\text{K} = 308.15 \pm 0.1$			
0.48	0.0238	0.9938	6.83	0.6885	0.9947
1.12	0.0587	0.9946	6.90	0.7249	0.9945
2.14	0.1266	0.9965	6.91	0.7297	0.9945
3.0	0.1989	0.9973	7.02	0.7973	0.9943
3.96	0.2883	0.9972	7.06	0.8011	0.9943
5.34	0.4279	0.9964	7.11	0.8183	0.9941
6.18	0.5398	0.9956	7.25	0.8485	0.9938
6.59	0.6219	0.9950			
		$T/\text{K} = 313.15 \pm 0.1$			
0.46	0.0238	0.9920	6.27	0.5097	0.9945
0.84	0.0480	0.9934	6.34	0.5263	0.9942
1.58	0.0941	0.9948	6.71	0.6052	0.9934
2.48	0.1506	0.9962	7.04	0.6904	0.9929
3.11	0.1928	0.9961	7.22	0.7498	0.9926
3.32	0.2081	0.9962	7.42	0.8048	0.9921
4.26	0.2866	0.9962	7.51	0.8396	0.9914
5.51	0.4151	0.9956	7.74	0.9007	0.9900
5.74	0.4425	0.9954	8.15	0.9605	0.9850
		$T/\text{K} = 318.15 \pm 0.1$			
1.05	0.0543	0.9912	6.04	0.4355	0.9933
1.61	0.0847	0.9924	6.69	0.5152	0.9919
2.61	0.1445	0.9940	7.38	0.6082	0.9904
3.76	0.2234	0.9944	8.11	0.7643	0.9894
4.92	0.3295	0.9939	8.15	0.7792	0.9894

method with liquid and vapor phase sampling. The procedure is the same as in our previous papers.[7−11] 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 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 ($\Delta P < 0.5$ bar). 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. 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 + 2-butanol binary system were measured at (298.15, 303.15, 308.15, 313.15, and 318.15) 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.

Figure 1 shows a detailed comparison of our data with existing literature data at 313.15 K. As can be seen, the new results of this work are in very good agreement with those of

Table 2. Data of Pure Components, GEOS Parameters, Average Absolute Deviations in Vapor Pressure (AADPV, %), and Average Absolute Deviations in Liquid Volume (AADVL, %) for Carbon Dioxide[22] and 2-Butanol[23]

subst.	T_c / K	P_c / bar	V_c / $cm^3 \cdot mol^{-1}$	Z_c	ω	α_c	m	AADPV / %	AADVL / %
CO_2	304.1	73.8	93.9	0.2741	0.239	7.0517	0.3146	1.1	1.9
2-C_4H_9OH	536.1	41.8	269	0.2523	0.577	9.0298	0.6533	6.5	4.7

Table 3. Binary Interaction Parameters and Average Absolute Deviations in Pressure (AADP, %) and Average Absolute Deviations in Temperature (AADT, %) for the Critical Curve

EoS	k_{12}	l_{12}	AADP %	AADT %
GEOS	0.050	−0.040	3.1	1.3
PR	0.025	−0.108	3.9	2.2
SRK	0.020	−0.111	5.7	3.0

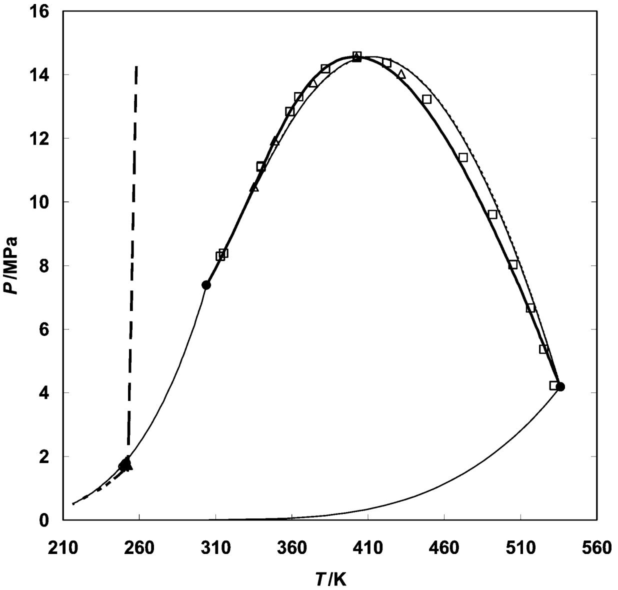

Figure 3. $P-T$ fluid phase diagram of the carbon dioxide (1) + 2-butanol (2) system: □, Stevens et al.;[13] Δ, Silva-Oliver et al.;[15] ●, critical points of pure components;[22,23] ▲, experimental UCEP, Stevens et al.;[13] —, vapor pressure curves of pure components; bold —, critical line predicted with the GEOS/2PCMR EoS; —, critical line predicted with the PR/2PCMR EoS; - - -, critical line predicted with the SRK/2PCMR EoS;bold - - -, LL and LLV lines predicted with GEOS/2PCMR EoS.

Stevens et al.[13,14] The data reported by Hiaki et al.[12] are in acceptable agreement with those of this work and Stevens et al.[13,14]

The modeling of the phase behavior of this system was made with the GEOS,[16-19] SRK,[20] and PR[21] EoS coupled with classical van der Waals mixing rules (2PCMR). The GEOS[16] 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

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

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

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

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.

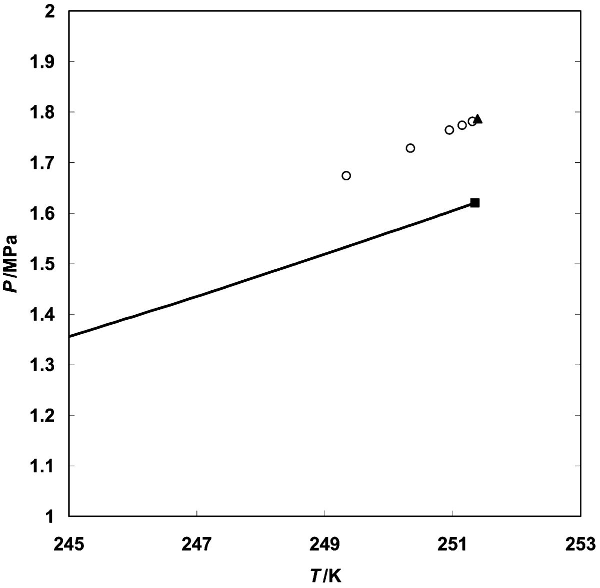

Figure 4. $P-T$ projection of the three phase curve for the carbon dioxide (1) + 2-butanol (2) system: ○, Stevens et al.;[13] Δ, experimental UCEP, Stevens et al.;[13] bold —, GEOS predictions; ■, calculated UCEP.

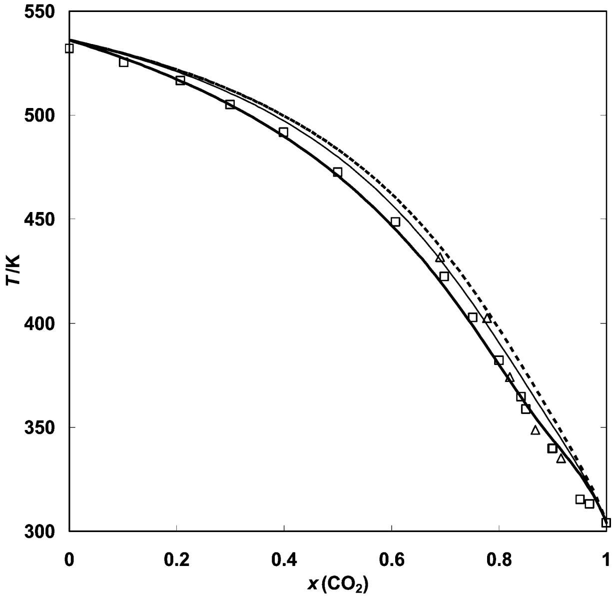

Figure 5. $T-x_1$ projection of the critical curve of the carbon dioxide (1) + 2-butanol (2) system: □, Stevens et al.;[13] Δ, Silva-Oliver et al.;[15] — (thick solid line), GEOS prediction; — (thin solid line), PR prediction; - - - (thick dashed line), SRK prediction.

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

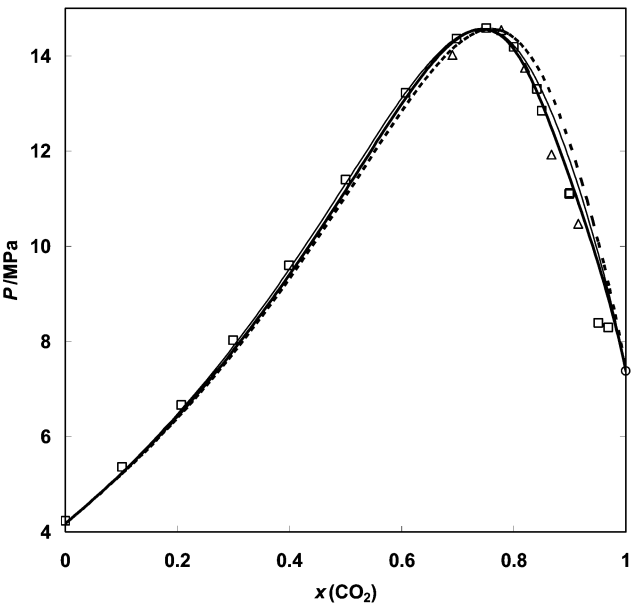

Figure 6. $P-x_1$ projection of the critical curve of the carbon dioxide (1) + 2-butanol (2) system: □, Stevens et al.;[13] Δ, Silva-Oliver et al.;[15] — (thick solid line), GEOS prediction; — (thin solid line), PR prediction; - - - (thick dashed line), SRK prediction.

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

at $T_r = 1$ and $V_r = 1$, the expressions of the parameters Ω_a, Ω_b, Ω_c, 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 volume on the saturation curve. For the carbon dioxide, the data on the saturation range, between the triple point and the critical point, were taken from Span and Wagner.[22] For 2-butanol, the data on the saturation range were taken from DIPPR correlations,[23] from 220 K (near the triple point of carbon dioxide) up to the critical point. The GEOS model reproduces well both the vapor pressures and the density for the carbon dioxide, while for the 2-butanol the liquid vapor pressures and the densities are less accurate. Although DIPPR[23] provides correlations between triple point and critical point, experimental data on the saturation curve for 2-butanol[24] are available only in the ranges (345.54 to 380.3) K and (422.11 to 535.9) K. The values of GEOS parameters, the data of pure components, the average absolute deviations in vapor pressures (AADPV, %), and the liquid volumes (AADVL, %) for the studied system are presented in Table 2.

As pointed out previously,[18] the relations (8) and (9) are general forms for all the cubic equations of state with two, three, and four parameters. To obtain the parameters of the SRK EoS from eqs (8) and (9), we set[16−19] the following restrictions: $\Omega_c = -(\Omega_b/2)^2$ and $\Omega_d = -\Omega_b/2$. It follows

$$\Omega_c = (1-B)^2(B-0.25) = -\frac{(Z_c - B)^2}{4} \tag{11}$$

$$\Omega_d = Z_c - 0.5(1-B) = -\frac{(Z_c - B)}{2} \tag{12}$$

It results: Z_c(SRK) = 1/3, and the relation for B (SRK)

$$B = 0.25 - \frac{1}{36}\left(\frac{1-3B}{1-B}\right)^2 \tag{13}$$

Solving iteratively, this equation gives B(SRK) = 0.2467, and correspondingly, Ω_a(SRK) = $(1 - B)^3$ = 0.42748 and Ω_b(SRK) = $Z_c - B$ = 0.08664.

For PR EoS we set the restrictions:[16−19] $\Omega_c = -2(\Omega_b)^2$and $\Omega_d = -\Omega_b$. It results

$$B = 0.25 - \frac{1}{8}\left(\frac{1-3B}{1-B}\right)^2 \tag{14}$$

$$Z_c = \frac{1+B}{4} \tag{15}$$

giving $B(PR)$ = 0.2296 and $Z_c(PR)$ = 0.3074.

The calculations were made using the software package PHEQ, developed in our laboratory.[25] The critical curves were calculated using the method proposed by Heidemann and Khalil,[26] with numerical derivatives given by Stockfleth and Dohrn.[27]

In this study, the GEOS, SRK, and PR equations are used in a semipredictive approach to obtain a set of binary parameters yielding good results in the binary system carbon dioxide + 2-butanol (including VLE in the entire temperature range, critical curve). The set of binary parameters for each equation was calculated using the $k_{12}-l_{12}$ method[28,9,10] to obtain the experimental value of the vapor−liquid critical pressure maximum (CPM) simultaneously with the temperature of UCEP. The binary system carbon dioxide + 2-butanol is a type II phase diagram, according to the classification of van Konynenburg and Scott.[29] Stevens et al.[13] have provided experimental evidence that the system carbon dioxide + 2-butanol exhibits liquid−liquid immiscibility. However, they measured only the pressures and temperatures on the LLV line between (249.34 and 251.39) K. The experimental temperature of UCEP (251.39 K[13]) and CPM (145.54 bar;[13] 145.42 bar[15]) have been traced by paths in the $k_{12}-l_{12}$ diagram, for each equation of state, and their intersection has given the values of the parameters, as can be seen in Figure 2. The values of the interaction binary parameters (k_{12} and l_{12}) fulfilling these requirements are presented in Table 3. Our parameters obtained for PR EoS are slightly different than those of Polishuk et al.,[28] due probably to the diverse critical data of pure components. These sets of interaction parameters were used to predict the topology of phase behavior (the critical, the liquid−liquid−vapor, the bubble- and dew-point lines). The $P-T$ fluid phase diagram is presented in Figure 3. In this figure are also illustrated the predictions of the critical curve with the SRK and PR equations of state. The average deviations in pressure and in temperature, respectively, on the critical curve are also presented in Table 3. The equation for calculating the average deviations in temperature is similar with that of pressure (eq 11). As can be seen, the smallest errors both in critical pressures and temperatures are obtained with GEOS equation. It should also be remarked that GEOS leads to

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) + 2-Butanol (2) System Calculated by GEOS, PR, and SRK Equations

T	*P* range	GEOS		PR		SRK		
K	bar	AADP %	AADY %	AADP %	AADY %	AADP %	AADY %	ref
278.21	11.57 to 38.44	8.8	–	11.6	–	11.6	–	13
283.14	12.47 to 43.39	8.6	–	11.3	–	11.3	–	13
293.24	14.22 to 54.89	8.0	–	10.6	–	10.7	–	13
298.15	7.40 to 62.80	8.7	0.1	12.3	0.1	12.8	0.1	this work
303.15	5.0 to 67.30	6.2	0.1	7.7	0.2	8.3	0.1	this work
303.18	15.82 to 67.69	7.5	–	10.0	–	10.3	–	13
308.15	4.80 to 72.50	8.7	0.1	12.5	0.1	13.1	0.1	this work
313.15	4.60 to 81.50	7.1	0.1	11.3	0.2	11.8	0.2	this work
313.20	40.30 to 76.9	5.3	0.2	8.3	0.2	9.1	0.2	12
313.22	17.37 to 81.17	6.7	–	9.4	–	9.8	–	13
318.15	10.50 to 81.50	6.6	0.1	10.7	0.1	11.5	0.1	this work
323.21	18.87 to 90.94	5.9	–	9.1	–	9.8	–	13
331.90	50.10 to 105.50	8.3	0.6	10.7	0.7	12.2	0.6	6
333.16	20.22 to 104.40	4.8	–	8.4	–	9.1	–	13
335.14	85.41 to 104.73	3.3	0.6	7.9	0.8	9.1	1.0	15
341.60	50.10 to 117.20	6.5	1.0	9.1	1.2	10.4	1.3	6
343.23	21.57 to 114.24	3.9	–	8.2	–	9.1	–	13
348.77	95.87 to 119.25	2.1	0.4	7.1	0.9	8.8	1.2	15
351.30	49.20 to 120.10	6.4	1.2	8.7	1.0	10.3	0.8	6
353.42	22.72 to 124.30	2.9	–	7.2	–	8.1	–	13
363.70	23.97 to 131.64	2.5	–	7.0	–	7.7	–	13
373.67	25.07 to 138.09	1.9	-	6.3	–	6.7	–	13
374.10	112.14 to 137.48	1.2	1.7	3.4	0.9	5.2	1.5	15
383.67	26.22 to 141.69	1.8	–	5.9	–	6.2	–	13
393.52	27.42 to 144.59	1.8	–	5.4	–	6.1	–	13
402.47	105.24 to 145.42	2.4	2.6	1.4	0.9	1.8	0.6	15
403.69	28.73 to 144.97	2.4	–	5.6	–	5.4	–	13
413.43	30.17 to 145.17	2.5	–	5.0	–	4.8	–	13
423.48	5.03 to 140.32	4.4	–	5.5	–	4.8	–	13
431.73	109.56 to 140.23	2.3	3.1	1.6	0.7	1.0	0.3	15
433.46	6.38 to 138.92	4.6	–	4.9	–	4.2	–	13
443.46	8.08 to 135.07	4.2	–	4.2	–	3.4	–	13
453.46	9.98 to 156.49	6.8	–	6.8	–	6.2	–	13
463.40	12.33 to 121.35	3.9	–	3.0	–	2.4	–	13
473.47	14.99 to 108.97	3.8	–	2.5	–	2.6	–	13
483.23	18.09 to 103.87	4.3	–	2.0	–	2.8	–	13
493.12	21.59 to 72.53	4.9	–	2.8	–	2.4	–	13
502.97	25.59 to 73.43	15.8	–	14.8	–	15.5	–	13
512.30	30.14 to 71.13	3.9	–	2.8	–	2.5	–	13

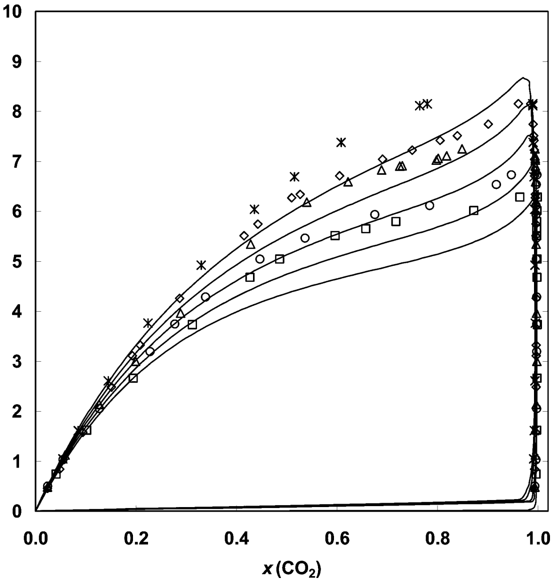

Figure 7. Comparison of our measured data for the carbon dioxide + 2-butanol system and predictions with GEOS/2PCMR ($k_{12} = 0.050$, $l_{12} = -0.040$): □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; ◇, 313.15 K; *, 318.15 K; −, GEOS/2PCMR equation.

better results with a set of interaction parameters smaller in absolute values than those used for PR and SRK equations. In Figure 4 is shown the *P*−*T* projection of the three phase LLV curve. It should be remarked that the differences in pressures are about 2 bar between the experimental data (available for a temperature range of 2 K) and GEOS predictions. The experimental temperature of the UCEP is reproduced, being used in the parameters estimation procedure.

The projection of the critical curve in the temperature−composition diagram (Figure 5) also shows that the GEOS equation is more accurate than both PR and SRK EoS. The pressure−composition projection (Figure 6) shows that all three equations are comparable, but GEOS and PR are better than SRK.

GEOS, PR, and SRK calculations with the sets of parameters presented in Table 3 were done for the new experimental data of this work and for 34 data sets from the literature at temperatures between (278.21 and 521.89) K. Table 4 presents the average absolute deviations in bubble point pressure (AADP, %) and vapor phase compositions (AADY, %) of the experimental data, comparing the prediction results. As can be seen, the predictions with the GEOS equation are better than those obtained with PR and SRK, and the results obtained with the PR equation are slightly better than those obtained with SRK. A higher deviation appears at 502.97 K where the data (three points) were measured near the critical point of the mixture[13] (see Table 3). The AADP (%) and AADY (%) are calculated by the equations

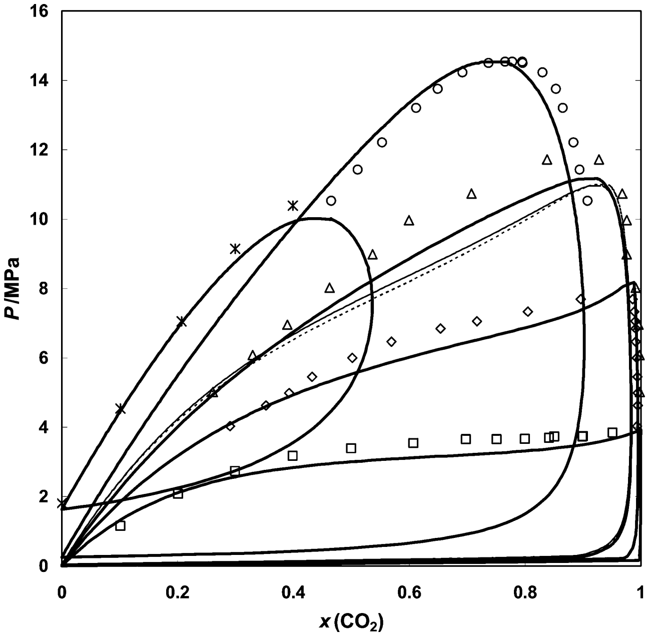

Figure 8. Comparison of selected literature data for the carbon dioxide + 2-butanol system: □, 278.21 K, Stevens et al.;[13] ◇, 313.2 K, Hiaki et al.;[12] Δ, 341.6 K, Chen et al.;[6] ○, 402.47 K, Silva-Oliver and Galicia-Luna;[15] *, 483.23 K, Stevens et al.;[13] bold —, GEOS predictions; - - -, SRK predictions; —, PR predictions.

$$\mathrm{AADP}\,(\%) = \frac{1}{N_{\mathrm{exp}}} \sum_{i=1}^{N_{\mathrm{exp}}} \left| \frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exp}}} \right| \cdot 100 \qquad (16)$$

$$\mathrm{AADY}\,(\%) = \frac{1}{N_{\mathrm{exp}}} \sum_{i=1}^{N_{\mathrm{exp}}} |Y_i^{\mathrm{exp}} - Y_i^{\mathrm{calc}}| \cdot 100 \qquad (17)$$

Several isotherms comparing the GEOS equation prediction results with experimental data are illustrated in Figure 7 (measured data of this work) and Figure 8 (selective literature data). As can be seen, the single set of interaction parameters leads to satisfactory prediction of VLE for the carbon dioxide + 2-butanol system. As observed for other systems,[8] the critical pressure of the mixture is slightly underestimated at lower temperatures but is accurately predicted as temperature increases. Also, it seems that vapor−liquid critical curves are easier to predict than subcritical VLE.[8,28] This result may be explained by the dependence of VLE not only on vapor−liquid critical data but also on other factors like liquid−liquid equilibria. Again, the liquid−liquid critical line for the carbon dioxide + 2-butanol 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 7 and 8. This observation can be also made for PR and SRK equations. However, all three equations used are very accurate in predicting the dew-point curves.

The modeling approach used in this work has the advantage to represent correctly the phase behavior and to avoid the false liquid−liquid splitting occurring when the experimental data are correlated.

Conclusions

New VLE experimental data for the binary system carbon dioxide + 2-butanol were measured at (298.15, 303.15, 308.15, 313.15, and 318.15) K and pressures between (4.6 and 81.5) bar, with a high-pressure static apparatus. Measured and literature VLE data for the carbon dioxide + 2-butanol system were modeled with cubic equations of state (GEOS, PR, SRK) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. One set of interaction parameters for each equation of state was used to predict the critical and subcritical phase behavior in the binary mixture carbon dioxide + 2-butanol in a wide range of temperatures. The predicted results were compared both with our experimental data and the available literature data for carbon dioxide + 2-butanol binary systems. The GEOS equation is capable of predicting the vapor−liquid critical curves more accurately than the PR and SRK EoSs.

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