Phase Behavior for the Carbon Dioxide + *N*-Pentadecane Binary System[†]

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Vapor−liquid (VLE), liquid−liquid (LLE), and vapor−liquid−liquid equilibria (VLLE) data for the carbon dioxide + *n*-pentadecane system at (293.15, 303.15, 313.15, 333.15, and 353.15) K up to 17.50 MPa and phase compositions of the two liquid phases and vapor phase as a function of temperature along the liquid−liquid−vapor (LLV) line 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*-pentadecane system were modeled with the Soave−Redlich−Kwong (SRK) 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 in the binary mixture carbon dioxide + *n*-pentadecane.

Introduction

Investigations of the solubility of low-volatile organic substances in compressed carbon dioxide are of considerable interest for different applications. Also, for theoretical purposes, fluid mixtures of carbon dioxide show a large variety of phase behavior and interesting thermodynamic properties and can be used as model systems for the correlation and calculation of fluid phase equilibria and mixture properties from molecular data.[1]

The carbon dioxide + *n*-pentadecane system shows a type-III fluid phase behavior,[2] according to the classification of van Konynenburg and Scott.[3] Among the carbon dioxide + alkane systems, the carbon dioxide + *n*-pentadecane system has not been widely studied. Hottovy et al.[2] have reported the liquid−liquid vapor (LLV) curve from the upper critical end point (UCEP) to the quadruple point (Q-point) solid−liquid−liquid−vapor for this system; van der Steen et al.[4] have measured the vapor−liquid−liquid equilibrium curve; Tanaka et al.[5] have measured the liquid compositions at 313.15 K; Scheidgen[6,7] has measured several isotherms at (292.0, 298.0, 316.0, and 393.0) K and the critical curve from 387.66 K and 23.29 MPa to 299.54 K and 99.5 MPa; and Secuianu et al.[8] have measured VLLE and VLE at (298.15 and 316.15) K.

In this study, we present new phase equilibrium data obtained using a static-analytical method, in a high-pressure visual cell, for the carbon dioxide + *n*-pentadecane binary system. New vapor−liquid (VLE), liquid−liquid (LLE), and vapor−liquid−liquid equilibria (VLLE) data for the carbon dioxide + *n*-pentadecane system at (293.15, 303.15, 313.15, 333.15, and 353.15) K up to 17.5 MPa and phase compositions of the two liquid phases and vapor phase as a function of temperature along the liquid−liquid−vapor (LLV) line were measured.

Measured and literature data for the carbon dioxide + *n*-pentadecane system were modeled with different cubic equations of state (Soave−Redlich−Kwong,[9] SRK, General Equation of State,[10−13] GEOS, Peng−Robinson,[14] PR) coupled with classical van der Waals mixing rules.

The models mentioned before were used for correlations and in a semipredictive approach to obtain one set of binary parameters to reproduce the complex phase behavior (critical curve, LLV line, isothermal VLE, and VLLE) of the carbon dioxide + *n*-pentadecane binary mixture. In this paper, only the prediction results by SRK/2PCMR are shown.

Experimental Section

Materials. Carbon dioxide ($w > 0.997$) was provided by Linde Gaz Romania, and *n*-pentadecane ($w > 0.990$) was an Aldrich product. The chemicals were used without further purification.

Apparatus and Procedure. A detailed description of the experimental apparatus is presented in earlier papers.[15,16] 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.[15−20] 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 *n*-pentadecane, and then it was slightly pressurized with carbon dioxide to the experimental pressure and 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. 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-

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Table 1. Mole Fraction of Component 1 in the Liquid Phase, x_{L1}, Mole Fraction of Component 2 in the Liquid Phase, x_{L2}, 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) + *n*-Pentadecane (2)

P/MPa	x_{L1}	x_{L2}	y_1
	T/K = 293.15 ± 0.1		
0.76	0.1451		0.9965
1.83	0.3061		0.9984
2.84	0.4021		0.9997
4.06	0.5459		0.9997
4.62	0.6096		0.9992
5.35	0.6837		0.9993
5.59	0.7482		0.9982
5.61	0.7583	0.9868	0.9979
5.82	0.7822	0.9862	
6.41	0.8138	0.9846	
8.21	0.8255	0.9794	
8.26	0.8261	0.9797	
11.18	0.8399	0.9676	
12.42	0.8437	0.9716	
13.73	0.8630	0.9718	
14.12	0.8686	0.9682	
	T/K = 303.15 ± 0.1		
0.72	0.1191		0.9904
1.70	0.2306		0.9980
2.85	0.3596		0.9978
3.97	0.4795		0.9981
4.81	0.5499		0.9976
5.81	0.6355		0.9990
6.85	0.7538		0.9990
7.04	0.7823	0.9822	0.9981
7.26	0.7958	0.9809	
8.12	0.8176	0.9810	
8.87	0.8318	0.9808	
10.03	0.8710	0.9797	

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).

Results and Discussion

The equilibrium compositions for the carbon dioxide + *n*-pentadecane binary system were measured at (293.15, 303.15, 313.15, 333.15, and 353.15) K, and the results are given in Tables 1 and 2. The values are typically averages of two or three measurements. For the phase equilibria (VLE, VLLE, and LLE) measurements, the uncertainty of the mole fraction is typically 1 % and always < 3 %. As usual, in the literature,[21] we calculated the mole fractions with four decimal places.

Figure 1 shows a comparison of our data with existing literature data at 313.15 K. As can be seen, the new results of this work are in good agreement with those of Tanaka et al.[5] The three-phase liquid−liquid−vapor (LLV) equilibrium curve was experimentally measured at temperatures from (292.85 to 308.65) K and pressures from (5.53 to 7.94) MPa (Table 3). The upper critical end point was found at 309.15 K and 8.02 MPa, in agreement with the values reported by Hottovy et al.[2] Our $P-T$ LLV data for carbon dioxide + *n*-pentadecane agree with those published by Hottovy et al.[2] and van der Steen et al.,[4] as shown in Figure 2, and confirm that this system shows type III fluid phase behavior, according to the classification of van Konynenburg and Scott.[3] Phase compositions of the two liquid phases and the vapor phase as a function of temperature along the LLV line are also compared with those of Hottovy et al.[2] and van der Steen et al.[4] in Figure 3.

Table 2. 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) + *n*-Pentadecane (2)

P/MPa	x_1	y_1	*P*/MPa	x_1	y_1
		T/K = 313.15 ± 0.1			
0.56	0.1088	0.9924	6.68	0.6343	0.9993
1.85	0.2144	0.9966	7.65	0.7078	0.9995
3.40	0.3386	0.9975	8.69	0.7777	0.9997
3.86	0.3839	0.9978	9.73	0.8029	0.9992
5.58	0.5221	0.9990	11.03	0.8394	0.9988
		T/K = 333.15 ± 0.1			
0.68	0.0768	0.9854	9.25	0.6799	0.9992
1.88	0.1894	0.9903	9.97	0.7052	0.9992
3.51	0.3243	0.9964	11.19	0.7534	0.9982
4.39	0.3768	0.9973	12.17	0.7931	0.9961
5.27	0.4402	0.9977	13.24	0.8238	0.9897
6.39	0.5140	0.9987	13.94	0.8425	0.9878
7.81	0.5878	0.9994			
		T/K = 353.15 ± 0.1			
0.93	0.0888	0.9508	10.23	0.6438	0.9991
1.88	0.2040	0.9840	11.69	0.6917	0.9984
3.48	0.3017	0.9952	13.16	0.7492	0.9974
5.49	0.4306	0.9985	14.56	0.7977	0.9960
7.27	0.5095	0.9991	16.03	0.8263	0.9927
8.81	0.5912	0.9992	17.50	0.8634	0.9889

Measured and literature data were correlated with the Soave−Redlich−Kwong (SRK),[9] the General Equation of State (GEOS),[10−13] and the Peng−Robinson (PR)[14] equations of state coupled with classical van der Waals mixing rules. In Figure

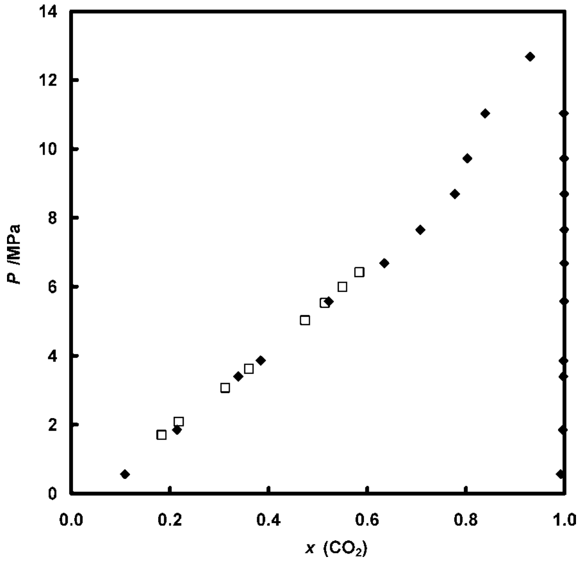

Figure 1. Comparison of measured and literature data for the carbon dioxide (1) + *n*-pentadecane (2) system at T = 313.15 K: ◆, this work; □, Tanaka et al.[6]

Table 3. Pressure and Temperature of the Three-Phase Liquid−Liquid−Vapor Curve for the Binary System Carbon Dioxide (1) + *n*-Pentadecane (2)

P/MPa	*T*/K	*P*/MPa	*T*/K
5.53	292.85	6.48	299.65
5.60	293.15	6.82	301.95
5.66	293.75	7.04	303.15
5.78	294.65	7.12	303.85
5.84	295.15	7.37	305.25
6.05	296.55	7.84	308.05
6.27	298.15	7.94	308.65
6.34	298.65	8.02[a]	309.15

[a] Upper critical end point (UCEP).

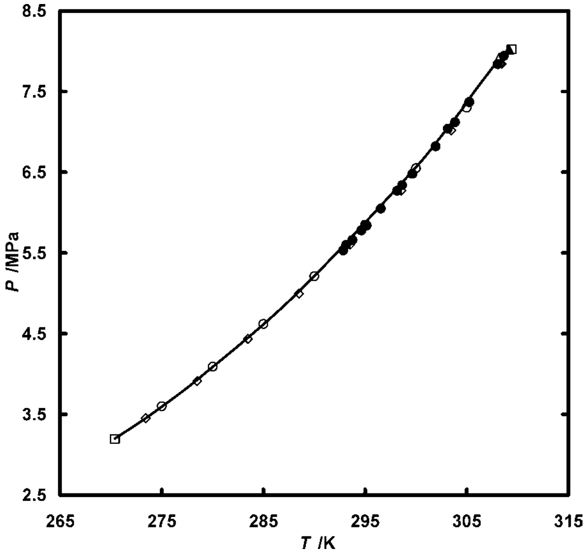

Figure 2. $P-T$ projection of the three-phase curve for the carbon dioxide (1) + *n*-pentadecane (2) system, comparing experimental results and predictions with SRK/2PCMR ($k_{12} = 0.096$, $l_{12} = 0.070$): ●, LLV line, this work; ▲, UCEP, this work; ○, LLV line, Hottovy et al.;[2] □, UCEP, Q-point, Hottovy et al.;[2] ◇, LLV line, van der Steen et al.;[4] Δ, predicted UCEP; −, predicted LLV line.

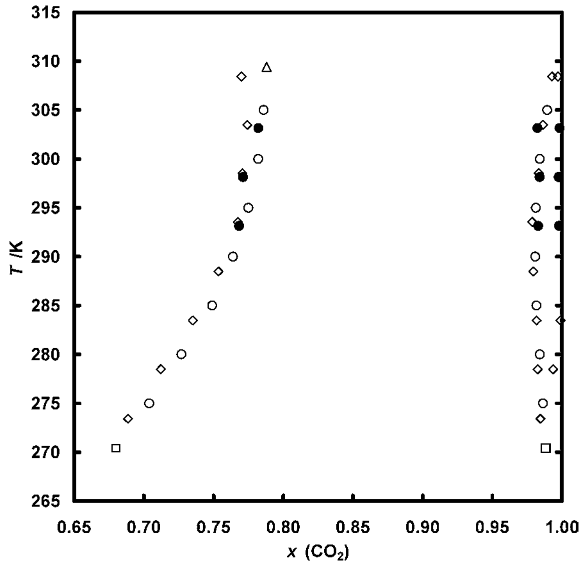

Figure 3. $T-x_1$ diagram of the three-phase equilibrium curve of the carbon dioxide (1) + *n*-pentadecane (2) system, comparing measured and literature data: ●, this work; ○, Hottovy et al.;[2] Δ, UCEP, Hottovy et al.;[2] □, Q-point, Hottovy et al.;[2] ◇, van der Steen et al.[4]

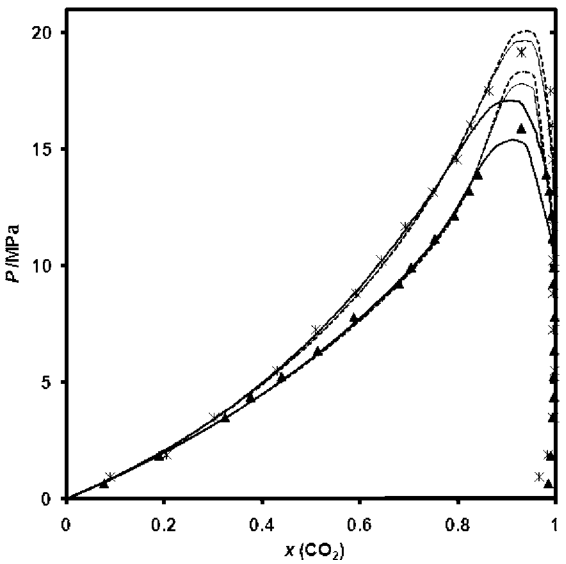

Figure 4. Comparison of measured data for the carbon dioxide (1) + *n*-pentadecane (2) system and correlation results with the EOS: ▲, 333.15 K, this work; ∗, 353.15 K, this work; –, GEOS/2PCMR; −, PR/2PCMR; - - -, SRK/2PCMR.

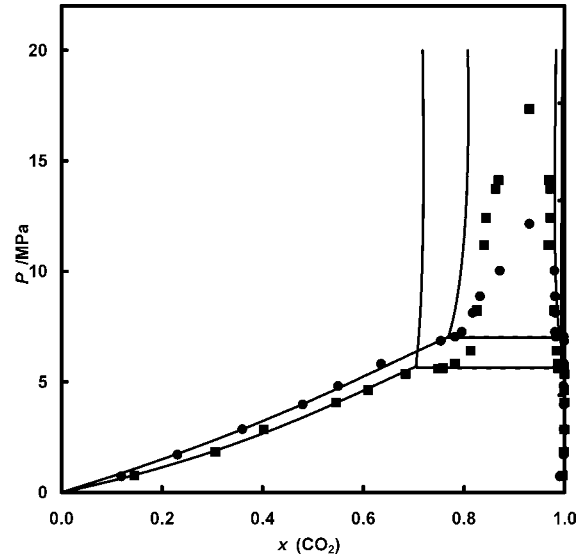

Figure 5. Comparison of our measured data for the carbon dioxide + *n*-pentadecane system and correlation results with SRK/2PCMR: ■, 293.15 K; ●, 303.15 K; −, SRK/2PCMR equation ($k_{12} = 0.1326$, $l_{12} = 0.0206$ at $T = 293.15$ K, $k_{12} = 0.1083$, $l_{12} = -0.0005$ at $T = 303.15$ K).

4, we show the comparison of the phase equilibrium data measured at (333.15 and 353.15) K and the correlations with the mentioned equations of state. The correlation results with SRK, PR, and GEOS are similar, except for the critical region. The critical point is better given by GEOS at 333.15 K, but with increasing temperature, SRK and PR are more successful. Also, the gas-phase compositions are better reproduced by SRK and PR equations. Consequently, in the next figures we present only the results obtained by the SRK equation. Figures 5 and 6 present the comparisons of the new experimental data measured in this work and correlations by SRK/2PCMR. For the isotherms below the temperature of the upper critical end point (UCEP), shown in Figure 5, the correlations are in good agreement with the experimental VLE data, but as can be seen, the LLE is not correctly calculated. The correlation results suggest that the calculated minimum in temperature of the liquid−liquid critical line is situated at a higher temperature compared with the experimental one. The correlations for the isotherms measured at temperatures higher than the UCEP temperature are good as well, except for the critical region which is overestimated. As shown in recent papers,[17−20,22] this approach fails to reproduce correctly the phase behavior, particularly the UCEP, the LLE, and the critical lines, and even the errors in pressure are small.

Therefore, a semipredictive approach was used to reproduce the type III phase behavior. The calculations were made using the software package PHEQ, developed in our laboratory.[23] The critical curves were calculated using the method proposed by Heidemann and Khalil,[24] with numerical derivatives given by Stockfleth and Dohrn.[25]

In this work, only the results obtained with the SRK/2PCMR equation of state are presented. One set of parameters ($k_{12} = 0.096$, $l_{12} = 0.070$) was used to predict VLE, VLLE, the critical curve, and the LLV line.[22] The parameters set was obtained by

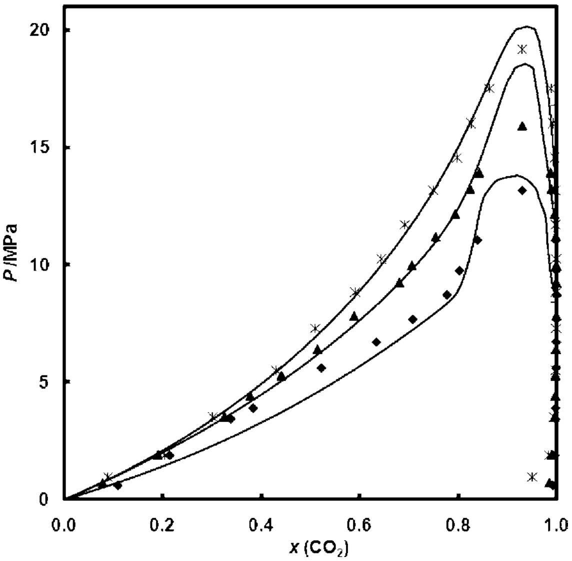

Figure 6. Comparison of our measured data for the carbon dioxide + *n*-pentadecane system and correlation results with SRK/2PCMR: ◆, 313.15 K; ▲, 333.15 K; ∗, 353.15 K; −, SRK/2PCMR equation ($k_{12} = 0.1051$, $l_{12} = 0.0136$ at $T = 313.15$ K, $k_{12} = 0.1022$, $l_{12} = 0.0011$ at $T = 333.15$ K, $k_{12} = 0.0999$, $l_{12} = 0.0154$ at $T = 353.15$ K).

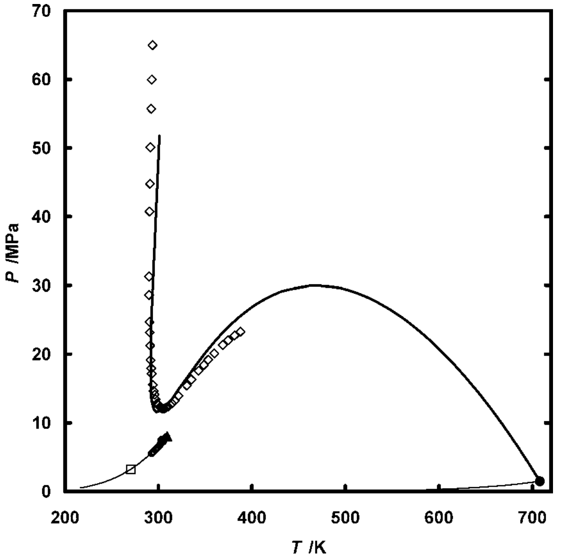

Figure 7. $P-T$ fluid phase diagram of the carbon dioxide (1) + *n*-pentadecane (2) system: ◇, Scheidgen;[7] ●, critical points of pure components; −, vapor pressure curves of pure components; ▲, experimental UCEP, this work; ○, LLV line, this work; Δ, UCEP, Hottovy et al.;[2] □, Q-point, Hottovy et al.;[2] −, critical line predicted with the SRK/2PCMR EoS ($k_{12} = 0.096$, $l_{12} = 0.070$).

a trial and error method to reproduce reasonably the minimum pressure of the critical curve and the minimum temperature of the liquid−liquid part of the critical curve (Figure 7). As can be seen, the topology of global phase behavior is reasonably predicted, as well as the LLV line and the UCEP (Figure 2). It can be remarked that small differences between the experimental and calculated liquid−liquid critical curve, due to its vertical inflection, lead to high differences in the critical pressure maximum (Figures 7 and 8). The predictions of VLE and LLE data (Figures 8 and 9) are less accurate due to the imposed restrictions.

Several isotherms comparing the SRK equation prediction results with experimental literature data are illustrated in Figure 10. As can be seen, the single set of interaction parameters leads to qualitative prediction of VLE for the carbon dioxide + *n*-pentadecane system. The modeling approach used in this work has the advantage to represent correctly the complex phase behavior of the studied system.

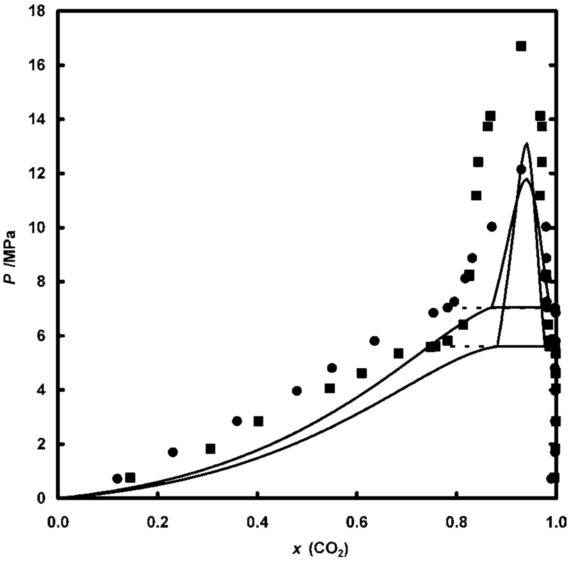

Figure 8. Comparison of our measured data for the carbon dioxide + *n*-pentadecane system and predictions with SRK/2PCMR ($k_{12} = 0.096$, $l_{12} = 0.070$): ■, 293.15 K; ●, 303.15 K; −, SRK/2PCMR equation.

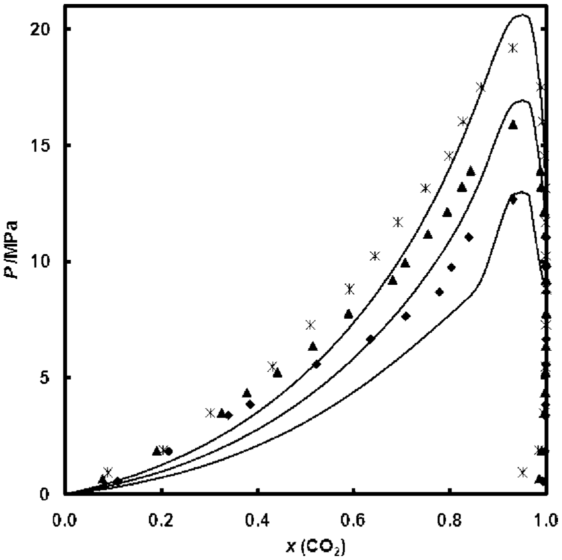

Figure 9. Comparison of our measured data for the carbon dioxide + *n*-pentadecane system and predictions with SRK/2PCMR ($k_{12} = 0.096$, $l_{12} = 0.070$): ◆, 313.15 K; ▲, 333.15 K; ∗, 353.15 K; −, SRK/2PCMR equation.

Conclusions

New VLE, LLE, and VLLE experimental data for the binary system carbon dioxide + *n*-pentadecane were measured at (293.15, 303.15, 313.15, 333.15, and 353.15) K and pressures between (0.56 and 17.50) MPa, with a high-pressure static apparatus. Measured and literature data for the carbon dioxide + *n*-pentadecane 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 the SRK equation of state was used to predict the critical and subcritical phase behavior in the binary mixture carbon dioxide + *n*-pentadecane. The

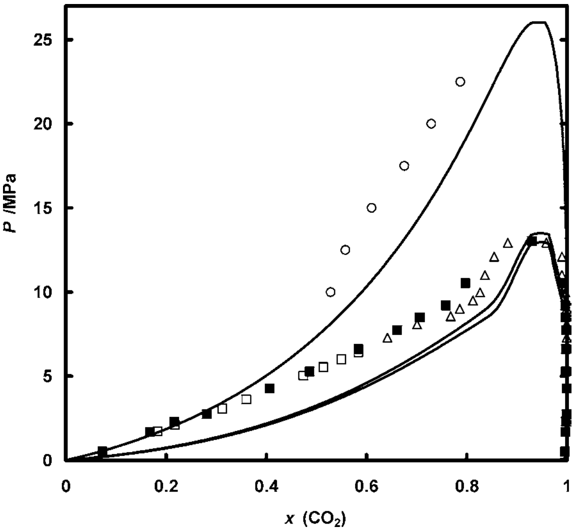

Figure 10. Comparison of selected literature data for the carbon dioxide + *n*-pentadecane system: □, 313.15 K, Tanaka et al.;[6] ■, 316.15 K, Secuianu et al.;[8] Δ, 316.0 K, Scheidgen;[6] ○, 393.0 K, Scheidgen;[6] −, SRK predictions ($k_{12} = 0.096$, $l_{12} = 0.070$).

predicted results were compared with both our experimental data and the available literature data for carbon dioxide + *n*-pentadecane binary systems.

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