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Experimental Vapor−Liquid Equilibria for the Carbon Dioxide + Octane and Carbon Dioxide + Decane Systems

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The vapor−liquid equilibria (VLE) for the carbon dioxide + octane, and carbon dioxide + decane systems were measured from (322 to 372) K and (319 to 372) K, respectively. The measurements were carried out with a static-type apparatus connected online to a gas chromatograph. A good agreement was found between the experimental measurements for the studied systems and those reported in the literature at 348 and 344 K for the carbon dioxide + octane and carbon dioxide + decane systems, respectively. Both systems were correlated using the Peng−Robinson equation of state with classical and Wong−Sandler mixing rules. The best VLE representation was obtained using the Wong−Sandler mixing rule with an absolute average deviation less than 1.8 % and 0.0020 mole fraction for pressure and equilibrium compositions, respectively.

Introduction

Accurate vapor−liquid equilibrium (VLE) data for the carbon dioxide + hydrocarbon systems are important for the design of separation processes and are useful for the enhanced oil recovery.[1] Supercritical fluid technology has been widely applied in the chemical, petroleum, and food industry. Carbon dioxide is the major solvent used as supercritical fluid because of its characteristics: low critical point, low price, environment-friendly solvent, nonflammable, and is inert.[2] Taking into account these advantages, we are studying the feasibility of sulfur compounds extraction from Mexican gasoline using supercritical carbon dioxide. Because of the several compounds involved in this oil cut, it is necessary to start with a model gasoline (alkanes + sulfur compounds), and the measurements of accurate VLE data from binary systems carbon dioxide + sulfur compound and carbon dioxide + alkane are important as basic information for this purpose. The modeling of these systems is a suitable tool to reduce the experimental measurements, although the interaction parameters for the binary mixtures are required. The determination of the binary interaction parameters requires accurate equilibrium data over a wide range of temperatures. In this work, we have measured the binary VLE for two carbon dioxide + alkane systems. The VLE determinations for the carbon dioxide + octane and carbon dioxide + decane systems were performed from (319 to 372) K in a static-analytic setup. Equilibrium data for these systems are also reported in the literature.[3−10] The VLEs for the carbon dioxide + octane system were compared with those presented by Weng and Lee[4] at ∼348 K. The VLE measurements for the carbon dioxide + decane system were compared with those reported in the literature[5−10] at ∼344 K. The experimental VLE data were correlated with the Peng−Robinson equation of state[11] using classical and Wong−Sandler[12] mixing rules. For this last mixing rule, the nonrandom two liquid (NRTL) model[13] was used to approach the excess Helmholtz free energy.

Experimental Section

Materials. Octane (C_8H_{18}) and decane ($C_{10}H_{22}$) with a certified purity of 99+ % were obtained from Sigma-Aldrich, USA. Air Products-Infra, Mexico, supplied carbon dioxide (CO_2) and helium with a minimum purity of 99.995 mol % and 99.998 mol %, respectively. Octane and decane were degassed and stirred under vacuum before the experimental measurements.

Apparatus and Procedure. The experimental apparatus is based on the static-analytic method and is mainly constituted by an equilibrium cell that can be operated up to 60 MPa and 523.15 K. The stainless steel cell has an internal volume of about 40 cm^3 and is equipped with two sapphire windows to allow for the visual observation of the phases involved in the studied mixture. The cell is connected online to a gas chromatograph (GC). A detailed description of the apparatus has been given by Galicia-Luna et al.[14]

The cell was initially loaded with the alkane (octane or decane) and degassed under vacuum and stirred with a magnetic rod for about 20 min. Then, a syringe pump (Isco, 100DM) was used to feed gradually carbon dioxide to the cell (with a previous degassing of the loading circuit). The cell temperature was kept constant by means of an air bath. Temperature measurements were performed with two platinum probes Pt100 (Specitec, France) placed in two thermometric wells at the top and bottom of the cell and were connected to a digital indicator (Automatic Systems, F250 ±0.03 K). Platinum probes were calibrated against a 25 Ω reference probe (Rosemount, model 162CE ±0.005 K) connected to a calibration system (Automatic Systems, F300S). Pressure was monitored by means of a thermoregulated transducer (Druck, PDCR 910-1756). The transducer was calibrated against a dead weight balance (Desgranges & Huot, Model 5304 Class S2, ±0.005 %). Uncertainties were estimated within ±0.03 K and ±0.04 % for temperature and pressure, respectively.

The system was stirred to decrease the time needed to reach the equilibrium conditions. After the pressure and temperature reached the required values, VLE measurements were performed. A small sample (1 μL) of the vapor or liquid phase

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Table 1. Experimental Vapor−Liquid Equilibrium for the CO_2 (1) + C_8H_{18} (2) System

T = 322.39 K			T = 348.25 K			T = 372.53 K		
x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa
0.1784	0.9945	2.013	0.1422	0.9846	2.075	0.1848	0.9749	3.146
0.3546	0.9952	3.912	0.2852	0.9874	4.073	0.2552	0.9768	4.262
0.5616	0.9945	5.730	0.3672	0.9878	5.308	0.3123	0.9773	5.288
0.6574	0.9936	6.609	0.4736	0.9862	6.993	0.3561	0.9774	6.063
0.7420	0.9921	7.446	0.6136	0.9821	9.099	0.4051	0.9772	7.027
0.8377	0.9885	8.167	0.6827	0.9782	9.937	0.4745	0.9734	8.385
0.8892	0.9860	8.529	0.7423	0.9732	10.704	0.5179	0.9700	9.421
			0.7789	0.9672	10.981	0.5669	0.9669	10.468
			0.8146	0.9577	11.460	0.6226	0.9620	11.595
						0.6868	0.9490	12.813
						0.7492	0.9394	13.275
						0.8287	0.9082	13.772

was taken from the cell with a ROLSI sampler-injector[15] and was sent to the GC (HP, 6890) through a thermoregulated transfer circuit for the composition analysis. The samples into the GC were analyzed with a thermal conductivity detector (TCD). The components from the sample were separated in a packed column (Porapak Q, 4 ft by 1/8 in diameter). Helium was used as the carrier gas at a rate of 30 mL/min. The TCD detector was previously calibrated with the pure compounds used in this work. The oven temperature was set to 473 K, and the temperatures for the injector and TCD detector were set to 483 K and 513 K, respectively. At least five consecutive samples were taken to obtain a consistent average composition. Composition deviation for the liquid and vapor phases was estimated to be less than 0.0039 mole fraction in both systems.

Carbon dioxide was again loaded into the cell to reach the new required pressure. The desired phase was sampled after temperature and pressure remained constant. The isothermal envelopes were measured by increasing pressure up to near the critical point of the mixture.

Results and Discussion

Experimental Data. Experimental VLE data for the CO_2 + C_8H_{18} system were obtained at 322.39, 348.25, and 372.53 K, and these data sets are reported in Table 1. They were compared with those reported by Weng and Lee[4] at ~348 K in Figure 1. Good agreement was found among the isothermal data, even for the vapor phase compositions for this system.

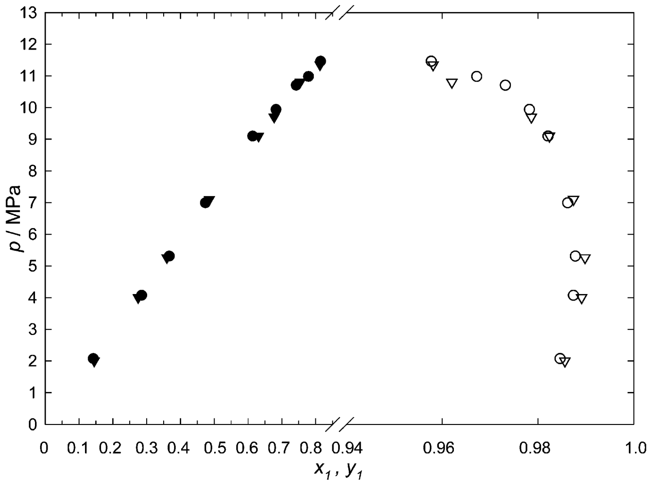

Figure 1. Vapor−liquid equilibrium data for the CO_2 (1) + C_8H_{18} (2) system at ~348 K: ●, this work; ▼, Weng and Lee.[4] Closed and open symbols denote the liquid and vapor phases, respectively.

Table 2. Experimental Vapor−Liquid Equilibrium for the CO_2 (1) + $C_{10}H_{22}$ (2) System

T = 319.11 K			T = 344.74 K			T = 372.94 K		
x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa
0.3395	0.9991	3.485	0.3421	0.9978	4.585	0.2146	0.9937	3.241
0.4243	0.9990	4.549	0.3993	0.9974	5.517	0.2774	0.9935	4.401
0.5262	0.9988	5.678	0.4934	0.9970	6.892	0.3351	0.9932	5.484
0.6338	0.9980	6.874	0.5815	0.9960	8.183	0.3799	0.9930	6.407
0.7336	0.9961	7.880	0.6474	0.9944	9.445	0.4449	0.9927	7.699
0.8847	0.9926	8.509	0.7373	0.9883	11.009	0.4862	0.9917	8.702
0.9240	0.9889	8.678	0.8383	0.9733	12.134	0.5128	0.9903	9.420
0.9731	0.9868	8.902	0.8956	0.9676	12.654	0.5752	0.9876	10.400
						0.6318	0.9830	11.894
						0.6974	0.9783	13.213
						0.7450	0.9711	14.240
						0.7910	0.9638	15.298
						0.8564	0.9271	16.060

The VLE measurements for the CO_2 + $C_{10}H_{22}$ system were carried out at 319.11, 344.74, and 372.94 K. The experimental results are presented in Table 2. Equilibrium measurements were in good consistency with those reported by Reamer and Sage,[5] Nagarajan and Robinson,[6] Chou et al.,[7] Jennings and Schucker,[8] Shaver et al.,[9] and Eustaquio-Rincón and Trejo[10] at ~344 K, as illustrated in Figure 2. It can also be observed in the enlarged image for the vapor phase composition for this system.

Modeling. The phase equilibria were correlated with the Peng−Robinson equation of state (PR EoS)[11] using classical and Wong−Sandler[12] mixing rules. The explicit form for this equation is expressed as follows

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

$$a(T) = 0.45724\,\frac{R^2 T_c^{\,2}}{p_c}\,\alpha(T_r) \tag{2}$$

$$b = 0.07780\,\frac{RT_c}{p_c} \tag{3}$$

$$\alpha(T_r) = [1 + \kappa(1 - T_r^{\,0.5})]^2 \tag{4}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where p and T are the pressure and temperature, respectively, the c and r subscripts denotes the critical and the reduced

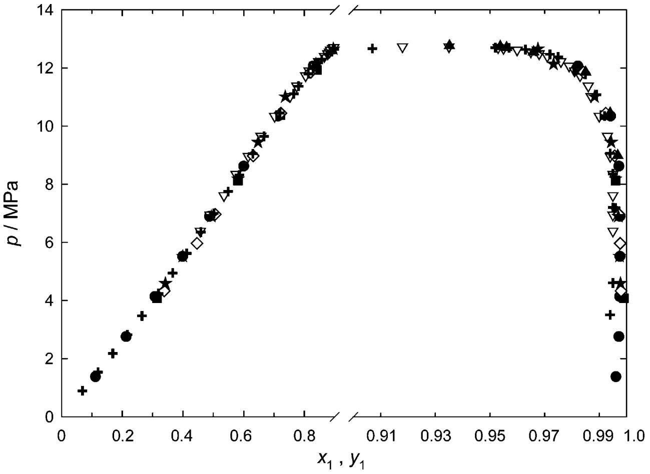

Figure 2. Vapor−liquid equilibria data for the CO_2 (1) + $C_{10}H_{22}$ (2) system at ~344 K: ●, Reamer and Sage;[5] ▽, Nagarajan and Robinson;[6] ■, Chou et al.;[7] ◇, Jennings and Schucker;[8] +, Shaver et al.;[9] ▲, Eustaquio-Rincón and Trejo;[10] ★, this work.

Table 3. Critical Properties and Acentric Factor for Pure Components[16]

	CO_2	C_8H_{18}	$C_{10}H_{22}$
T_c/K	304.12	568.70	617.70
p_c/MPa	7.374	2.490	2.100
ω	0.225	0.399	0.490

property for each component, respectively, R is the gas constant, v is the molar volume, α is a temperature dependent factor, and κ is a function of the acentric factor (ω). The critical properties and the acentric factor for each component are listed in Table 3.[16]

The classical mixing rule is defined for the a and b constants as follows

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) \qquad (6)$$

$$b_m = \sum_i x_i b_i \qquad (7)$$

where k_{ij} is the interaction parameter for the binary mixture.

The Wong−Sandler mixing rule[12] is represented as

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \qquad (8)$$

with

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)_{ij}}{2}(1 - k_{ij}) \qquad (9)$$

and

$$a_m = b_m \left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{CRT}\right) \qquad (10)$$

where $C = \ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR EoS. The excess Helmholtz free energy (A_∞^E) at infinite pressure can be expressed with the excess Gibbs free energy G^E at low pressure. In this work, we use the NRTL model[13] given by

$$\frac{A_\infty^E}{RT} = \sum_i x_i \frac{\sum_i x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \qquad (11)$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (12)$$

and

$$\tau_{ji} = \frac{A_{ji}}{RT} \qquad (13)$$

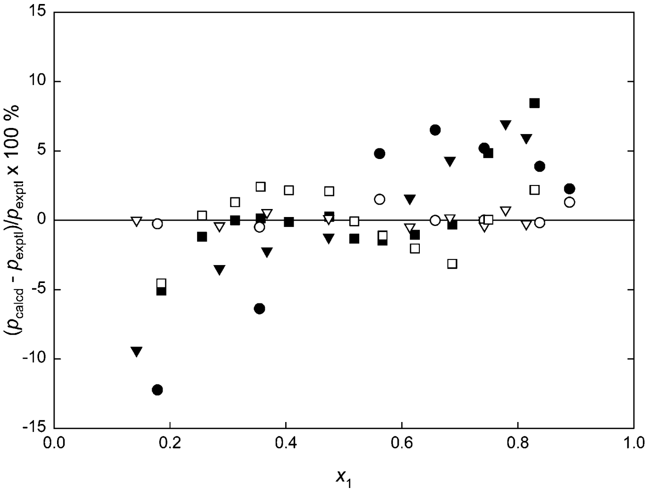

Figure 3. Pressure deviations between experimental data and those calculated with the PR EoS using the classical (closed symbols) and the Wong & Sandler (open symbols) mixing rules for the CO_2 (1) + C_8H_{18} (2) system at the following temperatures: ●, 322.39 K; ▼, 348.25 K; ■, 372.53 K.

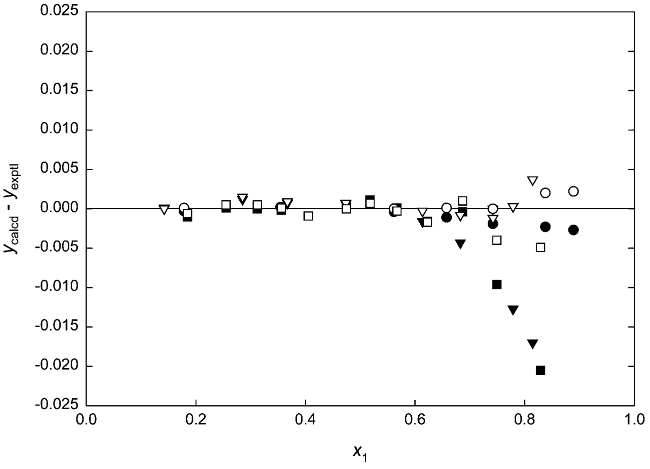

Figure 4. Composition deviations between experimental data and those calculated with the PR EoS using the classical (closed symbols) and the Wong & Sandler (open symbols) mixing rules for the CO_2 (1) + C_8H_{18} (2) system at the following temperatures: ●, 322.39 K; ▼, 348.25 K; ■, 372.53 K.

α_{ji} is the nonrandomness parameter, it was fixed at 0.3 for both binary systems, G_{ji} is the local composition factor, τ_{ji} are two binary interaction parameters, and $A_{ji} = (g_{ji} - g_{ii})$, g_{ji} is the interaction energy between the components i and j. These parameters were obtained by a VLE calculation algorithm using the Levenberg−Marquardt method[17] and minimizing the following objective function, F

$$F = \sum_{j=1}^{N_d}\left[\sum_{i=1}^{N_c}\left(\frac{y_{ij}^{calcd} - y_{ij}^{exptl}}{y_{ij}^{exptl}}\right)^2 + \left(\frac{p_j^{calcd} - p_j^{exptl}}{p_j^{exptl}}\right)^2\right] \qquad (14)$$

where N_d is the number of data points, N_c is the number of components, y is the vapor mole fraction, and the superscripts calcd and exptl denote the calculated and experimental data, respectively.

The calculated sets of data are in good agreement for the CO_2 + C_8H_{18} and CO_2 + $C_{10}H_{22}$ systems. The deviations between the experimental and calculated values in both systems for p and y are shown from Figures 3 to 6. The calculated data sets using the PR EoS with the Wong & Sandler mixing rule provided lower deviations than those obtained with the classical mixing rule using the same EoS. The optimized binary parameters for both mixing rules, and the absolute average deviations (AAD) for p and y are presented in Table 4. The

Table 4. Binary Interaction Parameters and the AAD

	classical mixing rule			Wong−Sandler mixing rule				
T/K	k_{12}	AAD (p)	AAD (y)	k_{12}	A_{12}/kJ·mol^{-1}	A_{21}/kJ·mol^{-1}	AAD (p)	AAD (y)
				CO_2 (1) + C_8H_{18} (2)				
322.39	0.1098	5.8933	0.0013	0.6520	7.2703	−0.6319	0.5352	0.0007
348.25	0.1241	3.9064	0.0042	0.6596	9.5910	−1.4838	0.3500	0.0010
372.53	0.1296	2.0185	0.0030	0.6668	10.4062	−1.9461	1.7842	0.0013
				CO_2 (1) + $C_{10}H_{22}$ (2)				
319.11	0.1064	2.4578	0.0014	0.6990	13.2909	−1.0309	0.5517	0.0010
344.74	0.0992	3.0250	0.0056	0.7207	10.5625	−1.7846	1.2882	0.0017
372.94	0.1069	1.6526	0.0014	0.7366	10.4049	−2.3771	0.6791	0.0020

AADs in pressure were calculated as follows

$$\text{AAD}\ (p) = \left(\frac{100}{N_\mathrm{d}}\right)\sum_{i=1}^{N_\mathrm{d}} \frac{|p^{\mathrm{exptl}} - p^{\mathrm{calcd}}|}{p^{\mathrm{exptl}}} \qquad (15)$$

and the AAD for the vapor phase mole fraction

$$\text{AAD}\ (y) = \left(\frac{1}{N_\mathrm{d}}\right)\sum_{i=1}^{N_\mathrm{d}} |y^{\mathrm{exptl}} - y^{\mathrm{calcd}}| \qquad (16)$$

The calculated VLE data using the Wong−Sandler mixing rule for the $CO_2 + C_8H_{18}$ system had an AAD within AAD (p) = 1.78 and an AAD (y) = 0.0013. For the $CO_2 + C_{10}H_{22}$ system, the AAD was less than AAD (p) = 1.28 and an AAD (y) = 0.0020.

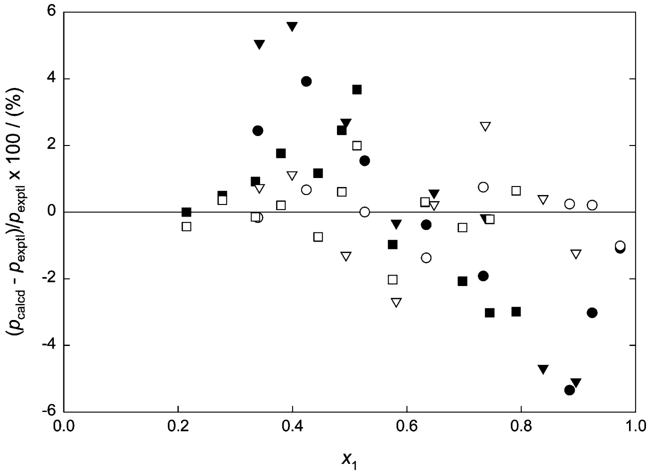

Figure 5. Pressure deviations between experimental data and those calculated with the PR EoS using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules for the CO_2 (1) + $C_{10}H_{22}$ (2) system at the following temperatures: ●, 319.11 K; ▼, 344.74 K; ■, 372.94 K.

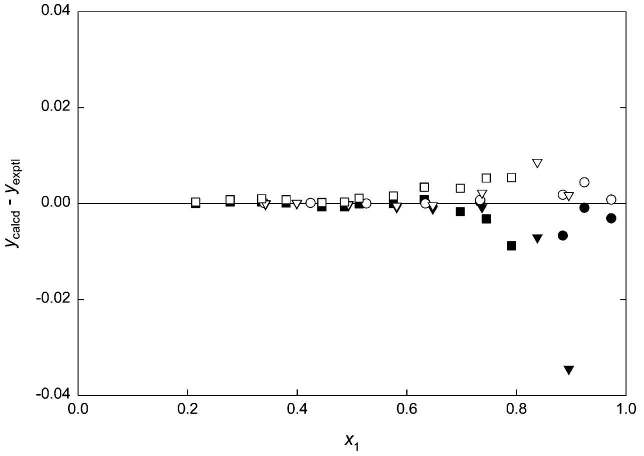

Figure 6. Composition deviations between experimental data and those calculated with the PR EoS using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules for the CO_2 (1) + $C_{10}H_{22}$ (2) system at the following temperatures: ●, 319.11 K; ▼, 344.74 K; ■, 372.94 K.

Conclusions

In this paper, VLE measurements for the $CO_2 + C_8H_{18}$ and $CO_2 + C_{10}H_{22}$ systems were performed using a static analytic setup at temperatures from (319 to 372) K in the pressures range of (2 to 16) MPa. The experimental data reported here were in good agreement with those reported in the literature. The experimental equilibrium data for these systems were correlated with the PR EoS using the classical and the Wong−Sandler mixing rules; the NRTL model was used to represent the excess Gibbs energy. The calculated VLE data using the Wong−Sandler mixing rule gave a better representation than those obtained using the classical mixing rule, especially close to the critical point of these mixtures. The obtained interaction parameters show a trend with respect to the temperature in the studied range, which could be used to extrapolate at other temperatures.

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