JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Vapor−Liquid Equilibria of Binary and Ternary Systems Containing Carbon Dioxide, Alkane, and Benzothiophene

Luis E. Camacho-Camacho,[†] Luis A. Galicia-Luna,[*,†] and Octavio Elizalde-Solis[‡]

[†]Laboratorio de Termodinámica, SEPI-ESIQIE, Instituto Politécnico Nacional, UPALM, Ed. Z, Secc. 6, 1 piso, Lindavista, C.P. 07738, México, D.F.

[‡]Departamento de Ingeniería Química Petrolera, ESIQIE, Instituto Politécnico Nacional, UPALM, Edif. 8, 2 piso, Lindavista, C.P. 07738, México, D.F.

ABSTRACT: Experimental vapor−liquid equilibrium (VLE) data of binary and ternary systems are reported covering all of the phase envelopes up to near the critical point. The carbon dioxide + dodecane, carbon dioxide + benzothiophene, and carbon dioxide + nonane + benzothiophene systems were studied at (318.14, 344.75, 373.23, and 417.91) K, 373.93 K, and (313.09, 343.73, and 373.74) K, respectively. The apparatus is based on the static−analytic method with an on-line ROLSI (rapid on-line sampler−injector) sampler to allow fast determination of the VLE. Standard uncertainties for the measured properties in this work were estimated to be $p \pm 0.01$ MPa, $T \pm 0.03$ K, liquid mole fraction $x_{CO_2} \pm 0.0036$, and vapor mole fraction $y_{CO_2} \pm 0.0016$. The experimental VLE data for carbon dioxide + dodecane were found to be in agreement with those available in the literature at 318 K. Furthermore, the corresponding results for the ternary system indicate a high selectivity of nonane in the vapor phase instead of benzothiophene. Data obtained in this work were correlated with the Peng−Robinson equation of state using the Wong−Sandler mixing rules.

INTRODUCTION

Experimental vapor−liquid equilibria (VLE), volumetric properties, and solubility data of alkanes in supercritical fluids such as carbon dioxide are important information in the petroleum process design area. Reliable experimental thermodynamic properties are also needed to test the approach of new or developed equations of state.

The present study belongs to a systematic experimental VLE and volumetric property determinations of alkanes (pentane, hexane, octane, nonane, undecane, and tridecane) in carbon dioxide.[1−5] These linear alkanes have been used in research as representative compounds of fuels,[6−8] while innovations regarding desulfurization pathways at the laboratory scale are commonly based on benzothiophene as a model sulfur compound.[9−14] Therefore, the aim of this work is to report accurate experimental VLE data for the carbon dioxide + dodecane, carbon dioxide + benzothiophene, and carbon dioxide + nonane + benzothiophene systems in a wide range of temperature and pressure. Nonane was mixed with the sulfur compound to simulate a fuel model and understand the selectivity of the solvent over both solutes.

The VLE for the ternary system mixture modeling require binary interaction parameters. Hence, the corresponding behavior for the carbon dioxide + benzothiophene was determined at 373.93 K, while Camacho-Camacho et al.[1] have already published the VLE for the binary carbon dioxide + nonane. Afterward, the ternary system behavior was predicted from the binary interaction parameters obtained in this work and those reported earlier.[1]

Some authors have published the phase equilibria for the carbon dioxide + dodecane system in different regions.[15−18] Nieuwoudt and du Rand[15] presented scarce isothermal phase equilibrium data near the critical pressure for the carbon dioxide + dodecane system from (313.2 to 343.2) K, Hottovy et al.[16] the three liquid−liquid−vapor phase equilibrium line at low temperatures, and Henni et al.[17] dew points far from the critical pressure at (313, 353, and 393) K. The only VLE data that cover the entire phase envelope are those reported by Gardeler et al.[18] at 318.15 K. These data were found to be in agreement with the experimental data obtained in this work. No VLE data have been published for the other binary and ternary systems.

EXPERIMENTAL SECTION

Materials. Anhydrous nonane (C_9H_{20}, certified purity 0.991 mole fraction), dodecane ($C_{12}H_{26}$, certified purity 0.9942 mole fraction), and benzothiophene (C_8H_6S, certified purity 0.995 mole fraction) were purchased from Sigma-Aldrich. Carbon dioxide (CO_2, mole fraction purity > 0.99995) and helium (He, mole fraction purity > 0.99998) were supplied by Air Products-Infra. Chemicals were used as received without any further purification. The water content for nonane was $1.9 \cdot 10^{-4}$ and $3.7 \cdot 10^{-4}$ for dodecane in mole fraction. It was determined by means of a Karl Fischer coulometer (831, Metrohm).

Apparatus. Experimental VLE data for the studied systems were measured isothermally by means of a static−analytic apparatus described elsewhere.[4,5] It consists of a 100 cm^3 titanium view cell (EC) coupled to a HP 5890 gas chromatograph (GC) and is capable to operate at temperatures up to 673 K and pressures up to 60 MPa. Figure 1 shows a scheme of the experimental apparatus. The gas chromatograph used to perform

Received: June 14, 2011
Accepted: September 27, 2011
Published: October 20, 2011

dx.doi.org/10.1021/je200586g | *J. Chem. Eng. Data* 2011, 56, 4109–4115

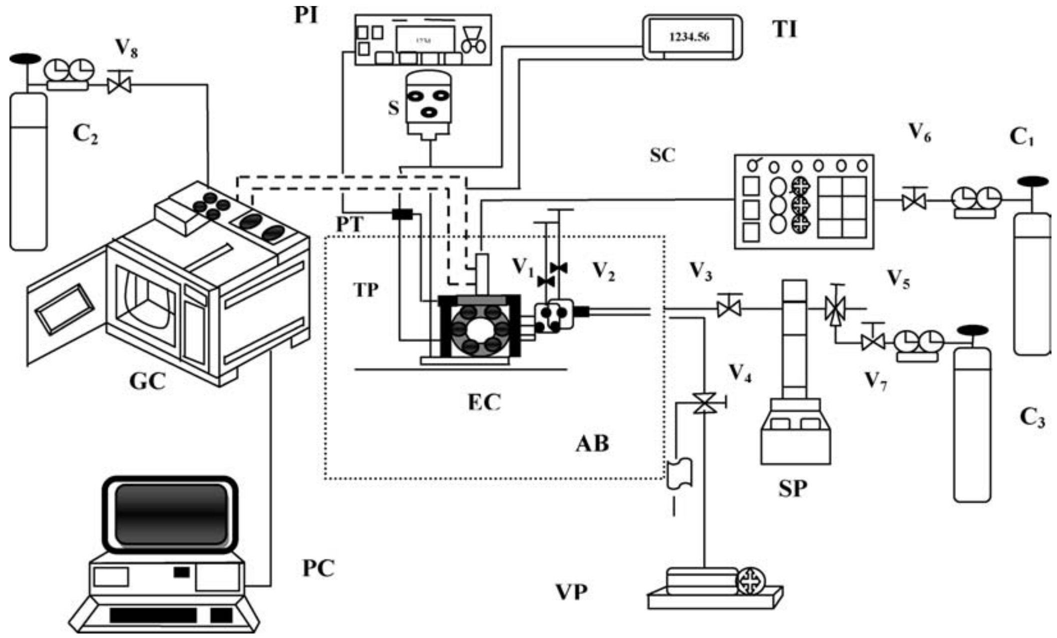

Figure 1. Experimental scheme of the static−analytic apparatus for phase equilibrium measurements:[3] AB, air bath; C_i, cylinder gases; EC, equilibrium cell; GC, gas chromatograph; PC, computer; PI, pressure indicator; PT, pressure transducer; S, stirring device; SC, sampler controller; SP, syringe pump; TI, temperature indicator; TP, temperature probe; V_i, needle valves; VP, vacuum pump.

the sample analysis was set at the following conditions: injector temperature (483 K); thermal conductivity detector (TCD) temperature (513 K); gradient in the oven temperature (350 K for 1 min, 70 $K\cdot min^{-1}$ up to 513 K for 3.67 min); Alltech packed column (Chromosorb Q 80/100, stainless steel 1/8 in. diameter × 2 ft length); carrier gas (helium at 30 $cm^3\cdot min^{-1}$); and reference TCD gas (helium at 45 $cm^3\cdot min^{-1}$). Prior to VLE determinations, GC calibration was completed according to the procedure described by Elizalde-Solis and Galicia-Luna.[5] Combined uncertainties for the mole fraction were estimated to be less than 0.0035 for $u(x_{CO_2})$ and 0.0016 for $u(y_{CO_2})$ in the whole range of measurements.

Measurements of pressure were performed by means of a pressure transducer (PDCR 4010-A093, DRUCK), and the standard uncertainty $u(p)$ was less than 0.01 MPa. Equilibrium temperatures were measured by two 100 Ω platinum probes (PT100, Specitec). The temperature uncertainty $u(T)$ was within 0.03 K. Uncertainties were evaluated according to the NIST Technical Note 1297.[19]

VLE Measurements. Experimental data were obtained isothermally according to the following procedure:

(a) About 50 cm^3 of the solute (alkane, benzothiophene, or its corresponding mixture with a volume relation of 1:1) was loaded to the equilibrium cell. Chemicals and the pipelines were carefully degassed under vigorous stirring for 1 h. Carbon dioxide flowed through the tubing to the EC for ensuring a complete evacuation of air at a desired pressure.

(b) The air bath (AB) temperature was initially set to the lowest value for each system. Thermal equilibrium was reached after almost 5 h when temperature values on the indicator were within its reported uncertainty. Then, the pressure in the EC was increased by adding CO_2. Pressure became stable after 1 h. Slow stirring was applied throughout the experimental measurements to ensure complete mixing of the compounds in both phases.

(c) Samples of the liquid phase in the EC were sent to the GC for the component quantification. It was carried out with an automatic online ROLSI (rapid on-line sampler−injector, Armines)[20] sampler injector which is moved in vertical position. At each temperature and pressure, several samples were taken and analyzed to reach the equilibrium composition. This criterium was determined when the last five consecutive had to be within 0.5 % of deviation between the maximum and minimum values of CO_2 composition for liquid phases and 0.05 % for the vapor phase; hence the combined uncertainty values could be a minimum.

(d) The sampler−injector was moved to the vapor phase, and the above-mentioned step was repeated. For this work, only the vapor phase and a single liquid phase were present in the EC.

(e) The pressure was increased by adding CO_2 to EC, and steps c and d were repeated. Finally, the temperature set-point of AB was changed to a new value, and procedures b to d were repeated again to accomplish VLE measurements.

■ MODELING

As the basis for the study, experimental VLE data were correlated with the Peng−Robinson equation of state[21] (PR EoS, eq 1) coupled to the classical (CMR) and the Wong−Sandler[22] (WSMR) mixing rules. The PR EoS is

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

The CMR are calculated with the next equations

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

$$b_m = \sum_i x_i b_i \tag{3}$$

Table 1. Critical Properties and Acentric Factor of the Pure Substances[23,24]

	CAS No.	T_c/K	p_c/MPa	ω
CO_2	[124-38-9]	304.12	7.374	0.225
nonane	[111-84-2]	594.60	2.290	0.445
dodecane	[112-40-3]	658.00	1.820	0.576
benzothiophene	[95-15-8]	754.00	4.140	0.296

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

Critical values of each compound were obtained elsewhere[23,24] and are listed in Table 1.

The WSMR are computed as:

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \sum_i x_i (a_i/b_i RT) - (A^E_\infty/CRT)} \tag{4}$$

where

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b_i - (a_i/RT)) + (b_j - (a_j/RT))}{2}(1 - k_{ij}) \tag{5}$$

$$a_m = b_m \left(\sum_i x_i \frac{a_i}{b_i} + \frac{A^E_\infty}{C} \right) \tag{6}$$

$C = \ln(2^{1/2} - 1)/2^{1/2}$ for the PR EoS. The excess Helmholtz free energy at infinite pressure, A^E_∞, can be expressed with the excess Gibbs free energy at low pressure, $G_\gamma{}^E$, by using the NRTL model:[25]

$$\frac{A^E_\infty}{RT} = \frac{G^E_\gamma}{RT} = \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \tag{7}$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{8}$$

α_{ji} was fixed at 0.3. G_{ji} are factors of local composition, and τ_{ji} are the binary interaction parameters. Parameters k_{ij}, τ_{ij}, and τ_{ji} were optimized by using the Levenberg–Marquardt method, and they are minimized with the following objective function,

$$\mathrm{OF} = \sum_{j=1}^{\mathrm{NP}} \left[\sum_{i=1}^{\mathrm{Nc}} \left(\frac{y_{ij}^{\mathrm{calcd}} - y_{ij}^{\mathrm{exptl}}}{y_{ij}^{\mathrm{exptl}}} \right)^2 + \left(\frac{p_j^{\mathrm{calcd}} - p_j^{\mathrm{exptl}}}{p_j^{\mathrm{exptl}}} \right)^2 \right] \tag{9}$$

where NP stands for the number of data points, Nc represents the number of compounds, p is the pressure at equilibrium, y is the vapor mole fraction, and superscripts calcd and exptl indicate calculated and experimental data, respectively. The absolute average deviation of bubble pressure was calculated as

$$\Delta p = \left(\frac{100}{\mathrm{NP}}\right) \sum_{i=1}^{\mathrm{NP}} \frac{|p_i{}^{\mathrm{exptl}} - p_i{}^{\mathrm{calcd}}|}{p_i{}^{\mathrm{exptl}}} \tag{10}$$

Table 2. Vapor–Liquid Equilibria for the CO_2 + Dodecane System[a]

p/MPa	x_{CO_2}	$u(x_{CO_2})$	y_{CO_2}	$u(y_{CO_2})$	K_{CO_2}	$K_{C_{12}}$
T = 318.14 K						
1.78	0.196	0.0010	0.997	0.0013	5.083	0.003
2.53	0.268	0.0006	0.998	0.0016	3.723	0.003
3.45	0.354	0.0022	0.999	0.0013	2.826	0.001
5.03	0.489	0.0011	0.999	0.0012	2.044	0.001
6.49	0.612	0.0020	0.998	0.0002	1.631	0.003
8.14	0.750	0.0015	0.995	0.0004	1.327	0.020
9.10	0.906	0.0023	0.989	0.0002	1.092	0.115
T = 344.75 K						
3.16	0.265	0.0005	0.995	0.0006	3.759	0.006
4.77	0.375	0.0018	0.997	0.0015	2.656	0.004
6.35	0.472	0.0012	0.998	0.0014	2.114	0.002
7.42	0.538	0.0024	0.998	0.0010	1.856	0.002
8.21	0.589	0.0035	0.998	0.0011	1.695	0.003
9.08	0.632	0.0011	0.998	0.0006	1.578	0.004
9.92	0.675	0.0010	0.997	0.0006	1.478	0.007
10.66	0.708	0.0011	0.995	0.0015	1.406	0.015
T = 373.23 K						
3.30	0.235	0.0018	0.990	0.0011	4.216	0.013
4.80	0.320	0.0016	0.995	0.0013	3.108	0.006
6.54	0.411	0.0025	0.996	0.0006	2.421	0.006
8.04	0.482	0.0013	0.996	0.0014	2.067	0.007
9.73	0.553	0.0027	0.996	0.0014	1.800	0.009
11.11	0.616	0.0020	0.995	0.0013	1.616	0.013
12.76	0.674	0.0031	0.993	0.0011	1.474	0.020
14.10	0.720	0.0014	0.990	0.0012	1.375	0.034
15.42	0.762	0.0026	0.974	0.0011	1.278	0.107
16.19	0.787	0.0013	0.967	0.0014	1.228	0.155
17.54	0.845	0.0015	0.958	0.0011	1.135	0.265
T = 417.91 K						
1.64	0.104	0.0018	0.969	0.0012	9.325	0.035
3.12	0.186	0.0033	0.986	0.0014	5.281	0.017
4.55	0.256	0.0028	0.990	0.0004	3.856	0.013
6.04	0.326	0.0022	0.990	0.0007	3.037	0.014
7.46	0.385	0.0027	0.990	0.0013	2.571	0.016
9.08	0.447	0.0013	0.989	0.0012	2.212	0.019
10.51	0.499	0.0026	0.989	0.0004	1.978	0.022
11.99	0.550	0.0015	0.988	0.0005	1.794	0.027
13.51	0.599	0.0028	0.986	0.0009	1.647	0.034
14.98	0.640	0.0026	0.983	0.0014	1.534	0.047
16.53	0.690	0.0025	0.979	0.0012	1.419	0.067
18.09	0.732	0.0033	0.972	0.0011	1.327	0.104
19.45	0.767	0.0027	0.960	0.0008	1.251	0.172
20.37	0.802	0.0020	0.943	0.0014	1.176	0.286

[a] Standard uncertainties are: $u(T) = 0.03$ K, $u(p) = 0.01$ MPa, $u(K_{CO_2}) \leq 0.02\ x(K_{CO_2})$.

The absolute average deviation for mole composition follows the next equation:

$$\Delta y = \left(\frac{1}{\mathrm{NP}}\right) \sum_{i=1}^{\mathrm{NP}} |y_i{}^{\mathrm{exptl}} - y_i{}^{\mathrm{calcd}}| \tag{11}$$

Table 3. Vapor−Liquid Equilibria for the CO_2 + Benzothiophene System[a]

p/MPa	x_{CO_2}	$u(x_{CO_2})$	y_{CO_2}	$u(y_{CO_2})$	K_{CO_2}	K_{BT}
			T = 373.93 K			
1.32	0.009	0.0031	0.957	0.0006	110.046	0.043
2.32	0.023	0.0026	0.966	0.0015	41.282	0.034
3.36	0.033	0.0032	0.987	0.0013	29.299	0.013
4.49	0.050	0.0025	0.993	0.0016	19.901	0.007
5.67	0.065	0.0014	0.994	0.0012	15.400	0.005
7.12	0.082	0.0035	0.994	0.0004	12.162	0.005
8.46	0.096	0.0029	0.993	0.0008	10.304	0.007
10.22	0.123	0.0027	0.988	0.0008	8.002	0.013
11.78	0.136	0.0018	0.983	0.0014	7.193	0.019
13.45	0.164	0.0020	0.971	0.0010	5.919	0.033
14.79	0.181	0.0022	0.915	0.0007	5.031	0.103

[a] Standard uncertainties are: $u(T) = 0.03$ K, $u(p) = 0.01$ MPa, $u(K_{CO_2}) \leq 0.02\ x(K_{CO_2})$.

Table 4. Vapor−Liquid Equilibria for the CO_2 + Nonane + Benzothiophene System[a]

p/MPa	x_{CO_2}	x_{C_9}	y_{CO_2}	y_{C_9}
		T = 313.09 K		
1.92	0.243	0.727	0.998	0.001
3.34	0.350	0.594	0.998	0.001
4.98	0.507	0.450	0.998	0.001
6.36	0.675	0.296	0.997	0.002
7.08	0.783	0.197	0.997	0.002
7.48	0.878	0.111	0.996	0.003
7.63	0.907	0.084	0.996	0.004
		T = 343.73 K		
1.61	0.144	0.804	0.994	0.005
3.00	0.246	0.698	0.995	0.004
4.44	0.354	0.590	0.996	0.003
5.96	0.458	0.492	0.995	0.004
7.37	0.547	0.411	0.994	0.005
8.83	0.633	0.333	0.993	0.006
10.53	0.745	0.230	0.987	0.012
11.46	0.816	0.166	0.975	0.022
11.99	0.887	0.103	0.960	0.036
		T = 373.74 K		
6.593	0.4027	0.553	0.989	0.010
9.133	0.5157	0.441	0.984	0.014
10.543	0.5929	0.370	0.983	0.016
11.946	0.6497	0.320	0.978	0.020
13.484	0.7282	0.248	0.966	0.032
14.565	0.7918	0.190	0.950	0.047
15.081	0.8261	0.159	0.932	0.062

[a] Standard uncertainties are: $u(T) = 0.03$ K, $u(p) = 0.01$ MPa, $u(x_{CO_2}) = 0.0036$, $u(y_{CO_2}) = 0.0011$, and the expanded uncertainties U_c are $U_c\ (x_{CO_2}) = 0.0072$, $U_c\ (y_{CO_2}) = 0.0022$ with a 0.95 level of confidence ($k \approx 2$).

Table 5. Bubble-Point Calculations for the Binary Systems Using the PR EoS

	classical			Wong−Sandler				
					NRTL			
T /K	k_{12}	%Δp	Δy	k_{12}	τ_{12}/ kJ·mol^{-1}	τ_{21}/ kJ·mol^{-1}	%Δp	Δy
				Carbon Dioxide + Dodecane				
318.14	0.0971	1.3	0.002	0.7723	10.2166	−1.3756	0.2	0.002
344.75	0.0903	1.0	0.001	0.7897	9.3484	−1.9794	0.4	0.002
373.23	0.0885	1.1	0.003	0.7961	9.7009	−2.6871	0.3	0.006
417.91	0.0833	3.0	0.004	0.8105	9.4023	−3.4698	0.3	0.007
T. I. P.[a]	0.1615	7.5	0.019	0.8447	9.1020	−1.0046	7.5	0.005
				Carbon Dioxide + Benzothiophene				
373.93	0.3031	24.9	0.021	1.8410	−5.0084	11.7121	6.1	0.021

[a] Temperature-independent parameters.

■ RESULTS AND DISCUSSION

Experimental VLE data were obtained isothermally with pressure increments. The carbon dioxide + dodecane system was measured at (318.14, 344.75, 373.23, and 417.91) K. Compositions of carbon dioxide, equilibrium ratios of each compound, and their corresponding standard uncertainties in both phases are presented in Table 2. VLE data for the second binary carbon dioxide + benzothiophene system at 373.93 K are listed in Table 3; this system has not been published in the literature. Table 4 summarizes the experimental data for the carbon dioxide + nonane + benzothiophene system at (313.09, 343.73, and 373.74) K. The mole fraction for benzothiophene in carbon dioxide mixtures decreases when nonane is added to the system.

The PR EoS coupled to the CMR and WSMR was used to represent experimental VLE data for the binary systems. Optimized parameters (k_{ij}, τ_{ij}, τ_{ji}) were obtained as temperature-dependent and independent parameters. Table 5 lists the absolute average deviation for the resulting correlations of the binary systems; the lowest pressure deviation was obtained at 318.14 K using the WSMR and the dependent parameters. The maximum average deviation belonged to the independent parameter, and no differences were found between the uses of any of the mixing rules for this instance.

The VLE behavior for the ternary system was predicted using bubble pressure calculations. These results are listed in Table 6. It was accomplished with the base model (PR EoS/CMR). The temperature-independent interaction parameter for the carbon dioxide + nonane mixture was obtained from the literature.[1] Lower deviations in pressure and composition were found at 313.09 K.

Isothermal (p, T, x_{CO_2}, y_{CO_2}) trends for the carbon dioxide + dodecane are plotted in Figure 2 where symbols and lines stand for experimental and calculated data, in that order. Calculations were carried out using the PR EoS + WSMR model with temperature parameter dependence. Our VLE isotherm at 318.14 K and that reported by Gardeler et al.[18] at 318.15 K are plotted in Figure 3. According to the trends and error bars, both sets of data are in agreement, and dew points follow the same trend; the enlarged image for the bubble region shows the error bars for the vapor mole fraction overlap. No other sources of data were found in the literature to compare our results in the studied temperature range. Equilibrium ratios ($K_i = y_i/x_i$) for the binary systems are depicted in Figure 4. Symbols represent experimental data, and lines stand for predicted values by the PR EoS + WSMR

Table 6. Bubble-Point Predictions for the Carbon Dioxide + Nonane + Benzothiophene System Using the PR EOS + Classical Mixing Rule

binary system	k_{ij}
CO_2 + nonane	0.0968[1]
CO_2 + benzothiophene	0.3031
nonane + benzothiophene	0.0000[a]

prediction for ternary system		
T/K	%Δp	Δy_{CO_2}
313.09	3.8	0.001
343.73	9.9	0.017
373.74	6.9	0.013

[a] Considered as zero due to the absence of VLE data.

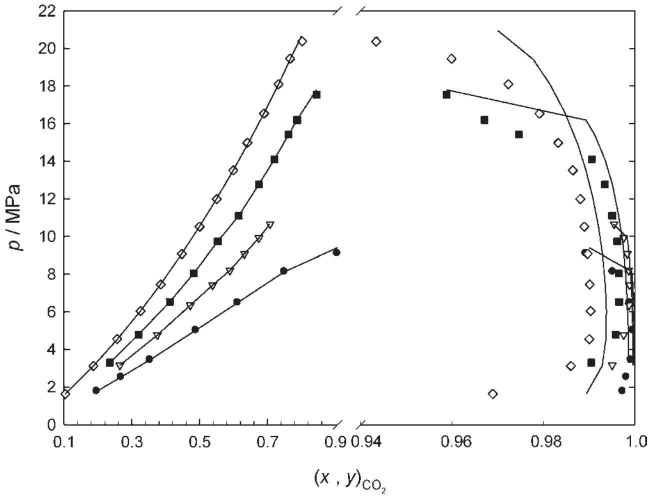

Figure 2. VLE for the CO_2 + dodecane system. Experimental data at: ●, 318.14 K; ▽, 344.75 K; ■, 373.23 K; ◇, 417.91 K. Solid lines represent the calculated data.

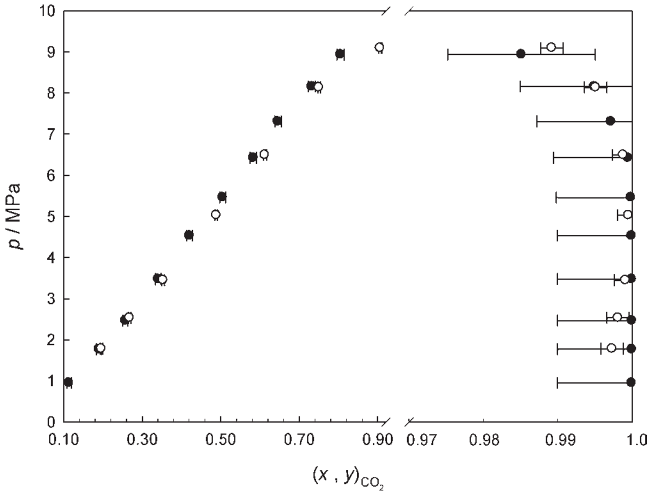

Figure 3. VLE for the CO_2 + dodecane system: ●, 318 K, Gardeler et al.;[18] ○, 318.14 K, this work. Horizontal lines represent error bars.

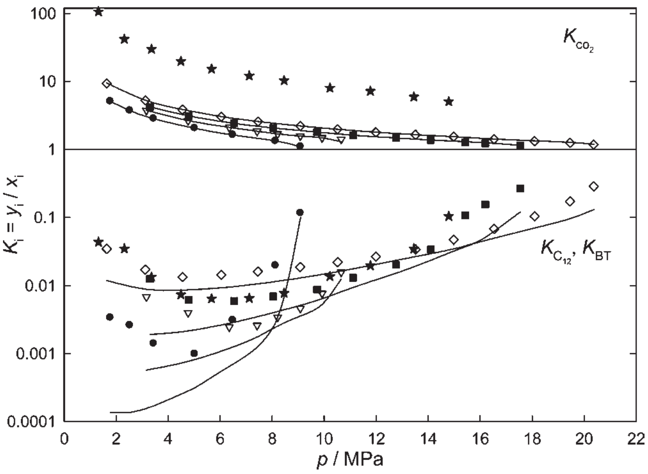

Figure 4. Experimental equilibrium ratios for the CO_2 + dodecane system: ●, 318.14 K; ▽, 344.75 K; ■, 373.23 K; ◇, 417.91 K. CO_2 + benzothiophene system at ★, 373.93 K. Solid lines represent the calculated data.

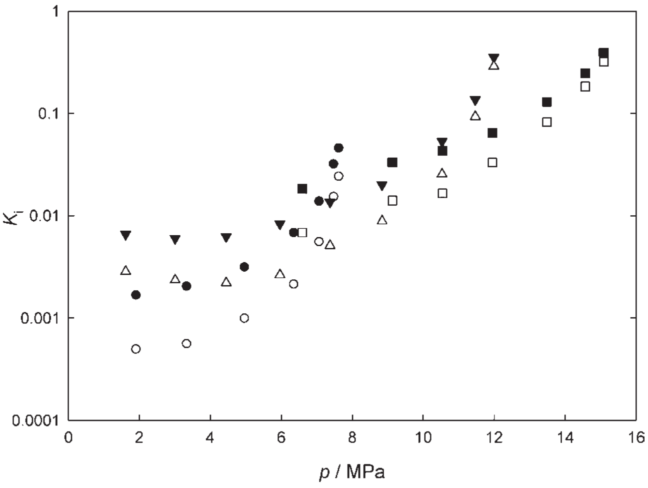

Figure 5. Experimental equilibrium ratios for the CO_2 + nonane + benzothiophene: ●, ○, 313.09 K; ▼, △, 343.73 K; ■, □, 373.74 K. Black symbols correspond to nonane, and open symbols denote benzothiophene.

model using the temperature-independent parameters. The smoothness of symbols confirms the internal consistency of data obtained in this work. The calculated values illustrate how much these deviated from the experimental data. Deviations observed in this figure are more evident than in Figure 2. The combined uncertainties for equilibrium ratios were estimated to be less than 2 % of the value reported in Table 2.

Equilibrium ratios are plotted in Figure 5 for nonane and benzothiophene in the ternary system. The experimental data could be considered suitable according to the smoothness of the isothermal trends. The separation factors ($S_{ij} = K_i/K_j$) for the CO_2 + nonane + benzothiophene system are plotted in Figure 6 for nonane over benzothiophene. The separation factor is observed to enhance as pressure decreases for each temperature, obtaining the highest value at 313 K in the low pressure region. In contrast, due to the compositions of benzothiophene in the vapor phase within the experimental uncertainty, the $S_{C_9/BT}$ values increase from low pressure, achieve a maximum of ($S_{C_9/BT}$ = 3.16) for 6 MPa, and decrease again as pressure increases at

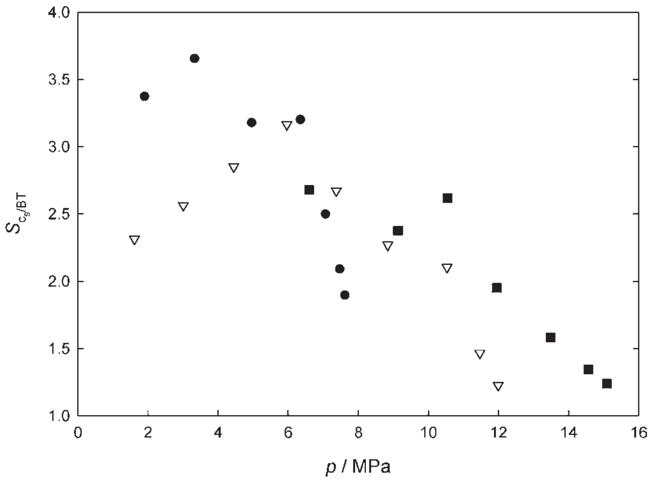

Figure 6. Separation factor for nonane over benzothiophene $S_{C_9/BT}$ in the CO_2 + nonane + benzothiophene system: ●, 313.09 K; ▽, 343.73 K; ■, 373.74 K.

343.73 K. Moreover, benzothiophene is been transferred to the vapor phase at high pressures, and it makes that the separation became low. Finally, the separation of nonane mixed with benzothiophene as a sulfur compound can be carried with high $S_{C_9/BT}$ values at low pressures (4 MPa, 313 K and 6 MPa, 343 K) using carbon dioxide. It indicates that a high content of nonane in the vapor phase can be obtained at low pressures compared against benzothiophene when carbon dioxide at supercritical conditions is used as a solvent.

■ CONCLUSIONS

Isothermal VLE data for the carbon dioxide + dodecane, carbon dioxide + benzothiophene, and carbon dioxide + nonane + benzothiophene systems were obtained at (318.14, 344.75, 373.23, and 417.91) K, 373.93 K, and (313.09, 343.73, and 373.74) K, respectively. Results for the carbon dioxide + dodecane system agree with the literature data at 318 K. No experimental VLE data have been reported for the other binary and ternary systems even at higher temperatures. The ternary system was studied to determine the possibility of separating one of the solutes. Taking into account the separation factors, it is feasible to separate nonane from the alkane + benzothiophene mixture using carbon dioxide as solvent media.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lgalicial@ipn.mx. Phone: (52) 55 5729-6000 ext 55133. Fax: (52) 55 5586-2728.

Funding Sources

The authors thank CONACyT and IPN for the financial support. L.E.C.-C. thanks ex-Director of ESIQIE J. Salvador Meza-Espinoza for a Ph.D. fellowship from 2006−2007.

■ REFERENCES

(1) Camacho-Camacho, L. E.; Galicia-Luna, L. A.; Elizalde-Solis, O.; Martínez-Ramírez, Z. New Isothermal Vapor-Liquid Equilibria for the CO_2 + *n*-Nonane, and CO_2 + *n*-Undecane Systems. *Fluid Phase Equilib.* **2007**, *259*, 45–50.

(2) Camacho-Camacho, L. E.; Galicia-Luna, L. A. Experimental Densities of Hexane + Benzothiophene Mixtures from 313 to 363 K and up to 20 MPa. *J. Chem. Eng. Data* **2007**, *52*, 2455–2461.

(3) Camacho-Camacho, L. E. Development of a Method to Measure Solid Solubilities and Solubilities of Solid + Liquid Mixtures in Supercritical Solvents or a Mixture of Liquid and Ionic Liquid up to 150 °C and 300 bar (In Spanish). Ph.D. Thesis, SEPI-ESIQIE Instituto Politécnico Nacional, México, 2009.

(4) Elizalde-Solis, O.; Galicia-Luna, L. A.; Camacho-Camacho, L. E. High-Pressure Vapor-Liquid Equilibria for CO_2 + Alkanol Systems and Densities of *n*-Dodecane and *n*-Tridecane. *Fluid Phase Equilib.* **2007**, *259*, 23–32.

(5) Elizalde-Solis, O.; Galicia-Luna, L. A. Solubility of Thiophene + Pentane and Thiophene + Octane Binary Mixtures in Supercritical Carbon Dioxide at Temperatures from 333 to 383 K. *Ind. Eng. Chem. Res.* **2005**, *44*, 5757–5760.

(6) Zhang, S.; Zhang, Z. C. Novel Properties of Ionic Liquids in Selective Sulfur Removal from Fuels at Room Temperature. *Green Chem.* **2002**, *4*, 376–379.

(7) Huang, C.; Chen, B.; Zhang, J.; Liu, Z.; Li, Y. Desulfurization of Gasoline by Extraction with New Ionic Liquids. *Energy Fuels* **2004**, *18*, 1862–1864.

(8) Zhang, S.; Zhang, Q.; Zhang, Z. C. Extractive Desulfurization and Denitrogenation of Fuels Using Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 614–622.

(9) Seeberger, A.; Jess, A. Desulfurization of diesel oil by selective oxidation and extraction of sulfur compounds by ionic liquids—a contribution to a competitive process design. *Green Chem.* **2010**, *12*, 602–608.

(10) Dai, W.; Zhou, Y.; Wang, S.; Su, W.; Sun, Y.; Zhou, L. Desulfurization of transportation fuels targeting at removal of thiophene/benzothiophene. *Fuel Process. Technol.* **2008**, *89*, 749–755.

(11) Varma, N. R.; Ramalingam, A.; Banerjee, T. Experiments, correlations and COSMO-RS predictions for the extraction of benzothiophene from n-hexane using imidazolium-based ionic liquids. *Chem. Eng. J.* **2011**, *166*, 30–39.

(12) Wang, H.; Prins, R. HDS of benzothiophene and dihydrobenzothiophene over sulfided Mo/γ-Al_2O_3. *Appl. Catal., A* **2008**, *350*, 191–196.

(13) Bettermann, I.; Staudt, C. Desulphurization of kerosene: Pervaporation of benzothiophene/*n*-dodecane mixtures. *J. Membr. Sci.* **2009**, *343*, 119–127.

(14) Hiyoshi, N.; Murakami, Y.; Yamaguchi, A.; Sato, O.; Rode, C. V.; Shirai, M. Purification of hydrocarbons from aromatic sulfur compounds by supercritical carbon dioxide extraction. *J. Supercrit. Fluids* **2010**, *55*, 122–127.

(15) Nieuwoudt, I.; du Rand, M. Measurement of Phase Equilibria of Supercritical Carbon Dioxide and Paraffins. *J. Supercrit. Fluids* **2002**, *22*, 185–199.

(16) Hottovy, J. D.; Kreamer, D. L.; Kohn, J. P. Three-Phase Liquid-Liquid-Vapor Equilibria Behavior of Certain Binary CO_2-*n*-Paraffin System. *J. Chem. Eng. Data* **1981**, *26*, 256–258.

(17) Henni, A.; Jaffer, S.; Mather, A. E. Solubility of N_2O and CO_2 in *n*-Dodecane. *Can. J. Chem. Eng.* **1996**, *74*, 554–557.

(18) Gardeler, H.; Fischer, K.; Gmehling, J. Experimental Determination of Vapor-Liquid Equilibrium Data for Asymmetric Systems. *Ind. Eng. Chem. Res.* **2002**, *41*, 1051–1056.

(19) Taylor, B. N.; Kuyatt, C. E. *Guidelines for evaluating and expressing the uncertainty of NIST measurement results*; NIST Technical Note 1297; NIST: Gaithersburg, MD, 1994.

(20) Guilbot, P.; Valtz, A.; Legendre, H.; Richon, D. Rapid On-Line Sampler-Injector: A Reliable Tool for HT-HP Sampling and On-Line GC Analysis. *Analusis* **2000**, *28*, 426–431.

(21) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(22) Wong, D. S. H.; Sandler, S. I. A Theoretically Correct Mixing Rule for Cubic Equations of State. *AIChE J.* **1992**, *38*, 671–680.

(23) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; pp A6, A17

(24) Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*; William Andrew: New York, 2008; p 38.

(25) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.