

# Modeling Study of CO<sub>2</sub>-Induced Asphaltene Precipitation<sup>†</sup>

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The insolubility of asphaltenes in light paraffin liquids and other incompatible fluids, such as carbon dioxide (CO<sub>2</sub>), is a source of problems during crude oil production operations. Asphaltene precipitation can cause formation damage and wellbore plugging, requiring expensive treatment and cleanup procedures. In the presence of light gases, such as methane, ethane, propane, and nitrogen (N<sub>2</sub>), asphaltenes are usually more stable as pressure and temperature increase; however, experimental measurements indicate that, in the presence of CO<sub>2</sub>, asphaltenes become more stable as the temperature decreases. In this work, the asphaltene phase behavior in a live reservoir fluid and a dead oil from South America is investigated in a range of pressures and temperatures in the presence of CO<sub>2</sub> using the perturbed chain–statistical associating fluid theory (PC–SAFT) equation of state (EoS). This thermodynamic model has been applied to asphaltene precipitation with different crude oil systems, such as those that involve methane, ethane, or N<sub>2</sub>. Simulation results using the PC–SAFT EoS model are in good agreement with experimental measurements. A thermodynamic analysis using a model live oil confirms and explains a crossover behavior observed in the simulation of the precipitation onset with CO<sub>2</sub>. Simulations show that CO<sub>2</sub> can act as an inhibitor or a promoter of asphaltene precipitation depending upon the range of temperature, pressure, and composition studied. At fixed pressure and live oil composition, CO<sub>2</sub> addition increases the asphaltene stability below the crossover temperature, whereas above this point, the asphaltene becomes less stable when the CO<sub>2</sub> concentration is increased.

## Introduction

Carbon dioxide (CO<sub>2</sub>) flooding has been used as a commercial process for enhanced oil recovery (EOR)<sup>1</sup> since the 1970s. Significant amounts of residual oil can be recovered by this procedure. In tertiary oil production, many light and medium reservoirs are subjected to miscible or near-miscible CO<sub>2</sub> flooding. In this process, CO<sub>2</sub> acts as a solvent, lowering the viscosity of the oil and making it mobile, thus significantly lowering the irreducible oil saturation. However, CO<sub>2</sub> flooding processes cause many changes in the flow and phase behavior of the reservoir fluids and can significantly favor the precipitation of asphaltenes.<sup>2,3</sup> Even though the literature is considerable on the subject, few studies have been reported on the simulation of asphaltene phase behavior changes caused by CO<sub>2</sub> addition.

Several experimental measurements have been reported in the last few decades. In 1997, Srivastava et al.<sup>4</sup> conducted static asphaltene precipitation tests for three samples of recombined crude oil (Weyburn reservoir fluid from Saskatchewan, Canada) using a high-pressure–volume–temperature (PVT) cell at the

reservoir temperature (138–145 °F). The reservoir fluid was reconstituted by recombining the separator oil and gas samples to a gas/oil ratio (GOR) of 107, 129, and 180 scf/bbl. The results from the mixtures indicate that the onset of asphaltene destabilization occurs at about 39–46 mol % CO<sub>2</sub> concentration for the three data sets. In 2003, Takahashi et al.<sup>5</sup> evaluated asphaltene precipitation during CO<sub>2</sub> injection using a crude oil from the Middle East carbonate reservoir. The onset pressure for this oil was measured in a PVT cell using a light-scattering technique with near infrared by gradually decreasing the pressure of the mixture at each predetermined CO<sub>2</sub> concentration. Their results showed that the amount of precipitated asphaltene became noticeable when the CO<sub>2</sub> mol % exceeded more than 50 mol %.

In 2005, Verdier et al.<sup>6</sup> studied the asphaltene phase behavior after injection of CO<sub>2</sub> into two dead oils (from South America and the Middle East) using a high-pressure cell and a filtration technique. They found that, as expected, asphaltenes were more stable as the pressure increased; however, for CO<sub>2</sub> injection, asphaltenes were more stable as the temperature decreased. The phase envelope of the Middle East crude was also investigated for a fixed CO<sub>2</sub> content (18 wt %). The same conclusions were found: the higher the pressure, the more soluble the asphaltenes, and the higher the temperature, the lower its solubility.

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To recreate this CO<sub>2</sub> asphaltene behavior, the perturbed chain–statistical associating fluid theory (PC–SAFT) thermodynamic model has been selected to simulate the precipitation boundaries as liquid–liquid equilibrium. This equation of state (EoS) has demonstrated its applicability to study asphaltene precipitation because of gas injection with different precipitants, such as methane, ethane, and N<sub>2</sub>.

**The PC–SAFT EoS Thermodynamic Model.** SAFT is a molecular-based EoS that has demonstrated its ability to accurately describe and predict the effects of large molecular-size differences and association on the phase behavior of complex mixtures.<sup>7</sup> Chapman et al.<sup>8,9</sup> derived the SAFT EoS by applying and extending Wertheim's first-order perturbation theory<sup>10,11</sup> to chain molecules. Gross and Sadowski<sup>12</sup> developed the perturbed chain modification of SAFT (PC–SAFT), by extending the perturbation theory of Barker and Henderson<sup>13</sup> to a hard-chain reference. PC–SAFT employs a hard-sphere reference fluid described by the Mansoori–Carnahan–Starling–Leland<sup>14</sup> EoS. This version of SAFT properly predicts the phase behavior of high-molecular-weight fluids similar to the large asphaltene molecules.

In PC–SAFT, three parameters are required for each nonassociating component (all of the species considered in this work are nonassociating compounds). These parameters correspond to the diameter of each segment in a molecule ( $\sigma$ ), the number of segments per molecule ( $m$ ), and the segment–segment interaction energy ( $\epsilon/k$ ). The pure component parameters are determined to match the saturated liquid density and vapor pressure data of the pure components for several homologous series.<sup>7,12</sup> One advantage of the SAFT-based EoS is the ability to easily correlate the molecular weight dependence of the pure component parameters. Well-behaved correlations exist for  $n$ -alkanes and polynuclear aromatics between  $m$ ,  $\sigma$ ,  $\epsilon/k$ , and the component molar weight in PC–SAFT. In this way, the parameters for the pseudo-components in the oil can be determined on the basis of their average molar mass and the aromatic and  $n$ -alkane correlations. The parameters for asphaltenes are tuned to titration data at ambient conditions and/or to asphaltene precipitation onset data at reservoir conditions depending upon availability.

PC–SAFT describes the residual Helmholtz free energy ( $A^{\text{res}}$ ) of a mixture of nonassociating fluid as

$$\frac{A^{\text{res}}}{RT} = \frac{A^{\text{seg}}}{RT} + \frac{A^{\text{chain}}}{RT} = m \left( \frac{A_0^{\text{hs}}}{RT} + \frac{A_0^{\text{disp}}}{RT} \right) + \frac{A^{\text{chain}}}{RT} + \frac{A^{\text{assoc}}}{RT} \quad (1)$$

where  $A^{\text{seg}}$ ,  $A^{\text{chain}}$ ,  $A_0^{\text{hs}}$ ,  $A_0^{\text{disp}}$ , and  $A^{\text{assoc}}$  are the segment, chain, hard-sphere, dispersion, and association contributions to the mixture Helmholtz free energy. The PC–SAFT association term is not used in this work because of the assumption that the molecular size and van der Waals interactions dominate asphaltene phase behavior in crude oil. The evidence obtained

**Table 1. Reservoir Fluid Characterization: Formation Reservoir “A”<sup>15</sup>**

measured depth (ft)	14 134
reservoir temperature (°F)	296
reservoir pressure (psia)	3256
bubble point pressure at 255 °F (psia)	3045
gas/oil ratio (scf/stb)	900
oil API gravity (deg)	32
wax content (% w/w)	12
cloud point (°F)	72
SARA contents (ASTM D4124-97)	
saturates (wt %)	57.4
aromatics (wt %)	30.8
resins (wt %)	10.4
asphaltenes ( $n$ -pentane insoluble) (wt %)	1.4

**Table 2. Reservoir Fluid “A” Composition<sup>15</sup>**

components	flashed liquid (mol %)	flashed gas (mol %)	monophasic fluid (mol %)
nitrogen	0.00	0.77	0.49
carbon dioxide	0.00	17.67	11.37
hydrogen sulfide	0.00	5.00	3.22
methane	0.00	42.49	27.36
ethane	0.14	14.54	9.41
propane	0.66	10.05	6.70
1-butane	0.23	1.13	0.81
$n$ -butane	1.48	4.11	3.17
1-pentane	1.17	1.26	1.22
$n$ -pentane	2.71	1.57	1.98
pseudo-C <sub>6</sub> H <sub>14</sub>	5.32	0.92	2.49
pseudo-C <sub>7</sub> H <sub>16</sub>	7.38	0.37	2.87
pseudo-C <sub>8</sub> H <sub>18</sub>	8.62	0.10	3.14
pseudo-C <sub>9</sub> H <sub>20</sub>	7.67	0.02	2.74
pseudo-C <sub>10</sub> H <sub>22</sub>	6.49	0.01	2.32
pseudo-C <sub>11</sub> H <sub>24</sub>	5.31	0.01	1.90
C <sub>12</sub> <sup>+</sup>	58.82	0.01	18.82
total	100.00	100.00	100.00
MW	229.21	31.69	102.04
mole ratio	0.3562	0.6438	
molar mass: C <sub>12</sub> <sup>+</sup>	337.98	167.11	337.94
density (g/cc): C <sub>12</sub> <sup>+</sup>	0.906		0.906

at this point<sup>16</sup> validates this assumption, leading to a simplified model with the minimum number of parameters.

**Reservoir Live Oil Investigation.** The effect of N<sub>2</sub> injection on asphaltene precipitation onset has been studied using reservoir live fluid “A”. Experimental and simulation results were previously reported.<sup>15,16</sup> This fluid was under production with primary depletion for more than 20 years; the reservoir performance indicated minimal aquifer support, and the reservoir pressure was expected to decline below the saturation pressure. An experimental study was carried out to evaluate the potential of improved oil recovery by pressure maintenance using N<sub>2</sub>. A summary of the reservoir “A” fluid properties and composition is provided in Tables 1 and 2.

The saturates, aromatics, resins, and asphaltenes (SARA) content indicates that the corresponding dead oil is saturate in nature (saturates > 50%) and that the asphaltene content is high enough that severe asphaltene problems are not expected (> 1%).<sup>17</sup> SARA values show a relatively stable fluid; however, these concentrations alone are not a complete indication for precipitation or deposition in the live system. Although the stock tank oil should be stable, the associated gas may cause

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**Table 3. PC-SAFT Characterization of the Live Sample at GOR = 900 scf/bbl**

	X <sub>mole</sub>	MW <sub>n</sub>	<i>m</i>	σ (Å)	ε/ <i>k</i> (K)
N <sub>2</sub>	0.004 95	28.01	1.2053	3.3130	90.96
CO <sub>2</sub>	0.145 83	44.01	2.0729	2.7852	169.21
methane	0.273 34	16.04	1.0000	3.7039	150.03
light	0.219 17	44.6	2.0546	3.6130	204.96
saturates	0.238 53	207.6	5.967	3.932	254.05
aromatics plus resins	0.117 50	270.5	6.473	3.87	332.52
asphaltenes	0.000 676	1700	29.5	4.30	392.56

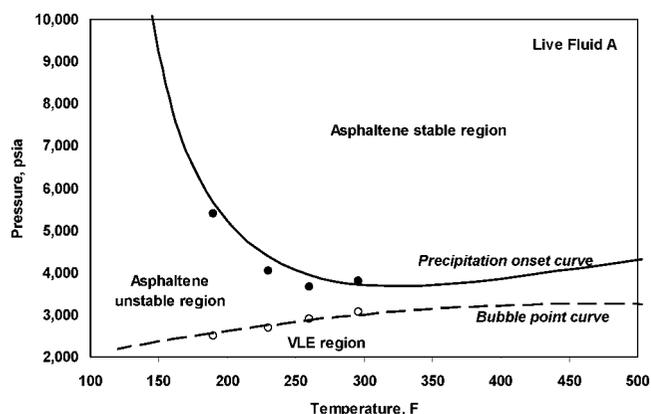
asphaltene precipitation under some conditions. All of these variables that drive asphaltene precipitation need to be integrated in a single model.

**Thermodynamic Model for Reservoir Fluids.** The PC-SAFT parameters for each pseudo-component (except for the asphaltenes) are determined from correlations with the average molecular weight. For instance, *m* for the saturates subfraction is obtained from a correlation of *m* with molecular weights of *n*-alkanes up to eicosane, and *m* for the aromatics and resins subfraction is obtained from a function of *m* with molecular weights of polynuclear aromatics and benzene derivatives.

The solid detection system (SDS) experimental technique was used to measure the condition for asphaltene precipitation.<sup>15</sup> Asphaltene parameters were then fit to meet experimental asphaltene precipitation onset measurements. The asphaltene parameters tuning procedure starts with the values determined in a previous work for a crude oil with similar API gravity.<sup>7</sup> These values were determined from titration with *n*-alkanes at ambient conditions. Then, light adjustments were made to match the onset at a high pressure/high temperature condition. Constraints such as the asphaltene solubility parameter, MW, and density are considered. The characterized asphaltene has a solubility parameter of 21.67 MPa<sup>1/2</sup> and a molar volume of 1442.6 cm<sup>3</sup>/mol, which corresponds to a mass density of 1.18 g/cm<sup>3</sup> for a MW of 1700 g/mol. This asphaltene is soluble in toluene at ambient conditions (concentration of 1 g/100 mL). Table 3 summarizes composition, molecular weight, and the PC-SAFT EoS parameters for each component and pseudo-component of the live sample.

Table 4 presents the binary interaction parameters determined by fitting binary vapor-liquid equilibrium (VLE) experimental data from the literature for each combination of the subfractions represented by a pure component. For example, the interaction parameter between light alkanes and saturates subfractions was estimated from the interaction parameter between propane and decane adjusted to VLE experimental data. The binary interaction parameters for asphaltenes are set equal to those for aromatics except for the asphaltene-N<sub>2</sub> binary parameter. This parameter was fit to experimental asphaltene precipitation data.

Figure 1 shows the agreement between experimental data and simulation results for fluid A, without gas injection. The simulation was performed using the values reported in Tables 3 and 4. The EoS accurately reproduces the bubble point pressures and the temperature dependence of the asphaltene



**Figure 1.** Onset of asphaltene precipitation and bubble points for reservoir fluid A. Experimental data were from ref 15.

precipitation pressure. Once we have proven that the experimental data can be well-correlated by the PC-SAFT EoS, we can study the effect of gas injection.

The asphaltene precipitation onset pressure increases when 10 mol % of either N<sub>2</sub> or methane is added to the original fluid as shown in parts a and b of Figure 2. We observe a different result upon the addition of 10 and 20 mol % CO<sub>2</sub>. As shown in Figure 2c, below a certain crossover, around 200 °F, the addition of CO<sub>2</sub> increases asphaltene stability compared to the original oil. Above this temperature, the asphaltene solubility decreases and the onset pressure goes to a minimum and increases at higher temperatures.

The addition of increasing amounts of gas at different temperatures was also simulated as shown in Figure 3. Experimental measurements obtained during the addition of N<sub>2</sub> to fluid A<sup>15</sup> are included in Figure 3b. Whereas the addition of methane and N<sub>2</sub> increases the precipitation onset pressure of a mixture at any temperature in the range studied, for CO<sub>2</sub>, this behavior is opposite at temperatures below the crossover point. The slope change in the precipitation onset curves predicted by PC-SAFT at decreasing temperature, above and below the crossover point, confirms the special behavior of CO<sub>2</sub>.

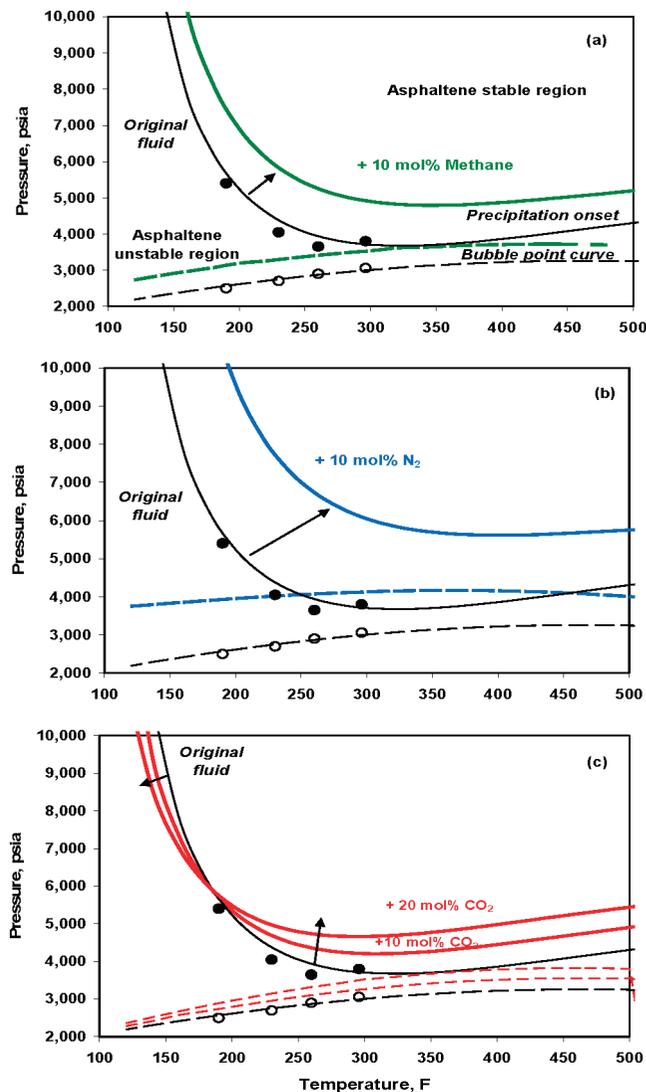
**Stock Tank Oil Investigation.** The effect of CO<sub>2</sub> addition on the asphaltene precipitation onset when added to dead oil was experimentally studied by Verdier et al.<sup>6</sup> The precipitation onset for two crude oils, from South America and the Middle East, was determined at different temperatures using a high-pressure cell and a filtration technique.

**STO Fluid Properties.**<sup>6</sup> The South American crude is a 27° API fluid with composition, molecular weight, and PC-SAFT parameter values for pseudo-components shown in Table 5. The binary interaction parameter values are kept as presented in Table 4.

Figures 4 and 5 present experimental and simulation results after the addition of 19 wt % of CO<sub>2</sub>. The effect on the precipitation onset and bubble point because of the addition of 3 wt % of N<sub>2</sub> and methane is presented in the same figure.

**Table 4. Binary Interaction Parameters (*k<sub>ij</sub>*)**

	<i>k<sub>ij</sub></i> values						
	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	light	saturates	aromatics plus resins	asphaltenes
N <sub>2</sub>		0.000	0.030	0.06	0.120	0.120	0.25
CO <sub>2</sub>			0.050	0.01	0.120	0.11	0.110
CH <sub>4</sub>				0.000	0.030	0.029	0.029
light					0.010	0.010	0.010
saturates						0.007	0.007
aromatics plus resins							0.000
asphaltenes							



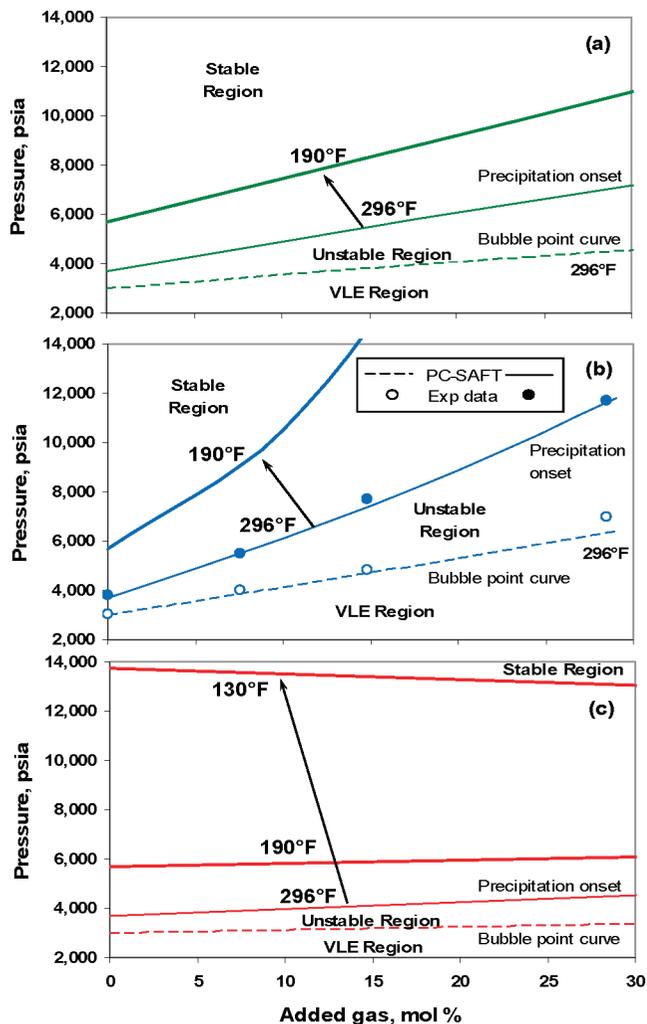
**Figure 2.** Fluid A phase behavior after the addition of (a) methane, (b)  $N_2$ , and (c)  $CO_2$ . The solid curves show the effect of gas addition. The dashed curves show the bubble point pressures of the original oil and oil with gas addition. Experimental data were from ref 15.

On the basis of these results, it is concluded that asphaltenes are more stable as the pressure increases; however, for  $CO_2$  injection, asphaltenes are more stable as the temperature decreases.

**Thermodynamic Analysis.** We have shown in previous examples that the  $CO_2$  injected to a crude oil (live or dead oil) can induce or prevent asphaltene precipitation; i.e., the  $CO_2$  can behave as an inhibitor or precursor of asphaltene precipitation, depending upon the temperature of the system for a fixed pressure and live oil composition. We have observed that, at temperatures below the crossover point, the  $CO_2$  acts as an inhibitor, whereas at temperatures above this point, it is a strong asphaltene precipitant. This dual effect is not observed with other gases, such as  $N_2$  or methane.

To elucidate this phenomenon and provide an explanation of this special behavior for  $CO_2$ , we propose a thermodynamic analysis based on the concept of the solubility parameter.<sup>18</sup> According to Hildebrand, two materials with similar solubility parameters gain sufficient energy on mutual dispersion to permit mixing.<sup>18</sup>

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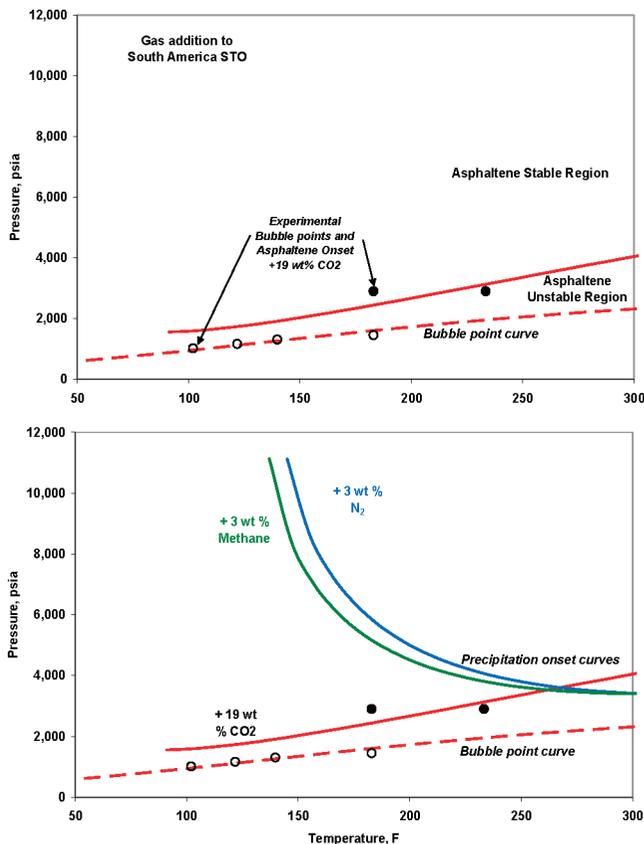
**Figure 3.** Temperature effect on asphaltene precipitation onset after the addition of (a) methane, (b)  $N_2$ , and (c)  $CO_2$  to reservoir fluid A at 190 and 296 °F. Experimental data were from ref 15. Lines represent simulations using the PC-SAFT EoS.

**Table 5. PC-SAFT Characterization of the South America STO Sample**

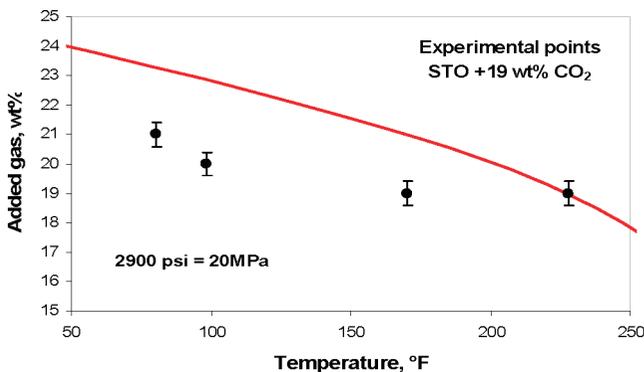
	wt (%)	MW <sub>n</sub>	<i>m</i>	$\sigma$ (Å)	$\epsilon/k$ (K)
saturates	35	160.4	4.984	3.899	246.95
aromatics	24	97.2	2.815	3.72	285.69
resins	32	670	6.473	3.86	253.00
asphaltenes	9	1700	29.5	4.30	395.00

To calculate the solubility parameters of the species involved, including the  $CO_2$ , and explain the effect of the solubility parameters in the stability of the mixture, we use a model live oil, which corresponds to a simplified version of a crude oil. The model live oil is composed of asphaltene, toluene, and precipitant. This representative oil version was originally studied and characterized by Ting et al.<sup>7</sup> The dead oil is composed by 1 g of C7-asphaltene/100 mL of toluene. The asphaltene molecular weight and specific gravity were found to be 4000 g/mol and 1.16, respectively. The model live oil was obtained by mixing 16.9 wt % of methane with the balance amount of dead oil. Parameters for toluene and other pure components are available in the literature,<sup>12</sup> and parameters for asphaltene were tuned to reproduce experimental data:  $\sigma = 4.05$  Å,  $\epsilon/k = 349.8$  K, and  $m = 75$ . The binary interaction parameter ( $k_{ij}$ ) for the methane-toluene pair was obtained from binary VLE data. In this case,  $k_{C_1\text{-total}} = 0.023$ .

Figure 6 shows good agreement between the simulation results and the experimental data for both the bubble point curve



**Figure 4.** Onset of asphaltene precipitation and bubble points for South America STO with 19 wt % of CO<sub>2</sub>. Experimental data from ref. 6. Lines represent simulations using the PC-SAFT EoS.

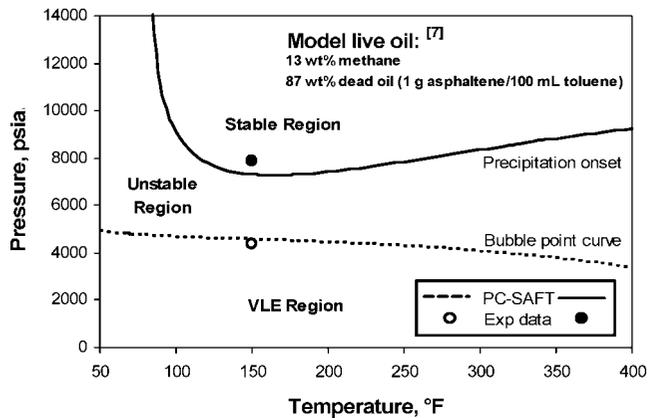


**Figure 5.** Amount of CO<sub>2</sub> added to a South America STO to reach the asphaltene onset. Experimental data from ref. 6. Lines represent simulations using the PC-SAFT EoS.

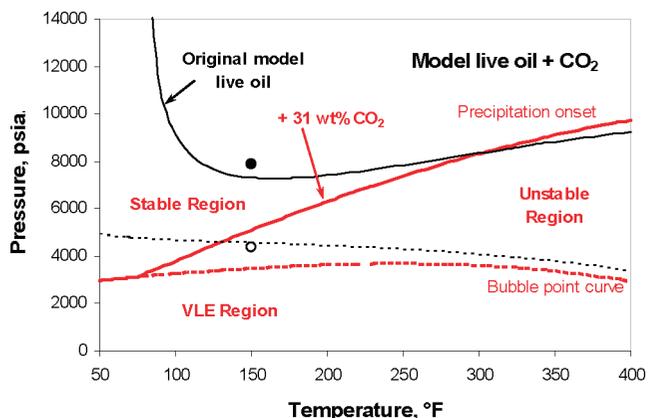
and the asphaltene precipitation onset for the model live oil described above.

After the addition of a certain amount of CO<sub>2</sub>, we observed a change in the corresponding *P-T* diagram, according to Figure 7. In this example, we arbitrarily added CO<sub>2</sub> to the live oil to a final concentration of 30.5 wt % of CO<sub>2</sub>. Because of this addition, the oil becomes stable at any pressure at temperatures below about 75 °F. Additionally, as we have discussed before, there is a crossover point when comparing both *P-T* diagrams. In this example, the crossover temperature is about 300 °F. This means that, if we add CO<sub>2</sub> at a temperature below 300 °F, the asphaltene becomes more stable, whereas the opposite behavior is obtained for temperatures above the crossover point.

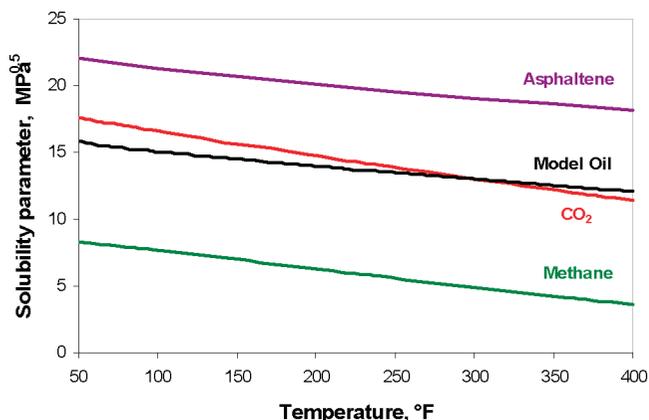
As we previously stated, this special behavior for CO<sub>2</sub> can be explained in terms of the solubility parameter concept. The solubility parameters for asphaltene, oil, CO<sub>2</sub>, and methane were



**Figure 6.** *P-T* diagram for a model live oil (asphaltene/toluene/methane). The points are experimental data, and the curves are calculations with the PC-SAFT EoS.



**Figure 7.** Comparison between the original live oil and the live oil after the addition of CO<sub>2</sub>. The oil becomes more stable at temperatures below 300 °F and less stable above this temperature.



**Figure 8.** Onset solubility parameters for different species as a function of the temperature.

calculated at the onset pressure as a function of the temperature using the PC-SAFT EoS. The results are plotted in Figure 8. According to simulation results, the solubility parameter of CO<sub>2</sub> is greater than the solubility parameters of the model oil at temperatures below 300 °F. Thus, adding CO<sub>2</sub> to the model oil at temperatures below 300 °F increases the solubility parameter of the mixture, and because of its increasing proximity with the solubility parameter of the asphaltene, the mixture becomes more stable. On the other hand, at temperatures above 300 °F, the solubility parameter of the oil decreases with the increasing amount of CO<sub>2</sub> added. In this case, the oil becomes unstable and the asphaltene readily precipitates. The solubility parameter

of methane is always lower than the solubility parameter of the oil; therefore, the injection of methane increases the oil instability at any temperature. For this reason, CO<sub>2</sub> can act as an inhibitor or a promoter of asphaltene precipitation, depending upon the temperature of the system, whereas methane is always a strong precipitant agent.

### Conclusions

(1) CO<sub>2</sub> addition to a crude oil can increase or decrease the stability of asphaltenes depending upon the characteristics of the fluid and temperature. The addition of CO<sub>2</sub> into a reservoir oil can cause asphaltene precipitation and deposition for temperatures above a certain crossover point; however, for lower temperatures, the addition of CO<sub>2</sub> increases asphaltene solubility. This behavior is different to what we observe for methane and N<sub>2</sub>. (2) The CO<sub>2</sub> behavior can be explained using the concept

of the solubility parameter. Below the crossover point, the solubility parameter of CO<sub>2</sub> is greater than the solubility parameter of the oil. Therefore, the addition of CO<sub>2</sub> under those conditions increases the solubility of asphaltene. Above the crossover temperature, the addition of CO<sub>2</sub> reduces the solubility parameter of the oil. (3) The PC-SAFT EoS accurately models the phase behavior of oils containing asphaltene and dissolved gases. The PC-SAFT thermodynamic model provides valuable insight into the phase behavior of these complex systems.

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