

Modeling Study of CO₂-Induced Asphaltene Precipitation[†]

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The insolubility of asphaltenes in light paraffin liquids and other incompatible fluids, such as carbon dioxide (CO₂), 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 (N₂), asphaltenes are usually more stable as pressure and temperature increase; however, experimental measurements indicate that, in the presence of CO₂, 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 CO₂ 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 N₂. 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 CO₂. Simulations show that CO₂ 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, CO₂ addition increases the asphaltene stability below the crossover temperature, whereas above this point, the asphaltene becomes less stable when the CO₂ concentration is increased.

Introduction

Carbon dioxide (CO₂) flooding has been used as a commercial process for enhanced oil recovery (EOR)¹ 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 CO₂ flooding. In this process, CO₂ acts as a solvent, lowering the viscosity of the oil and making it mobile, thus significantly lowering the irreducible oil saturation. However, CO₂ flooding processes cause many changes in the flow and phase behavior of the reservoir fluids and can significantly favor the precipitation of asphaltenes.^{2,3} Even though the literature is considerable on the subject, few studies have been reported on the simulation of asphaltene phase behavior changes caused by CO₂ addition.

Several experimental measurements have been reported in the last few decades. In 1997, Srivastava et al.⁴ 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 % CO₂ concentration for the three data sets. In 2003, Takahashi et al.⁵ evaluated asphaltene precipitation during CO₂ 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 CO₂ concentration. Their results showed that the amount of precipitated asphaltene became noticeable when the CO₂ mol % exceeded more than 50 mol %.

In 2005, Verdier et al.⁶ studied the asphaltene phase behavior after injection of CO₂ 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 CO₂ injection, asphaltenes were more stable as the temperature decreased. The phase envelope of the Middle East crude was also investigated for a fixed CO₂ 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 CO₂ 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 N₂.

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.⁷ Chapman et al.^{8,9} derived the SAFT EoS by applying and extending Wertheim's first-order perturbation theory^{10,11} to chain molecules. Gross and Sadowski¹² developed the perturbed chain modification of SAFT (PC–SAFT), by extending the perturbation theory of Barker and Henderson¹³ to a hard-chain reference. PC–SAFT employs a hard-sphere reference fluid described by the Mansoori–Carnahan–Starling–Leland¹⁴ 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 (σ), the number of segments per molecule (m), and the segment–segment interaction energy (ϵ/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.^{7,12} 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 , σ , ϵ/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 asphaltene 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^{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^{seg} , A^{chain} , A_0^{hs} , A_0^{disp} , and A^{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”¹⁵

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” Composition¹⁵

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 ₆ H ₁₄	5.32	0.92	2.49
pseudo-C ₇ H ₁₆	7.38	0.37	2.87
pseudo-C ₈ H ₁₈	8.62	0.10	3.14
pseudo-C ₉ H ₂₀	7.67	0.02	2.74
pseudo-C ₁₀ H ₂₂	6.49	0.01	2.32
pseudo-C ₁₁ H ₂₄	5.31	0.01	1.90
C ₁₂ ⁺	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 ₁₂ ⁺	337.98	167.11	337.94
density (g/cc): C ₁₂ ⁺	0.906		0.906

at this point¹⁶ validates this assumption, leading to a simplified model with the minimum number of parameters.

Reservoir Live Oil Investigation. The effect of N₂ injection on asphaltene precipitation onset has been studied using reservoir live fluid “A”. Experimental and simulation results were previously reported.^{15,16} 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 N₂. A summary of the reservoir “A” fluid properties and composition is provided in Tables 1 and 2.

The saturates, aromatics, resins, and asphaltene (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%).¹⁷ 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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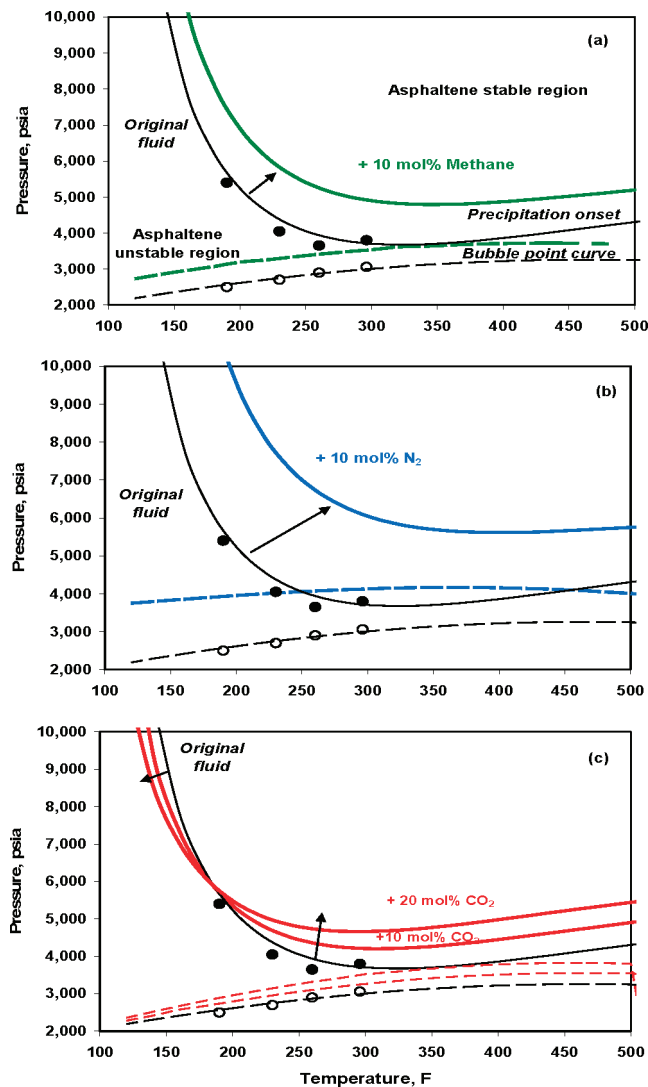


Figure 2. Fluid A phase behavior after the addition of (a) methane, (b) N_2 , and (c) CO_2 . The solid curves show the effect of gas addition. The dashed curves show the bubble point pressures of the original oil and oil with gas addition. Experimental data were from ref 15.

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.¹⁸ According to Hildebrand, two materials with similar solubility parameters gain sufficient energy on mutual dispersion to permit mixing.¹⁸

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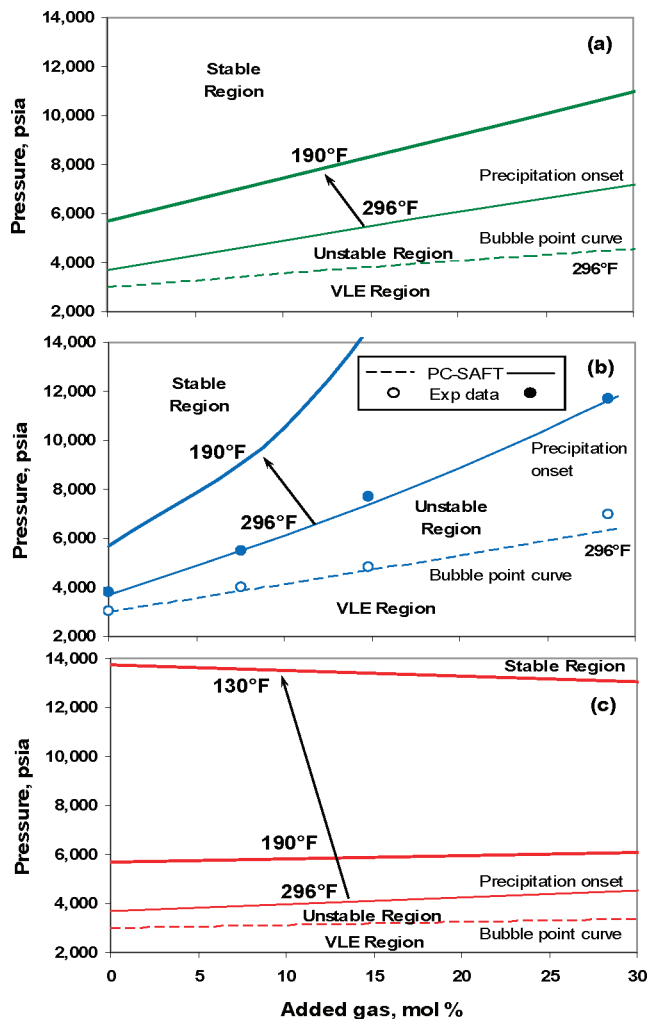


Figure 3. Temperature effect on asphaltene precipitation onset after the addition of (a) methane, (b) N_2 , and (c) CO_2 to reservoir fluid A at 190 and 296 °F. Experimental data were from ref 15. Lines represent simulations using the PC-SAFT EoS.

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

	wt (%)	MW _n	<i>m</i>	σ (Å)	ϵ/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.⁷ 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,¹² 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

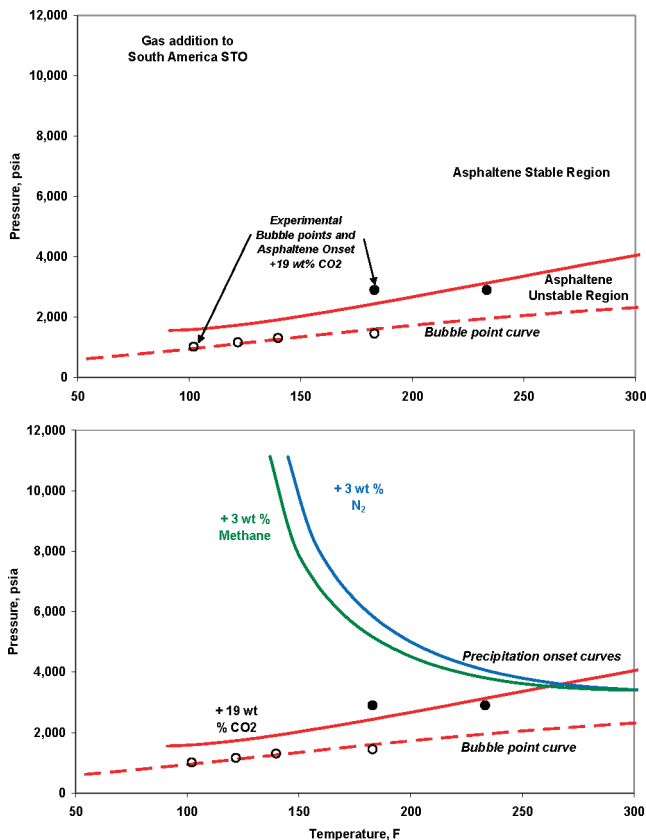


Figure 4. Onset of asphaltene precipitation and bubble points for South America STO with 19 wt % of CO₂. Experimental data from ref. 6. Lines represent simulations using the PC-SAFT EoS.

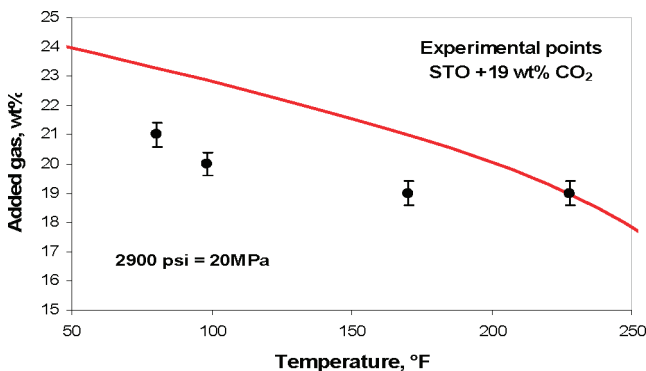


Figure 5. Amount of CO₂ added to a South America STO to reach the asphaltene onset. Experimental data from ref. 6. Lines represent simulations using the PC-SAFT EoS.

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

After the addition of a certain amount of CO₂, we observed a change in the corresponding *P-T* diagram, according to Figure 7. In this example, we arbitrarily added CO₂ to the live oil to a final concentration of 30.5 wt % of CO₂. 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 CO₂ 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 CO₂ can be explained in terms of the solubility parameter concept. The solubility parameters for asphaltene, oil, CO₂, and methane were

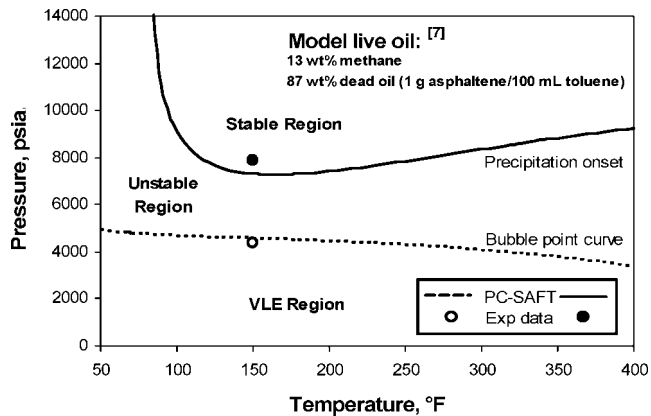


Figure 6. *P-T* diagram for a model live oil (asphaltene/toluene/methane). The points are experimental data, and the curves are calculations with the PC-SAFT EoS.

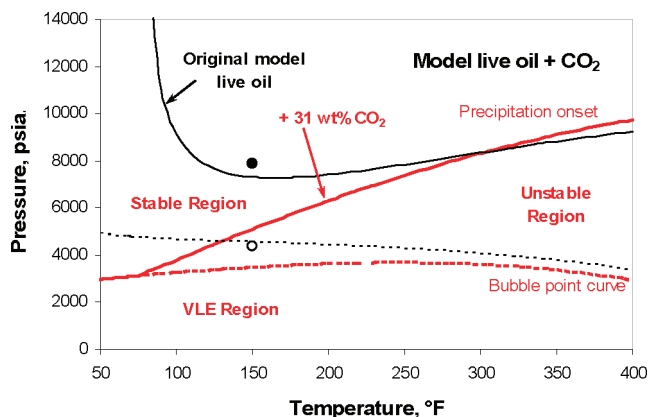


Figure 7. Comparison between the original live oil and the live oil after the addition of CO₂. The oil becomes more stable at temperatures below 300 °F and less stable above this temperature.

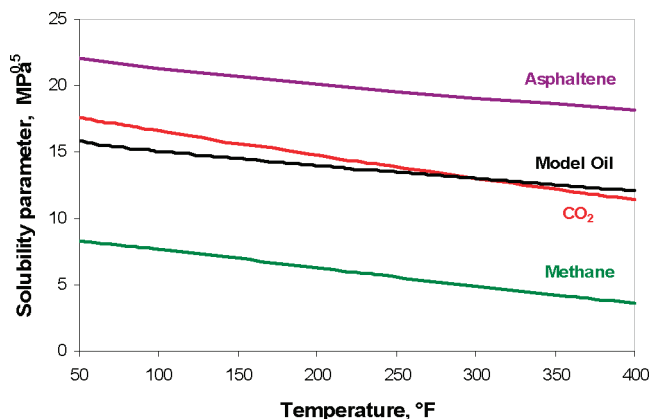


Figure 8. Onset solubility parameters for different species as a function of the temperature.

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 CO₂ is greater than the solubility parameters of the model oil at temperatures below 300 °F. Thus, adding CO₂ 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 CO₂ 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, CO₂ 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) CO₂ 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 CO₂ into a reservoir oil can cause asphaltene precipitation and deposition for temperatures above a certain crossover point; however, for lower temperatures, the addition of CO₂ increases asphaltene solubility. This behavior is different to what we observe for methane and N₂. (2) The CO₂ behavior can be explained using the concept

of the solubility parameter. Below the crossover point, the solubility parameter of CO₂ is greater than the solubility parameter of the oil. Therefore, the addition of CO₂ under those conditions increases the solubility of asphaltene. Above the crossover temperature, the addition of CO₂ 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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