

# Study of Asphaltenes Aggregation in Toluene/*n*-Heptane/CO<sub>2</sub> Mixtures under High-Pressure Conditions

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**ABSTRACT:** In this work, we present a novel experimental method to obtain an asphaltene precipitation envelope (APE) of complex systems composed of a mixture of toluene and *n*-heptane in the presence of CO<sub>2</sub> at high pressure and different temperatures. The method has the feasibility to detect phase changes of asphaltenes in a pressure range from 1 MPa to 100 MPa and temperatures from 283 K to 473 K. For the first time, a complete APE using experimental data was obtained. The solubility behavior of the asphaltenes with the pressure of the system is in agreement with previous studies. However, the temperature aggregation behavior at high pressure showed a minimum near 353 K that contrasts with reported data. This complex tendency can be explained by changes in viscosity, density, and aggregate composition with temperature. Also, the coexistence of two subfractions (denoted A1 and A2) in the asphaltenes and their differences in solubility modifies the solubility, and the entropy variation of the system can help to understand the asphaltene aggregation behavior at higher temperatures.

## INTRODUCTION

Asphaltenes are defined as the heaviest aromatic fraction of crude oil. This is soluble in organic solvents having solubility parameter values in the range of 17.5–21.6 MPa<sup>1/2</sup>, such as toluene, and it is insoluble in saturated hydrocarbons, such as *n*-heptane or *n*-pentane. Consequently, asphaltenes are considered as a solubility class of complex mixture of thousands of compounds, which are highly polydisperse, with a molar mass distribution ranging between 200 g mol<sup>-1</sup> and 1000 g mol<sup>-1</sup>.<sup>1,2</sup> From the molecular point of view, asphaltenes are represented by a mixture of polycyclic systems joined by flexible aliphatic chains, such as rosary- or archipelago-type molecules and condensed polycyclic structures, and bridging aliphatic rings or continental-type structure.<sup>3–5</sup> Acevedo et al. have presented evidence of two asphaltene subfractions using the *p*-nitrophenol (PNP) method.<sup>6,7</sup> One of these subfractions, called A1, has a low solubility in toluene at room temperature (0.05 g L<sup>-1</sup>) and a molar mass of ~2600 g mol<sup>-1</sup>.<sup>3,8</sup> Subfraction A2 has the usual toluene solubility of asphaltenes (between 57 and 100 g L<sup>-1</sup>, under the same conditions) and molar mass close to 1000 g mol<sup>-1</sup>. According to these results, the authors propose a model where asphaltene colloids could be represented by particles with a core rich in subfraction A1 and a periphery rich in solvent media and subfraction-A2-type molecules.<sup>9</sup> Fractal packing, mainly promoted by subfraction A2, allows the solvent penetration to the colloidal periphery, and this forms a barrier to inhibit the interaction of subfraction A1 particles and, therefore, asphaltene aggregation.<sup>6,10</sup>

The tendency of asphaltene to flocculate and precipitate in the presence of light liquid paraffin, such as *n*-heptane, and other incompatible fluids, such as carbon dioxide (CO<sub>2</sub>), is a well-known source of operational problems in the oil industry. Destabilization of asphaltene in crude oils can cause reservoir plugging, in the form of deposits in well production, generally around the bubble point depth or during the transportation and

treatment.<sup>11–14</sup> Therefore, it is important to study asphaltene aggregation at high pressure in the presence of CO<sub>2</sub>.

In recent years, applications of enhanced oil recovery (EOR)<sup>15</sup> have been widely used to improve oil recovery. One of the popular EOR procedures is the miscible-CO<sub>2</sub> flooding method. The CO<sub>2</sub> is more soluble in oil than water, so CO<sub>2</sub> acts as a solvent in this process,<sup>16</sup> reducing the oil viscosity and making it mobile.<sup>17</sup> However, CO<sub>2</sub> injection may cause undesirable effects that are favorable for phase separation of the asphaltenes.<sup>18,19</sup> Consequently, the precipitation of asphaltenes is a common event in most CO<sub>2</sub> flooding.<sup>18–22</sup> For this reason, the oil industry has employed efforts to have a practical tool that enables one to estimate asphaltene precipitation, especially under conditions of pressure and temperature during the CO<sub>2</sub> injection.

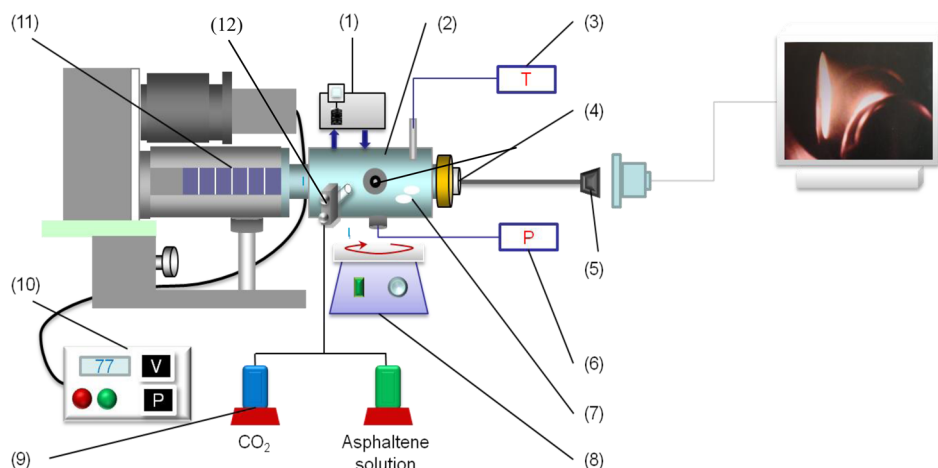
The aggregation behavior of asphaltenes, as a function of pressure, temperature, and composition, is a complex process and still not fully understood. Hence, there are various models reported in the literature for predicting the amount of asphaltene precipitation. Some of the developed models are based on Flory–Huggins polymer solution theory,<sup>23,24</sup> thermodynamic colloidal models<sup>11</sup> and thermodynamic micellization models,<sup>25,26</sup> and the application of advanced equations of state (EOSs).<sup>27–30</sup> However, application of these models to real samples requires an enormous amount of experimentation and time-consuming work to analyze the results.

Asphaltene-aggregated phase formation during the natural production process depends strongly on pressure and temperature.<sup>31</sup> The asphaltene phase behavior under reservoir conditions can be represented in a graph of pressure versus temperature. The asphaltene onset at high pressure and

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**Figure 1.** Experimental setup. Legend: (1) thermostat, (2) high-pressure cell, (3) thermometer, (4) sapphire windows, (5) endoscope, (6) pressure gauge, (7) magnetic bars, (8) magnetic stirrer, (9) high-precision balance with CO<sub>2</sub> mini-cylinder, (10) control panel, (11) mobile piston, and (12) valves.

temperature are used to draw a diagram that represents the phase stability.<sup>32</sup> This diagram has been called the asphaltene phase envelope (APE).<sup>31</sup> The first experimental study about the effect of pressure in asphaltene precipitation was made by Billheimer et al.,<sup>33</sup> in mixtures of bitumen with tetralin and using *n*-pentane as a precipitant. The authors reported a constant decrease in asphaltene precipitation with the increase of pressure.

Buenrostro-González et al.<sup>31</sup> studied the asphaltene precipitation through a series of high-pressure/high-temperature flocculation experiments in two Mexican crude oils. It was observed a dependence of the asphaltene onset with temperature from experimental APEs. This behavior was related to the increased asphaltene solubility with temperature, so the asphaltene onset requires extreme reservoir conditions to promote phase changes.

Verdier et al.<sup>34</sup> studied the asphaltene phase behavior after injection of CO<sub>2</sub> in two dead crude oils (from South America and the Middle East) up to 383 K and 60 MPa, using a high-pressure cell with a filtration technique to remove the asphaltene that has precipitated. For both crude oil samples, the asphaltene was shown to be more stable at high pressure and low temperature.

González et al.<sup>35</sup> has reported that CO<sub>2</sub> can destabilize or stabilize asphaltene in oil, depending on the temperature of the system. They observed a CO<sub>2</sub> inhibition effect on asphaltene precipitation with temperature in the temperature range of 311–533 K. This phenomenon may be explained by changes in the solubility parameter of CO<sub>2</sub> at ~422 K. At this temperature, the solubility parameter of the mixture increases and the asphaltene become more stable. On the other hand, at temperatures above this point, the solubility parameter of CO<sub>2</sub> is lower than the crude oil and causes precipitation of the asphaltene.

At this point, and according to the literature, it is important to note that the stability of the asphaltene, in the presence of CO<sub>2</sub>, is proportional to the pressure (i.e., at high pressure, the asphaltene are more soluble). However, the temperature effect on asphaltene behavior is a subject of controversy. There are three reported tendencies: (a) an increase in asphaltene solubility with temperature, (b) a decrease of the solubility with temperature, and (c) a temperature crossover point, where the CO<sub>2</sub> can act as a flocculation inhibitor or as an asphaltene

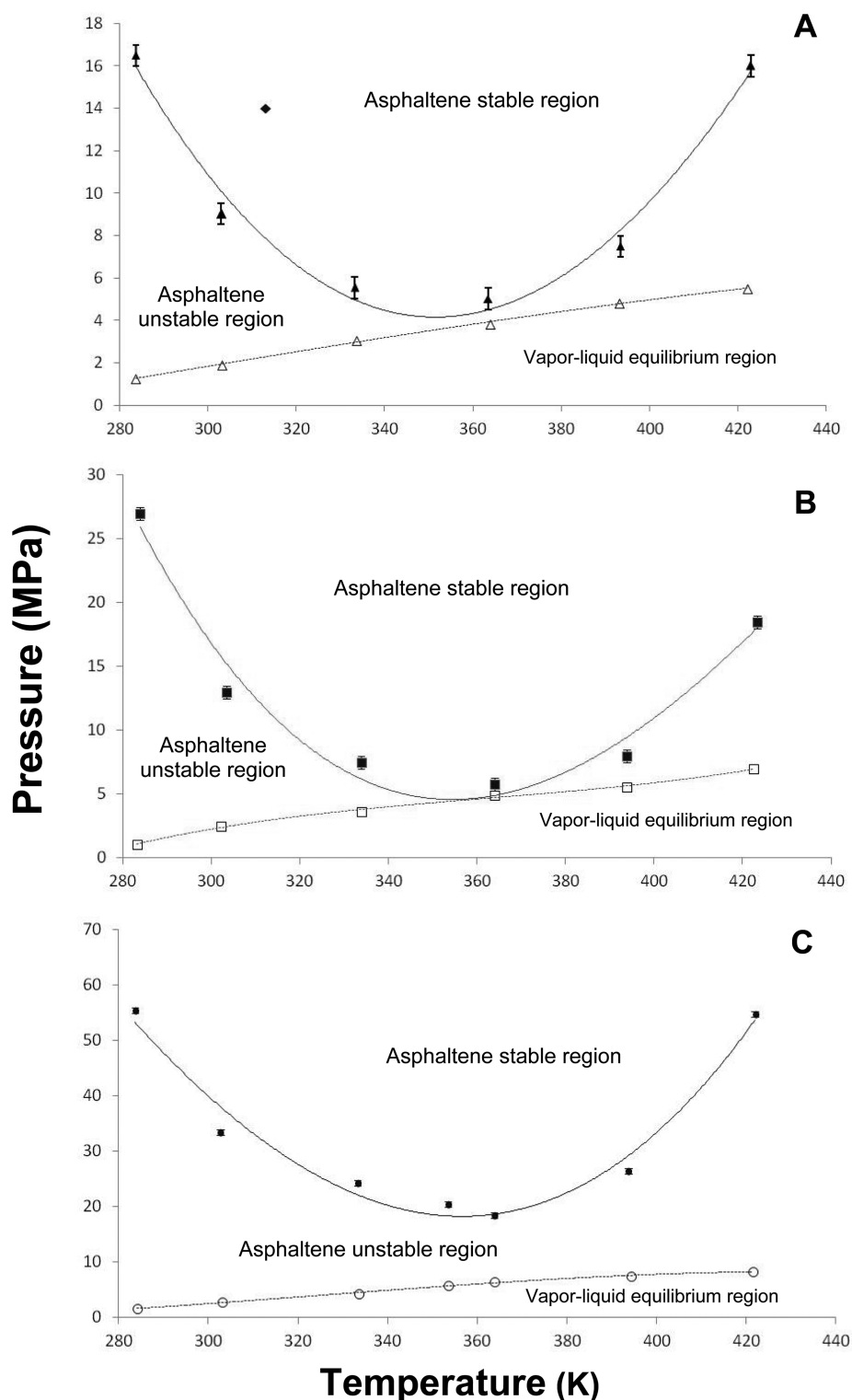
precipitant. From our point of view, all these tendencies are correct and dependent on pressure and crude oils properties. These effects are derived from the complex nature of asphaltene subfractions.

Given all of the aforementioned information, the main goal of this work is to study the asphaltene phase behavior in the presence of CO<sub>2</sub> at high pressures, as function of the temperature. In this effort, we present a complete set of this type of experimental data at high pressures and temperatures. The sample involved asphaltene extracted from a Venezuelan unstable crude oil dissolved in a toluene:*n*-heptane mixture (Heptol) (used as a synthetic model oil).<sup>21</sup> The asphaltene flocculation onset of solutions with 10, 15, and 20 wt % CO<sub>2</sub> were studied. The temperatures varied in the range of 283–423 K, using an especially designed high-pressure cell system. Results reveals a critical temperature value of ~353 K. Also, data showed an interesting behavior of the asphaltene with temperature at pressures above the bubble point. These results are strongly consistent with recent reports on the influence of subfractions A1 and A2 in the asphaltene aggregation model.<sup>10,31,36,37</sup>

## EXPERIMENTAL SECTION

**Experimental setup.** Figure 1 presents a simplified scheme of the experimental setup used in this work. It was provided by Top Industries (Paris, France) and allows visual detection of the asphaltene flocculation onset and the bubble point. The setup can be divided into three main parts. The first one corresponds to an automated high-pressure cell (denoted as “2” in Figure 1), designed to work at a maximum pressure of 100 MPa and temperatures up to 473 K. The volume of the cell is controlled by a mobile piston (denoted as “11” in Figure 1), to adjust the volume between 7.85 cm<sup>3</sup> and 35.2 cm<sup>3</sup>, and it automatically reaches the pressure at the equilibrium condition of the system. The cell is equipped with two sapphire windows (denoted as “4” in Figure 1) to give full visibility of the fluids inside.

The second part involves a high-pressure container made of carbon fiber and a high precision balance (denoted as “9” in Figure 1) to weigh the gas injected at pressures not exceeding 30 MPa. Finally, a display system allows detection of asphaltene flocculation onset. This part consists of an analogical camera coupled to an endoscope (denoted as “5” in Figure 1) parallel to cell axis. The cell has two sapphire windows: one of them is for visual inspection by using the endoscope, and the other sapphire window, oriented 90° from the other, is present to illuminate the inside of the cell, using a white light source. In addition, there are two valves (denoted by “12” in Figure 1)



**Figure 2.** Asphaltene phase envelope (APE) for Furrial asphaltene solution (concentration, 0.04 wt %; solvent, toluene:*n*-heptane (6:4)): (A) 10 wt % CO<sub>2</sub>, (B) 15 wt % CO<sub>2</sub>, and (C) 20 wt % CO<sub>2</sub>. Filled symbols represent the asphaltene onset points, and open symbols represent bubble points.

connected to the cell for sample and CO<sub>2</sub> gas introduction and removal.

The temperature in the cell was adjusted by a constant recirculating thermostatic bath of ethylene glycol mixture and controlled in a range of 283–473 K using a probe (denoted as “3” in Figure 1) (Pt 100, with an accuracy of 0.1 K). The pressures obtained with a Kulite pressure gauge (denoted as “6” in Figure 1) (HEM 375), which operates between 0.1 MPa and 100 MPa.

**Sample.** The APE study was performed with a sample from Furrial field in the Eastern Venezuelan Basin). This crude oil presents serious problems of asphaltene precipitation. Furrial crude oil has 4% asphaltene and 24° API. The asphaltene sample was obtained by precipitation with *n*-heptane from the crude oil, using a well-known method (ASTM IP-143).<sup>38</sup>

**Asphaltene Phase Envelope (APE).** APE were obtained from asphaltene solution prepared by dissolution in toluene:*n*-heptane

mixture (Heptol 4:6). This mixture has a similar Furril asphaltene flocculation onset (46 wt % of *n*-heptane) and is used as synthetic model oil. The asphaltenes concentration was fixed at 0.04 wt %. The APE was studied at three final concentrations of CO<sub>2</sub> added in the pressure cell: 10 wt %, 15 wt %, and 20 wt %, calculated based on 9 g of asphaltenes solution. These CO<sub>2</sub> quantities cover a wide range of possibilities: at low concentrations, no precipitation of particles was observed, and high concentrations, precipitation was obtained.

**Experimental Procedure.** Prior to any experiment, the cell and all the connecting lines was cleaned with toluene and light suction is applied to dislodge the solvent. For each analysis, 9.0 g of the asphaltene toluene:*n*-heptane solution was introduced at atmospheric pressure in the cell by using a positive-displacement piston. The temperature was increased to the selected work value. Then, the sample is pressurized by a negative (backward direction) piston displacement and it was equilibrated at the temperature of the cell after CO<sub>2</sub> is injected through the valves to the cell at constant pressure. The quantity of CO<sub>2</sub> injected into the pressure cell was determined by CO<sub>2</sub> weight difference of the mini-cylinder, using a high-precision balance.

Two magnetic bars were used for continuous stirring, to avoid the deposition of asphaltene particles. The pressure was increased to 60 MPa for 2 h to complete the fluids dissolution and allow the system to reach an equilibrium state. The latter was considered when the entire sample was dissolved. At this point, a constant negative piston displacement rate of 1.5 MPa min<sup>-1</sup> was used to decrease the pressure slowly and isothermally up to the desired pressure. The system then was placed in standby mode for 24 h, to ensure the equilibrium state and finally a visual inspection was made through the endoscope. The images from this endoscope permit a resolution on the order of micrometers. Each point on the APE curve was obtained at constant temperature from high pressure to low pressure, and the pressure was delimiting as a function of the appearance (or disappearance) of asphaltene particles (with a precision of ±0.5 MPa). In a similar way, the same was applied to the bubble point that corresponds to the pressure in which gas bubbles appear at each selected temperature.

## RESULTS AND DISCUSSION

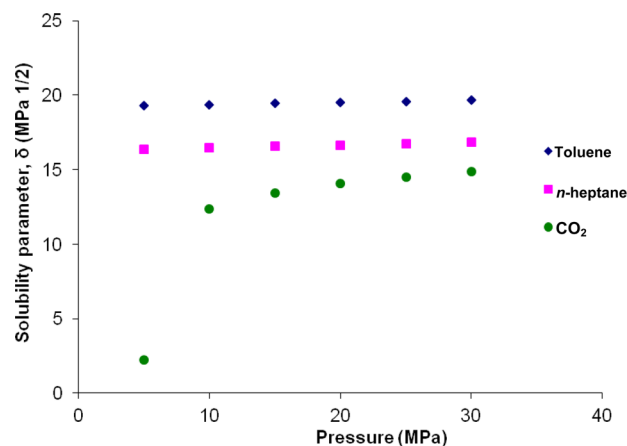
The first part of this study focuses on the selection of the working concentration to obtain the APE, given the complexity and opacity of the asphaltenes solutions, as well as the limitations of the experimental setup. The concentration was carefully chosen, based on the solution opacity, as the maximum value that allows the visual detection of asphaltene particles using the endoscope and white light illumination. For this, testing involved the passage of light through the cell having the asphaltenes solution ranging from 0.1 wt % to 0.05 wt %, in the presence of CO<sub>2</sub>. It was found that the maximum asphaltene concentration was 0.04 wt %.

Figure 2 presents APE curves obtained from an asphaltenes toluene/*n*-heptane solution at three CO<sub>2</sub> concentration (10, 15, and 20 wt %), while setting the temperatures in the range of 283–423 K. The continuous curves represent the asphaltenes precipitation values and define the stability area. Above this curve, the asphaltenes are dissolved in solution, and below this curve, they are precipitated. The dashed curves show the bubble point and define the vapor–liquid equilibrium zone.

Figure 2 also shows that the asphaltenes are more soluble at high pressure for all concentrations of CO<sub>2</sub>. For example, in Figure 2a, at 14 MPa bar and 313 K (diamond), the asphaltenes solution resides in a stable region. However, if the pressure drops (isothermally) to 8 MPa, asphaltenes precipitation onsets are obtained and two phases coexist in the system until the bubble point pressure is reached (dashed curve, 2 MPa). At this point, gaseous CO<sub>2</sub> starts to break free of the solution.

The above-described behavior was observed in all of the temperature ranges studied and for 15 and 20 wt % CO<sub>2</sub>

mixtures (see Figures 2b and 2c). Thus, it is possible to conclude that an increase in pressure enhances the asphaltenes stability, by increasing the solubility of the medium. This trend is consistent with the literature,<sup>31,34,35,39,40</sup> and it can be explained by changes in density and solubility parameters of all the components of the mixture during the process.<sup>39,41</sup> To illustrate this, Figure 3 shows the changes of solubility



**Figure 3.** Variation of the solubility parameter of toluene, *n*-heptane, and CO<sub>2</sub> with pressure at 303 K, theoretically calculated using the PR EOS.

parameter ( $\delta$ ) calculated for toluene, *n*-heptane, and CO<sub>2</sub> with pressure at 303 K. The  $\delta$  was calculated using the Peng–Robinson (PR) cubic EOS (eq 1).<sup>42</sup> The values to feed into the equation at different pressures and temperatures were obtained from the National Institute of Standards and Technology (NIST).<sup>43</sup>

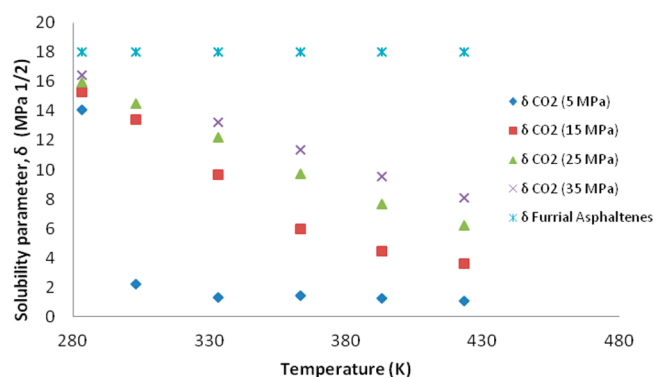
$$\delta^2 = \frac{\sqrt{2}}{4b} \left( a - T \frac{da}{dT} \right) \left[ \ln \left( \frac{V(T, P) + b(\sqrt{2} + 1)}{V(T, P) + b(\sqrt{2} - 1)} \right) \right] \left( \frac{1}{V(T, P)} \right) \quad (1)$$

It can be seen that insignificant variations of solubility parameter ( $\delta$ ) for toluene and *n*-heptane are observed with pressure; in contrast, the  $\delta$  value for CO<sub>2</sub> increases proportionally with pressure. Accordingly, this component of the mixture is responsible for the variations in the solubility parameter of the complete system toluene/*n*-heptane/CO<sub>2</sub>, particularly at pressures below 15 MPa. The solubility parameter of the mixture follows the rule of mixture in volume<sup>34,44,45</sup> and this is in agreement with eq 2; that is, when the CO<sub>2</sub> is present, the solubility parameter of the mixture decreases the asphaltene solubility, given that the solubility parameter reported for Furril asphaltenes is ~18 MPa<sup>1/2</sup>.<sup>9</sup> This effect is more significant when the pressure in the system decreases.

$$\delta_{\text{mezcla}} = \varphi_{C_7} \delta_{C_7} + \varphi_{\text{Tol}} \delta_{\text{Tol}} + \varphi_{\text{CO}_2} \delta_{\text{CO}_2} \quad (2)$$

The effect of temperature on the APE is very complex, in contrast to the results with pressure. The experimental values showed an increase of asphaltenes solubility for pressure values above the bubble point for temperatures up to 353 K. Over this point, the asphaltenes solubility started to diminish in all CO<sub>2</sub> concentrations. This tendency cannot be explained based only

on the solubility parameter of the mixture. In an attempt to try to explain this behavior, Figure 4 shows the variation of



**Figure 4.** Variation of the solubility parameters of CO<sub>2</sub> and Furrrial asphaltenes with temperature, using the PR EOS.

solubility parameter calculated for CO<sub>2</sub> and asphaltenes solutions, at different pressures, as a function of temperature. It can be noted that solubility parameter curve for CO<sub>2</sub> never intercepts the asphaltenes curve.

Generally, asphaltenes precipitation curves at high pressure presented in the open literature are simulated values of crude oils solutions using EOSs such as PC-SAFT. According to these models, the solubility parameter of CO<sub>2</sub> ( $\delta_{\text{CO}_2}$ ) below the threshold temperature is greater than the solubility parameter of crude oil ( $\delta_{\text{crude oil}}$ ). Therefore, the addition of CO<sub>2</sub> under pressure increases the solubility parameter of the mixture, so the asphaltenes solubility also increases. At higher temperature,  $\delta_{\text{crude oil}}$  decreases with the addition of CO<sub>2</sub> and the asphaltenes solubility decreases, leading to precipitation.<sup>35,40</sup> It is evident that experimental results do not match these computer-generated data.

The presence of critical temperature may be explained by taking into account the following aspects:

- An increase in temperature improves the miscibility, in the absence of specific intermolecular forces. Two fluids can be mixed easily at high temperature, because of the entropy of mixture contribution in the Gibbs energy.
- In contrast, an increase in temperature also causes a decrease in the density (and viscosity) of the liquids, and the fluid solubility parameter reduces the effective solvency. At constant temperature, the asphaltenes solubility decreases with the density of the solvent.

One can conclude that the observed solubility behavior is the result of the competition between two opposite phenomena: changes in entropy and changes in density. The former may be predominant at temperatures of <80 °C, and the latter controls the system at higher values.

Recent studies reported by Acevedo et al.<sup>10,36</sup> and Zanganeh et al.<sup>21</sup> also helps to clarify the effect of temperature on the high-pressure and high-temperature system. Our results are consistent with the solubility differences reported for the asphaltenes subfractions A1 and A2, hence the differences in molecular structure.<sup>21</sup> The first group of authors demonstrated that these asphaltenes subfractions have notable solubility differences. These subfractions are stable in solution, but any change in the solubility parameter of the medium may induce destabilization of the system. In this connection, our experimental APE behavior suggests that the solubility of

subfraction A2 increases with temperature, causing that A2 subfraction to drop out from the periphery of the particle into solution and, consequently, a decrease of asphaltenes aggregate size. At higher temperatures, the low solution viscosity and high entropy of the system promotes collisions between particles rich in subfraction A1 which are devoid of subfraction A2, allowing effective particle interactions between subfraction A1 low-solubility-type molecules, increasing the aggregation. Differences in the molecular structures of the asphaltenes could promote the attraction and interaction between molecules and increase the aggregation, flocculation, and deposition of asphaltenes.<sup>21</sup>

## CONCLUSIONS

For the first time, an asphaltenes precipitation envelope (APE) curve was constructed from direct experimental data. A high-pressure cell was used to study the effects of temperature (up to 423 K) and pressure (up to 55 MPa), in the presence of CO<sub>2</sub>, and a novel methodology was developed to detect the phase change. An increase in the pressure at constant temperature always leads to an increase in asphaltenes solubility and stability in the fluid. The critical asphaltene solubility and aggregation behaviors with temperature over the bubble point was observed at constant pressure. This tendency can be explained by changes in viscosity and density with temperature that may alter the asphaltenes aggregates composition, mixture miscibility, and the entropy of the system. Also, the differences between the solubility of subfractions A1 and A2 suggest that the aggregates present in solution are constituted by subfraction A1, so the asphaltenes stability in solution decreased at temperatures of >353 K.

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### Notes

The authors declare no competing financial interest.

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