

CO₂ influence on asphaltene precipitation

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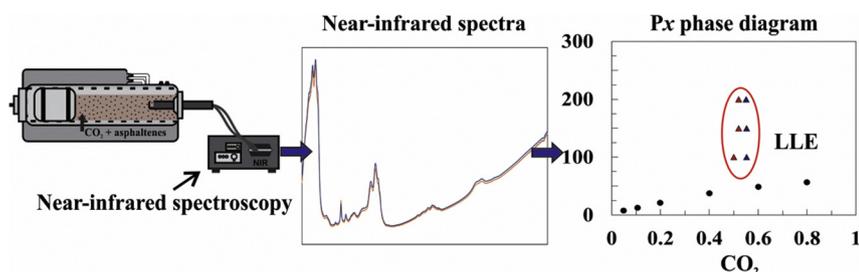
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GRAPHICAL ABSTRACT



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ABSTRACT

The energy industry has registered a considerable growth of petroleum production from reservoirs located in deep and ultra-deepwater, mainly in Brazil. The Brazilian Pre-Salt fields, specifically, have shown high carbon dioxide content which favors the precipitation of organic particles such as asphaltenes. This scenario has turned flow assurance into a major technical and economic challenge for the exploitation of those fields. In this work a variable-volume cell equipped with a near-infrared probe was used to study the onset of asphaltene precipitation induced by carbon dioxide, evaluating the effects of pressure, temperature, asphaltene concentration, and system composition. Furthermore, the Cubic Plus Association (CPA) was applied to model the asphaltene precipitation. The results show that temperature and the oil model system composition were the parameters that most influenced the asphaltene stability, and that the CPA adequately described the asphaltene precipitation.

1. Introduction

Asphaltene precipitation is a challenging problem that has created serious flow assurance problems to the oil industry during these last decades. This petroleum fraction is not chemically well-defined, presenting a compositional variety which is dependent on the origin of the oil. Therefore, it is typically accepted as a solubility class. Asphaltenes are classified as insoluble compounds in light hydrocarbons like n-pentane, n-heptane, and n-decane but soluble in aromatic solvents like

toluene, benzene, and xylene. They are formed by condensed aromatic rings which are surrounded by aliphatic chains and are the most polar as well as the heaviest (between 100 and 10,000 g mol⁻¹) components in petroleum. Asphaltenes also may contain heteroatoms of nitrogen, sulfur and oxygen in their molecules [1–6].

The asphaltene precipitation is induced by variations of thermodynamic conditions such as pressure, temperature, and composition changes during oil exploitation. The precipitation is responsible for clogging porous formation; porosity and permeability reduction of the

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reservoir; and damage in pumps caused by deposition [2,5,7]. In this scenario, the presence of carbon dioxide (CO₂) in oil reservoirs is a relevant issue to consider due to its potential to induce asphaltene destabilization. The high CO₂ contents in some reservoirs of the Brazilian Pre-Salt fields favor the asphaltene precipitation and deposition. Consequently, some studies have been carried out in order to evaluate the impact of carbon dioxide on the crude oil production [8,9].

Likewise, Loureiro et al. [10] analyzed the influence of CO₂ upon asphaltene destabilization in the model system through UV–vis spectroscopy as well as the efficiency of commercial additives (CAAS) as precipitation inhibitor. Zanganeh et al. [2] observed the effect of carbon dioxide on asphaltene precipitation with high-pressure microscopy. Shen & Sheng [11] evaluated the effect of CO₂ and CH₄ on asphaltene destabilization by filtration technique in oil samples taken from shale reservoirs. Most methodologies applied to study the impact of CO₂ on asphaltene precipitation process require sampling techniques and/or they are hard to implement in the petroleum industry.

In this scenario, near-infrared spectroscopy (NIR) arises as a potential tool for detection of asphaltene precipitation in crude oil. NIR is an analytical technique that has received great attention from the scientific community over the last decades due to a large amount of information that can be extracted from a spectra set. For instance, it has a good reproducibility; enables fast on-site and on-line analysis; and allows the analysis of materials in different conditions regarding shape, size and physical state [12,13]. The operation mechanism of NIR spectroscopy is based on the interaction between radiation and the molecules of the analyzed sample. Such interaction is registered by a variation on light absorption which, in turn, is related to the similarity between the infrared radiation and the electric field generated by the atoms interactions [14].

Borges et al. [15] used a NIR probe to detect phase transition of a system composed of CO₂ and distilled fractions from a Brazilian crude oil. The results highlighted the similarity between the phase transition data obtained through NIR and visual method. It proved the effectiveness of NIR for detecting vapor-liquid equilibrium. In addition, NIR has been successfully used to determine asphaltene precipitation onset. Aske et al. [16] studied the influence of pressure upon the asphaltene aggregation in model systems (toluene/pentane) and crude oil by using NIR chemometric analysis. Hassanvand et al. [17] evaluated the instability of asphaltenes in oil with NIR. Their focus was to study the effect of temperature on the precipitation onset at the temperature levels of 418.87 K, 416.15 K, and 363.15 K.

Further, it was highlighted by Bahrami et al. [18] that temperature may increase or decrease asphaltene precipitation depending on the counterbalance effect of density and solution entropy. Moreover, CO₂ seemed to be a strong precipitant at high temperatures. Soroush et al. [19,20], in turn, studied oil model system composed by mimetic and real asphaltene molecules. They reported that carbon dioxide acts as a co-solvent at low concentrations and as an anti-solvent at high concentrations for asphaltenes. Despite the considerable amount of published studies on asphaltene precipitation, the effect of CO₂ upon asphaltene stability at high pressures remains poorly studied and understood. Therefore, this work aims to study the influence of the variation of thermodynamic conditions (pressure, temperature, and composition) on the asphaltene precipitation induced by CO₂ in oil model systems. The asphaltene onset precipitation was detected by NIR and the Cubic Plus Association Equation of State (CPA) was applied to model the asphaltene precipitation.

2. Experimental

2.1. Materials

Asphaltene fractions were extracted from a Brazilian crude oil by using an n-heptane precipitation method based on the ASTM D6560/IP-143 procedure. Tables 1a and 1b presents the crude oil characteristics

Table 1a
Crude oil characteristics.

Properties	API gravity (°)	BSW (%)	TAN (mgKOH/g)	SARA composition (wt %)			
				S	A	R	A
Oil N	23.4	0.6	0.8	47.2	26.9	23.1	2.8

Table 1b
Elemental analysis (CHNS) for the asphaltene fraction.

Composition (wt %)	C	H	N	S	H/C
Asphaltene N1	82.8	8.7	1.6	1.1	1.3

as well as the asphaltene elemental composition. Carbon dioxide ($\geq 99.9\%$) and propane ($\geq 99.9\%$) were supplied by White Martins Praxair Inc. for the phase behavior studies. Toluene, n-heptane, and cyclohexane were obtained from Sigma-Aldrich Co. ($\geq 99\%$).

2.2. Experimental procedure

2.2.1. Oil model system

As aforementioned, the asphaltene extraction was based on the ASTM D6560/IP-143 procedure. The oil model solutions were prepared as a way to simulate crude oils with asphaltene concentrations of 500 ppm; 1,000 ppm; 5,000 ppm; and 10,000 ppm. The extracted asphaltene fraction was solubilized in toluene and sonicated by an ultrasonic bath for 30 min to ensure the complete solubilization. After that, the initial solution was left to rest for 15 h. Then, cyclohexane or n-heptane was added, and a new sonication step was carried out for more 15 min. The solutions of heptol (heptane + toluene) and cetol (cyclohexane + toluene) were prepared in an equivolumetric basis.

2.2.2. Phase equilibria data

The visual synthetic method, as well as near-infrared spectroscopy, were used to determine the CO₂ influence upon the asphaltene precipitation at high-pressure conditions. The experimental apparatus consisted of a high-pressure variable-volume equilibrium cell which was able to operate at pressures up to 300 bar and temperatures up to 373 K. A hollow stainless-steel cylinder consisted in the high-pressure equilibrium cell and had two sapphire windows on the sides, the near-infrared probe was inserted at one end and the other was closed with a movable piston. The movable piston was used to pressurize the system with the aid of a syringe pump (Teledyne ISCO 260D) filled up with propane. A J-type thermocouple with an uncertainty of 0.1 K was placed inside the cell to monitor the temperature, which was controlled by using a water bath (JULABO) connected to an aluminium jacket. A pressure transducer (NOVUS, TP HUBA) with the uncertainty of 0.1 bar was used to monitor the system pressure. Sensors were calibrated by using sensor references following ASTM standard methods (ASTM E230 e E2744). The equilibrium cell was equipped with a near-infrared transmittance probe connected to an FT-NIR spectrophotometer (Thermo Scientific model Antaris MX Process Analyzer) which operated in the spectral region of 10,000–4,000 cm⁻¹. It is worth mentioning that for the NIR transmittance mode, the infrared light is transmitted through the sample, then reflected by a mirror and retransmitted before being detected [21]. The apparatus used in this work was built according to previously published phase behaviour works [22,15] and it is presented in Fig. 1.

For the vapor-liquid equilibrium measurements, the system composition was prepared by adding a known mass (Shimadzu balance model AX 200, with an uncertainty of 0.0001 g) of equivolumetric solution of cyclohexane/toluene – cetol – into the equilibrium cell. Then, pre-defined amounts of CO₂ were added by using a syringe pump. The temperature was kept constant during the measurements (± 0.5 K). To

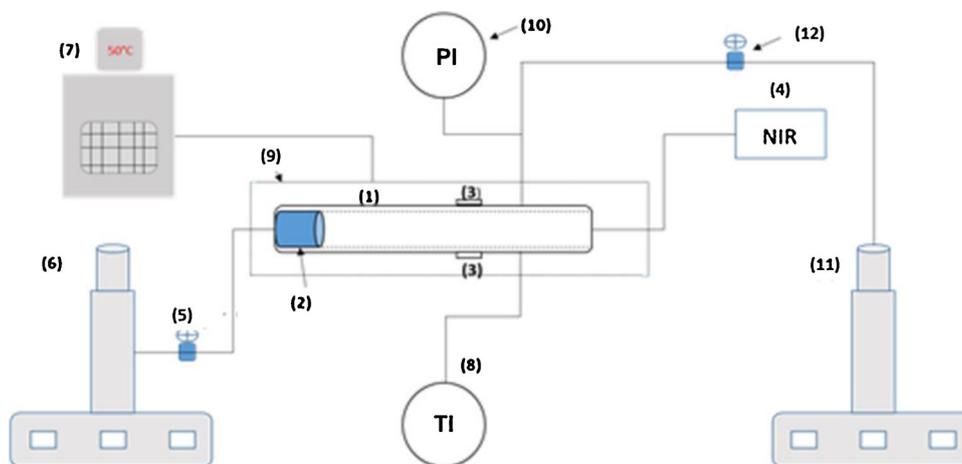


Fig. 1. Schematic apparatus: (1–3) variable-volume high-pressure cell; (4) near-infrared spectrophotometer; (5–6) pressurizing system; (7–9) heating system; and (10–12) CO₂ feeding system.

detect the phase transitions the system pressure was increased until a liquid-homogeneous phase was formed. Then, the pressure was reduced at a constant rate of 0.3 bar min⁻¹ until the appearance of the new phase. This procedure was repeated three times, at least.

For the asphaltene precipitation essays, the initial solution was the oil model system already described (2.2.1). A fixed amount of oil model solution was added into the cell and maintained at a constant pre-defined pressure (100, 175, 200, and 250 bar). Those pressure levels were selected in order to mimic the production conditions. A magnetic bar was used to promote a continuous homogenization. As soon as the defined pressure and temperature were reached, intermittent additions of CO₂ were made. For the visual method, the asphaltene precipitation was detected by a digital microscope (Dino-Lite Pro, AM-413FIT) with near-infrared LEDs (850 nm). Also, after each CO₂ injection, a near-infrared spectra set was collected to analyze the spectral behavior in order to determine the phase transition through the baseline changes. The NIR spectra were collected up to 30 min after each CO₂ injection. Considering the maximum useful volume of the high-pressure cell (50 mL), and that the carbon dioxide injection amount was around of 0.5 g in each step, it was estimated that uncertainty in the carbon dioxide molar fraction was around 0.01 in each solvent addition/measurement.

3. Phase behaviour modelling

The experimental results obtained in this work were modelled in the commercial software Multiflash™ to estimate the asphaltene precipitation onset as well as the vapor-liquid equilibrium. The thermodynamic model used was the Cubic Plus Association equation of state (CPA) which has been efficiently applied to describe undefined mixtures such as crude oil and petroleum fractions, and that can describe the solvation and association of asphaltenes molecules [18]. The model presents a physical term, based on the SRK EoS, as well as association term, based on perturbation theory, as applied with SAFT [23,24]. Interaction coefficients for asphaltene-asphaltene (K_{AA}) and asphaltene-resin (K_{AR}) were previously obtained with this model by Zhang et al. [25]. CPA is described by the following equations [26]:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \left(\frac{RT}{V_m} \right) \left(1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial (1/V_m)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

where P, T, and V_m are pressure, temperature, and molar volume, respectively. The association strength ($\Delta^{A_i B_j}$) between two sites belonging to two different molecules is related to X_{A_i}, which is the fraction of non-bonded A sites of molecule i with other active sites (site of monomeric

fraction) [27].

The non-bonded fraction, from the association term, is obtained from:

$$X_{A_i} = \frac{1}{1 + \frac{1}{V_m} \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (2)$$

with the association strength being obtained from:

$$\Delta^{A_i B_j} = g(V_m) b_{ij} \beta^{A_i B_j} \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) \right] \quad (3)$$

Where $\beta^{A_i B_j}$ and $\varepsilon^{A_i B_j}$ are the volume of association and energy of association, respectively. $g(V_m)$ is a radial distribution function.

Classical mixing rules were applied for the calculation of parameters (a and b) for mixtures.

$$a = \sum_{ij} \sqrt{a_i a_j} (1 - k_{ij}) x_i x_j \quad (4)$$

$$b = \sum_i b_i x_i \quad (5)$$

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

The version of the model here applied is the same as the one from Zang et al. [25]. Thus, a_i and b_i are pure component parameters given by the equations:

$$a_i = a_{ci} \alpha_i \quad (6)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (7)$$

The alpha function in Eq. 4 can use up to five parameters and is given by:

$$\alpha_i(T) = a_{ci} (1 + T'c_1 + T'^2c_2 + T'^3c_3 + T'^4c_4 + T'^5c_5)^2 \quad (8)$$

$$\text{where } T' = 1 - \sqrt{\frac{T}{T_{ci}}}$$

and

$$a_{ci} = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \quad (9)$$

where P_{ci} and T_{ci} are, respectively, the critical pressure and critical temperature of component i.

The alpha function parameters were fitted directly to saturation pressure data. To fit liquid densities a Péneloux type volume shift [28] must be used. However, in this work, only phase equilibria is analyzed, which is not affected by such an approach. Table 2 presents CPA parameters of the pure compounds. As none of the compounds studied

Table 2
CPA parameters of pure component.

Compound	a_c (Pa m ⁶ mol ⁻²)	b . 10 ⁵ (m ³ mol ⁻¹)	c_1	c_2	c_3	c_4	c_5	Ref.
cyclohexane	2.225	9.80	0.905	1.953	13.89	44.95	56.54	[44]
toluene	2.522	10.39	1.009	2.106	14.07	45.37	57.11	[44]
CO ₂	0.371	2.97	0.904	1.345	5.61	0.00	0.00	[44]

in this work are considered to be associative, no association term is applied, however the oil model system description can be used as feed data to develop a robust model to describe real system (petroleum/CO₂).

4. Results and discussions

As already mentioned, the so-called synthetic method was chosen for measuring the phase equilibria of the systems studied in this work. Due to its advantages when compared with analytical methods, the synthetic method is widely used for investigations that involve asphaltene stability in high-pressure conditions [29]. Aiming to validate the experimental apparatus, visual detection of phase transitions for a system composed of cyclohexane + toluene + CO₂ were carried out (Table S1). These measurements were compared with those performed by NIR spectroscopy according to the methodology proposed by Borges et al. [15]. Table 2 shows the comparison of the vapor-liquid equilibrium (VLE) data at the carbon dioxide molar fraction of 0.2 and 0.4 that was detected visually and spectroscopically. The equilibrium pressures measured by both methods do not present significant differences.

As this work aimed to detect asphaltene instability induced by carbon dioxide through NIR spectroscopy, it was also necessary to certify that the experimental apparatus was suitable for detecting phase transitions of dark fluids. At this step, the oil model solution was composed by 1,000 ppm of asphaltene in an equivolometric mixture (v/v) of cyclohexane and toluene. For the visual method, analysis of acquired images of the system were carried out to identify the appearing of asphaltene particles. At the same time, the spectroscopic detection was performed through the near-infrared light attenuation caused by the precipitated particles. Such attenuation degree is directly related to the flocculation level of asphaltene, as explained elsewhere [25]. However, it is not practical to evaluate the light attenuation magnitude only through a simple analysis of the spectra set, as can be seen in Fig. 2a. To overcome this limitation, chemometric tools were applied such as the sum of absorbances. Fig. 2b shows the sum of light absorbances at the wavenumber from 6,150 to 7,690 cm⁻¹ in function of the CO₂ concentration in the solution. The wavenumber range was selected in a spectral region that does not show absorbance peaks of the compounds present in the oil model system, and includes the wavenumber usually used for detecting asphaltene precipitation onsets (6250 cm⁻¹) [30].

Fig. 2b depicts a slight absorbance decrease caused by the decrease in density of the system as the concentration of carbon dioxide solubilized into the system was increased until the molar fraction of 0.42. When precipitated asphaltene particles were formed in solution, it was observed a sudden absorbance increase. Such particles were detected at a CO₂ concentration of around 0.46. It was also observed that a subsequent addition of CO₂ caused an increase in the slope of the diagrams due to the formation of precipitates in the system. This is linked to the increase in the number of asphaltene particles that precipitated, which ends up inducing a greater light attenuation [31]. Therefore, the asphaltene onset precipitation is defined henceforth as the molar fraction of CO₂ in which an increase of the near-infrared absorbance is noticed along time, i.e., when the system enters a dynamic state.

Fig. 3 presents the comparison of visual and near-infrared

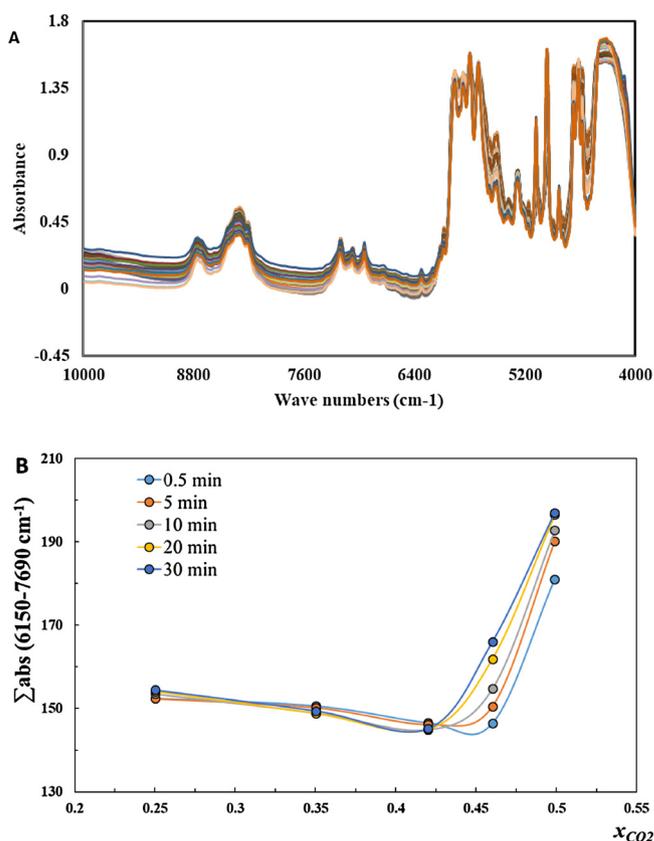


Fig. 2. Near-infrared detection of asphaltene precipitation at temperature and pressure conditions of 303 K and 100 bar, respectively. (A) Spectra set of oil model system composed by cyclohexane + toluene + asphaltene and carbon dioxide at a varied CO₂ molar fraction; (B) variation of the sum of absorbance at the wavenumber range of 6,150–7,690 cm⁻¹ in function of CO₂ molar fraction for the same model oil.

measurements at 303 K and 100 bar for the asphaltene concentration of 1000 ppm. NIR detected asphaltene precipitation before the visual method with a difference around of 0.05 M of CO₂. Such difference was observed due to the digital microscope's limitation in detecting small particles in dark systems. Further, the asphaltene precipitation onset will be analyzed herein in a P-x diagram in order to evaluate the thermodynamic parameters that rule the asphaltene precipitation induced by CO₂: pressure; temperature; asphaltene concentration; and, oil model system composition.

Fig. 3 also presents a comparison of vapor-liquid equilibrium data measured by both visual and NIR methods with good correlation between them. A previous study about the influence of asphaltene presence on this phase transition was performed. No significant influence was verified, most probable due to the low asphaltene concentration. In this way, experimental data for bubble point presented in this work is from cyclohexane/toluene/CO₂ system. Thus, the knowledge of vapor-liquid equilibrium data for the study allow ones to define temperature and pressure conditions in which the system remains in a single phase.

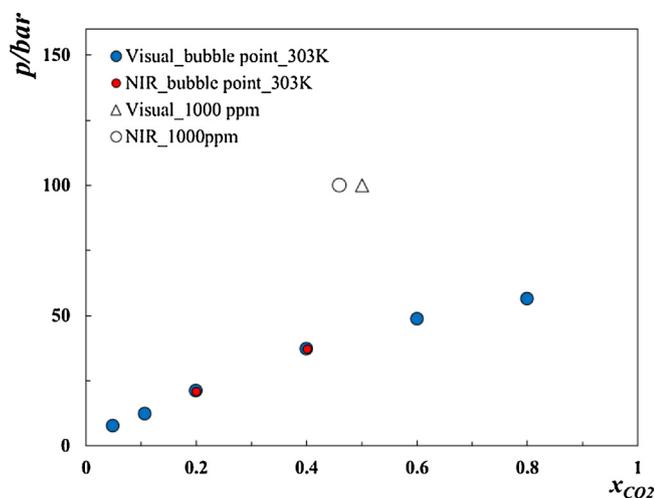


Fig. 3. pTx phase diagram for the systems with asphaltenes at 303 K and 100 bar. Comparison between visual and NIR detection for the systems cetol/ CO_2 (bubble point) and cetol/ CO_2 /asphaltene.

4.1. Pressure effect

The influence of pressure on the asphaltene stability was analyzed at the temperature of 303 K and asphaltene concentration of 1000 ppm, as reported in Table S2. Fig. 4 shows that the pressure of 100 and 250 bar did promote a slight increase in the asphaltene precipitation onset. It was observed that the concentration of carbon dioxide at which the asphaltene particles were detected for the lower pressure was of 0.46 and of 0.48 for the higher pressure. A possible explanation for the small influence of pressure is that the studied pressures are above the Lower Onset Point (LOP). Consequently, the pressure variation was not as relevant in model system as it has been verified for asphaltene stability in real crude oil system [32–34].

4.2. Temperature effect

Temperature is recognized as a relevant parameter for the asphaltene stability and has been object of several studies. In this work, the temperature influence upon asphaltene precipitation was studied at the pressure of 250 bar and two temperature levels: 303 and 348 K. These thermodynamic parameters were chosen in order to better emulate the reservoir conditions. Fig. 5 shows that the temperature enhancement improved the stability for the studied asphaltenes since more carbon dioxide was necessary to precipitate them. The asphaltene precipitation onset was of 0.48 for the lower temperature (303 K) and of 0.52 for the

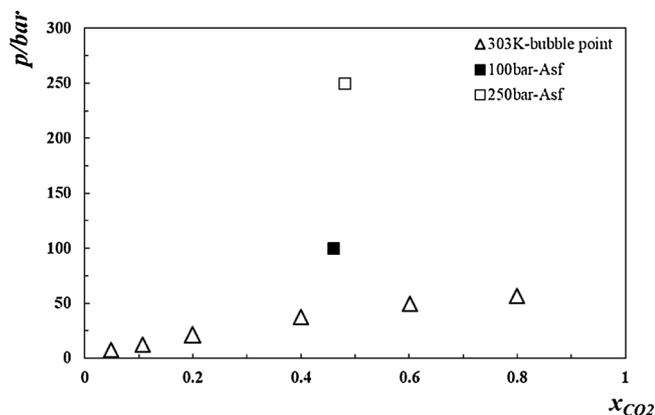


Fig. 4. Pressure influence on liquid-liquid equilibrium of asphaltene precipitation induced by carbon dioxide in a model oil system composed by cyclohexane + toluene + asphaltene at 303 K.

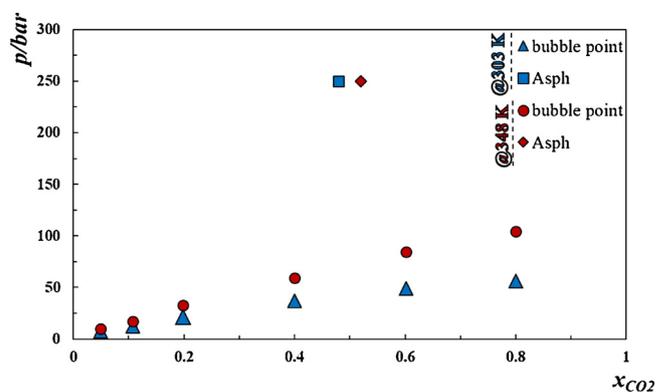


Fig. 5. Temperature influence on liquid-liquid equilibrium of asphaltene precipitation induced by carbon dioxide in a model oil composed by cyclohexane + toluene + asphaltene at 250 bar.

higher one (348 K).

The reason for the noticed higher asphaltene stability promoted by temperature is explained by the modification of interaction forces between CO_2 and asphaltene aggregates [35]. Although carbon dioxide molecules are usually considered non-polar, they present a dipolar moment that becomes more relevant conferring CO_2 a slight polar character at supercritical conditions. Since carbon dioxide is liquid at pressure and temperature conditions of 250 bar and 303 K, respectively, its non-polar behaviour reduces the asphaltene stability. On the other hand, the CO_2 is a supercritical fluid if the temperature is increased to 348 K at the same pressure. Hence, the polar-polar interaction among asphaltenes and supercritical carbon dioxide reduced the asphaltene precipitation extent. The results presented by this study are in accordance with other literature reports. According to Yang et al. [5], the balance of asphaltene-asphaltene attractive and repulsive forces explains the stabilization of asphaltene aggregates at higher temperatures. In such case, the temperature enhancement promotes a greater motion of the asphaltene aliphatic side-chains. It generates a repulsive force between asphaltene aggregates, thus avoiding the flocculation phenomena. This effect is also known as steric repulsion.

4.3. Effect of asphaltene concentration

The asphaltene concentration was evaluated at 1000; 5000 and 10,000 ppm at 175 bar and 343 K, respectively. The results are presented in Fig. 6 and Table S2. One can notice that the change in asphaltene concentration promoted a non-significant modification on the dynamic range of precipitation, which was around 0.45 for all cases. However, such concentration variation can cause structural changes in

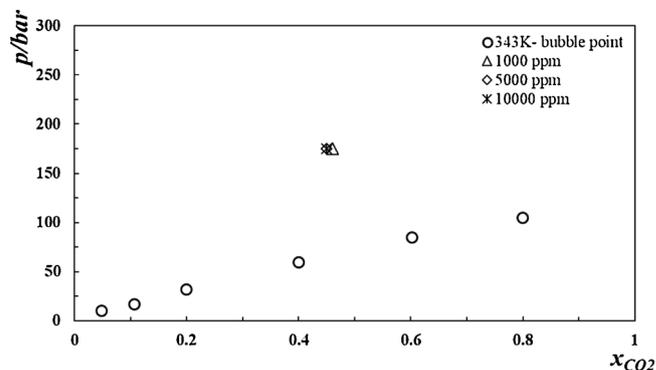


Fig. 6. Influence of asphaltene content on liquid-liquid equilibrium of asphaltene precipitation induced by carbon dioxide in a model oil composed by cyclohexane + toluene + asphaltene at 175 bar, 343 K, and asphaltene concentration of 1,000; 5,000; and 10,000 ppm.

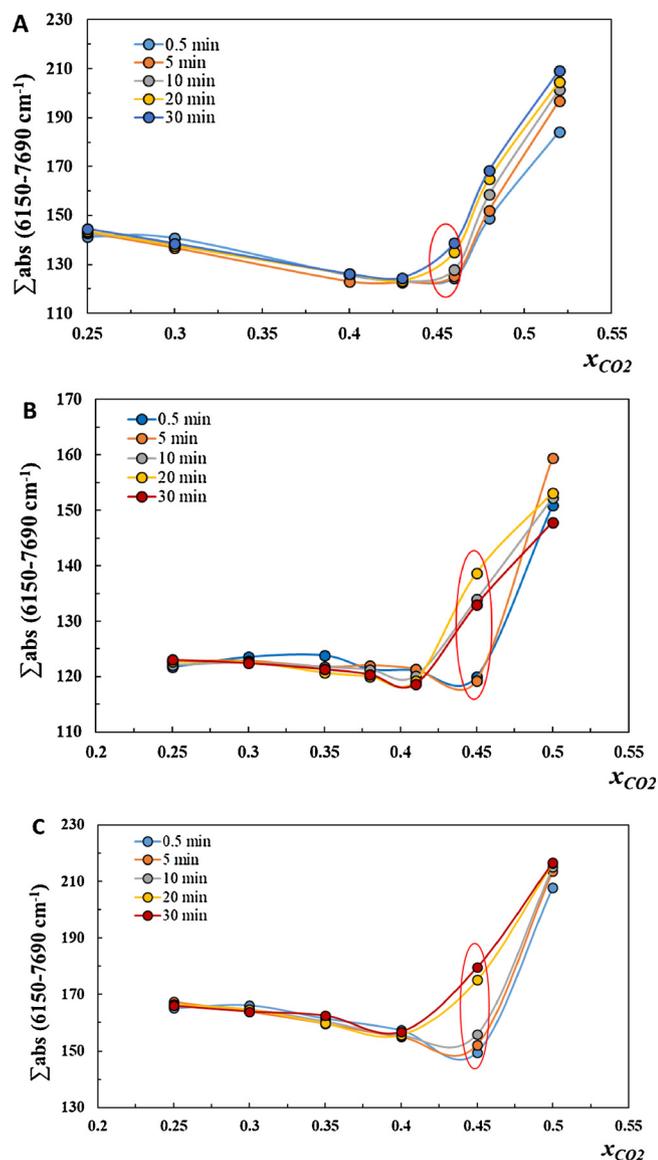


Fig. 7. Absorbance variation in function of carbon dioxide molar fraction for asphaltene precipitation onset in model oil (cyclohexane + toluene + asphaltene) with asphaltene concentration of (A) 1000 ppm, (B) 5000 ppm, and (C) 10,000 ppm at 175 bar and 343 K.

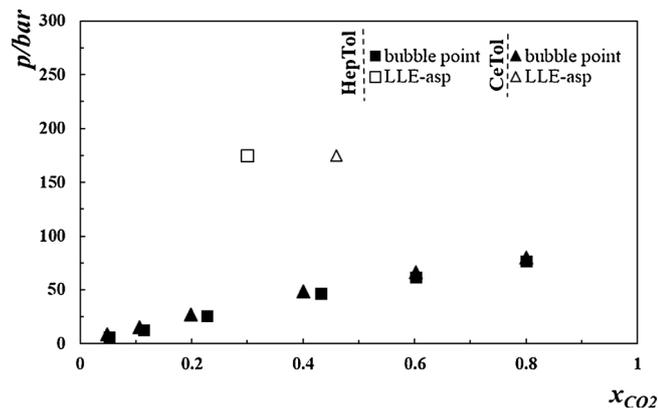


Fig. 8. Liquid-liquid equilibrium of asphaltene precipitation induced by carbon dioxide in two different model oils composed by cyclohexane + toluene + asphaltene and heptane + toluene + asphaltene at 175 bar and 343 K.

Table 3a

VLE-BP for CO₂ (1)/cetol (2) system at 303 K. Comparison between synthetic-visual (Pa) and spectroscopic (Pb) methods.

X _a (1)	P _a (bar)	X _b (1)	P _b (bar) /ε _{abs}
0,1997	21,0 ± 0,1	0,1984	21,2 ± 0,1
0,4005	37,3 ± 0,1	0,3997	37,1 ± 0,3

Table 3b

Pure component physical properties.

Compound	MM (g/mol)	T _c (K)	P _c (Pa)	ω
CO ₂ ^a	44.0098	304.128	7,377,300	0.223
Cyclohexane ^a	84.1614	553.56	4,070,000	0.209
Toluene ^a	92.1409	591.79	4104000	0.263

^a Multiflash™ database [44].

Table 4

Binary interaction parameters (k_{ij}) estimated for each temperature.

k _{ij}	303 K				%AAD
	CO ₂	Cyclohexane	Toluene	Asphaltene	
CO ₂	0	0.1093	0.1095	0.100	5.53
Cyclohexane		0	0	-0.050	
Toluene			0	-0.150	
Asphaltene				0	

k _{ij}	343 K				%AAD
	CO ₂	Cyclohexane	Toluene	Asphaltene	
CO ₂	0	0.1093	0.1095	0.150	1.85
Cyclohexane		0	0	0.000	
Toluene			0	-0.100	
Asphaltene				0	

asphaltene aggregates and consequently unbalance their attractive-repulsive forces equilibrium [36]. Also, the asphaltene diffusivity is enhanced by the concentration increase. As a result of it, the aggregation rate and flocculation extent are modified, as can be seen in Fig. 7. Fig. 7 also shows that the absorbance increase trend at the precipitation onset is greater for higher asphaltene concentrations. This was due to the presence of a larger number of precipitated particles which, in turn, promotes a bigger extent of light attenuation [37,38].

4.4. Oil model system composition

The influence of the oil model system composition upon the asphaltene stability was analyzed in order to simulate different crude oil types. Experiments were previous conducted using a mixture of cyclohexane and toluene as a representative oil system. A mixture of heptane and toluene (heptol 1:1 v/v) was also used under pressure of 175 bar and temperature of 343 K. The results are shown in Fig. 8. They point out that the replacement of cyclohexane by n-heptane lead to a marked difference in the asphaltene precipitation onset. Fig. 8 shows that n-heptane reduced the molar fraction of carbon dioxide required to trigger the dynamic precipitation from 0.46 to 0.3. The experimental data are reported in Table S2.

Mitchell & Speight [28,39] studied the influence of several solvents upon asphaltene stability and observed that the cycloparaffins like cyclopentane and cyclohexane presented solvency power similar to that of aromatic solvents, but distinct from n-alkanes such as pentane and heptane. Furthermore, Wang [40] reported that interactions between toluene and asphaltenes lead to an increase in the repulsive forces between asphaltene-asphaltene, that results in the stabilization enhancement of the asphaltenes in solution. In such scenario, the interaction

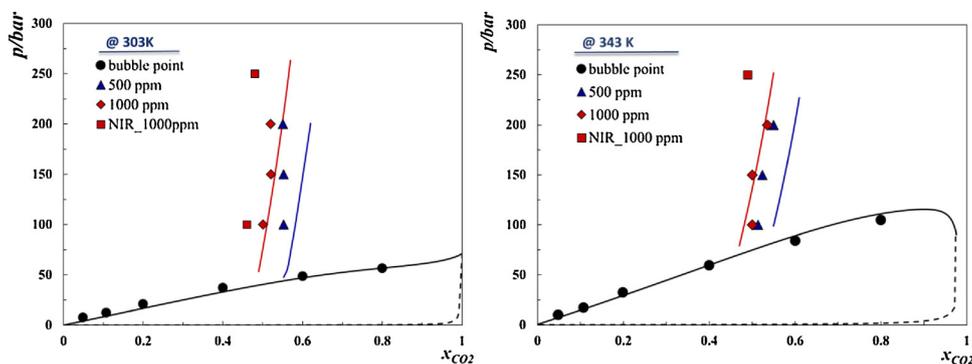


Fig. 9. pTx phase diagram for the systems CO_2 /cyclohexane/toluene/asphaltenes at 303 K and 343 K as well as asphaltene content of 500 and 1000 ppm. (■) NIR detection of asphaltene precipitation; (♦) visual detection/1000 ppm; (▲) visual detection/500 ppm; (●) bubble point of CO_2 /cyclohexane/toluene. The solid lines represent the CPA results applying temperature dependent binary interaction parameters (see Tables 3a and 3b).

between the asphaltene molecules are weaker than the asphaltene-solvent interactions, then preventing the particle precipitation [41]. On the other hand, it is recognized that heptane reduces the steric repulsion between asphaltene molecules. Hence, the increase in the asphaltene-asphaltene attractive forces caused by a higher alkane/toluene ratio in an oil model system enhances the asphaltene flocculation [36]. Therefore, heptane shows a greater precipitant potential for asphaltenes even in crude oil model systems.

4.5. Modelling

The phase behaviour of the model systems composed by cyclohexane + toluene + asphaltene + CO_2 was measured for the asphaltene concentrations of 500 ppm and 1000 ppm at pressures up to 250 bar and temperatures of 303 K and 343 K by the visual method, as reported in Table S3. The Cubic Plus Association Equation of State was adjusted to the experimental data by fitting the binary interaction parameters (k_{ij}) that better described the onset of asphaltene precipitation in each temperature. Table 3a and 3b shows the pure components physical properties and Table 4 presents the binary interaction parameters used in the CPA model for both temperatures. The critical properties of asphaltene component were estimated by Multiflash™ software as presented in Zhang et al. [25].

The calculated pTx diagram is presented in Fig. 9, where is possible to observe the asphaltene onset data. The model provides an excellent description of the bubble point curves and presented an absolute average deviation of less than 6% for the asphaltene onset precipitation data, correctly describing the effect of the asphaltene concentration upon its flocculation. A better model description of the asphaltene onset for real crudes would require a more detailed information on the asphaltene nature [42,43]. Due to that, it was needed to introduce relevant temperature dependences for the binary interaction parameters, in order to describe the phase equilibria.

5. Conclusions

Near-infrared spectroscopy was used to detect upper asphaltene precipitation onset in oil model systems induced by carbon dioxide. It was confirmed that after the first detectable asphaltene particle precipitates out of solution, the contact time between asphaltene and CO_2 rules the precipitation kinetics. The oil model system composition was the parameter that most affected the asphaltene stability among those studied.

Phase diagrams were modelled by the CPA equation of state. The model was shown to be capable of describing the asphaltene precipitation onset in good agreement with the experimental data.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.supflu.2018.08.005>.

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