

Paraffin effects on the stability and precipitation of crude oil asphaltenes: Experimental onset determination and phase behavior approach[☆]

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ABSTRACT

Asphaltene precipitation has been related with flow assurance problems in all the stages of crude oil production and processing. The destabilization of asphaltenes in crudes depends on temperature, pressure and composition variations. The latter variable was specifically studied in this work throughout compositional modifications of Brazilian dead oils, by adding three different paraffins on the crudes (*n*-hexadecane, docosane and a commercial paraffinic pool). These paraffins were firstly added in a crude oil, here named *P1* (16.5 °API, 6.34 wt % asphaltenes), and the resulting modified crudes were analyzed in terms of asphaltene yield and stability using *n*-heptane as precipitant. Asphaltenes precipitation onset was affected by the inclusion of all the paraffins tested in the same extension; at the maximum paraffin addition of 10 wt%, onset decreases by 5 ± 1 *n*-heptane wt %. Similar results were verified for other two different oils *P2* (17.7 °API, 6.29 wt% asphaltenes) and *P3* (16.7 °API, 1.55 wt% asphaltenes). The solids obtained from the different systems were analyzed by FT-IR spectroscopy, observing that the alkyl content of the asphaltenes was not affected by the inclusion of heavy paraffins. Precipitation behavior was evaluated by using literature reported thermodynamic models based on modifications of the Regular Solution Theory. This model reproduced qualitatively the experimental precipitation behavior and the asphaltene solvency affectation by paraffin addition in the crudes.

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1. Introduction

Asphaltenes are recognized as the heaviest and the most polar group of all crude oil components [1]. For decades, they have been related with industrial problems in all stages of crude production, transportation and refining [2–6]. Typically treated as a solubility group, asphaltenes could be defined as the fraction of crude oil normally soluble in aromatic solvents such as toluene and benzene, and insoluble in light paraffins such as *n*-heptane and *n*-pentane [1,7]. This definition includes a wide distribution of molecules types, chemical structures and properties [8,9], where the molecular weight of the individual molecules vary from 500 to 1000 Da [10].

Asphaltenes can aggregate and form nanosized particles, and those aggregates continue to grow to form clusters (normally 4–10 nanoparticles per clusters) that leads to their precipitation and deposition [9,10]. It is well known that asphaltenes precipitation could be related with pressure [11] or temperature changes [12,13], and also compositional variations in the crude oil [14–16]. Those events are normally observed during the pressure depletion in crude oil production. Crude oil composition changes could be also expected in crudes blending, usually used to improve crude oil properties, e.g., viscosity and light distillation cuts [17,18]. Blending incompatible oils, or crude oil with light or middle distillates (typically paraffinic), could also lead to asphaltenes precipitation due to crude compositional changes and a consequent reduction in the solvency of the resulted crude oil mixture [15,19].

In order to investigate the principles that governs asphaltene precipitation, several approaches have been used. In most of the cases, researchers normally add a paraffinic precipitant to dead oil samples (cooled and degasified crude oil) to induce the asphaltenes

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flocculation, trying to simulate the natural aggregation events that occurs industrially [11,20–22]. During crude oil production, this phenomenon is caused by the pressure depletion and possibly some asphaltenes could precipitate before reach surface facilities conditions. Adding a precipitant, e.g., *n*-paraffins (*n*-pentane, *n*-hexane, *n*-heptane) to a depressurized crude oil allows to force out of solution the remaining asphaltenes and consequently to study precipitation mechanisms involved [23].

Crude oil solvency could be affected its mixture with *n*-paraffins. Additionally, the chain length of the precipitant has an influence in the yield and properties of the precipitated asphaltenes. It has been reported that at high precipitant proportion, shorter *n*-alkanes increase asphaltenes precipitation yield [17]. When the chain length of the paraffin increases above 7 or 10 carbons, it has been shown that higher chain length paraffins could initiate the asphaltene precipitation at lower concentrations [24]. Based on this behavior, it has been considered that asphaltenes precipitation yield with *n*-alkanes decreases with the increase of the chain length until a minimum value, and then increases with the chain length of the paraffin. This kind of measurements has been performed using several detection techniques, especially to measure the minimum paraffin concentration that could be added to initiate the precipitation of asphaltenes in crude oil, which is the onset of asphaltene precipitation. Optical microscopy [25], light scattering [26], refractive index [27], centrifugation test [28], and UV–vis spectrophotometry [22] has been widely used for this purpose.

Solubility information of crude asphaltenes in different *n*-paraffins solvents, derived from the aforementioned tests, is commonly used to model the asphaltene precipitation as a phase transition in thermodynamic models [18,20,29]. Experimental precipitation yield curves are normally used to fit and adjust asphaltenes properties, such as molecular mass distribution, density or solubility parameters [30,31]. Fitted curves could be used to predict the asphaltene behavior in other conditions, such as variations in precipitating solvents, temperature and pressure [11,18,20,21].

Despite the fact that the asphaltenes solvency has been widely studied when used *n*-paraffins as solvent, the solvency effects of endogenous heaviest paraffins are still under revision. Solvency power of the crude is crucial in asphaltene stabilization, and it depends on the solubility contribution of each crude constituent [19]. In typical paraffinic oils, it is expected around 20 wt % of paraffin wax in its constitution, varying the carbon number from C15 to C60 [32–34]. It has been demonstrated that the asphaltenes and the paraffinic waxes of the crude oil interacts under synergic mechanisms that leads to solid precipitation [33,35,36]. Although the mechanism is still unknown, waxes can contribute to modify the asphaltene behavior [37] and could also coprecipitate as a solid complex of the mixtures [38]. A typical approach to investigate the parallel effects of precipitation of asphaltene and paraffins is the simplification to model solution [17,22] or solids mixtures [38], avoiding the natural solvency properties of others crude oil constituents.

The aim of this work is to evaluate the inclusion of heaviest paraffins as constituents of dead crude oil samples and to investigate their influence on asphaltene solubility and stability. Long chain paraffins, typical of paraffinic crudes, were integrated to crude oil samples, and the solvency for asphaltenes of the resulted modified oils was investigated by analysis of the asphaltene yield behavior using *n*-heptane as precipitant. Effects of heavy paraffins on the collected precipitated solids was also verified by FT-IR analyses, to obtain information of eventual wax coprecipitation with asphaltenes solids. Asphaltenes precipitation, from unmodified crudes samples and paraffinic modified oils, was modelled thermodynamically using a phase equilibria approach and a Regular

Solution based model, which was used to evaluate the solvency effects of the different paraffins tested.

2. Materials and methods

Three different Brazilian crude oils were modified with paraffins and the asphaltene yield and precipitation onset were determined using *n*-heptane as precipitant. The procedure for crude characterization, paraffin incorporation and asphaltenes solubility test are described in the following sections. Asphaltenes precipitation behavior was modelled using modifications of the Regular Solution Theory also described below.

2.1. Crude oil samples and characterization

Three different crude oils supplied by Petrobras were used in this work, namely *P1*, *P2* and *P3* respectively. These oil samples were pretreated and characterized before paraffin addition. Crudes thermal history was erased by heating the samples until 60 °C for 4 h. In the same way, dissolution of possible wax crystals and evaporation of light ends were attempted as a result of the heating [39]. Subsequently, API gravity and viscosity at both 20 and 60 °C were analyzed using an Anton-Paar SVM 3000 viscodensimeter. This equipment was equipped with a density measurement cell using the U-tube principle with an uncertainty of 0.0001 g/cm³. Measurement of viscosity was performed based on a modified Couette principle, with a small volume (2.5 ml) measurement cell composed by to rotating tubes, ones of them rotating at constant speed around the sample and another bob which rotates more slowly, allowing to measure viscosity with an 0.1% accuracy and a repeatability error of 2%. Calibration of the equipment was made with standard oils (CN-6773) supplied by Anton-Paar. From viscosity analyses, wax appearance temperature (WAT) has been determined, by finding the temperature that intercept two different linear region on the logarithm of the viscosity and the inverse of the absolute temperature plot [40,41].

As part of the crudes characterization, asphaltene content was measured following a single stage *n*-heptane addition stated by Alboudwarej et al. [42] and briefly described here. A 3 g sample of pretreated crude was mixed with *n*-heptane at 1:40 ratio (g:cm³). This mixture was sonicated for 45 min at room temperature, left to equilibrate for 24 h, and then filtered using a Millipore 0.22 µm mesh filter under vacuum. The filter paper and filtered asphaltenes was Soxhlet-washed with hot *n*-heptane (~75 °C) until the solvent in the upper section of the extractor becomes colorless. Extracted maltenes were mixed with the filtered washings for saturates, aromatics and resins (SAR) analysis. The washed asphaltenes was extracted by hot toluene in the Soxhlet, recuperating the dissolved asphaltenes in a previously weighted flask. The mass of the asphaltenes was determined by weighting the flask content after drying at 60 °C under vacuum. It was not detected toluene insoluble residues after Soxhlet extraction on any of the three crude oils studied here.

Crudes SAR content was also performed using liquid chromatography fractionation (ASTM D2007M) [43]. Analytical grade (>99.8%) solvents were used (*n*-heptane, toluene, dichloromethane and methanol) supplied by Sigma-Aldrich, with no further purification. Also, acetone precipitation technique [44,45] was used to determine the total amount of waxes following the modified UOP 46–64 method as described elsewhere [46]. Table 1 summarizes crude oil characterization analyses. Experimental uncertainties were determined by four independent repeat measurements.

Table 1
API density, viscosity, SARA, WAT and wax content measurements for crude oils.

crude oil	P1	P2	P3
° API	16.5	17.7	16.7
viscosity (20 °C), mPa·s	2200	1770	1600
viscosity (60 °C), mPa·s	107	102	90
S ± 2, wt %	32	37	43
A ± 2, wt %	27	25	26
R ± 3, wt %	35	32	30
A ± 0.05, wt %	6.34	6.29	1.55
WAT ± 1, °C	24	25	28
wax content, wt %	3.4	2.5	1.1

2.2. Crudes modifications with paraffins

Crude oils were modified with commercial paraffins and then the resulted asphaltenes solvency on the crudes was tested. For that, two pure commercial paraffins were used in the recombination procedure: *n*-hexadecane (C16, Sigma-Aldrich 99%, melting point 18 °C) and docosane (C22, Sigma-Aldrich 99%, melting point 42–45 °C). In addition, a commercial paraffin pool ASTM-D87 (melting temperature range of 53–57 °C supplied by Sigma Aldrich) was tested as well. Paraffins carbon number was selected from reported distribution of native paraffins from typical paraffinic crudes [32,33]. All paraffins were used without any further purification.

Each paraffin was firstly integrated in crude oil *P1* by a mass proportion of 2, 4 and 10 wt %, this paraffins mas proportions were selected based on reported paraffin content of paraffinic crude oils [32–34]. For crude modification, 120 g of oil and the calculated mass of each paraffin were heated to 60 °C. Then the paraffin was added slowly to the oil sample and homogenized by using a handle spatula, for at least 30 min, to avoid local concentration of the paraffins [17]. The modified crudes were cooled and equilibrated at room temperature for 24 h.

Crude oil *P1* and its modified composition by the addition of C16, C22 and the paraffin pool were evaluated in terms of asphaltene precipitation yield and asphaltenes precipitation onset by *n*-heptane addition. For oil samples *P2* and *P3*, only the best results obtained for *P1* sample have been tested. The modified crudes were named using the following sequence: firstly, the crude oil sample precursor (*P1*, *P2* or *P3*), then the paraffin mass fraction (2, 4 or 10) and finally the paraffin addition (C16, C22 or Pool), e.g., *P1-10C16*. All the modified crudes were characterized in terms of API gravity, viscosity and WAT by the same procedure described in Section 2.1.

2.3. Asphaltene yield and precipitation onset determination

Asphaltene yield and precipitation onset was investigated for each crude its modifications with paraffins. Asphaltene onset was defined here as the percentage by mass of *n*-heptane at which asphaltene initiate the precipitation. Centrifugation and gravimetric measurements were performed to quantify the percentage by mass of precipitated asphaltenes when mixed with *n*-heptane (99.8% supplied by Dinâmica Brazilian Ind.), from 10 to 90 *n*-heptane wt %. To initiate the solubility tests, 1.5–6 g of each crude was initially diluted with *n*-heptane at a given ratio, then mixed by sonication for 15 min, and finally left to settle for 24 h at room conditions. After that, those mixtures were centrifuged for 30 min at 3000 rpm. The resulting supernatant was separated, and the obtained solids were washed with *n*-heptane. The washed solids were sonicated and centrifuged after 24 h of equilibration as stated before. The obtained precipitates (*i*-C7, *n*-heptane insoluble solids) were dried at 60 °C for few days until the mass variations were less than 0.1 mg. Asphaltene yield was calculated as the

percentage by mass of *i*-C7 precipitate per mass of the crude oil. Asphaltenes precipitation onset was estimated by linear extrapolation of the asphaltene yield curves to zero yield [47]. It was identified the points to the linear adjust after the first inflection point on the asphaltene yield curves, for *P1* and *P2* crudes it was used the points between 65 and 85 wt % of *n*-heptane, and for *P3* crudes the points between 75 and 90 *n*-heptane wt % and the repeats. For asphaltenes precipitation yields and onset determination, the experimental uncertainties were determined by triplicate repetitions obtaining ±0.2 wt % for *P1* and *P2* asphaltenes yields, 0.05 wt% for *P3* asphaltenes yields, and ±1 *n*-heptane wt % for asphaltenes onset in all the cases, calculated at 95% of confidence.

The previous tests were performed on both the unmodified based crude oils and the paraffinic modified crudes. Following this, the precipitation onset of each crude was compared by the difference $\Delta\text{Onset} = \text{Onset}_{\text{modified}} - \text{Onset}_{\text{base}}$, in *n*-heptane wt %. In order to evaluate any chemical variation in the obtained precipitated *i*-C7 solids by the addition of the heaviest paraffins, i.e. paraffins coprecipitation, the asphaltenic solids were analyzed by FT-IR supported in KBr plates using an IR Solution Shimadzu spectrometer. The alkyl content of the *i*-C7 solids was determined by the perceptual area of 2920/2850, 1453 and 1374 cm⁻¹ bands in the FT-IR spectrum as described elsewhere [38,40,48].

2.4. Regular solution model for paraffinic modified oils

Asphaltenes yield and precipitation curves where modeled using a modified regular solution approach, as described by Akbarzadeh et al. [49] and further applications [20,31,50]. The model was originally fitted for unmodified crude asphaltene yields, and later employed predictively to estimate the effects of the inclusion of C16, C22 and the paraffin pool. This model considers a liquid-liquid equilibrium between a heavy dense phase (consisting mostly of asphaltene and resins), and a light phase (composed by the solvent and all the oil fractions). The crude was divided into SARA molar fractions and the equilibrium constant for each fraction was determined as follows:

$$K_i^{hl} = \frac{x_i^h}{x_i^l} = \exp \left(\frac{v_i^h}{v_m^h} - \frac{v_i^l}{v_m^l} + \ln \left(\frac{v_i^l}{v_m^l} \right) - \ln \left(\frac{v_i^h}{v_m^h} \right) + \frac{v_i^l}{RT} (\delta_i^l - \delta_m^l)^2 - \frac{v_i^h}{RT} (\delta_i^h - \delta_m^h)^2 \right) \quad (1)$$

where *x* is the molar fraction, *v* is the molar volume, δ is the solubility parameter, *T* is the absolute temperature, *R* is the universal gas constant, subscript *i* indicate the *i*th component (saturates, aromatics, resins, asphaltene or *n*-heptane as solvent) and *m* mixture properties, superscripts *l* and *h* denote the light and heavy phase, respectively.

The mole fraction, the molar volume and the solubility parameter for each component are required to apply this model. For *n*-heptane as pure component, the properties are reported in literature. For saturates, aromatics and resins, reported average properties are used [49,51,52]. Recent papers report that there is not any considerable variations in those fractions properties when compared with previous data for SAR properties of different crudes from around the globe [49,51]. The solvent and SAR properties were listed in Table 2.

For asphaltenes, the average molar weight was determined by fitting the model to the asphaltene yield curves of unmodified oils. A gamma distribution, widely used to describe the molar weight distribution of asphaltenes [30,31,49], is described here as follows [54]:

Table 2Density, molar weight and solubility parameter for *n*-heptane [53] and SAR fractions [51,52] at 25 °C and 1 atm.

compound/group	density, kg/m ³	molar weight, g/mol	solubility parameter, MPa ^{0.5}
<i>n</i> -heptane	678.0	100.0	15.2
saturates	880.0	460.0	16.4
aromatics	990.0	522.0	20.3
Resins	1044.0	1040.0	19.3

$$f(MW_a) = \frac{(MW_a - MW_m)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left(-\frac{MW_a - MW_m}{\beta}\right) \quad (2)$$

where MW_m is the molecular weight of the monomeric asphaltene unit, α determines the shape of the distribution, $f(MW_a)$ is the frequency at given molecular weight MW_a , and β is stated by:

$$\beta = \frac{MW_{avg} - MW_m}{\alpha} \quad (3)$$

where MW_{avg} is the average molecular weight of the asphaltenes aggregates. Previous usages of the gamma distribution recommend the subdivision of the asphaltene molecular weight in a range from 1800 to 30000 Da [55]. In this work, high resin crudes were tested, low asphaltene aggregation was reported under conditions specified elsewhere [49,56], and the asphaltene molecular weight domain was reduced to 750–7200 Da. Those values are in accordance with literature [10] and better fitting was obtained.

Asphaltene solubility parameter and density were estimated using correlations from the literature. For asphaltenes density ρ_a in kg/m³, the following recommended exponential relation as function of the molar weight of the asphaltene aggregates was implemented [30]:

$$\rho_a = \left(1100 + 100 \left(1 - \exp\left(\frac{-MW_a}{3850}\right)\right)\right) \quad (4)$$

For the solubility parameter of asphaltenes, Tharanivasan et al. correlation of solubility parameter to density was employed [20]:

$$\delta a = (A(T)\rho_a)^{1/2} \quad (5)$$

and,

$$A(T) = 0.579 - 0.00075T \quad (6)$$

where $A(T)$ function is considered approximately equal to the monomer specific heat of vaporization in J/kg, δ_a is the solubility parameter for the asphaltenes in MPa^{0.5} and ρ_a the asphaltenes density in kg/m³.

With all fraction properties correlated or specified, the phase distribution was performed using recommended Rachford-Rice flash calculations [55]. The asphaltenes molar weight distribution was fitted to the asphaltene yield of the unmodified crudes and then used to model the paraffinic modified oils. The model was fitted by the minimization of the average absolute relative deviation percent %AARD as objective function

$$\%AARD = 100 \cdot \sum \frac{1}{N} \left| \frac{(y_{i \text{ exp}} - y_{i \text{ modeled}})}{y_{i \text{ exp}}} \right| \quad (7)$$

where $y_{i \text{ exp}}$ represents the experimental asphaltene yield, $y_{i \text{ modeled}}$ the modeled asphaltene yield, and N the number of experimental data. The onset accuracy of the fitted model was evaluated using the absolute relative deviation %ARD with respect to the experimental values

$$\%ARD = 100 \cdot \left| \frac{(Onset_{i \text{ exp}} - Onset_{i \text{ fitted}})}{Onset_{i \text{ exp}}} \right| \quad (8)$$

The Regular Solution model was fitted to unmodified crude oil asphaltenes yield data, and the molar weight distribution of the asphaltenes was obtained. Then, the model was implemented by using the fitted asphaltenes properties to predict the precipitation behavior when the C16, C22 and the paraffin pool was integrated in the calculation. Both pure paraffins (i.e., C16 and C22) were treated as pure components using the properties listed in Table 3. The paraffin pool addition was considered as a proper increase on the saturate group of crude SARA fractions and then normalized. The average absolute deviation AAD was calculated for both the fitted and the predicted asphaltene yields as follows:

$$AAD = \sum \frac{1}{N} \left| (y_{i \text{ exp}} - y_{i \text{ modeled}}) \right| \quad (9)$$

Finally, the predicted onset variation $\Delta Onset$ as function of the crude paraffin addition was calculated and compared with experimental trends.

3. Results and discussion

3.1. Crudes modifications and asphaltenes precipitation yields

Properties of crude *P1* and its respective modifications with paraffins, *n*-hexadecane, docosane and the paraffin pool, were listed in Table 4. As expected, it can be noted that all paraffin addition contributes to a reduction in the crude density, even for the paraffin pool. Only the WAT for modified crudes with paraffin pool were above ambient temperature (25 °C), suggesting the presence of wax crystals only for modified crudes with the paraffin pool. Crystallization of waxes could be related to the viscosity increase observed at temperatures below the WAT and associated with a non-Newtonian behavior [45,57]. Recovered i-C7 solids from asphaltene solubility test of paraffin pool modified oils were considered for FT-IR analysis to evaluate any possible conjugate precipitation processes (wax precipitation and asphaltenes).

For pure *P1* crude and *n*-hexadecane modifications, asphaltenes yield curves are presented in Fig. 1. With the addition of the foreign paraffin, such as *n*-hexadecane, is expected from mass balance a resulting decrease in the other crude fractions like aromatics, resins and asphaltenes. This behavior is experimentally observed for asphaltenes yield in modified crudes at higher proportion of precipitant (90wt% *n*-heptane). At this point, the asphaltenes yields (based on the total mass of modified oil including the added paraffin), have a reduction when compared to the unmodified crude oil, due to the mass contribution of the C16 paraffin. In terms of solubility of the asphaltenes, it could be observed that asphaltenes onset precipitation shift is more pronounced as *n*-hexadecane content increases, precisely asphaltenes precipitation start point or onset is detected at lowers *n*-heptane regions. Asphaltene precipitation onset of the unmodified *P1* crude was detected at 63 ± 1 wt % of *n*-heptane, while for *P1*-C1610 mixture the onset decreased to 58 ± 1 wt %.

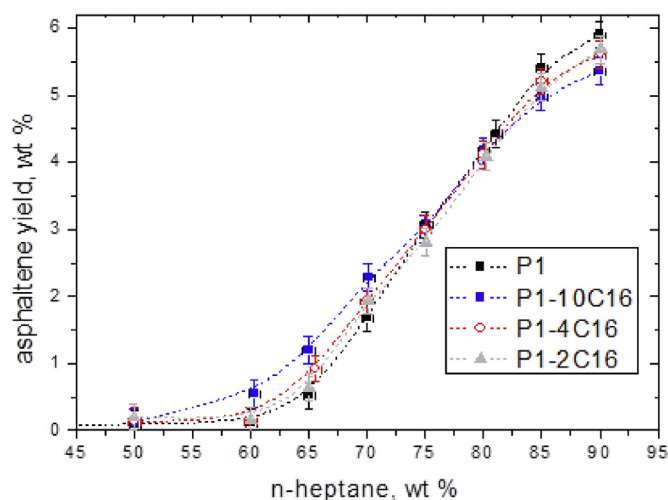
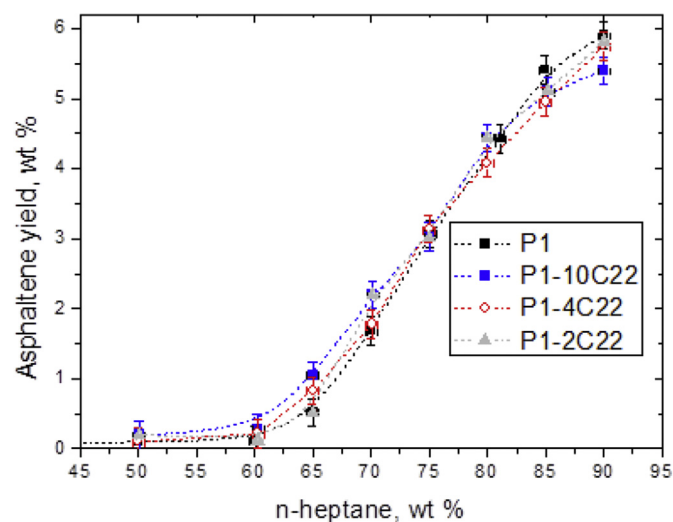
It is important to notice that the same behavior has been

Table 3Density, molar weight and solubility parameter for *n*-hexadecane, docosane and paraffin pool.

compound	density, kg/m ³	molar weight, g/mol	solubility parameter, MPa ^{0.5}
<i>n</i> -hexadecane ^a	769.8	226.4	16.3
docosane ^a	778.0	310.0	16.2
paraffin pool ^b	880.0	460.0	16.4

^a From [53].^b Same properties than saturates group as listed in Table 2.**Table 4**API, viscosity and WAT of P1 modified with *n*-hexadecane, docosane and the paraffin pool.

crude oil and paraffins additions	added paraffin content, wt%	° API	viscosity (20 °C) mPa·s	viscosity (60 °C) mPa·s	WAT ± 1 °C
P1 (unmodified)	—	16.5	2200	107	24
P1 + C16	10	20.4	476	58	15
	4	18.4	1020	77	23
	2	17.8	1370	90	24
P1 + C22	10	20.0	700	58	20
	4	18.2	1250	85	21
	2	17.6	1490	98	23
P1+ Pool de Parafin as	10	19.2	28600	64	34
	4	17.9	1820	86	32
	2	17.7	1600	98	26

**Fig. 1.** Asphaltene precipitation yield in *n*-heptane from crude P1 and modifications with *n*-hexadecane C16. Experimental uncertainties were within ± 0.2 wt %. Lines plotted as eye-guide.**Fig. 2.** Asphaltene precipitation yield in *n*-heptane from crude P1 and modifications with docosane C22. Experimental uncertainties were within ± 0.2 wt %. Lines plotted as eye-guide.

observed for *P1* crudes modified with docosane and the paraffin pool. Asphaltenes yield for *P1* crude modified with docosane and with paraffin pool are presented in Figs. 2 and 3, respectively. When paraffin content reach 10 wt %, it is observed a left shift for asphaltene precipitation onset, reaching 59 ± 1 wt % for P1-10C22 and 58 ± 1 wt % for P1-10Pool, showing a considerable variation when compared to unmodified oil. This asphaltenes precipitation onset reduction could be related to an affection of the crude solvency for asphaltenes. In the same way, as one can note, from *n*-hexadecane to the heavier paraffin pool, asphaltene onset variation at the maximum paraffin addition was within the experimental error, with mean onset variation $\Delta Onset$ around $-5 \pm 1\%$ *n*-heptane. For lowers paraffins additions, such as 2 wt % or 4 wt % of paraffins, the asphaltenes onset variation was not considerable and the effects in asphaltene precipitation were minimal. It is important to mention that for all (*n*-hexadecane, docosane and paraffin pool)

used in this work, onset was affected in the same proportion regardless the paraffin type.

Asphaltenes onset affection due to paraffins incorporation in the crude was also verified after the addition of *n*-hexadecane and the paraffin pool to the crudes *P2* and *P3*. Those paraffins were particularly selected in order to corroborate the similar effects of the heaviest and lightest paraffins, in terms of molecular weight, obtained on *P1*. Crude oil properties (API, viscosity and WAT) of original and modified crudes *P2* and *P3* are listed in Table 5 and Table 6, respectively. It was also detected an increase on WAT temperature for the crudes modified with the heaviest paraffin pool, and a simultaneous increase in viscosity at lowers temperatures than the WAT. Non-Newtonian behavior of crudes oils could be related to the marked increase of viscosity when measured at 20 °C.

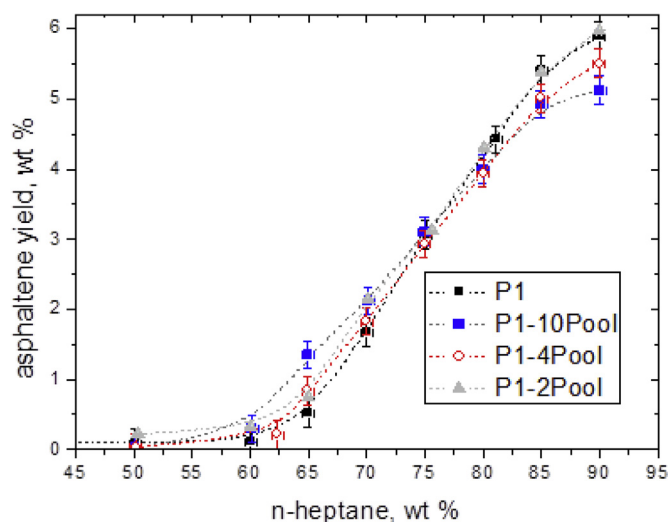


Fig. 3. Asphaltene precipitation yield in *n*-heptane from crude P1 and modifications with paraffin pool. Experimental uncertainties were within ± 0.2 wt %.

Asphaltenes precipitation yield and onset were evaluated for P2 and P3 modified crude oils. Fig. 4 depicts asphaltenes precipitation results for P2 and P3 when modified with 10 wt % of paraffins pool. Similar results were obtained when compared to P1 and its modifications, i.e., the precipitation onset has a distinguished diminution with the increase of the foreign paraffin content. For P2 modified crudes, it was obtained the same onset variation $\Delta Onset$ of $-5 \pm 1\%$ for P2-10C16 and for P2-10Pool respectively. The onset variation was again the same after the addition of those two different paraffins. Crude P3 has the lowest asphaltene content, and the addition of paraffins did not display a remarkable effect in the change of the onset (with onset variations $\Delta Onset$ within the experimental error).

Onset variations are summarized in Fig. 5 and as one can observe, the equivalent effects of the *n*-hexadecane and the paraffin pool become significant when added to the tested crudes. Solid marks represent the onset variation $\Delta Onset$ when the crude was

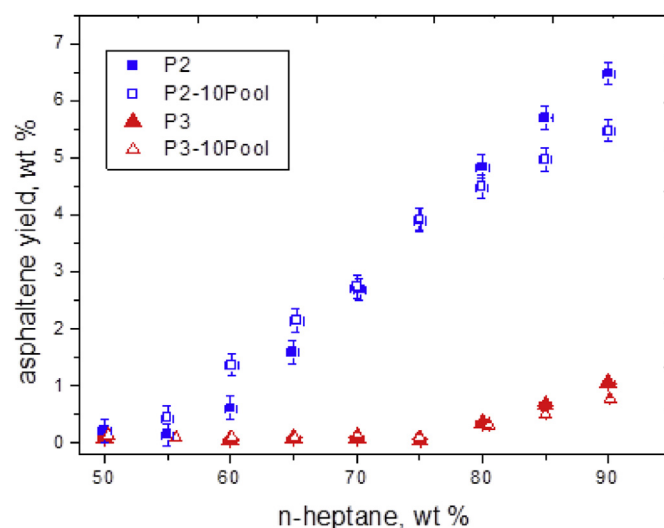


Fig. 4. Asphaltene precipitation yield in *n*-heptane from crude P2 and P3 and modifications with paraffin pool. Experimental uncertainties were within ± 0.2 wt % for P2 asphaltene yield and ± 0.05 wt % for P3 asphaltene yield.

modified with the heaviest paraffin pool, and the circled marks represent crudes modified with C16. In both cases, variation of the onset was the same for each modified crude, leading the asphaltenes precipitation at lower solvent additions when the crude paraffin content increases. Paraffins tested in the modified crudes have similar effects on the reduction of crude asphaltenes solubility, despite their differences in chain length and structures. This observation might be related to the similarity between the solubility parameter for all paraffins tested. For *n*-hexadecane the solubility parameter has a value of $16.3 \text{ MPa}^{1/2}$, and even when paraffin chain length increases in six carbons (docosane), the solubility parameter remains with a value of $16.2 \text{ MPa}^{1/2}$, as reported in Table 3. This similarity was also identified when compared to the solubility parameter for crude oil saturate fraction, with values of $16.4 \text{ MPa}^{1/2}$. Generally speaking, one may suggest that the structure differences in the paraffins tested have no major influence in the asphaltene crude solvency when compared under the same mass

Table 5

API, viscosity and WAT of P2 modified with *n*-hexadecane and the paraffin pool.

crude oil and paraffins additions	added paraffin content, wt%	° API	viscosity (20 °C) mPa·s	viscosity (60 °C) mPa·s	WAT ± 1 °C
P2 (unmodified)	—	17.7	1770	102	25
P2 + C16	10	20.0	397	42.7	14
	4	18.7	920	72	21
	2	18.2	1090	80	22
P2 + Paraffin pool	10	21.2	83000	63	38
	4	19.2	1770	81	29
	2	18.5	1540	89	26

Table 6

API, viscosity and WAT of P3 modified with *n*-hexadecane and the paraffin pool.

crude oil and paraffins additions	added paraffin content, wt%	° API	viscosity (20 °C) mPa·s	viscosity (60 °C) mPa·s	WAT ± 1 °C
P3 (unmodified)	—	16.7	1600	90	28
P3 + C16	10	21.7	580	30.5	11
	4	19.7	1190	66	20
	2	16.9	1400	78	22
P3 + Paraffin pool	10	20.5	28200	40.9	40
	4	19.1	1200	52	32
	2	18.1	1400	70	27

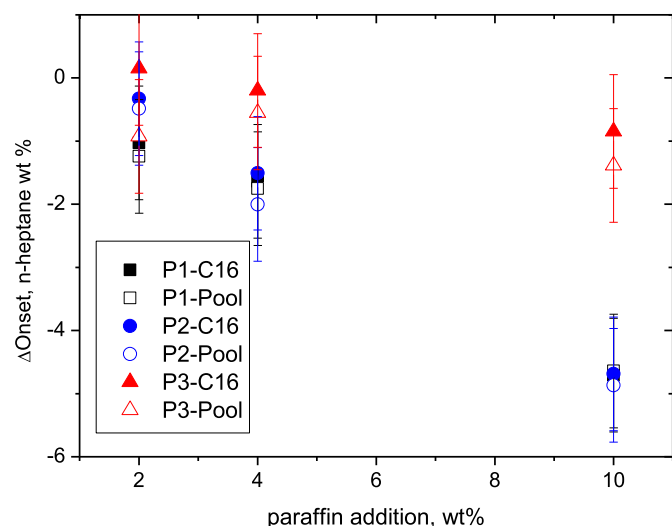


Fig. 5. Variation on the asphaltene precipitation onset as function of the paraffin addition on the modified crude.

addition, as long as the solubility parameter of the tested species are too close together.

3.2. Precipitates characterization

One of the biggest concerns of the heaviest paraffin addition to the crudes was the paraffin coprecipitation and the mass contribution for recovered i-C7 solids in asphaltene solubility tests. It has been reported previously in the literature that simultaneous events of asphaltene and paraffin wax precipitation can be detected [35,38]. WAT measurements showed that modified crudes with the paraffin pool could have crystal wax at ambient conditions. For that reason, the asphaltenic precipitated solids from the oils with the maximum addition of paraffin pool, i.e. P1-10Pool, P2-10Pool and P3-10Pool, were analyzed in terms of alkyl content by FT-IR. The i-C7 solids were collected just after the precipitation onset and at the maximum precipitation yield and later compared with the i-C7 solids obtained from the unmodified crude.

Fig. 6 presents FT-IR spectra for the mentioned solids from the P1, P2 and P3 crudes respectively, recovered at 90 wt % of *n*-heptane addition. Table 7 summarizes alkyl content of each specific analyzed solid. From this figure, it could not be observed any variations in the asphaltene alkyl content, when compared to the unmodified oil i-C7 solids. Considering the solid paraffin pool as a series of alkyl chains, the weight contribution in the precipitated asphaltenes was negligible and no coprecipitation was detected. Consequently, one can consider that asphaltenes onset variation detected by the incorporation of paraffins in the crude oil was only a solvency effect, and not a parallel wax precipitation event.

3.3. Thermodynamic modelling

The effects of paraffin incorporation in the crudes over the asphaltene precipitation was also investigated using a reported modification of the Regular Solution Theory. The Regular Solution model was adjusted to match the experimental yield data of unmodified oils, identifying the fitted average molecular weight of the asphaltenes. With the molar weight of the asphaltenes fraction of the original crudes, the model was used to predict the behavior when the different paraffins were added. The fitted average asphaltene molar weight and the fitted model deviations respect the experimental data were listed in Table 8. One can note that the

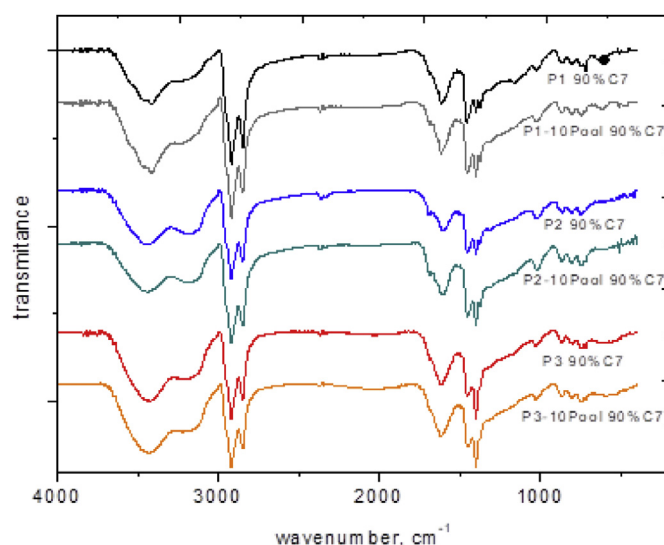


Fig. 6. FT-IR spectrum for precipitated i-C7 solids from P1 and P1-10Pool at 70 and 90 wt % of precipitant (*n*-heptane).

Table 7

Alkyl content of precipitated i-C7 solids from unmodified crudes and crudes modified with paraffin pool.

crude source of the precipitated i-C7 solids	% alkyl ± 1 , wt %	
	<i>n</i> -heptane proportion, wt %	
	70 ^a	90
P1	35	32
P1 10%Pool	34	31
P2	27	27
P2 10%Pool	26	28
P3	23	25
P3 10%Pool	24	25

^a 80 *n*-heptane wt % for P3 samples, before asphaltenes precipitation onset.

fitted average molar weight for the asphaltenes may be associated to the aggregation of 2–4 monomers with molar mass of 750 Da. As reported in the literature [55,56], the model is sensible to the resins content of the crude by a diminution of the aggregation number and the average molar mass of the asphaltenes. In this work, the range of the asphaltene molar weight had to be adjusted to lower values than those previously obtained by using the model (above 1800 Da [46,47]) due to the highly resins content in the crudes. In that way, a better fitting was obtained and similarly an aggregation behavior that corresponds with reported literature [10].

In Fig. 7, the fitted asphaltene yield curves and the model prediction for the case of crudes modification with 10 wt % of *n*-hexadecane are presented. From these results, it could be observed that for all crudes the model predictions are in concordance with the experimental results. The model shows the same experimental trend in diminution of asphaltenes precipitation onset and total yield obtained.

Table 8

Average fitted molar weight for asphaltenes on base crudes, fitting deviations and onset %ARD.

crude oil	Asphaltenes MW_{avg} g/mol	AAD	% AARD	onset % ARD
P1	1859	0.1	1.8	3
P2	2316	0.1	2.9	4
P3	2533	0.1	14.4	1

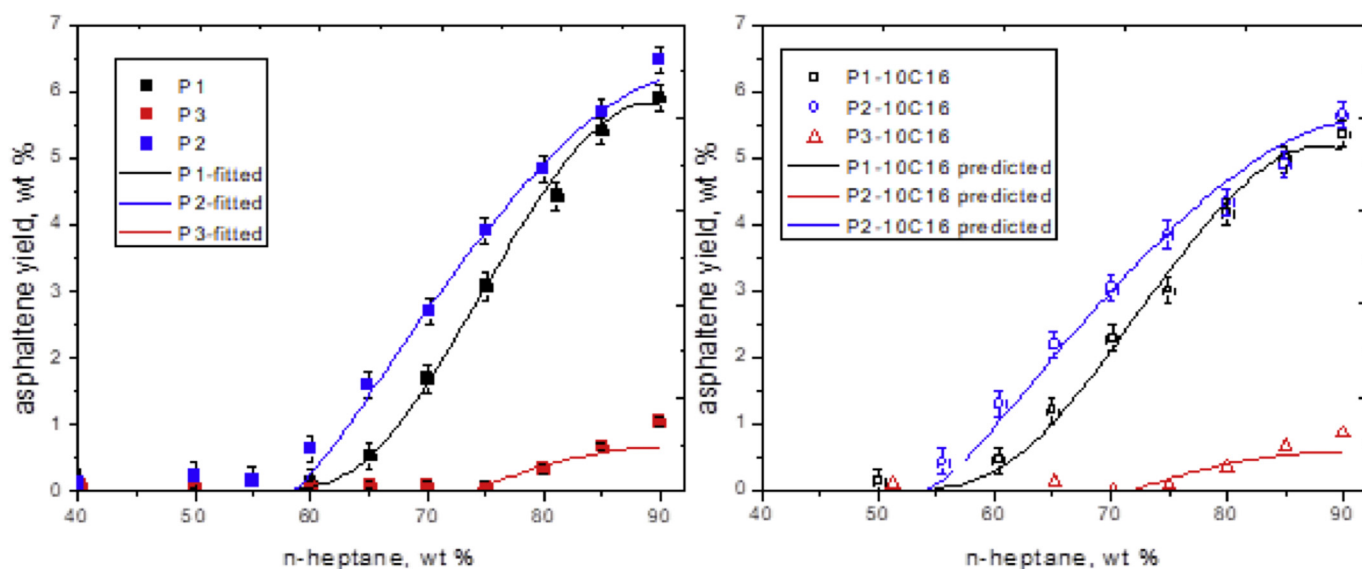


Fig. 7. Fitted and predicted asphaltene precipitation yields for unmodified crudes and crudes modified with *n*-hexane in 10 wt %.

Table 9

%AAD deviations between predicted and experimental asphaltene yield curve for crudes modified with paraffins.

system, oil + paraffin	AAD			%AAD		
	paraffin content, wt %					
	10	4	2	10	4	2
P1+C16	0.2	0.1	0.1	6.5	7.2	6.5
P1+C22	0.2	0.1	0.1	5.6	5.5	4.5
P1+Pool	0.3	0.2	0.1	9.6	8.0	7.2
P2+C16	0.5	0.1	0.1	4.0	4.1	2.6
P2+Pool	0.3	0.2	0.1	8.1	3.5	4.0
P3+C16	0.1	0.1	0.1	55.0	49.9	20.6
P3+Pool	0.1	0.1	0.1	45.5	17.7	21.8

Similar results were obtained when predicted the asphaltene behavior of the other paraffin additions. Deviations AAD and % AARD of all the predictions are presented in Table 9. For crudes P1 and P2, the best estimation results were obtained by using the model, with AAD deviations less than 0.285 that represents a % AARD of 9.62% between the predicted and experimental

asphaltene yield behavior. For crude P3, the largest deviations were observed once the model overestimates the variations in the onset regions and does not match the asphaltene yields in higher heptane region. A possible explanation to the model prediction fail might be attributed to generalizations in the crude fraction properties used, along with uncertainties in the asphaltene and onset measurement in low asphaltene crudes [54].

The predicted onset variations were calculated in the same way as for the experimental determinations. The predicted onset variation ΔOnset as function of the *n*-hexadecane addition and the paraffin pool addition are presented in Figs. 8 and 9, respectively. As can be noted, the model reproduces well the change of the onset when the paraffin content of the crude increases. Nevertheless, the model overestimates the onset variation for low content crudes like P3 as commented before, whereas for crudes with higher asphaltene content (P1 and P2), a satisfactory prediction has been observed, with asphaltene onset precipitation decreases with increases of paraffin content. Additionally, the model was also capable to reproduce the similar solvency effects between the incorporation of *n*-hexadecane and the paraffin pool as seen experimentally.

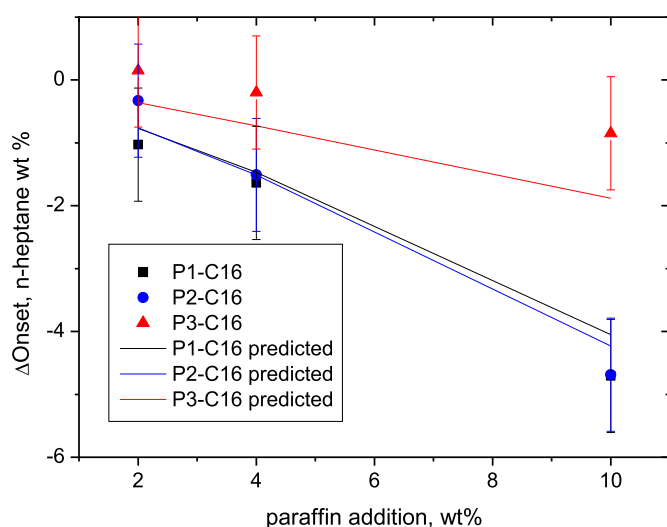


Fig. 8. Predicted and experimental asphaltene onset variation ΔOnset as function of the *n*-hexadecane addition on the modified crude.

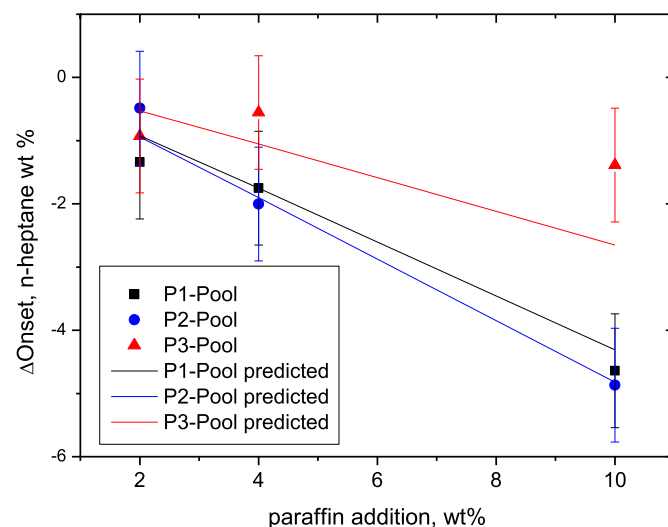


Fig. 9. Predicted and experimental asphaltene onset variation ΔOnset as function of the paraffin pool addition on the modified crude.

4. Conclusions

Compositional modifications by the inclusion of different paraffins (*n*-hexadecane, docosane and paraffin pool) in crudes and their effects on the asphaltene stability were evaluated, by analyzing variations in the solvency and precipitation behavior of crude asphaltenes. Asphaltene yields (evaluated by precipitation test in *n*-heptane) showed a decreasing on the asphaltene precipitation onset in paraffinic modified crudes once the paraffin proportion increases in the samples, possibly due to instability of asphaltenes caused by the addition of paraffin along with native asphaltenes content. Not to mention that incorporation of heaviest solid paraffins has not impact on the alkyl content, indicating negligible precipitation of wax crystals in the asphaltene solubility test. In spite of the differences in the paraffin structures and the chain lengths, similarities in the solubility parameter among those paraffins resulted in equivalent effects on the crude solvency power. Variations in asphaltene precipitation onset were the identical when compared *n*-hexadecane addition and the addition of a heavier paraffin pool. Equal effects in asphaltenes stability was obtained at the same mass proportion of those paraffins as crudes constituents. Asphaltene behavior in paraffinic modified crudes was also well described by using Regular Solution model, being capable to predict the reduction in the asphaltene precipitation onset.

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Nomenclature

x	molar fraction, mol/mol	eq. (1)
v	molar volume, cm ³ /mol	eq. (1)
T	absolute temperature, K	eq. (1)
R	universal gas constant, cm ³ .MPa/K.mol	eq. (1)
MW _m	molecular weight of the monomeric asphaltene unit, g/mol	eq. (2)
f (MW _a)	frequency at given molecular weight	eq. (2)
MW _a	molecular weight for asphaltenes, g/mol	eq. (2)
A(T)	asphaltene monomer specific heat of vaporization as function of T, J/kg	eq. (5)
y _{iexp}	experimental asphaltene yield, wt %	eq. (7)
y _{i modeled}	modeled asphaltenes yield, wt %	eq. (7)
N	number of experimental data	eq. (7)
%AARD	average absolute relative deviation	eq. (7)
%ARD	absolute relative deviation percent	eq. (8)
AAD	average absolute deviation	eq. (9)
Greek letters		
δ	solubility parameter, MPa ^{1/2}	eq. (1)
α	distribution shape factor	eq. (2)
β	distribution shape factor	eq. (2)
ρ _a	asphaltenes density, kg/m ³	eq. (4)
δ _a	asphaltenes solubility parameter, MPa ^{1/2}	eq. (5)
Subscripts		
i	ith component	eq. (1)
m	mixture properties	eq. (1)
Superscripts		
l	light phase	eq. (1)
h	heavy phase	eq. (1)

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