A model system to assess the phase behavior of asphaltenes in crude oil

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HIGHLIGHTS

- A model-system reproducing petroleum phase behavior is presented.
- Each petroleum requires a suitable model-solvent for asphaltenes equilibrium.
- The asphaltenes precipitation depends on the hole crude oil composition.
- The asphaltenes phase behavior is related to only one solubility parameter.

ARTICLE INFO

ABSTRACT

Determination of the precipitation onset in heavy crude oils is difficult due to their high viscosity. Dilution is one method utilized to enable this analysis. However, it is known that the asphaltenes phase behavior is a function of the type of molecule added to the oil, due to the changed composition. Therefore, the dilution should be done with a suitable solvent. Crude oil can be seen as a system of asphaltenes dispersed in the other components. In this work, these other components as a group are called the "Petroleum Media that Disperses the Asphaltenes" (PMDA). A previously developed methodology was successfully applied to another type of crude oil, showing that the solubility parameter of the PMDA, and thus of the mixture of model solvents to be added to the oil without affecting the asphaltenes phase behavior, is different for each type of crude oil. The results obtained also show that obtaining a model system containing the model solvent mixture with solubility parameter equal to the oil's PMDA and the asphaltenes separated beforehand is only possible using the fraction of asphaltenes precipitated with alkanes as small as C1.

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1. Introduction

Asphaltene deposits in the reservoir, flow lines, refining equipment and storage tanks can drastically affect petroleum production [1,2]. Deposition of asphaltenes can be induced by changing pressure, temperature and/or oil composition and mixtures of different crude oils [3]. The asphaltenes' tendency to aggregate has been interpreted in function of colloidal and interfacial behaviors, for petroleum and model systems, that is, asphaltenes dispersed in model solvents [4–11]. When studying petroleum, the asphaltene precipitation onset induced by the addition of a hydrocarbon solvent (pentane, hexane, heptane, etc.) is an important parameter, since many mathematical models used to predict asphaltene precipitation are based on precipitation data [12–18].

Flocculation of asphaltenes takes place when the solvent added changes the crude oil's composition, and as a consequence changes the solubility parameter of the petroleum media that disperses the asphaltenes [19,20]. The solubility parameters of the petroleum and the asphaltene fraction are the properties most widely applied in theoretical work to describe asphaltene precipitation. Several studies using model systems that, in general, do not represent the real conditions and characteristics of the petroleum and its production have been performed. A better understanding of the interactions between asphaltenes and other petroleum components, as well as the interactions between asphaltenes and solvents, is still necessary. In this case, establishing a model system that can be applied evaluate asphaltenes' phase behavior is important.

A previous paper [21] presented a method to determine the solubility parameter of the mixture of solvents that do not affect the asphaltene phase behavior when added to the crude oil of interest. This method was applied to only one type of crude oil, by determining the solubility parameter of the petroleum media that disperses the asphaltenes (PMDA).

This work presents the results of experiments applying that method to another type of crude oil, for the purpose of confirming its broader applicability. It is well known that models systems of

asphaltenes dispersed in solvents do not satisfactorily reproduce the behavior of asphaltene phases in crude oil. This article presents the results of a careful experiment investigating to what extent various model systems of asphaltenes dissolved in organic solvents (varying the asphaltene fraction and solvent type) present behavior different than that in crude oil. This article also presents the composition that a model system should have to reproduce the phase behavior of the target petroleum sample, with this model system composed of a model solvent with solubility parameter equal to that of the PMDA and the asphaltenes extracted from the same petroleum. This method can be very useful to analyze asphaltene stabilization in heavy oils.

2. Experimental

2.1. Materials

Two crude oils supplied by Petrobras were used in this work. The samples had some small differences in composition and density, as shown in Table 1.

The various solvents used were P.A. grade chemicals purchased from Vetec Química Fina, Brazil, and were used without any further purification. The density and solubility parameter components of these solvents are listed in Table 2 [22–24].

2.2. Extraction of the asphaltenes from the crude oil samples

The asphaltenes and sub-asphaltenic fraction were separated from both crude oil samples following the IP 143 [25] standard procedure for asphaltene preparation, using pentane, hexane, heptane, octane and decane as precipitating agents to obtain the C5–C10 asphaltenic fractions.

2.3. Determination of asphaltene precipitation onset by near infrared spectrometry (NIR)

The asphaltene precipitation onset (PO) was determined using a Bruker MATRIX-F near infrared spectrophotometer containing an external probe (pathway of 2 or 5 mm), coupled to a Jasco PU2087 isocratic pump, which titrates the sample with the flocculant solvent at a flow rate of 2 mL/min. The flocculation is monitored by the absorption intensity against volume of flocculant, at 1600 nm. All analyses were carried out at least twice and the results are reported as the average value.

The precipitation onset (PO) expressed as mL C7/g of oil corresponds to the volume of flocculant required to induce incipient precipitation of the asphaltenes detected as the minimum in the absorbance vs. concentration curve.

2.3.1. Analysis of pure Petroleum B

Due to the size of the assay recipient, the analyses were carried out with about 4 g of petroleum. The asphaltene precipitation onset refers to ratio between the volume of flocculant, at minimum absorption intensity, and the mass of petroleum Eq. (1).

$$PO = \frac{\text{heptane volume at minimum absorption intensity (mL)}}{\text{Mass of petroleum (g)}}$$

(1)

2.3.2. Analysis of Petroleum B diluted with solvent

For the petroleum diluted with a solvent, the expression "1 g of petroleum" was replaced by "1 g of oil phase". The oil phases were prepared by weighting the petroleum mass and adding a predetermined volume of solvent or solvent mixture. The mass of oil phase was calculated from the density of the components and the composition of the mixture. The mixture was submitted to ultrasound for 15 min. The asphaltene precipitation onset was calculated from the volume (mL) of n-heptane, added to 1 g of oil phase required to achieve the minimum absorption intensity, as shown in Eq. (2).

$$PO = \frac{\text{heptane volume at minimum absorption intensity (mL)}}{\text{Mass of petroleum (g)} + \text{mass of model-solvente (g)}}$$

(2)

2.3.3. Analysis of the model system of asphaltenes dispersed in the model solvents

The model systems were prepared with the asphaltenes dispersed in the particular model solvent chosen. For each type of petroleum, different model systems were prepared containing varying fractions of asphaltenes extracted beforehand (C5–C10). The asphaltenes' concentration followed the same concentration present in the corresponding original oil sample (Table 1), that is, 3.1 m/m% for the fractions extracted from Petroleum A and 7.3 m/m% for the fractions extracted from Petroleum B.

2.4. Calculation of the solubility parameter of the solvent mixtures

The solubility parameters of the mixtures were calculated by the weighted average of the solubility parameters (δ) and the respective volumetric fractions (Φ) of their pure components, according to Eq. (3) [26].

$$\delta_{mix} = \delta_1 * \phi_1 + \delta_2 * \phi_2 + \cdots + \delta_v * \phi_v$$

(3)

2.5. Approximate calculation of the solubility parameter of the petroleum media that disperses the asphaltenes (PMDA) (δ_{PDMA})

The solubility parameter at which the asphaltenes started precipitating was calculated according to Eq. (4).

$$\delta_{mix} = (\delta_{MPDA} * \varphi_{MPDA}) + (\delta_{hept} * \varphi_{hept})$$

(4)

The δ_{mix} was approximately calculated by the results from the diluted Petroleum B experiments.

3. Results and discussion

The method presented here, previously established for Petroleum A [21], first involves determining the asphaltene precipitation onset in pure petroleum and petroleum diluted with cyclohexane. By using the data of the solubility parameter range of the asphaltene precipitation of the petroleum diluted with cyclohexane, the δ_{PDMA} is calculated using Eq. (4). After that, the asphaltene precipitation onset is determined for the oil diluted with model solvent, to obtain the δ_{PMDA}. In the present work, all these steps were done for Petroleum B and compared with results previously obtained for Petroleum A [21]. We also investigated the most suitable model solvent used to prepare model systems, con-

Table 1
Characteristics of Petroleum A and Petroleum B.

Petroleum samples	Density (g/mL)	°API	Saturates (m/m%)	Aromatics (m/m%)	Resins (m/m%)	Asphaltenes (m/m%)
A	0.934	19.4	40.2	33.3	23.4	3.1
B	0.974	13.2	35.7	24.6	32.4	7.3

Table 2
Density [22] (ρ), Hildebrand solubility parameter [23] (δ) and Hansen solubility parameters [24] of the solvents.

	n-Heptane	n-Decane	Cyclohexane	Toluene[a]	Dioxane
Density, ρ (g/mL)	0.68	0.73	0.78	0.87	1.03
Hildebrand solubility parameter, δ (MPa$^{1/2}$)	15.3	15.8	16.8	18.3	20.7
Dispersion cohesion solubility parameter, δ_D (MPa$^{1/2}$)	15.3	15.7	16.8	18.0	19.0
Polar cohesion solubility parameter, δ_P (MPa$^{1/2}$)	0.0	0.0	0.0	1.4	1.8
Hydrogen bonding cohesion solubility parameter, δ_H (MPa$^{1/2}$)	0.0	0.0	0.2	2.0	7.4

[a] Distilled under metallic sodium.

taining asphaltenes extracted from the petroleum. This last step was done for both petroleum samples A and B.

3.1. Asphaltene precipitation onset in pure Petroleum B (PO_{pure})

The volume of n-heptane required to attain the minimum absorption intensity in the flocculation of Petroleum B with that solvent was 15.4 mL (Fig. 1). According to Eq. (2) with a petroleum mass of 4 g, the precipitation onset (PO) of Petroleum B occurred with 3.8 mL of heptane/g of oil. This value, higher than that determined previously for Petroleum A (2.7 mL of heptane/g of oil) [21], could be expected based on the colloidal dispersion model discussed in the literature [8,10,11,27,28], according to which asphaltenes are dispersed in the oil and stabilized by the balance among saturates, aromatics and resins. Petroleum B contains a lower percentage of saturates in its composition than Petroleum A (Table 1), making the asphaltenes of Petroleum B more stable than those of Petroleum A, thus requiring more flocculant (a saturate) to destabilize the phase balance.

3.2. Asphaltene precipitation onset in Petroleum B diluted with cyclohexane

The estimation of the solubility parameter of the petroleum media that disperses the asphaltenes (δ_{PDMA}) was performed by first determining the precipitation onset values of the asphaltenes contained in Petroleum B diluted in cyclohexane. In a previous study [21] we observed that the asphaltenes precipitate at a determined value of the solubility parameter of the solvent + flocculant mixture, and this value varies with the dilution, but tends to become constant for higher dilutions. Such results are in agreement with literature [29–32] Therefore, in this study we only used dilutions of 1:25 and 1:30 g of petroleum:volume of cyclohexane. The results are presented in Table 3.

Applying the value of 15.95 in Eq. (4) yields an approximate value for δ_{PDMA} of 18.55 MPa$^{1/2}$. This value is higher than that
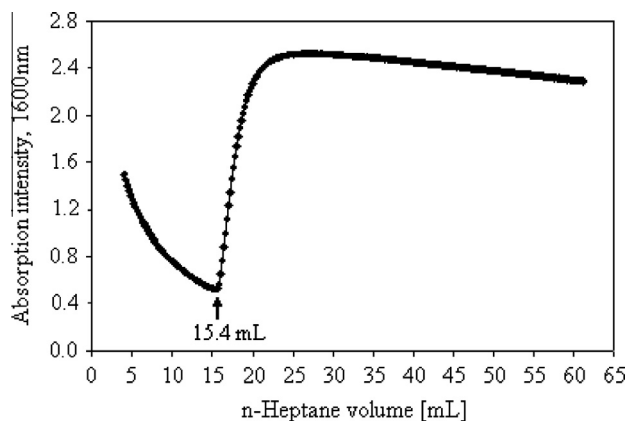

Fig. 1. Curve of absorption intensity against n-heptane volume added to the pure petroleum B, at 1600 nm.

found previously [21] for Petroleum A (17.8 MPa$^{1/2}$), probably because of the higher concentration of saturates present in Petroleum A, which makes the solubility parameter of the petroleum media that disperses the asphaltenes (PDMA) lower.

3.3. Asphaltene precipitation onset of Petroleum B diluted with the model solvents

In order to find a model solvent for Petroleum B, meaning a solvent that does not change the asphaltene phase behavior, we prepared several solvent mixtures with solubility parameters between 17.59 MPa$^{1/2}$ and 19.51 MPa$^{1/2}$, since the calculated value was 18.55 MPa$^{1/2}$. The solvents used were n-decane (D), cyclohexane (C), toluene (T) and dioxane (Di). Table 4 shows the asphaltene precipitation onset results for Petroleum B diluted with the different model solvents, at a dilution of 1:1 grams of petroleum:volume of model solvent, flocculated with n-heptane. All the values of the organic phase (petroleum + model solvent) are corrected to mass of solvent, instead volume.

It can be seen that the model solvent that, added to Petroleum B, leads to an asphaltene precipitation onset value very near that obtained for pure Petroleum B is toluene, whose solubility parameter is 18.3 MPa$^{1/2}$. This value is very near that calculated by the proposed method (18.55 MPa$^{1/2}$). This small difference can be attributed to the fact that the calculation method applied does not take into consideration the mass of petroleum contained in the mixture with cyclohexane. Nevertheless, the proposed calculation method is able to reduce the number of tests necessary to find the best model solvent that, when mixed with the petroleum, does not change the asphaltene phase behavior.

The results obtained for Petroleum B confirm that the calculation method proposed previously, based on preliminary results with only one type of crude oil (Petroleum A), can be utilized to find a good approximation of the solubility of a model solvent that does not affect the asphaltene phase behavior when added to that crude oil. This procedure is especially useful to predict the phase behavior of highly viscous crude oils, which need to be diluted to carry out asphaltene precipitation onset tests. In this case, it is expected that the effect of dilution, which is observed when adding a random solvent to the oil [29,30], is minimized.

To assess the influence of the type of solvent used to prepare the mixtures on the asphaltene precipitation onset results, comparison can be made of the two solvent mixtures that lead to very similar precipitation onset values: toluene (δ = 18.3 MPa$^{1/2}$) and DTC:Di (54:46) (δ = 18.92 MPa$^{1/2}$). Gradual variations in the asphaltene precipitation onset are only observed for mixtures containing the same constituents (or constituents with similar polar contributions), in different composition. This result suggests that the overall solubility parameter value is not the only factor to be considered, as observed in our previous work [21], besides the factors observed by other authors [29–34]. Since our experiments were done at the same conditions, the influence of the type of solvent used to prepare the solvent mixtures could be related to the different intramolecules interactions occurring in each solvent, as proposed by Hansen [24]. So, to extend this study to the use of

Table 3
Precipitation onset of Petroleum B diluted with cyclohexane, and solubility parameters of solvent + flocculant mixture at the precipitation onset.

Dilution (g:mL)	Volume of CH (mL)	Volume of HEP (mL)	Φ of CH in the final mixture	Φ of HEP in the final mixture	δ CH (MPa$^{1/2}$)	δ HEP (MPa$^{1/2}$)	δ CH + HEP at onset (MPa$^{1/2}$)
1:25	25	33.0	0.43	0.57	16.8	15.3	15.95
1:30	30	41.8	0.42	0.58			15.93

CH = cyclohexane; HEP = heptane; δ = solubility parameter; Φ = volume fraction.

Table 4
Asphaltenes precipitation onset of Petroleum B diluted with different model solvents.

Model solvent	Model solvent δ (MPa$^{1/2}$)	Mass of organic phase (g)	Volume of HEP (mL)	Asphaltenes onset (mL HEP/g OP)
DTCDi(34 66)	19.51	1.89	7.30	3.86
DTCDi(54 46)	18.92	1.85	7.00	3.79
DTCDi(58 42)	18.81	1.85	6.80	3.68
DTCDi(62 38)	18.70	1.84	6.70	3.64
TOLUENO	18.30	1.80	6.92	3.82
DTC(5 90 5)	18.00	1.79	6.59	3.68
DTC(5 85 10)	17.93	1.79	6.54	3.65
DTC(5 80 15)	17.86	1.79	6.46	3.61
DTC(10 80 10)	17.80	1.79	6.41	3.58
DTC(10 75 15)	17.73	1.77	6.35	3.59
DTC(10 65 25)	17.59	1.77	6.12	3.46

HEP = n-heptane; OP = organic phase; D = decane; T = toluene; C = cyclohexane; Di = dioxane. DTCDi mixtures are related to DTC (10:65:25) added to dioxane at the proportion expressed in brackets.

Table 5
Composition of model systems.

Petroleum	Model solvent	Asphaltenes concentration (m/m%)[a]	Onset of original petroleum (ml heptane/g oil)
Asphaltenes A [21]	DTC (10:65:25)[b]	3.1	3.2
Asphaltenes B	DTC:Di (54:46)[c]	7.3	3.8

[a] Asphaltenes concentration in original petroleum samples – Table 1.
[b] Ref [21].
[c] In this case, DTC composition is 10:65:25.

more polar solvents should take in account not only the overall solubility parameter, but also the individual contributions of δ_D, δ_P and δ_H, related to dispersion interactions, polar cohesive energies and electron exchange parameters, respectively.

3.4. Asphaltene precipitation onset of asphaltenes dispersed in the model solvents

We also studied the asphaltenes extracted from both Petroleum A and Petroleum B, called Asphaltenes A and Asphaltenes B, respectively. From each crude oil, the fractions isolated were C5–C10. The characteristics of the systems are described in Table 5. For Asphaltenes A, the model solvent was used whose constituents have very low contribution of hydrogen bonds (toluene, $\delta_H = 2.0$ - MPa$^{1/2}$) [24], while for Asphaltenes B, the model solvent used was one with a relatively high hydrogen bond contribution (dioxane, $\delta_H = 7.4$ MPa$^{1/2}$) [24], as shown in Table 2. Two model solvents could have been chosen for Petroleum B: toluene and DTC:Di (54:46), since when both of these were added, the asphaltenes phase behavior was similar to that observed for pure Petroleum B (Table 4). The DTC:Di (54:46) mixture was selected to verify the possible influence of a solvent with a more substantial hydrogen bond contribution.

The aim of this study was to validate the model solvents. We considered that a model system, prepared with asphaltenes and a suitable model solvent, should exhibit similar behavior as the original petroleum. As already known, model systems present different onsets when prepared with different asphaltene fractions: the higher the hydrocarbon length that isolates asphaltenes,

the lower is the asphaltene precipitation onset of the model system. This behavior can be interpreted based on two different perceptions, taking in account literature statements [8,35,36].

(i) The most polar molecule of asphaltenes, which is present in all fractions, is the first to precipitate with the addition of a flocculant such as heptane, i.e., a flocculant with a relatively low solubility parameter. This more polar molecule is more stable in the fraction with broader distribution of structure types and polarity, thus requiring a greater quantity of flocculant to destabilize the system and consequently cause the precipitation of this more polar molecule. This same molecule in a fraction with narrower distribution of polarity and structure types will be more susceptible to having its equilibrium perturbed, i.e., with a lower quantity of flocculant.

(ii) In comparison with the average polarity of the different asphaltene fractions, the fractions separated with n-alkanes with greater size have a higher average solubility parameter. This fraction's equilibrium is affected by smaller volumes of flocculant.

From the results obtained, the asphaltene precipitation onset was plotted against the number of carbon atoms of the flocculant used to extract the asphaltenes. Fig. 2a and b shows the results for asphaltenes A and B, respectively.

The results suggest that to obtain the best model system using the model solvents employed in this work, it is necessary to use asphaltenes extracted from the petroleum with hydrocarbons hav-
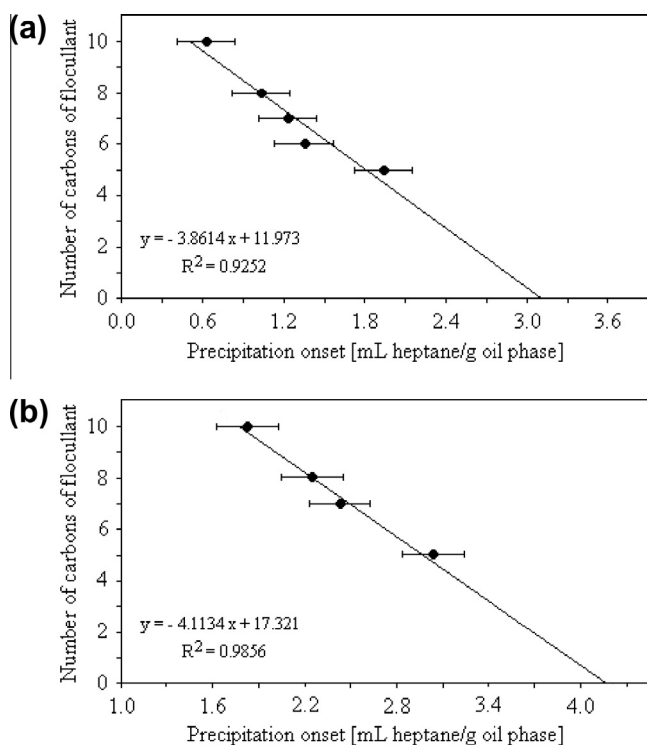
Fig. 2. Number of carbons of flocculant used to extract asphaltenes against asphaltenes precipitation onset of model system: (a) Asphaltenes A and (b) Asphaltenes B.

ing very short chain lengths (C1, C2). This proves the suitable behavior of the model solvents determined for each type of petroleum.

4. Conclusions

The phase behavior of crude oil diluted with solvents can be maintained as long as an adequate solvent is used. The solubility parameter of the solvent is the main factor in this choice. However, consideration should also be paid to the contributions of the different interactions (Hansen parameters). Different crude oils have distinct solubility parameters and thus require solvents with compatible thermodynamic qualities. Mixtures of solvents can be used to produce the most suitable model solvent for each type of petroleum. The identification of this model solvent is generally done by trial and error, but the method used in this work allows reducing the range of solubility parameters that need to be investigated. Obtaining model systems using asphaltenes dispersed in the model solvent for a given crude oil that reproduce the asphaltenes phase behavior in this same crude oil would only be possible when the asphaltenes are extracted with hydrocarbons as small as those of C1.

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