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Characterization of Crude Oils and the Precipitated Asphaltenes Fraction using UV Spectroscopy, Dynamic Light Scattering and Microscopy

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Abstract

Analysis of crude oil composition provides important information that impacts on the recovery, handling, and transportation of hydrocarbons. Crude characterization also provides data in the analysis of geochemistry of the source of origin. Crude oil characterization by optical methods is usually difficult because of its dark color; however, those characterizations are crucial because they give information that can affect some analysis procedures. Ultraviolet-visible (UV-vis) spectroscopy is a simple and practical technique that allows the characterization of crude oil through dilution in solvents. A comparative study of crude oil solutions contrasted with their asphaltene fractions was performed. Each solution was analyzed in triplicate, on a UV-vis spectrophotometer. Calibration curves for both raw solutions showed no significant variations, indicating stability. Additionally, the results of dispersion and migration phenomena indicated stability only for crude oil solutions. The aggregate size dispersion was different for each type of crude and varied with respect to time. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed the type of morphology present for each type of asphaltene.

Keywords: heavy oil, asphaltenes, UV-vis spectroscopy, aggregation, dynamic light scattering, SEM, TEM

1. Introduction

1.1. General aspects of crude oil

The name crude oil is used for naturally occurring and unprocessed petroleum. Crude oils are mixtures of many components, hydrocarbons (mostly alkanes, cycloalkanes, and aromatics) and other organic compounds containing nitrogen, oxygen, sulfur, and traces of metals [1].

Traditionally, these compounds are classified in several complex groups. The most popular is the method of separation into four groups: saturates, aromatics, resins, and asphaltenes (SARA) [2].

In refineries, one of the main criteria for control process is the content of asphaltene. **Table 1** shows the composition differences normally found in conventional oils, heavy oils, and residues.

1.2. Importance of the characterization of crude oil and asphaltenes

Asphaltenes are petroleum hydrocarbons with extremely complex molecular structure containing sulfur (0.3–10.3%), oxygen (0.3–4.8%), nitrogen (0.6–3.3%), and metal elements such as Fe, Ni, and V in small quantities [4, 5].

The association of metal porphyrins with asphaltenes is probably the reason behind the great difficulty in extracting or separating metal porphyrins from oil or waste oil. Metal porphyrins entrapment by asphaltenes was predicted long ago when the presence of free radicals in asphaltenes was discussed [6]. The porphyrins carry nickel and vanadium in the same proportions as established in the depositional environment. During generation and migration, these porphyrin structures are incorporated into the crude oil and carried along to the reservoir, preserving this information about the proportions of nickel and vanadium in the source rock. The nickel and vanadium content are also important in establishing a value for the oil. Nickel and vanadium will poison catalysts during the refining process. As such, high concentrations of nickel and vanadium in crude oil will reduce the market value of the oil [7].

On the other hand, the aromatic moiety, through π - π^* and dipole interactions, was thought to be one of the dominant contributors to asphaltenes self-association. Hence, proper characterization

Sample	Typical composition range (wt%)		
	Asphaltene	Resin	Oil fraction ¹
Conventional oil	<0.1–12	3–22	67–97
Heavy oil	11–45	14–39	24–64
Residue	11–29	29–39	<39

¹Correspondent to the fraction composed of saturate and aromatic.

Table 1. Composition for conventional oil, heavy oil and residue (Adapted from Speight Ref. [3]).

of the asphaltene molecular structure and its aromaticity is fundamental in understanding the self-association phenomenon [8].

The compositional analysis of crude oils provides important information that impacts petroleum exploitation at every step along the value chain, from exploration through production, transportation, and refining. In upstream operations, geochemical inversion of crude oil to the provenance of petroleum is invaluable in petroleum system analysis, especially where source-bed information may be difficult or impossible to obtain during exploration. In reservoir management, crude oil composition is essential for fluid correlation and the construction of functional, effective static reservoir models [9].

Heavy oils usually display a greater content of asphaltenes and resins than conventional oils, which directly impacts recovery, transport and refining processes. Colloidal properties of asphaltenes and resins have been the subject of intense debate in the literature [10].

In refineries, some issues include the reduction of the overall rates of hydrotreating reactions, deactivation of catalysts from surface deposition, and increased coke formation (asphaltenes are a coke precursor). In general, asphaltene precipitation limits the ultimate level of conversion. From this operational definition, asphaltenes are anticipated as a group of complex compounds, which are highly polydispersed and cannot be absolutely prescribed by some simple physicochemical parameters. There are fewer large aggregates and narrower distributions once asphaltenes are in infinitely diluted systems of higher temperatures and better solvents; however, they still exhibit a real polydispersity. The average molecular weight (MW) is not necessarily a good parameter to characterize asphaltenes, simply because asphaltenes are defined through their solubility in aliphatic hydrocarbons [11]. Asphaltenes, usually derived either from coal or from petroleum vacuum distillation residues, are wide spread, and a class of compounds that are by their solubility, insoluble in n-heptane, and soluble in toluene [12, 13].

1.3. Types of characterizations for crude oil and asphaltenes

Depending on the origin of the crude oil from which they are precipitated, asphaltenes can exhibit wide differences in composition and structure. The amount and length of the alkyl side chains as well as the number of aromatic rings may change in such a way that the variations of molecular weight and aromaticity factor of asphaltenes are notorious [14].

Crude oil is a complex mixture of compounds difficult to characterize using optical methods because of its dark color. Ultraviolet-visible (UV-vis) spectroscopy is simple, practical, and inexpensive. It allows the characterization of crude oil through dilution in solvents like cyclohexane. Recently, a study was conducted on the development of a spectroscopic method for the quantification of functional groups characteristic of asphaltenes, making direct quantification from oil a simple and practical method [15]. The strongest absorption of metal porphyrin occurs in the vicinity of 425 nm and is called Soret band [16]. In addition to the well-defined amounts of energy to increase its vibrational and rotational moiety, a molecule can also absorb some energy to increase the excitation of its electrons. The energy changes involved are considerably greater than those involved in vibrational and rotational energy changes and correspond to radiation in the ultraviolet (200–400 nm) and visible (400–750 nm) regions [17].

Other research about combustion characterization and kinetics of four different origin crude oil samples was determined using thermogravimetry-differential thermal analysis (TGA-DTA) and thermogravimetry-Fourier transform infrared (TGA-FTIR) and thermogravimetry-mass spectrophotometry (TGA-MS) techniques [18].

Four crude oil samples from the oil fields Intisar A, Intisar D, and Intisar E (Sirte Basin, Libya) were investigated in order to define depositional environment, lithology, thermal maturity, and geologic age of the corresponding source rocks. Saturated biomarkers (n-alkanes, isoprenoids, steranes, and triterpanes) were determined using gas chromatography-mass spectrometry (GC-MS) and gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS). Aromatic hydrocarbons (phenanthrene, methylphenanthrenes, methyl dibenzothiophenes, and trimethyl naphthalenes) were analyzed by GC-MS [19].

***A large amount of research is currently oriented to the study of asphaltene aggregation in different solvents [20]. The aggregation of asphaltene solutions in toluene was investigated. The particle diameter grows with increasing concentrations of asphaltene, and the increase rate varies with asphaltene concentration. This trend proves the presence of interactions that promote the formation of aggregates. With increasing concentration of asphaltene the formation of small particles is no longer dominant since, at higher concentrations, strong attractive interactions from small particles may cause the formation of larger particles [21].

Most research has been focused on native asphaltenes. Some researchers determined the molecular weight, density, and solubility parameter distributions of asphaltenes from thermo and hydrocracked oils [22]. Other researchers precipitated asphaltene fractions from heavy oil using a series of solvents that are similar from the thermodynamic viewpoint but are discriminated by their solubility parameters [2].

Asphaltene aggregation is usually discussed by means of the appearance of flocculation, which is regulated by thermodynamics of phase transition and can be observed by optic and spectroscopic techniques. However, growth and precipitation of aggregates not only depend on thermodynamic parameters (e.g., concentration and temperature) but also kinetic factors [23].

Recently, a study was conducted on the development of a spectroscopic method for the quantification of functional groups characteristic of asphaltenes, making direct quantification from oil a direct and practical method [24]. Nondiluted light and heavy crude oils and their blends were studied with additives of pyrolysis oil and Kemelix, both acting as asphaltene dispersants [25].

The classic form used to study the composition of an extremely complex mixture such as oil is to separate it into discrete simple fractions that can be analyzed, but the main objective of this work was to develop a spectroscopic method for the quantification of functional groups characteristic of asphaltenes, making a direct and practical method for quantification from oil. This investigation was conducted as a comparative study of two heavy crude oil solutions (HC1 and HC2) and asphaltene precipitated (AHC1 and AHC2) using UV-vis spectroscopy and dynamic light scattering (DLS). Particle size of the aggregates was performed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM).

2. Methodology

2.1. Materials

Cyclohexane with 99.9% of purify supplied by Tedia, analytical balance, OHAUS Adventurer Pro, AV264C model and UV-vis Spectrophotometer, model GBC Cintral 303 were used for the quantification of characteristic functional asphaltene groups in crude oil. A dynamic light scattering (DLS) Zetasizer Nano Malvern for determining the particle size and Heavy Fuel Formulation Classic Turbiscan and software Turbisoft Classic for analyzing crude oil migration phenomena were used.

Table 2 shows SARA fraction of HC1 and HC2 heavy crudes determined by ASTM-D2007-98 with 18°API density, which was used in this work.

2.2. Extraction of asphaltene from heavy crude oils

Asphaltenes were precipitated by ASTM D2007-80 standard method (American Society for Testing and Materials [ASTM], 1983).

2.3. UV-visible spectroscopy analysis of the crude-solvent solutions

Beginning with a standard 100 mg L⁻¹ solution of crude in cyclohexane, dilutions of 10–100 mg L⁻¹ were prepared. Successively and in triplicate, each dilution was analyzed on a UV-vis spectrophotometer to obtain the different absorbance (A) signals vs wavelength (λ), in the range of 200–450 nm. The information was graphed to obtain an absorbance vs concentration curve, the equation of a straight line and the value of the coefficient of determination (R²). For each concentration, the highest absorbance peak was sought, which was important for the calibration curves.

2.4. UV-visible spectroscopy analysis of the asphaltenes-solvent solutions

Based on a standard solution of 100 mg L⁻¹ asphaltenes in cyclohexane, solutions 10–100 mg L⁻¹ were prepared. Successively and in triplicate, each solution was analyzed on a UV-vis spectrophotometer for the different absorbance signals (A) versus wavelength (λ), in the range of 200–600 nm. The obtained data were plotted to graph a curve to show variations of absorbance

SARA fraction	HC1	HC2
Saturated	21.66	23.69
Aromatic	30.57	38.74
Resins	24.35	14.06
Asphaltenes	23.41	23.51

Table 2. SARA fraction in weight % of the analyzed crude oils.

versus concentration. The equation of a line was determined, and the coefficient of determination (R^2) was established. For each concentration, the highest absorbance peak was sought, which was important for the calibration curves.

2.5. Dynamic light scattering analysis (DLS) of crude oils and precipitated asphaltenes solutions

DLS analysis was conducted to determine the state of aggregation and stability of crude oil and asphaltenes in cyclohexane from a standard solution of 100 mg L^{-1} , performing triplicate measurements. For both solutions, ultrasonic vibration was applied for 20 min.

2.6. Crude oils migration phenomena analysis

Migration phenomena in crude oil were determined by measuring the variation of the transmittance versus the height of the signal for each sample. These measurements were carried out as a function of time, as the mechanism of this instrument is to take readings of transmitted and backscattered light at a maximum sample height of 80 mm. This scan can be repeated with a programmable frequency to obtain a macroscopic fingerprint of the sample. It was a 2-h analysis (12 scans at intervals of 5 min) and then, 1 min each 24 h for a period of 30 days. Experiments were performed at room temperature ($\sim 25^\circ\text{C}$).

2.7. Scanning electron microscopy and energy dispersive X-ray spectroscopy

Microstructure and surface elemental characterization of asphaltenes were performed through scanning electron microscopy (SEM) by using a JEOL JSM 6390-LV. Samples were dispersed and adhered to a double-sided graphite tape placed over a brass sample holder.

2.8. High-resolution transmission electron microscopy

The shape and size of asphaltene nanoparticles were examined through high-resolution transmission electron microscopy (HTEM) by using a JEOL JEM-2200FS equipment. Asphaltenes suspensions in ethanol were prepared by applying 5 min of ultrasonication, and one drop of each solution was placed on the grid and left to dry for 10 min with an incandescent light lamp.

3. Results and discussion

3.1. UV-vis spectroscopy analysis of crude-solvent and asphaltene-solvent solutions

By using UV-vis spectroscopy, the analyses of crude-solvent and asphaltene-solvent solutions were possible. Calibration curves were constructed for both solutions. In approximately 120 min of UV-vis spectroscopy analysis, no significant changes were detected.

Figures 1 and 2 show the wavelength versus absorbance plot for crude-solvent solutions in cyclohexane, varying their concentration from 10 to 70 mg L^{-1} for HC1 and HC2 oils. In the operating UV-vis region of the test, three signals were observed and identified: at approximately

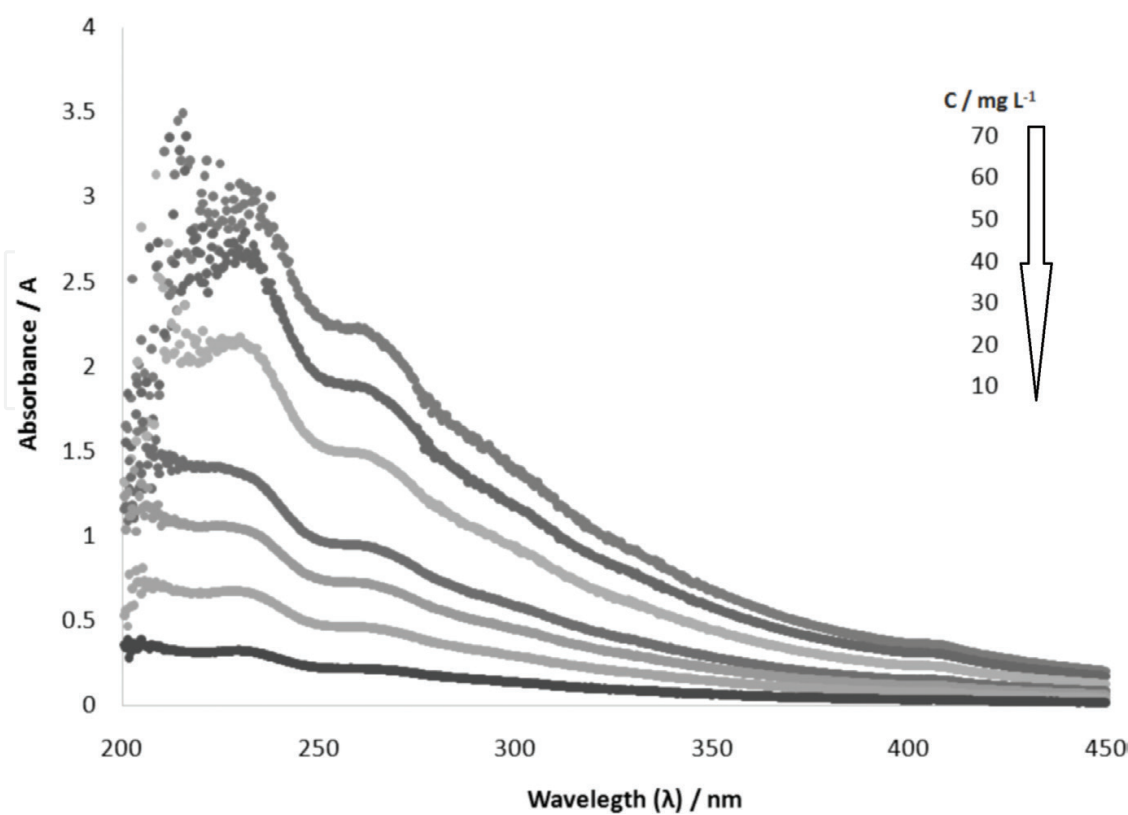


Figure 1. UV spectrum for HCl oil solutions, at different concentrations (decreasing order from 70 to 10 mg L⁻¹).

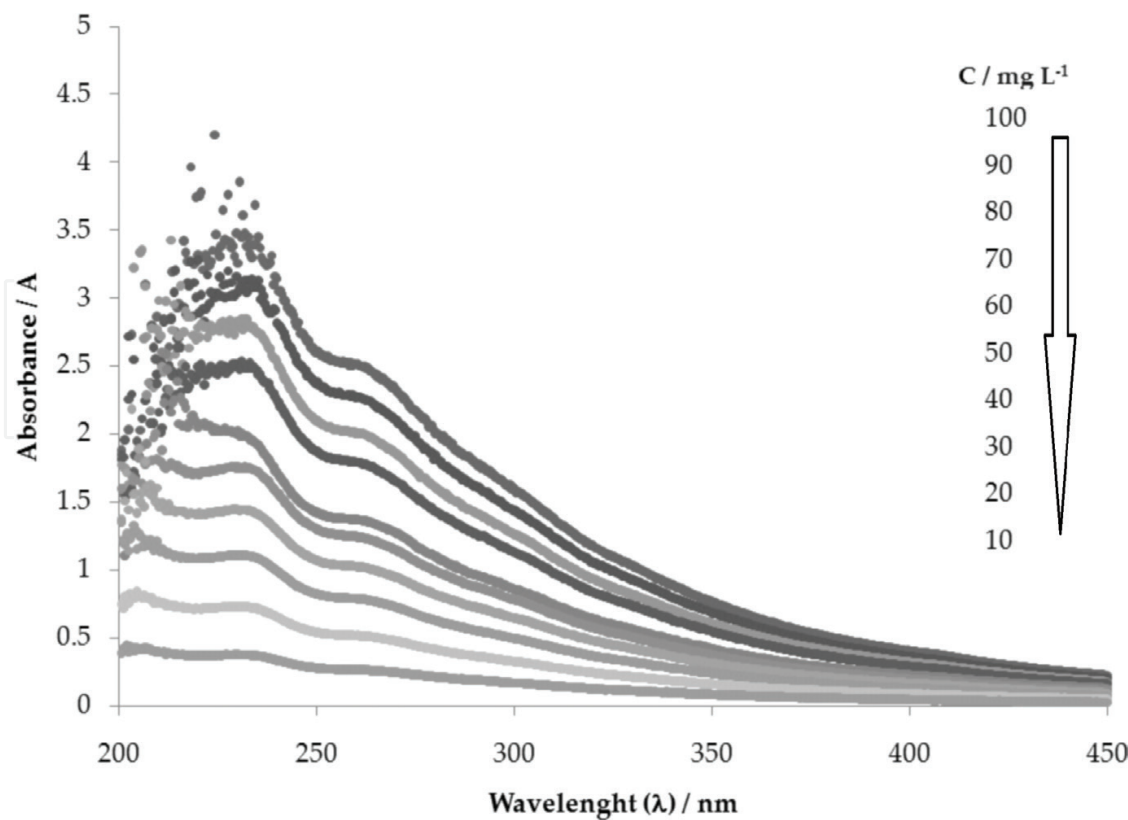


Figure 2. UV spectrum for HC2 oil solutions, at different concentrations (decreasing order from 100 to 10 mg L⁻¹).

230 nm, the signal corresponding to benzenic compounds; at 260 nm, the one of naphthenic compounds; and at 410 nm, the Soret band, showing information of metal porphyrin compounds [26–30] for HC1 oil and only the first two for HC2 oil. It was noticed that, as the oil concentration in the solutions decreased, the intensity of the three signals did the same, as effect of concentration for both crudes. Nevertheless, maximum absorbance signals could not be detected neither above 70 mg L⁻¹ concentrations for HC1 oil due to noise nor below 10 mg L⁻¹ because of the low concentration of HC1 oil, which precludes the detection of species by this technique [26].

Due to a smaller amount of resins in the HC2 oil composition, it was possible to display signals from 100 mg L⁻¹. For HC2 oil solutions above the concentration of 100 mg L⁻¹, it was not possible to detect signals due to the presence of noise. Below the concentration of 10 mg L⁻¹, no signs were present.

Figures 3 and 4 show the absorbance versus concentration graph for asphaltene solutions (AHC1 and AHC2), varying the concentration from 10 to 100 mg L⁻¹.

For AHC1 (**Figure 3**), three signals were detected: the one attributed to benzenic compounds at 235 nm, naphthenic compounds at 262 nm, and the Soret band at 410 nm, which corresponds to metal porphyrins present in asphaltene solutions [26, 30, 31]. For AHC2 solutions (**Figure 4**), only the two signals were detected at 235 and 262 nm. With this information, calibration curves for each compound and their respective linear equations were calculated.

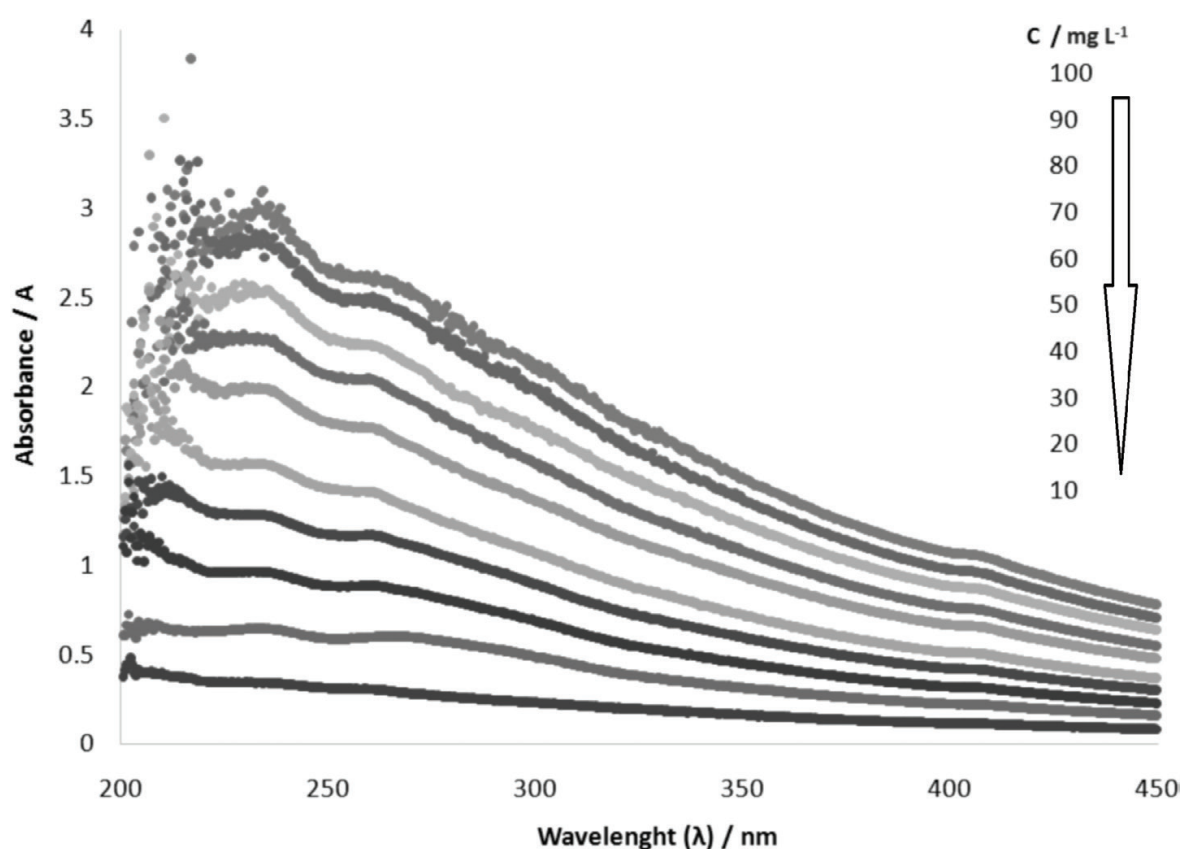


Figure 3. UV spectrum for AHC1 solutions, at different concentrations (decreasing order from 100 to 10 mg L⁻¹).

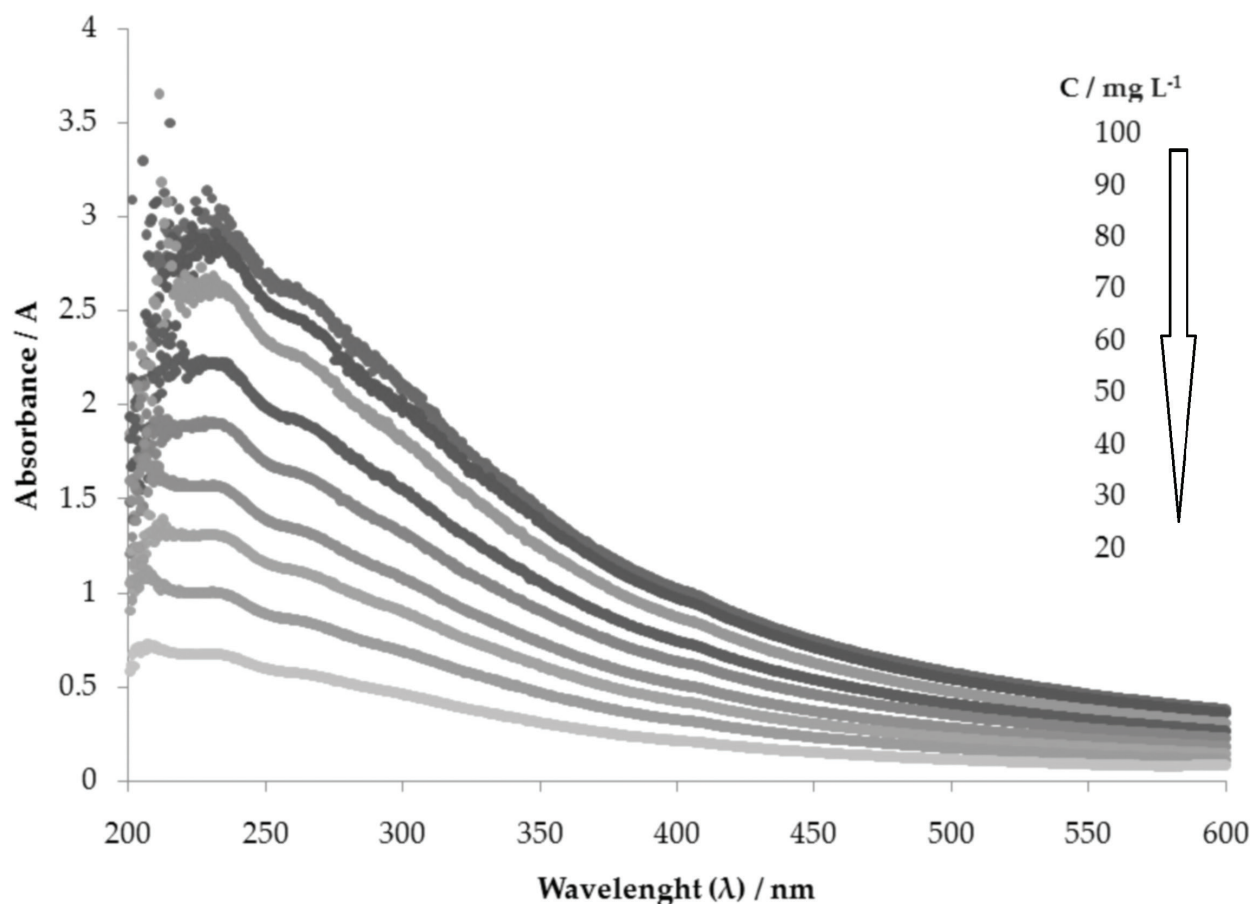


Figure 4. UV spectrum for AHC2 solutions, at different concentrations (decreasing order from 100 to 20 mg L⁻¹).

For concentrations under 50 mg L⁻¹ of AHC1 solutions, no Soret band was found, and similarly, no signals were detected for samples prepared at concentrations below 10 mg L⁻¹, due to the low concentration of asphaltenes; therefore, it was not possible to detect species by this method. As mentioned earlier, signal detection was impossible for HC1 oil solutions at concentrations exceeding 70 mg L⁻¹; however, for asphaltene solutions, the three signals were found, even above those concentrations. This phenomenon is attributed to the fact that crude is a complex mixture of various compounds including saturates, asphaltenes, resins, and aromatics, and as the saturation of a crude solution increases, noise becomes more evident in the spectrum, hindering the signal recognition. It was also observed that the amplitude of the maximum absorbance signals for crude solutions was more intense compared to absorbance maximum for asphaltene solutions. That is to say, higher absorbance maximum was observed when working with whole crude, because of the overlapping of individual absorbances, corresponding to many of the different components of crude. That complex composition includes the saturate fraction, which is nonpolar and is composed of linear alkanes, branched alkanes, and cycloalkanes [30]. The saturates tend to absorb strongly in the deep UV region, with high-frequency electronic transitions, as their electrons are tightly bound and require more incident energy to be excited. Meanwhile, aromatic hydrocarbons form structures of one or more rings, where multiring structures are often referred to as polycyclic aromatic hydrocarbons. Similar to saturates, a redshift is noted as complexity increases, and more rings are

added to the molecule [32, 33]. Bathochromic shift exists in signals of benzenic and naphthenic compounds for both asphaltene solutions at longer wavelengths because of more interactions between asphaltenes caused by the absence of resins.

It was possible to obtain signals at the concentration of 100 mg L^{-1} for AHC2 solutions. For concentrations below 20 mg L^{-1} , it was not possible to detect signals.

Figure 5(a) and **(b)** show the calibration curves of HC1 and HC2 oil solutions, respectively. Coefficient values for each compound are presented, since little dispersion of data was found. The HC1 oil solutions at concentration of 40 mg L^{-1} and HC2 oil solutions at concentration of 60 mg L^{-1} appear to be slightly deviated, which can be attributed to the presence of aromatics that favor aggregation in crude.

Figure 6(a) and **(b)** show the calibration curves of asphaltene solutions for HC1 and HC2, respectively. Coefficient values for each compound are presented. No dispersion of data was found.

3.2. Study of aggregate dispersion in crude and asphaltene solutions

DLS analysis was carried out in order to evaluate the average size of crude and asphaltene solutions in cyclohexane over time. **Figure 7(a)** shows the behavior of average size particles (Z_{AV}) over time (t) for HC1 oil solutions in cyclohexane at 100 mg L^{-1} . Z_{AV} was plotted from $t = 0 \text{ min}$, when the particle size was 51.16 nm , to $t = 100 \text{ min}$, when the average aggregate size showed an increase to 72.27 nm . In general, this behavior corroborates the instability of the unfractionated HC1 oil, although that its components coexist in equilibrium, which permits to perform analyses with good and reproducible results. Recently, a study was conducted to evaluate the aggregation state of Mexican crude oil solutions from two different sources and SARA compositions, by using dynamic light scattering (DLS) [34].

Figure 7(b) shows Z_{AV} (nm) behavior of HC2 oil solutions versus time. During the first 40 min, there was a Z_{AV} increase from 173.16 to 542 nm . After 40 min, Z_{AV} stabilized in the range

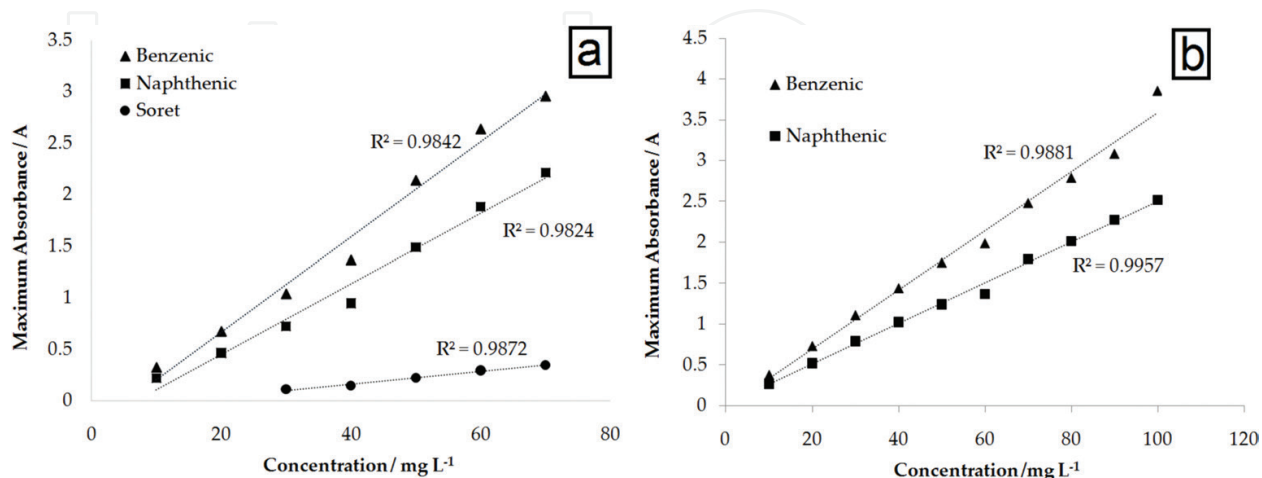


Figure 5. Calibration curves for benzenic, naphthenic and petroporphyrinic compounds in heavy crude oil solutions. (a) HC1 and (b) HC2.

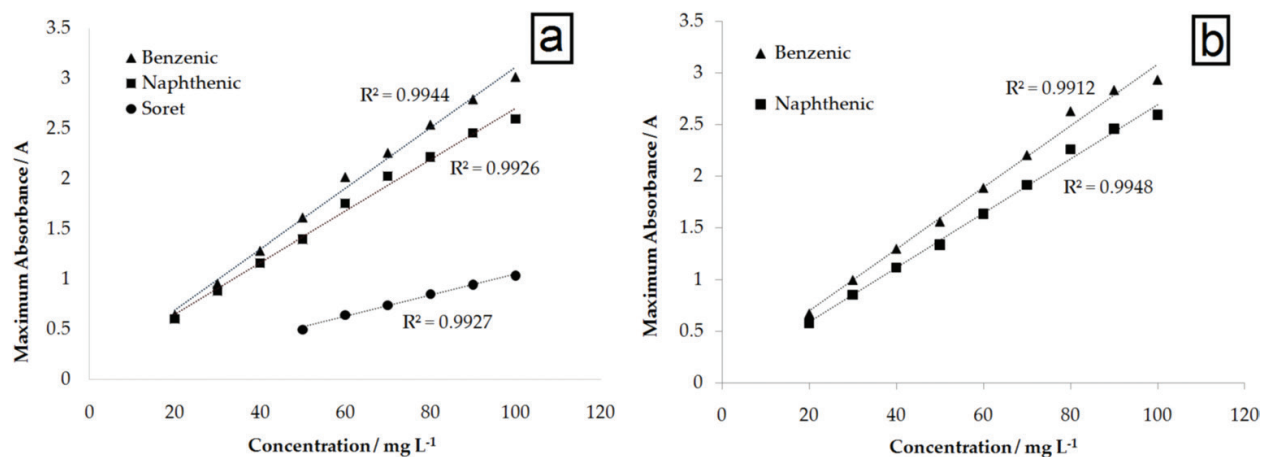


Figure 6. Calibration curves for benzenic, naphthenic and petroporphyrinic compounds in asphaltene solutions. (a) AHC1 and (b) AHC2.

of 563–624 nm. Molecules of the asphaltene fraction are dispersed in crude oil as stabilized colloids, and they can form aggregates by steric effect according to their sizes, polar characteristics, and solvent polarity [35].

The solutions of HC2 oil showed bigger size of aggregates in comparison with the solutions of HC1 oil, due to a smaller amount of resins present in the HC2 oil as confirmed by SEM. Banda et al. [34] studied different crude oil concentrations by using DLS. Results indicate that the aggregation state of the studied solutions is influenced by crude oil composition, specifically by the amount of resins. The resins are less soluble in n-alkanes than in cyclohexane and therefore are more likely to interact with asphaltenes to keep them in the form of small aggregates [5].

In the case of asphaltene solutions for both oils, the average aggregate size changed so rapidly that it was impossible to determine it. The aggregate size instability of asphaltenic solutions is a result of the absence of resins, which are known to favor stability [1, 37]. Therefore, the average aggregate size was no longer uniform, and unlike the behavior observed in unfractionated crude oil, the values corresponding to asphaltene solutions did not fit any tendency [1, 25–38].

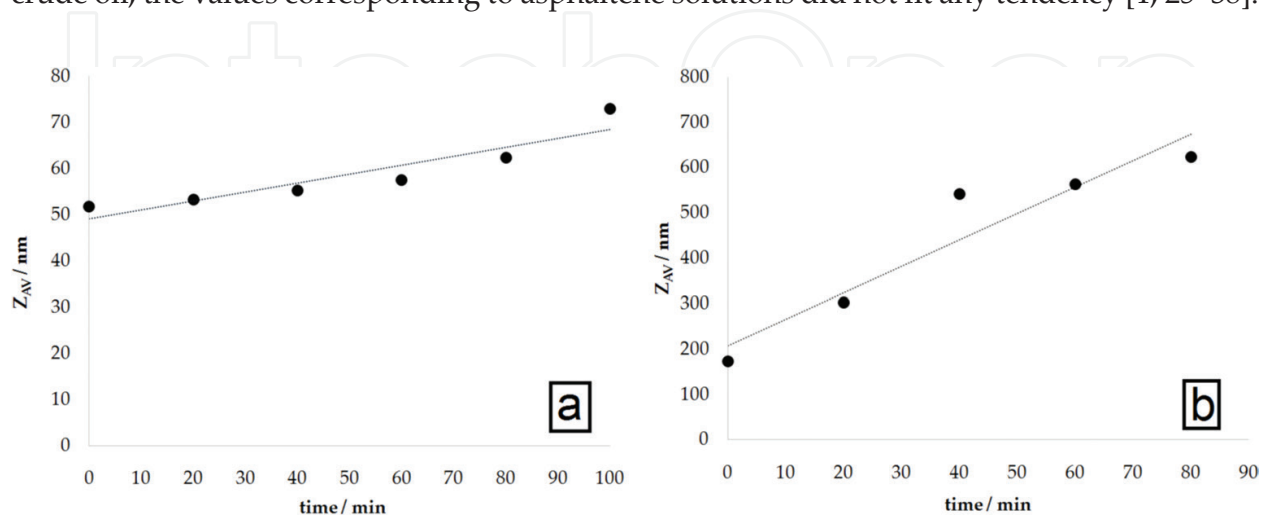


Figure 7. The average aggregate size (Z_{AV}) over time for (a) HC1 and (b) HC2 oil solutions.

3.3. Scanning electron microscopy (SEM)

Figure 8(a) and (b) shows a SEM micrograph of AHC1 asphaltenes. In the figures, a slightly porous surface can be observed. It is possible to appreciate agglomerates of various shapes and sizes. The larger agglomerates correspond to asphaltenes. At the top of the **Figure 8(a)**, large agglomerate of asphaltene is presented with lamellar morphology. On the surface, smaller agglomerates with smooth surface that correspond to resins can be noted.

Figure 8(c) and (d) shows a SEM micrograph of AHC2 asphaltenes, where a surface with lower precipitation degree is presented. SEM micrographs show stacked sheets of asphaltenes over the surface.

Two types of asphaltenes extracted from crude oil of different sources and SARA compositions were studied, by using SEM and HTEM. Significant differences in morphology and aggregate size for each type of asphaltene were noted. Results from these techniques reveal particulated low-porosity smooth surfaces due to the presence of resin, as well as the determination of the characteristic elements found in asphaltenes [34].

3.4. High-resolution transmission electron microscopy (HTEM)

Figure 9(a) and (b) shows AHC1 crude oil asphaltenes HTEM micrographs. The presence of asphaltene aggregates is constituted by nanometric particles. The presence of agglomerates of various sizes and shapes is found. Differences in image contrast are probably because of mate-

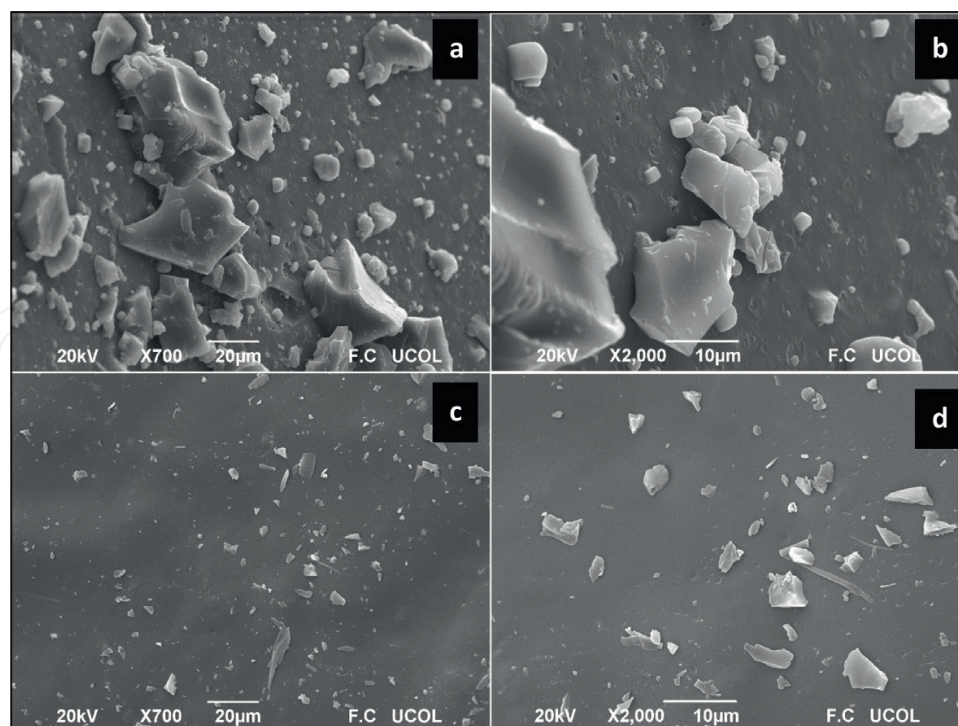


Figure 8. Morphology of (a and b) AHC1 and (c and d) AHC2 crude oil asphaltenes.

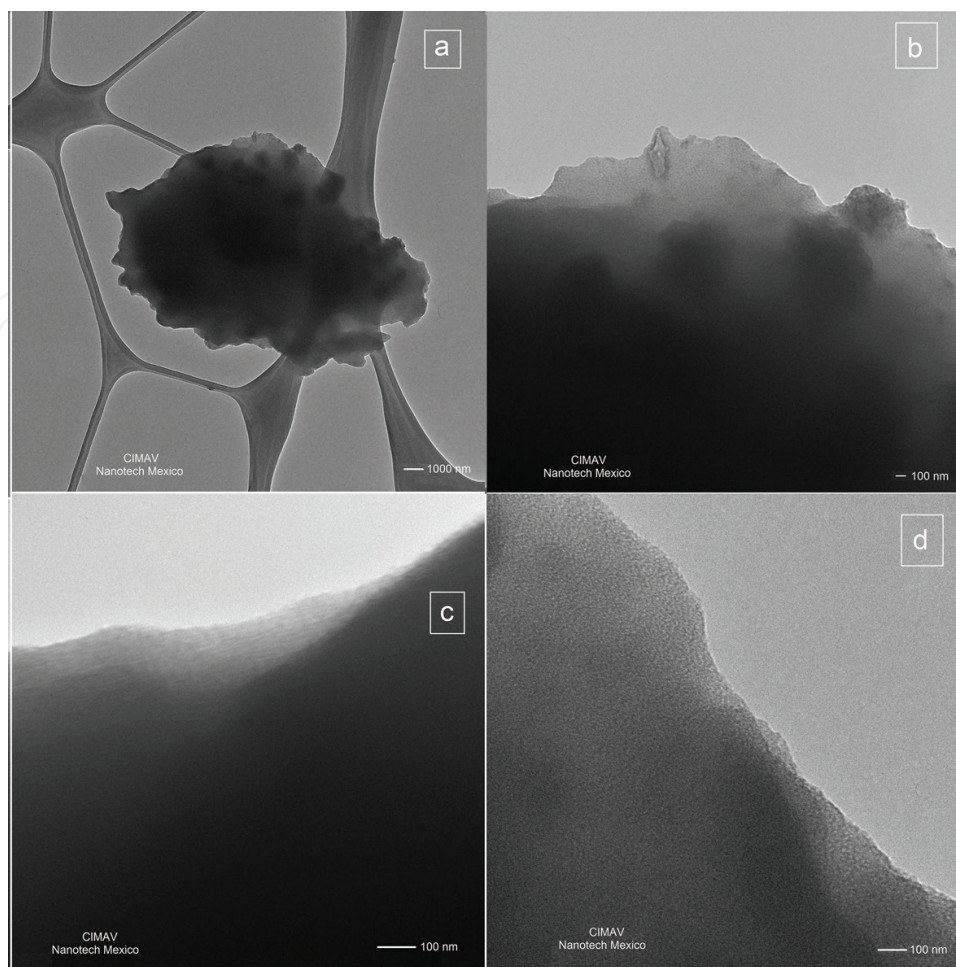


Figure 9. Morphology of AHC1 (a and b) and AHC2 (c and d) crude oil asphaltenes.

rial superposition for both images [39]. **Figure 9(a)** shows the grid of Cu/C with the sample. Agglomerates of approximately 1000 nm in size are presented. At the top of **Figure 9(b)**, layered structures are presented. In the center of micrograph, agglomerates with regular edges and approximately 500 nm sizes are found. At the bottom of the figure, there are agglomerates greater than 100 nm size.

Figure 9(c) and **(d)** shows AHC2 crude oil asphaltenes HTEM micrographs. **Figure 9(c)** proves the existence of crystalline zones in AHC2 asphaltene particles. Reticular stripes appear at the bottom of the image, indicating the nanocrystalline limits of the stacked layers [13]. **Figure 9(d)** shows the aggregates are constituted by nanometric particles. The presence of lamellar morphology is observed. There are stacked sheets at the top of the image, and there are agglomerates of approximately 200 nm. In the center of the micrograph, agglomerates are observed with a lamellar morphology and approximately 300 nm size. HTEM indicated the presence of asphaltene aggregates constituted by nanometric particles and asphaltene stacking as well as ultrafine nanocrystalline-oriented structures. Dark zone at the bottom of micrograph shows asphaltene stacking. The jagged surfaces along the edge of the structure correspond to nanocrystal-oriented structures.

3.3. Analysis of migration phenomenon in heavy crude oil

Furthermore, in **Figure 10**, the graph of percent transmittance versus cell length for stability assessment and crude oils separate fronts of this study is presented. Generally and conclusively, both crude oils were very stable. There was no change of percent transmittance ($>8\%$) within 30 days of analysis. No phenomena of measurable migration (separation, flocculation, coalescence, or sedimentation) were observed [36, 40]. To confirm the results yielded by the Turbiscan instrument, the migration speed of the agglomerates of HC1 was determined to be $3.69 \times 10^{-6} \text{ mm min}^{-1}$ and for HC2 of $8.683 \times 10^{-7} \text{ mm min}^{-1}$ (**Table 3**).

Low values of migration velocity and high sample stability were observed in **Figure 10**, which allow us to establish that the oils are stable over a wide range of time (there is no separation of components, mainly resins and asphaltenes). Studies conducted by the working group have shown that the rates of sedimentation of asphaltenes of various Mexican crudes in toluene and n-heptane are of the order of $5.94 \times 10^{-2} \text{ mm min}^{-1}$. These studies showed monodispersion and stability, because the asphaltenes tend to form large aggregates quickly, which facilitates precipitation [27].

Recently, a study of migration rate in a period of 30 days of two crudes from different sources and SARA composition. For both crude oils are very stable and did not show changes in the percentage of transmittance during the 30 days of analysis [15].

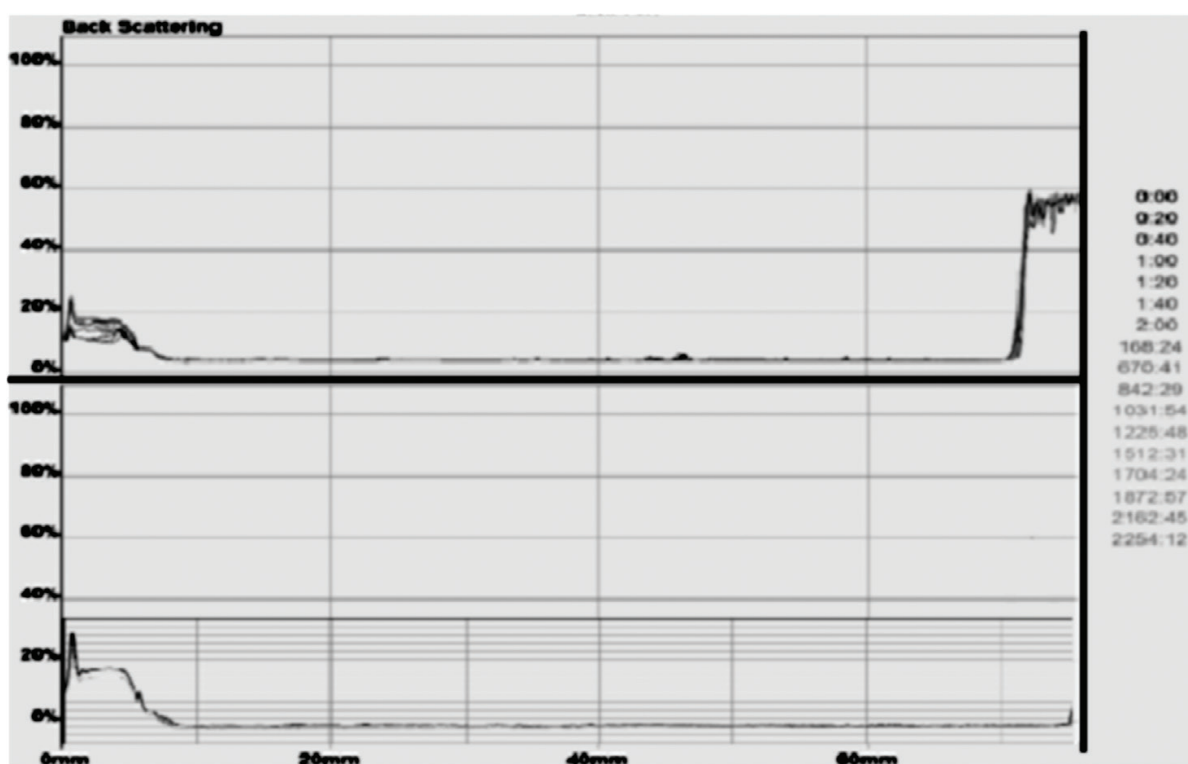


Figure 10. Curve of percent transmittance versus cell length (mm). Stability analysis of HC1 and HC2 oils obtained from the Turbisoft and Migration softwares of Classic Turbiscan software.

Sample	Oil	Migration velocity, mm min ⁻¹
1	HC1	3.69×10^{-6}
2	HC2	8.68×10^{-7}

Table 3. Migration velocity values of HC1 and HC2 oils.

4. Conclusions

UV-vis spectroscopy is an important tool that can be used to characterize crude oil solutions and their asphaltenes fractions. Characteristic signals of benzenic, naphthenic, and Soret compounds, which correspond to petroporphyrins, were identified in solutions of crude oil and extracted asphaltenes, using UV-vis spectroscopy. Bathochromic shift exists in signals of benzenic and naphthenic compounds for both asphaltene solutions at longer wavelengths because of more interactions between asphaltenes caused by the absence of resins. It was also observed that the amplitude of the maximum absorbance signals for crude solutions was more intense compared to absorbance maximum for asphaltene solutions. Higher absorbance maximum were observed for whole crude, because of the overlapping of individual absorbances, corresponding to many of the different components of crude. Stability in solutions was also established under test conditions using UV-vis spectroscopy.

DLS analysis indicated a slight increase in aggregate particle size during the first 100 min for solutions of HC1 oil. For HC2 solutions, Z_{AV} values were unstable during the first 80 min. The amount of resins present in each crude affects the aggregate size and the stability of the solutions with respect to time. Z_{AV} of asphaltene solutions changes rapidly due to the absence of resins for both crudes.

SEM showed a lamellar morphology in both asphaltenes. A greater quantity of resins was observed on the surface of AHC1. It was possible to observe differences in the morphology of the resins for AHC1 and AHC2. HTEM indicated the presence of asphaltene aggregates constituted by nanometric particles and asphaltene stacking as well as ultrafine nanocrystalline-oriented structures in AHC1 and AHC2.

A migration study was carried out for 30 days, indicating stability of asphaltenes in both crudes, backing up the results obtained in all the undertaken characterizations.

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