

Physicochemical Characterization of Heavy Oil and the Precipitated Asphaltenes Fraction using UV Spectroscopy and Dynamic Light Scattering

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Abstract. 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 by 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.

Keywords: Heavy oil, asphaltenes, UV-vis spectroscopy, aggregation, dynamic light scattering.

1 Introduction

Some of the most common problems occurring in refineries include the reduction of the hydrotreating reactions overall rates, deactivation of catalysts due to surface deposition, and an increase of coke formation (asphaltene are a coke precursor). In general, asphaltene precipitation limits the ultimate level of conversion. From this operational definition, asphaltene are known as a group of complex compounds, which are highly polydispersed and cannot be predicted by simple physicochemical parameters. High temperature systems where asphaltene are infinitely diluted in an appropriate solvent, are less prone to induce the formation of large aggregates, and tends to show narrow distributions; however, they still exhibit a real polydispersity. The average molecular weight (MW) is not necessarily the best parameter to characterize asphaltene, because the definition of these compounds is based on a simple principle: their solubility in aliphatic hydrocarbons [1]. Asphaltene, usually derived either from coal or from petroleum vacuum distillation residues, are wide-spread, and a class of compounds that are defined by their solubility, i.e. insoluble in n-heptane and soluble in toluene [2, 3]. The aromatic moiety, through π - π^* and dipole interactions, is thought to be one of the dominant contributors to asphaltene self-association. Hence, proper characterization of the asphaltene molecular structure and its aromaticity is fundamental in understanding the self-association phenomenon [4].

Therefore, the best linear n-alkane solvent of asphaltene, can keep a portion of them in a molecular state, favoring, at the same time, the association of higher molecular weight species. Then, the low molecular weight asphaltene remain as individual molecules or in very low aggregation state (dimer

or trimer). Furthermore, 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 [5-9].

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 [10]. Other researchers precipitated asphaltene fractions from heavy oil using a series of solvents that are similar from the thermodynamic viewpoint but discriminated by their solubility parameters [11-13].

Recently, a study for the development of a spectroscopic method for the quantification of the characteristic functional groups of asphaltenes was conducted by making direct quantification from oil [14, 15]. Non-diluted light and heavy crude oils and their blends were also studied with additives of pyrolysis oil and Kemelix, both acting as asphaltene dispersants [13, 16, 17].

The composition of an extremely complex mixture such as that of the oil, is typically determined by separating the mixture into simple discrete fractions that can be independently analyzed, but the main objective of this work was to develop a spectroscopic method for the quantification of functional groups characteristic of asphaltenes, making direct quantification from oil, making it a direct and practical method. This investigation was conducted as a comparative study of heavy crude oil and asphaltene precipitated solutions using UV-Vis spectroscopy and dynamic light scattering (DLS).

2 Experiments

2.1 Materials and Methods

Cyclohexane of 99.9% purity, supplied by Tedia, and an analytical balance, OHAUS Adventurer Pro, AV264C model, were employed. A UV-Vis Spectrophotometer, model GBC Cintral 303 was used for the quantification of the asphaltene characteristic functional groups in crude oil. A dynamic light scattering (DLS) Zetasizer Nano Malvern was utilized for the particle size determination, and a Heavy Fuel Formulation Classic Turbiscan was used for analyzing the crude oil migration phenomena.

Table 1 shows the SARA fractions, determined by ASTM-D2007-98, of the heavy crude oil, 18°API density, that was used in this work.

Table 1. SARA fraction in weight % of the analyzed crude oil

SARA fraction	weight %
Saturated	21.66
Aromatic	30.57
Resins	24.35
Asphalthenes	23.41

2.2. Methodology

Extraction of Asphaltene from Heavy Crude Oil

Asphaltenes were precipitated according to the ASTM D2007-80 standard method (American Society for Testing and Materials [ASTM], 1983). **UV-vis spectroscopy analysis of crude-solvent solutions** Dilutions of 10-90 mg L⁻¹ were prepared from a 100 mg L⁻¹ standard solution of crude in cyclohexane. Successively and by triplicate, each diluted sample was analyzed by means of a UV-vis spectrophotometer to obtain the absorbance (A) vs wavelength (λ) behavior within the range of 200-450 nm. From the absorbance vs concentration curve, the equation of a straight line and the value of the coefficient of determination (R²), were calculated. Calibration curves were prepared using the information given by the maximum absorbance value of each concentration.

UV-Visible spectroscopy analysis of the asphaltenes-solvent solutions

Based on a standard solution of 100 mg L⁻¹ of asphaltenes in cyclohexane, solutions of 10 to 100 mg L⁻¹ were prepared. Successively and by triplicate, each solution was analyzed on a UV-Vis spectrophotometer, in order to identify the absorbance (A) versus wavelength (λ) signals in the range of 200–450 nm. From the obtained data, a curve that reflected the variations of absorbance as a function of concentration, was obtained. Then, the equation of a line as well as its coefficient of determination (R²) were computed. Calibration curves were prepared using the information given by the maximum absorbance value of each concentration.

Dynamic light scattering Analysis (DLS) of the heavy crude oil and precipitated asphaltenes solutions

The DLS analysis was conducted with the aim of determining 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. Ultrasonication was used to stir both solutions for 20 minutes.

Analysis of heavy crude oil migration phenomena

Migration phenomena in crude oil were determined by measuring the variation of the transmittance versus the intensity of the signal of each sample, using a Turbiscan instrument. These measurements were carried out as a function of time. The mechanism of this instrument consists of detecting the 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. The analysis was performed for 2 hours (12 scans at intervals of 5 minutes), and then 1 minute each 24 hours for a period of 30 days. Experiments were performed at room temperature (~25°C).

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 minutes of UV-vis spectroscopy analysis, no significant changes were detected.

Figure 1 shows the wavelength versus absorbance plot for crude-solvent solutions in cyclohexane, varying their concentration from 10 to 70 mg L⁻¹. In the operating UV-vis region of the test, three signals were observed and identified: at approximately 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 [12, 14, 15, 18-20]. It was noticed that, as the oil concentration in the solution decreased, the intensity of the three signals did the same, as effect of concentration. Nevertheless, maximum absorbance signals could not be detected neither above 70 mg L⁻¹ concentrations due to noise, nor below 10 mg L⁻¹ because of the low concentration of crude, which precludes the detection of species by this technique [12].

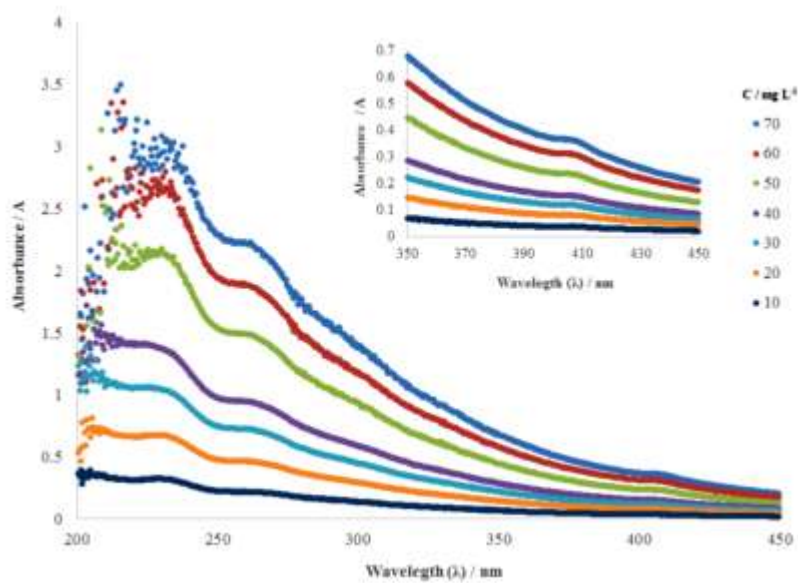


Figure 1. UV spectrum for heavy crude oil solutions, at concentrations of 10 to 70 mg L⁻¹

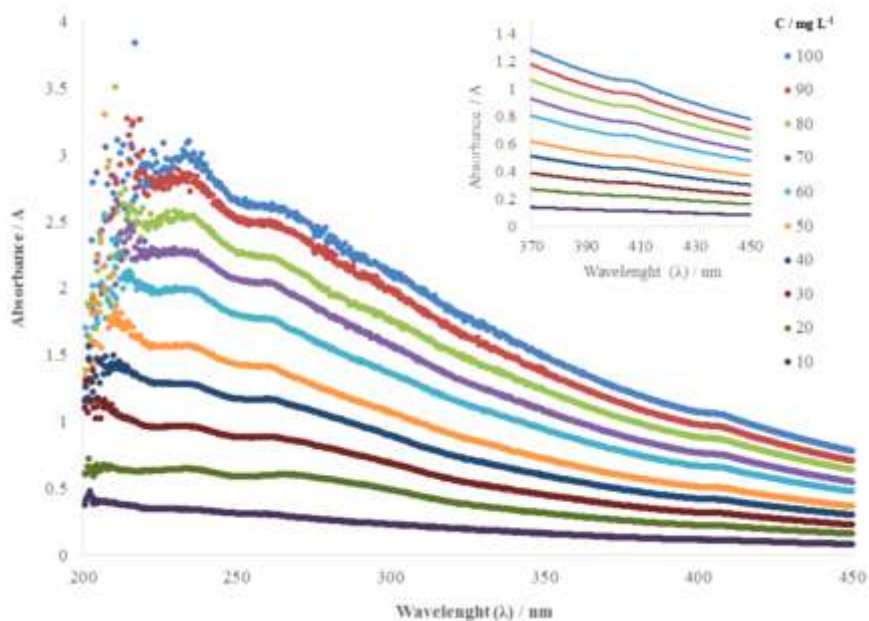


Figure 2. UV spectrum for heavy asphaltene solutions, at concentrations of 10 to 100 mg L⁻¹.

Figure 2 shows the absorbance versus concentration graph for asphaltene solutions in cyclohexane, varying the concentration from 10 to 100 mg L⁻¹. 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 [6, 12, 20]. With this information, calibration curves for each compound and their respective linear equations were calculated. For concentrations under 50 mg L⁻¹, 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 crude 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 were 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 [20]. The saturates tends 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 red shift is noted as complexity increases and more rings are added to the molecule [13, 21]. Bathochromic shift exists in signals of benzenic and naphthenic compounds for asphaltene solutions at longer wavelengths because of more interactions between asphaltenes caused by the absence of resins.

Figures 3 and 4 show the calibration curves of crude solutions and asphaltene solutions, respectively. Coefficient values for each compound are presented, since little dispersion of data was found. Crude solutions at concentration of 40 mg L⁻¹ appears to be slightly deviated, which can be attributed to the presence of aromatics that favor aggregation in crude.

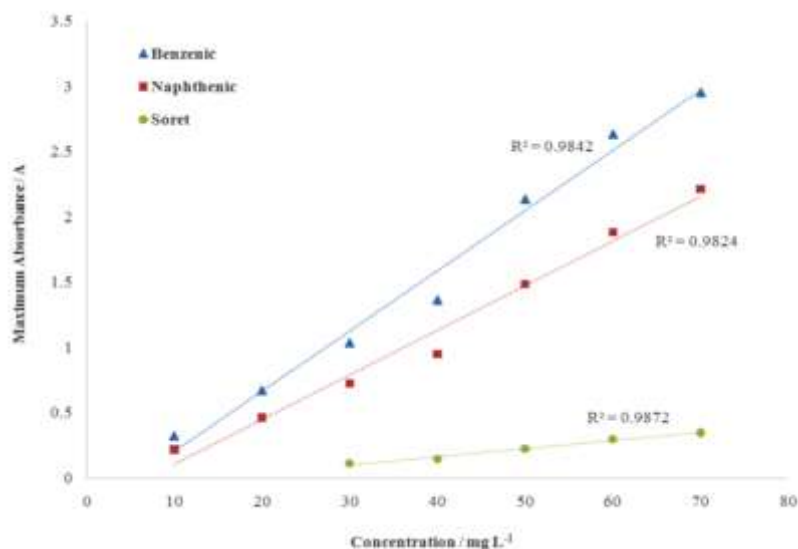


Figure 3. Calibration curve for benzenic, naphthenic and petroporphyrinic compounds in crude solutions.

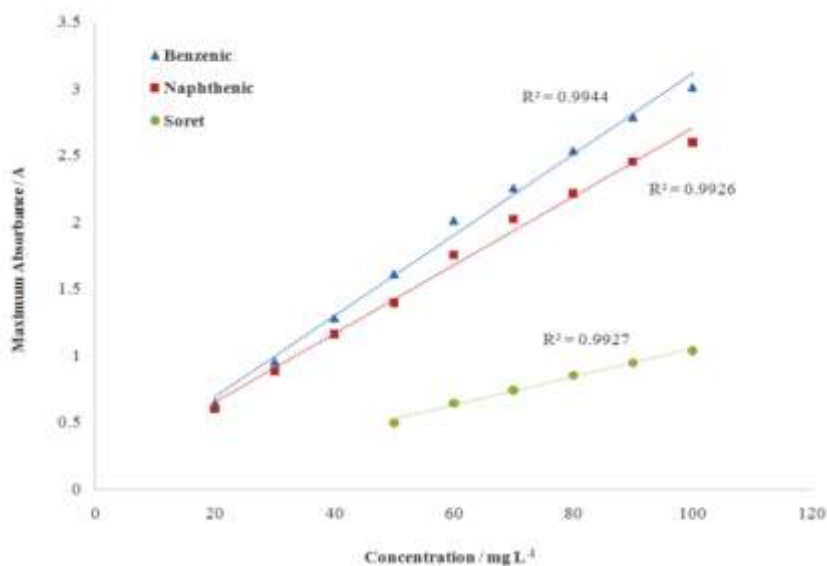


Figure 4. Calibration curve for benzenic, naphthenic and petroporphyrinic compounds in asphaltene solutions.

3.2 Study of aggregate dispersion in crude and asphaltene solutions.

DLS analysis was carried out in order to evaluate the stability of crude and asphaltene solutions in cyclohexane over time. Figure 5 shows the behavior of average size particles (Z_{AV}) over time (t) for crude 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 stability of the unfractionated crude oil, given 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) [22].

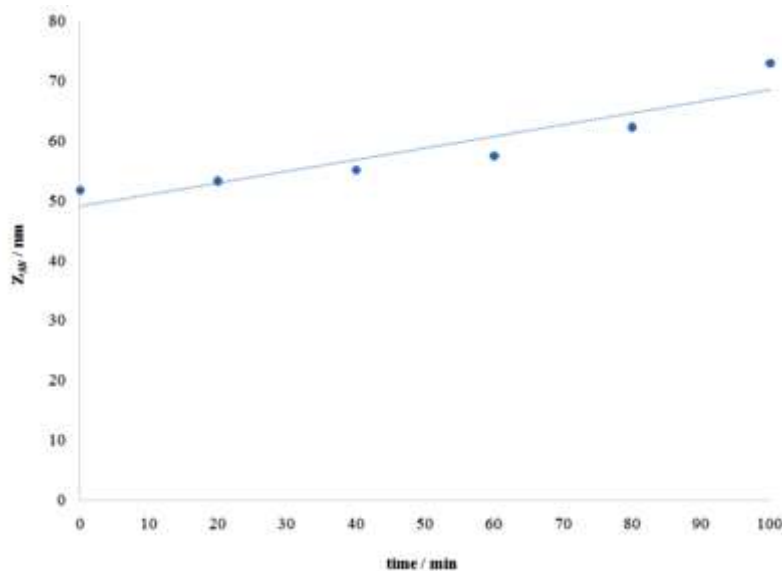


Figure 5. Represents the average aggregate size (Z_{AV}) over time for crude solutions.

In the case of asphaltene solutions, 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 [23, 24]. 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 [7-9].

3.3 Analysis of migration phenomenon in heavy crude oil

Furthermore, in Figure 6, the graph of percent transmittance versus cell length for stability assessment and crude oils separate fronts of this study are presented. Generally, and conclusively the heavy crude is 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 [5, 25]. To confirm the results yielded by the Turbiscan instrument, the migration speed of the agglomerates of heavy crude oil was determined to be $3.69 \times 10^{-6} \text{ mm min}^{-1}$.

Low values of migration velocity and high sample stability were observed in Figure 6, which allow us to establish that the oil is stable over a wide range of time (there is no separation of components, mainly resins and asphaltenes).

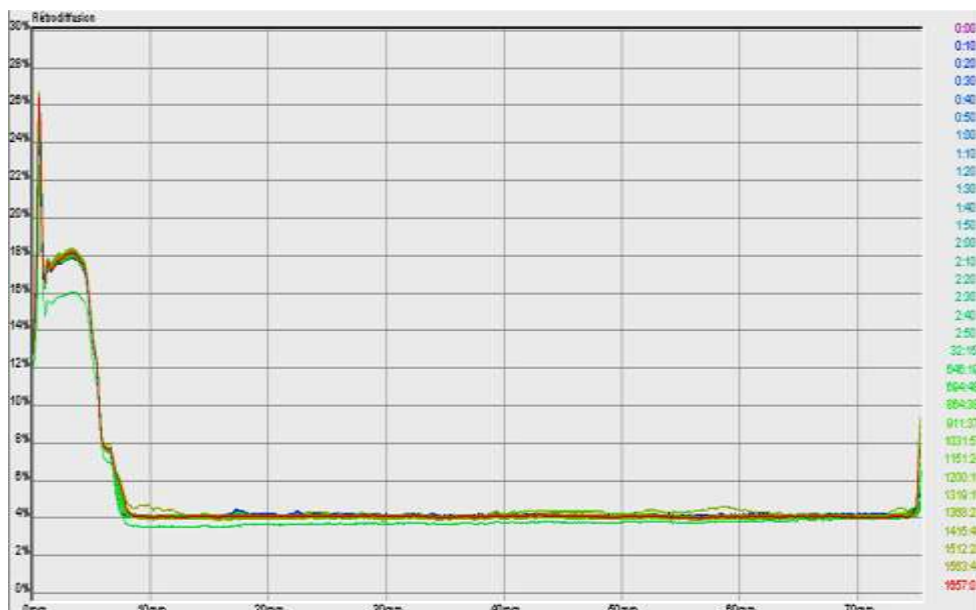


Figure 6. Curve of percent transmittance versus cell length (mm). Stability analysis of the heavy crude oil obtained from the Turbisoft and Migration softwares of Classic Turbiscan software.

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 of the asphaltenes tends to form large aggregates quickly, which facilitates precipitation.

4. Conclusions

It was possible to identify signals of benzenic, naphthenic and Soret compounds which correspond to petroporphyrins for solutions of heavy crude oil and extracted asphaltenes using UV-vis spectroscopy. Stability in solutions of crude oil and asphaltenes was also established under test conditions using UV-vis spectroscopy. DLS indicates a slight increase in aggregate particle size during the first 100 minutes for solutions of crude oil, while the Z_{AV} of asphaltene solutions changes rapidly due to the absence of resins. A migration study was carried out for 30 days, indicating stability, backing up results obtained in all the characterizations undertaken.

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