



Absorbance and fluorescence spectroscopy on the aggregation behavior of asphaltene–toluene solutions

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Abstract

Evidence of crude oil stability and the tendency of asphaltene aggregation in crude oil have been investigated by absorption and fluorescence spectroscopy. Octylated asphaltenes were also used as reference because of their low aggregation tendency. Changes in the absorbance vs. concentrations in toluene solutions show that aggregation starts around 50 mg/l for Furiial asphaltene and approximately at 75 mg/l for Hamaca asphaltenes. Red shift and quenching in the fluorescence peak maximum observed for solutions when asphaltenes concentrations are increased demonstrate that the aggregation process starts at low concentration regime. These experimental results are consistent with the fact that Hamaca asphaltenes have lower tendency to aggregate than asphaltenes from Furiial crude oils. Our results verify that the tendency to form aggregates diminishes in the octylated form.

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1. Introduction

Asphaltenes are typically defined as the non-volatile fraction of crude oils insoluble in *n*-heptane. The asphaltene fraction consists of many different molecules of different molecular weight and polarity having the same solubility properties in the oil or precipitation solvent [1].

Asphaltenes are important in the oil industry, due to their deleterious effects in many industrial operations (production, refining, and transportation). Many of these problems are related to the capacity of the sample to form aggregates and clogging of rock pores and production facilities, catalysis fouling, and deposit formation during storage, among other inconveniences. Therefore, an important research effort has been dedicated to the study of the relevant factors controlling process [2–4].

One of the main conclusions of investigation on the asphaltene colloidal state is that asphaltenes self-associate in solution to give rise to more or less extended aggregates. Different concentrations have been proposed for the point

below which asphaltenes are fully dissociated. Recently, Acevedo et al. [5] based on thermo-optical diffusivities data, proposed that the asphaltene aggregation starts at concentrations lower than 100 mg/l. Different studies on the aggregation process behavior in simple molecules like dyes and other organic compounds using UV–vis spectroscopy has been reported in the last years [6–8]. Changes in the UV–vis absorption spectra due to aggregation in dyes, these kind of samples have been clearly demonstrated. In the field of crude oils investigation, UV–vis technique has been applied for the studies of asphaltene adsorption on different substrates without taken into account the sensitivity of this technique to the aggregate formation [9–11].

Recently, studies have exploited optical techniques, some new, some traditional, to expand greatly the understanding of crude oils and asphaltenes aggregation behavior [14–19]. Techniques like light absorption and fluorescence are widely used to elucidate the fundamental properties of crude oils and asphaltenes [20–23]. Previous studies using optical spectroscopic techniques performed in asphaltene have evidenced small differences in absorption and emission spectra for different kind of crude oil and asphaltenes solutions. Despite that all crude oils possess the same chromospheres, they are in very different concentration

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showing little variations in the spectral location of the absorption [20,21,23].

Several aspects of the molecular absorption and fluorescence of asphaltenes have been examined by Mullin et al. [20] and Yokota et al. [21]; however, little spectroscopic studies have been carried out to understanding the asphaltenes aggregation process in low concentration regime.

In order to study the aggregation phenomena of asphaltene, Ignasiak et al. [12] modify the molecular structure by treatment of the asphaltene with potassium naphthalide in order to reduce the tendency to form aggregates. Acevedo et al. [13] consider as possible octylation reaction shown in Fig. 1. The compound **I** was taken as a prototype for asphaltenes fraction. Step 1 is an electron transfer from potassium naphthalide **II** to the sulfur atom in the asphaltene, which leads to anion radical **III**. Step 2 is a C–S bond breaking; in step 3 the radical **V**, much more stable than **IV** due to delocalization, is formed. Further reduction of **V** by potassium is achieved in step 4 and finally, step 5 corresponds to an SN2 type reactions leading to the incorporation of the *n*-octyl group. Although other reactions are possible, Acevedo shows to this work that this sequence is consistent with the C-13 spectra of octylated asphaltenes (OA) and according to the elemental analysis.

This methodology is usefully in the study of the aggregation process of asphaltene in toluene at low concentrations by permitting to compare the aggregation process in asphaltene crude oils before and after modification.

In this work, we employ absorption and fluorescence techniques to study aggregation process in asphaltenes solutions at relative low concentration regimes. Changes in the extinction coefficient and peak shift in the fluorescence spectra with concentration demonstrate the beginning of aggregation of asphaltene at concentrations as low as 50 mg/l. Octylated asphaltene shows the same behavior, but the aggregation start at higher concentrations.

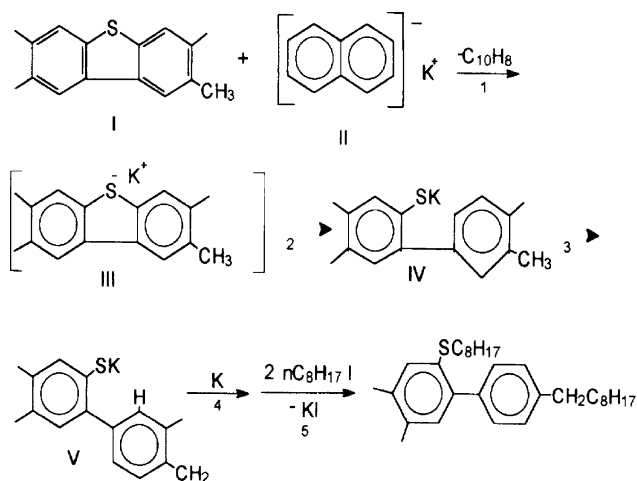


Fig. 1. Octylation mechanisms of asphaltenes.

2. Experimental method

2.1. Sample preparation

Asphaltene samples were extracted from two Venezuelan heavy crude oils: Furrial and Hamaca. They were obtained by precipitation with *n*-heptane in the usual way [24]. Furrial crude oil has severe flocculation problems, whereas Hamaca is a stable crude oil with less precipitation problem. The octylated asphaltene were obtained starting from the above asphaltene and using the procedure described previously [13]. Some properties of these crude oils are summarized in Table 1.

Solutions from asphaltene and octylated asphaltene were prepared by dissolution of the dried solid samples in toluene. The solutions were left in ultrasonic bath for 30 min to assure complete dissolution. Finally, the samples were diluted with toluene to concentrations ranging from 10 to 500 mg/l.

2.2. Absorption and fluorescence measurements

Absorption spectra of samples were taken using a diode array spectrometer (Ocean Optics 2200 UV–vis) of 0.5 nm spectral resolutions and spectral regions between 300 and 900 nm. All the measurements were made at room temperature. The absorption spectra of asphaltenes were corrected with solvent (toluene) spectra. Quartz sample cells with different optical path 0.1–0.5 cm were used.

Fluorescence measurements were made using a classic optic mount at 90° signal observation. As excitation source, a CW ion argon laser (Innova 305 from Coherent) operated in a single line mode (514.5 nm) was used at 150 mW. The spectra were recorded on an optic fiber spectrometer (Ocean Optics, Inc. model 2200) and total fluorescence signal is collected by a silicon photodetector (Thorlabs, Inc.). The experimental setup allows obtaining the fluorescence spectrum and the total fluorescence intensity. The solution sample cells were contained in a 1-cm path-length glass cell.

Table 1
Properties of materials used

Asphaltene	API ^a	% ^b	H/C ^c	f _a ^d	N	S	O
Furrial	21	9	0.97 ^e	56	1.7	3.4	2.5
Hamaca	9	10	1.13	56 ^f	1.96	4.5	1.89
Octylated Asphaltene		H/C		N		S	O
Furrial		1.199	0.92		2.52		5.56
Hamaca		1.398	1.28		2.92		1.91

^a Of crude oil.

^b Respect to crude oil.

^c Hydrogen to carbon ratio.

^d Aromaticity (% of aromatic carbons).

^e From Ref. [25].

^f Obtained by NMR as usual.

3. Results and discussion

3.1. Absorbance

The absorption spectrum of the Furrial and Hamaca asphaltenes in toluene solution of 50 mg/l are shown in Fig. 2. The spectrum exhibits a maximum of absorbance around 310.0 nm and a broad band with more of 100 nm at the full half width maximum intensity. The absorption spectrums for the octylated asphaltenes in toluene solution are similar. The spectral location of the absorption maximum varies considerably and almost continuously for the different crude oils [20]. The similarity of the absorption spectra of the asphaltenes studied evidence that the same type of chromospheres presents in the asphaltene fractions [21].

Absorbance as a function of the concentration for Furrial asphaltenes solution at 532 nm is shown in Fig. 3A. An apparent linear behavior is observed. The inset displays that the absorbance signal increase linearly with the concentration, but a break point is located around 53 mg/l. This slope change can be related to changes in the absorption coefficient due to asphaltenes aggregation. Fig. 3B shows the variation of absorbance for octylated Furrial asphaltenes solutions. For this sample, a linear behavior is observed in all concentration range, without break point. These results verified that the tendency to form aggregates diminishes in the octylated form.

Fig. 4A and B shows the variation of absorbance for Hamaca asphaltenes and octylated Hamaca asphaltenes

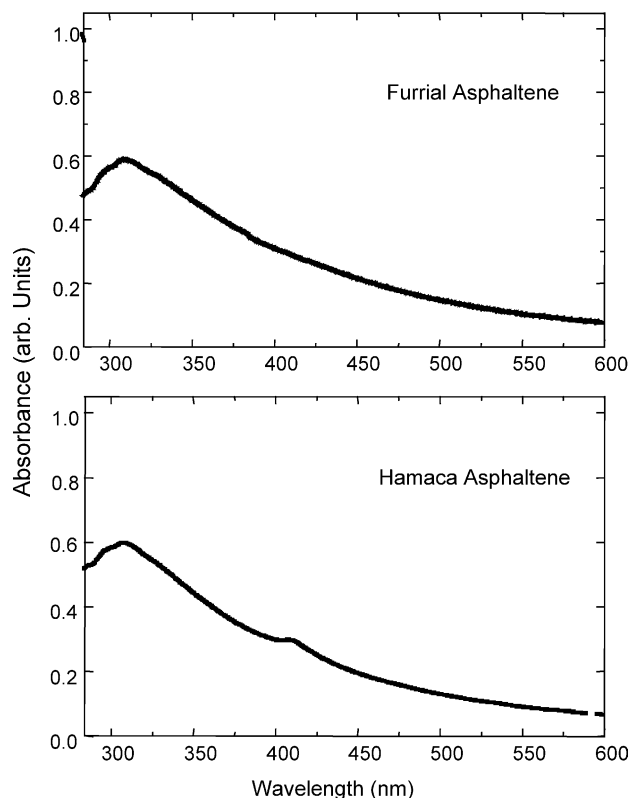


Fig. 2. Absorption spectrum of the Furrial and Hamaca asphaltenes in toluene solution of 50 mg/l.

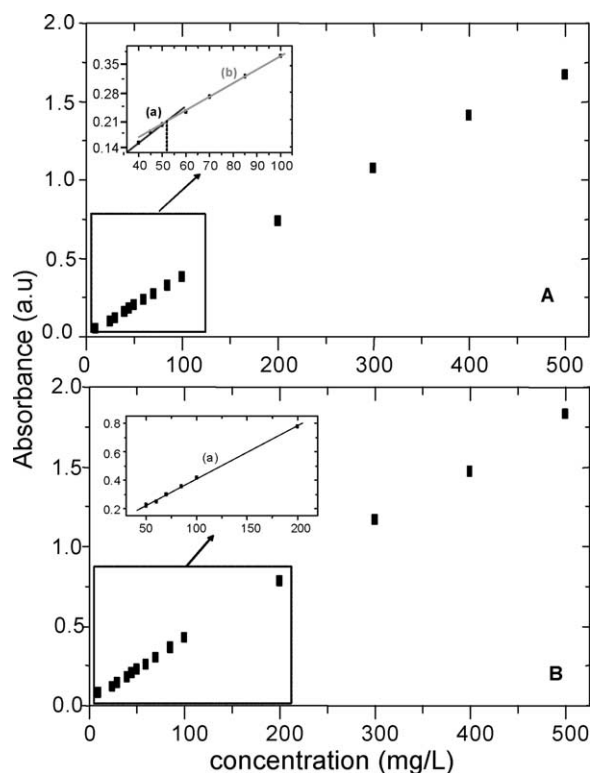


Fig. 3. Absorbance vs. concentration (mg/l) for solution toluene of Furrial asphaltenes (A) and their octylated forms (B) at 532 nm using a 1 mm cell.

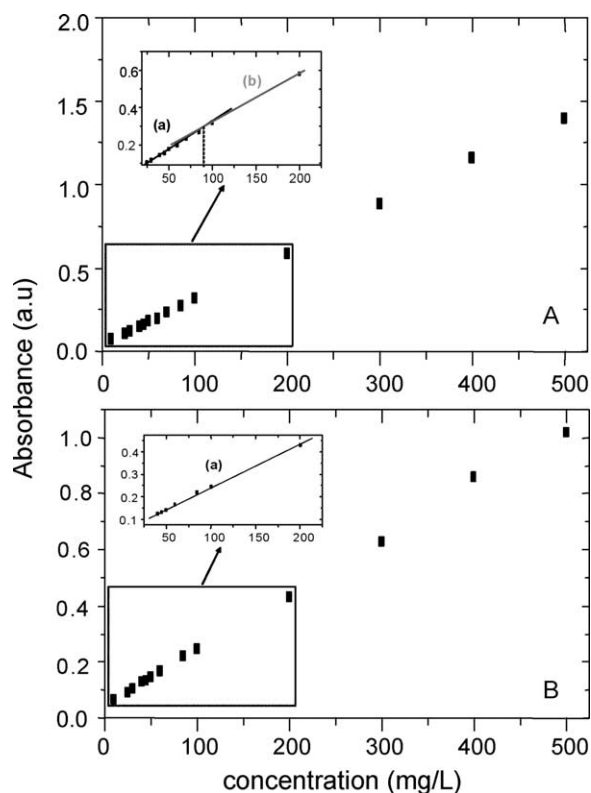


Fig. 4. Absorbance vs. concentration (mg/l) for solution toluene of Hamaca asphaltenes (A) and their octylated forms (B) at 532 nm using a 1 mm cell.

solutions, respectively. Similar behaviors were obtained for this asphaltenes, but the break point in the absorption vs. concentration curve is now observed at higher concentration (~ 75 mg/l). It is clear too, that the magnitude of the slope change is lower compare to those observed for Furrial asphaltenes. These experimental results are consistent with the fact that Hamaca asphaltenes has lower tendency to aggregate than asphaltenes from Furrial crude oils.

3.2. Fluorescence

Figs. 5A and 6A show the fluorescence spectra for Furrial and Hamaca asphaltenes in toluene solutions at different concentrations. Both spectra have the same characteristics, a broad band with at least three different local maximum were observed, the first corresponds to the excitation wavelength and the others to the sample response: 530.6 and 564.6 nm. The presence of these bands can be attributed in the presence of different fluorophores presents in the asphaltenes.

The fluorescence spectrum of the Furrial and Hamaca asphaltenes in their octylated forms exhibits a main band at 564.0 nm. When the concentration is increased, the emission at 530.6 nm suffers a relative decreases. These decreases can be explained because of changes in the structure asphaltene due to aggregation.

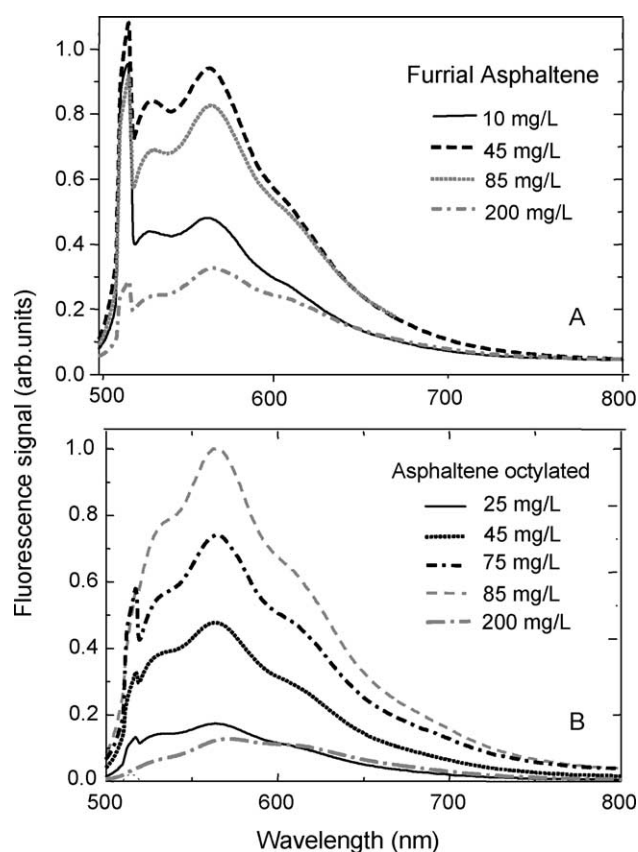


Fig. 5. Fluorescence spectra of toluene solution of Furrial asphaltenes and their octylated forms for different concentrations.

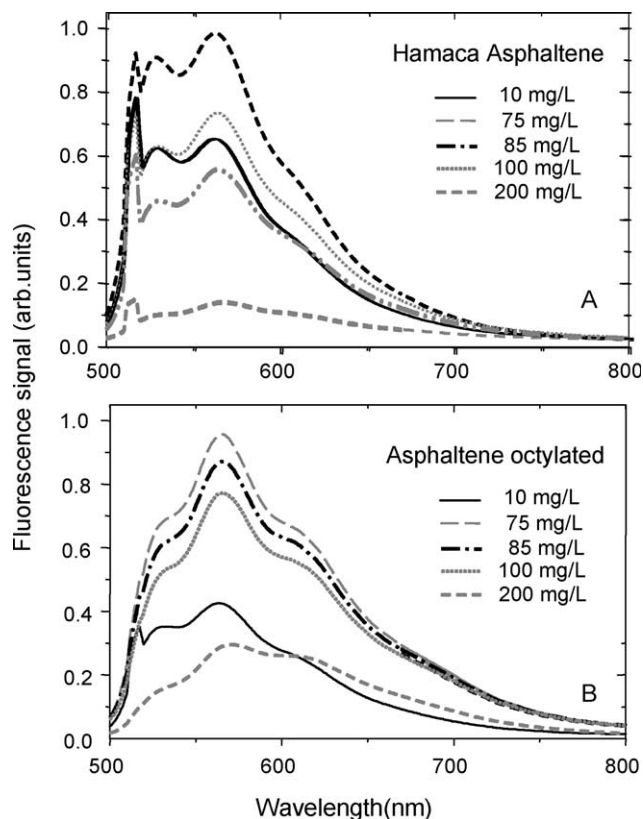


Fig. 6. Fluorescence spectra of toluene solution of Hamaca asphaltenes and their octylated forms for different concentrations.

Fig. 7 shows the shift in the fluorescence peak maximum of solutions of different concentration for Furrial asphaltenes and their octylated forms. This figure shows that the fluorescence spectrum of the samples is shifted to smaller energies (red shift) when asphaltenes solution concentration is increased. This red shift is observed when the solution concentrations reach 50 mg/l. In order to discard any effect of saturation, we carried out these experiments with a 1 mm optical path cell. We found that

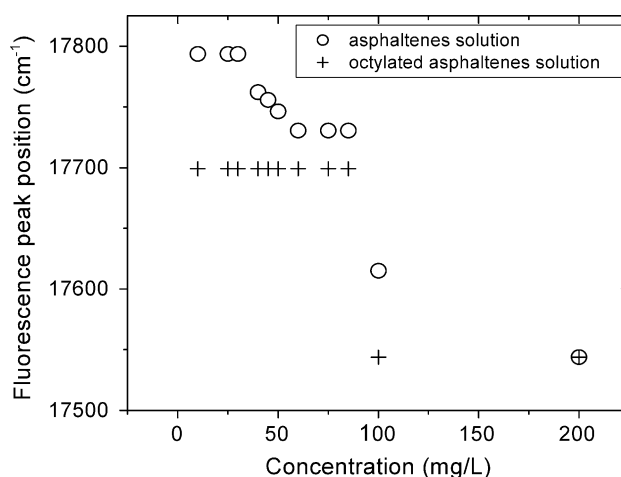


Fig. 7. Fluorescence peak position of toluene solution of Furrial asphaltenes and their octylated forms for different concentrations.

the fluorescence spectrum of high optical density samples (high concentration solution) recorded had the same shape as that observed in the experiments using 1 cm optical path. Therefore, the spectral shift is not attributed to re-absorption and re-emission phenomena [10,11].

It is known that energy transfer interactions of fluorophores produce large, measurable spectral effects in complex fluorophore mixtures such as asphaltenes. Energy transfer between dissimilar molecules always occurs from the molecule of large HO–LU gap to the molecule of smaller HO–LU gap, where the excess energy is rapidly thermalized. Consequently, photoemission subsequent to energy transfer is characterized by a red shift relative to the spectrum obtained from the initially excited molecule [20].

In this sense, the effect of the spectral red shift of the emission observed is consequence of the energy transfer interactions between aggregate of asphaltenes. This change in the fluorescence maximum shows the start of aggregation process at 50 mg/l that is consistent with absorption results obtained. For octylated Furrial asphaltenes, the effect of the spectral red shift of the emission is observed at higher concentrations (100 mg/l) demonstrating the suppressive effect of octylation process. A similar behavior was observed for Hamaca asphaltenes (Fig. 8), but in this case, the change of peak shift in the fluorescence spectra occurs at higher concentrations (~100 mg/l).

Fig. 9 shows the total fluorescence intensity as a function of the solution concentration for Furrial asphaltenes and octylated asphaltenes. It is noticeable the difference between the emission intensity of both samples. In case of Furrial asphaltene, the signal increase linearly with the concentration up to 40 mg/l, then the signal remains approximately constant with high dispersion. At this point, the asphaltenes start to form aggregates with a considerable dimension that cause high light scattering. This behavior can be explained if we compare the equilibrium between the monomers and n -mers in solution [21]. It must be noted that the fluorescence intensity of the samples decreases at

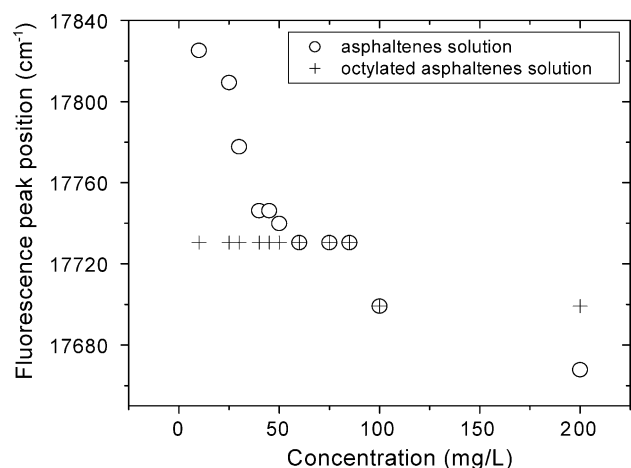


Fig. 8. Fluorescence peak position of toluene solution of Hamaca asphaltenes and their octylated forms for different concentrations.

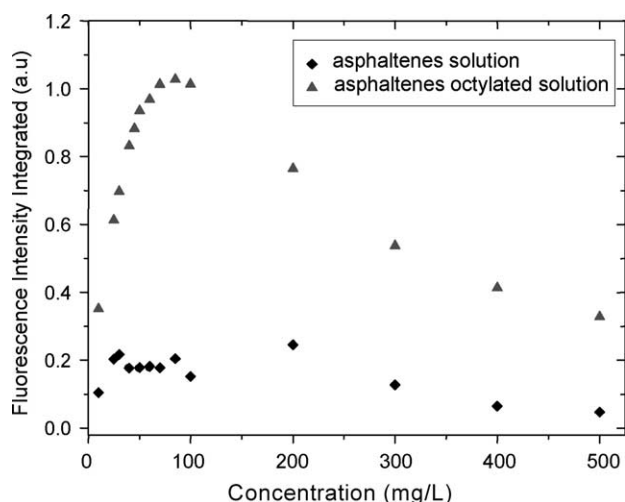


Fig. 9. Fluorescence intensity integrated vs. concentration (mg/l) for Furrial asphaltenes in toluene.

higher concentrations. The main mechanisms that may quench the fluorescence emission at these concentrations are aggregate formation. Dynamic quenching effect appears when the asphaltenes start to form aggregate diminishing the number of fluorophores in solution. In the same figure, Furrial octylated asphaltenes shows a different behavior. The increment in the signal is observed when the concentration is approximately at 100 mg/l, above this concentration the intensity diminishes, probably due to monomers concentration is reduced to forming aggregates. These aggregates act like a quencher, diminishing the fluorescence intensity.

Fig. 10 shows the results for Hamaca asphaltenes and octylated asphaltenes. In this case, the slope changes are observed at higher concentrations (~75 and ~110 mg/l are observed for asphaltene and octylated asphaltenes, respectively) compared to those obtained for Furrial asphaltenes. This fact can be clearly related to the more

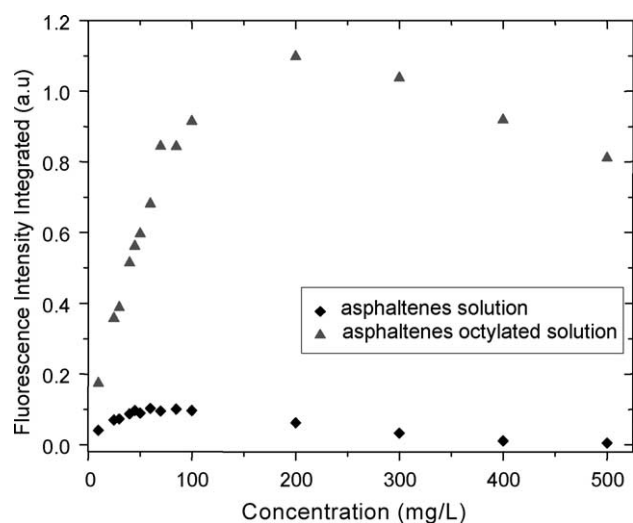


Fig. 10. Fluorescence intensity integrated vs. concentration (mg/l) for Hamaca asphaltenes in toluene.

stability of this crude oil. Hamaca crude oils show fewer tendencies to form aggregates, while Furrial asphaltenes begins to aggregate at very low concentration.

The literature on the aggregation point of asphaltenes is not clear. Different authors report that aggregation appears at higher concentration values as 500 mg/l, in this regard our results based on direct measurements in the solutions confirm that the aggregation processes of asphaltenes start a relative low concentration as 50 mg/l.

4. Conclusions

Our experiments allow concluding, that asphaltenes in toluene solutions starts to aggregate at considerably low dilution (50 mg/l). The change point of absorbance and fluorescence of the samples studied can be related with crude oil stability or the tendency to precipitate. The aggregation process occurs in both crude oil, Furrial and Hamaca, but in the case of the more stable crude oil (Hamaca), the quenching demonstrates that the process due to aggregation occurs at higher concentrations. The changes encountered in the absorption and fluorescence spectra permits to affirm that the aggregation process is observed in both asphaltenes and octylated asphaltenes. For octylated forms the aggregation start at higher concentrations.

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