Study of the aggregation and adsorption of asphaltene sub-fractions A1 and A2 by white light interferometry: Importance of A1 sub-fraction in the aggregation process

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HIGHLIGHTS

- Asphaltene adsorption measured on the surface using white light interferometry.
- Experiments show the aggregate formation in a good solvent a low concentration.
- The existence of asphaltene nanoaggregates in good solvent is cleaver demonstrated.
- The role of A1 and A2 subfractions in the aggregation process is clearly showed.

GRAPHICAL ABSTRACT
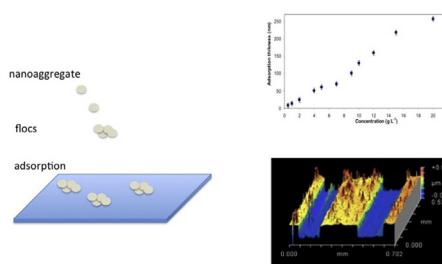
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ABSTRACT

In the present work we show the application of white light interferometric microscopy to study the adsorption of asphaltene on to glass surfaces. Asphaltenes, isolated from two different crude oils and dissolved in chloroform, were studied. The adsorption behavior of the total asphaltene and two sub-fractions is presented and the adsorption behavior is correlated with the solubility of each sub-fraction in different solvents. The existence of nanoaggregates of asphaltenes, even in a good solvent such as chloroform, is presented. The importance of each asphaltene sub-fraction in the aggregation and subsequent deposition is clearly shown. The characteristics of the adsorbed film illustrate differences in the average molecular structures of each sub-fraction and their impact on the solute–solute interaction and consequently the solubility. The results demonstrate, for the first time, the importance of A2, the asphaltene sub-fraction which is soluble, in the impact in the aggregate adsorption.

1. Introduction

Asphaltenes are considered to be the most aromatic and polar fraction present in crude oil. This fraction has been defined, in terms of solubility, as the fraction of crude oil insoluble in paraffin of low molecular weight (e.g. *n*-heptane). Recently, Acevedo et al. [1] proposed a model for asphaltene colloids in toluene which consists of two sub-fractions with different solubilities, called A1 and A2. The sub-fraction A1, which is insoluble in aromatic solvents such as toluene, cumene and others, is found in greater proportion than a second sub-fraction A2, which is soluble in these solvents and acts as an adjunct in the dispersion of A1. In this model the tendency of the asphaltenes to aggregate is explained as a result of the strong intermolecular interaction between the fraction A1 counteracted by the ability of fraction A2 to penetrate and disperse these aggregates. This prevents efficient packing and results in a porous aggregate, which can be penetrated by the solvent, so forming a dispersion of small particles, with size of the order of nanometers. The flocculation process requires

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desorption of the soluble fraction, A2, and the loss of solvent from the periphery of the colloid promotes the aggregation, thus forming the nanoaggregates.

Different studies of asphaltene aggregates in the form of colloids [2–5] report a characteristic size of 3–10 nm for the smaller colloidal particles, depending on the nature of the solvent or thermodynamic conditions. These studies were carried out for asphaltene in toluene solutions, with concentrations below 50 mg/L, and with the size measured using a range of techniques. Acevedo et al. [6] in 2010 studied the molecular mass (MM) properties of the A1 and A2 fractions of asphaltenes. They showed evidence of A2 aggregation in chloroform, characterized by a weaker aggregation tendency than the mixed asphaltenes and A1. Recently, the same author reported changes of size distribution for asphaltenes and their sub-fractions with temperature [7]. They found that in all chloroform solutions, the sizes of the particles are in the range 2–12 nm. The differences in diameter and particle density between the A1 and A2 fractions were in agreement with structural and solubility behavior.

The adsorption of asphaltenes on solids is the result of favorable interactions of the asphaltene species or its aggregates with chemical species on or near the mineral surface. There are a number of interaction forces, individually or in combination, that can be responsible for this. Adsorption on to the surface depends strongly on the nature of the solvent and the concentration, due to the aggregation tendency of the asphaltenes. The major forces which contribute to the adsorption process include electrostatic (Coulomb), charge transference, van der Waals, repulsion or steric interactions and hydrogen bonding [8].

The understanding of the influence of aggregate formation on the adsorption requires us to develop experiments at higher solution concentrations, as well as presenting an accurate characterization of the surfaces and the amounts of adsorbent [9,10]. Higher concentrations of asphaltene complicate the problem, due to multilayer formation, time dependence, aggregate formation and precipitation [9,11–13].

Jouault et al. [14] proposed a mechanism of asphaltene adsorption on to solid surfaces, namely hydrophilic and hydrophobic silica using neutron reflectivity measurements. Their results indicate that under good solvent conditions, the adsorption isotherms show that the interaction potentials between the asphaltenes and the surfaces are slightly higher for hydrophilic surfaces. All the samples show the same local structure, which is a single layer of asphaltene aggregates of equal thickness. Their results show that the shape of the isotherms depends on the nature of the adsorption layer and interaction force between the asphaltene and the surfaces. The shape of the isotherm provides qualitative information on the nature of the adsorbing species and with its interaction with the surface. For both cases (hydrophilic and hydrophobic silica), the adsorption behavior appears to be defined by Langmuir isotherms. These authors conclude that the adsorption process induces a densification of the aggregates at the interface with changes in solvent conditions; the structure of the adsorbed asphaltene exhibits a transition from one layer to a multilayer structure, when the concentration exceeds the flocculation onset. This is a good illustration of the strong relationship between the structure and dynamics of the growth of asphaltene aggregates in solution and their adsorption profiles at the solid–liquid interface [14].

Castro et al. [15] reported studies related to the prediction of adsorption isotherms of asphaltenes on porous surfaces. They presented a molecular thermodynamic approach for modeling of the adsorption isotherms of asphaltene on Berea sandstone, siltstone, bedford, dolomitic limestone rock using a model for asphaltene precipitation and an approach to quasi two-dimensional confined liquids. The authors applied their model of adsorption isotherms to asphaltene experimental data acquired from samples of Mexican heavy crude oil. The experimental results indicate the tendency to follow Langmuir-type adsorption isotherms. Their model requires the identification of ten molecular parameters related to particle size, the potential used to describe the particle–surface interactions, in addition to particle–particle interactions in the dissolved and adsorbed phases. However, they highlight the fact that this study focused on interaction energy forces involved in particle–surface interaction, showing that the values of these forces are consistent with molecular mechanics calculations for asphaltene adsorbed on to different surfaces and solutions.

One point of interest is the shape of the aggregates and this issue is still being debated. Spheres, disk or rod-like particles can fit the experimental results but for models such as that from Yen a cylindrical shape is preferred [5]. Recent studies based on an analysis of neutron and X-ray spectra report asphaltene aggregate dimensions and shapes under several solvent conditions [16,17]. There is evidence of two relevant scales; one (2–3 nm) defines dense nanoaggregates and the other (5–10 nm) belongs to clusters of nanoaggregates. A fractal organization from nanoaggregates to clusters has also been reported.

The main goal of this work is to study the principal mechanism involved in the adsorption of asphaltene and its sub-fractions on to a glass surface. The experiments were carried out using chloroform, as this is a very good solvent for asphaltene and its sub-fractions A1 and A2, even at high concentrations. Also, chloroform allows experiments at high concentrations with a minimum asphaltene aggregation effect. The results clearly show first, the importance of the A1 sub-fraction as responsible for the asphaltene aggregation and subsequent deposition and, secondly, the effect of the surface on the increase of density of the molecules near it and consequent increase in the tendency to form aggregates, even in this good solvent.

2. Experimental

2.1. Materials

Toluene, *n*-heptane, chloroform and cumene HPLC grade were obtained from Aldrich, *p*-nitrophenol (PNP) from Merck-Schuchardt and sodium hydroxide from Riedel-de Haen. Glass slides of the type used for microscopy were obtained from Merck. Two crude oils with significantly different asphaltene stabilities were selected, namely crude oils from Carabobo and Furrial. Carabobo is an extra heavy crude oil, with 8 API gravity; it contains 11% asphaltene with a low tendency to form aggregates. Furrial is a medium crude oil, 21 API gravity, with 3.5% of asphaltene and a high tendency for formation of aggregates and flocculation. These remarkable differences in crude oil characteristics and tendency to aggregate make these samples of great interest [18].

Asphaltenes were precipitated from the crude oil by a well known method [19]. Asphaltene sub-fractions were obtained using the methodology proposed by Acevedo et al. [20,21]. Solutions of 8000 mg/L of asphaltenes in cumene saturated with *p*-nitrophenol (PNP) were prepared. After 3 days, the mixtures were filtered by suction. The precipitate corresponds to the fraction A1 + PNP and the solution is composed of A2 + PNP + cumene. PNP was extracted by acid–base reaction. Each fraction was dissolved in the minimum amount of chloroform, and then successive extractions were carried out with an aqueous solution of 5% (w/v) sodium hydroxide. After performing the extractions, the organic phase was taken from both fractions and the solvent (chloroform) was left to evaporate, giving fractions A1 and A2 free of PNP.
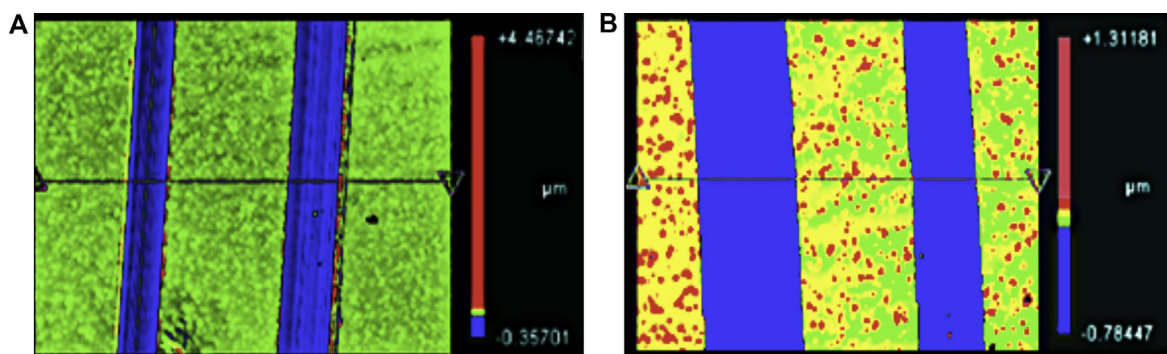
Fig. 1. Interferometric image for typical asphaltene adsorbed sample. Blue zone correspond to exposed glass surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.2. Adsorption experiments

Asphaltenes and asphaltene sub-fractions (A1 and A2) were dissolved in chloroform. This solvent is suitable for all the asphaltene sub-fractions, at concentrations from 500 to 20,000 mg/L. Solutions were stored in clean amber bottles for later use.

Glass slides were cut into pieces of the same size then washed with alcoholic potash to remove grease residues, dirt and any particles. After this process, the plates were left immersed in fresh chloroform for later use. The glass slides were placed in contact with solutions of asphaltenes, and A1 and A2 sub-fractions, for a period of 96 h to ensure complete adsorption. After this time, the slides were withdrawn and the excess solution on the plates was cleaned with fresh solvent. Three identical tests were made for each concentration of asphaltene solution in order to estimate the reproducibility of the adsorption.

2.3. Interferometric measurements

The basic principle of white light interferometric microscopy is well documented [22]. A white light beam emerging from the source is split into two. One goes to the internal reference surface (perfectly flat) and the other goes to the sample under study. After reflection the two beams recombine inside the interferometer, producing the phenomenon of constructive and destructive interference, which generates a pattern of bright and dark fringes. The light intensity of each point depends on the path difference between the two beams. The pattern is recorded digitally by an array of photodiodes connected to a microprocessor. Small displacements in the reference surface produce changes of the fringe pattern, which can be related to the sample surface topography. The interferograms were stored on the computer and processed individually to obtain the sample surface profiles, measuring depth, etc.

A white light interferometer, New View 600 model Zygo Metro-Pro, was used to measure the adsorbed asphaltene film thicknesses. After adsorption of sample on to the glass plate, a fine piece of steel was used to mechanically remove a fine line of the adsorbed film. The thickness of the film was then measured by comparison of images of the glass and adsorbed asphaltene surface. Fig. 1 shows images obtained for two typical glass plates with different amounts of adsorbed asphaltene. The different highs (in microns) on the observed surface are indicated by the color scale shown at the right of each figure. A blue color indicates the deeper and the red indicates the higher surface of the observed sample area. In both figures the blue lines correspond to the glass surface which has been exposed due to asphaltene removal. This is better observed when the image is rotated (see Figs. 6 and 7). For determination of the adsorbed asphaltene film thickness, two points are defined on to the surface at both sides of the blue lines (uncover part). The instrument software allows the differences in height to be determined. At least 12 measurements were made on different zones of each plate surface. The adsorbed asphaltene film thickness is reported as the average of all measurements and the standard deviation is used as an error estimation.

3. Results and discussion

The asphaltene film thickness is related to the amount of asphaltene adsorbed. This was plotted as a function of asphaltene solution concentration in order to obtain solute–solid adsorption isotherms (SSA) of the asphaltene on the glass surface. Each experimental point is the average of three adsorption experiments. The standard deviations were calculated and are indicated as error bars for each experimental point.

Fig. 2 shows the SSA isotherm for asphaltenes from Carabobo crude oil. First of all, very good reproducibility was observed for the experimental results in the concentration ranged studied. This technique measures directly the thickness of the layer and the precision is higher than other techniques where the data are obtained from the difference in the quantity of the solute in the solution after the adsorption. For the adsorbed asphaltene sample, the adsorption thickness increases in proportion to the concentration in solution in the range between 500 and 5000 mg/L. At this point an apparent saturation is reached when the thickness of the layer is approximately 60 nm. This size of adsorbed layer is evidence of aggregate adsorption. After this point, the thickness of the layer grows until saturation is reached at concentrations near 16,000 mg/L where the thickness of the layer is approximately 220 nm. This is a well understood phenomenon interpreted as increased aggregation and deposition of huge aggregates. These phenomena have previously been reported in the literature [11–13] in experiments using toluene as solvent. At this point, it is important to note the
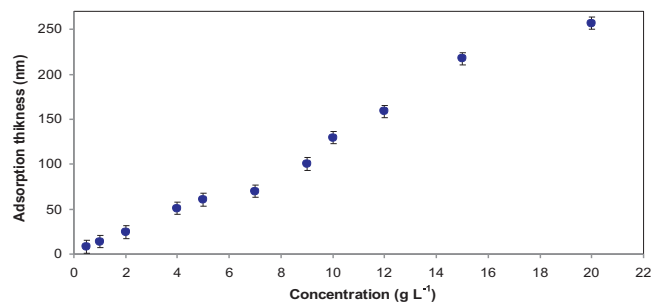

Fig. 2. Solute–solid adsorption isotherm for asphaltenes from Carabobo crude oil. Solvent: chloroform, $T = 26\,°C$, $t = 96\,h$.

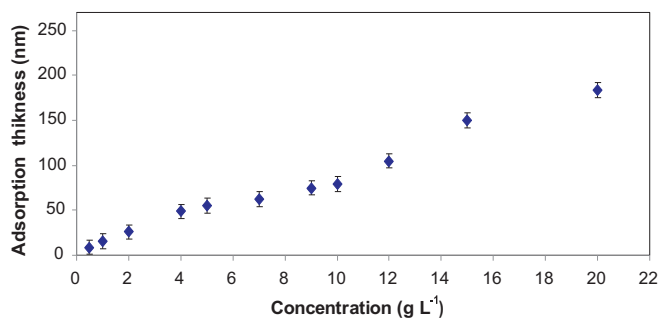**Fig. 3.** Solute–solid adsorption isotherm for asphaltenes from Furrial crude oil. Solvent: chloroform, $T = 26 °C$, $t = 96$ h.

small uncertainty in the thickness of the layer measured using the technique described above.

The importance of this result lies in the solvent used for the adsorption experiments. In chloroform the solubility of asphaltenes is very high and the polar nature of the solvent reduces the aggregation tendency of the asphaltenes. Although thin layers are readily formed from aggregates, it is the increase in density of particles near the surface that induces the formation of these relatively huge aggregates. The thicknesses of layers formed at low concentration (500 mg/L) are of the order of a few nanometers (3–10 nm), which is consistent with data reported previously [5,7].

In order to evaluate and compare the adsorption behavior of asphaltenes from different origins, a similar adsorption experiment was performed for asphaltenes from the unstable crude oil (Furrial). The SAA isotherm for the Furrial asphaltenes are shown in Fig. 3. The adsorption behavior is similar to the Carabobo asphaltenes, showing three different zones. The first area covers concentrations between 500 and 4000 mg/L where the adsorption increases linearly with the concentration of asphaltene in solution. There is a second zone with an apparent saturation in the range 4000–9000 mg/L, reaching about 60 nm thickness. Finally, the third zone (9000–20,000 mg/L) presents a sharp rise of the adsorption, reaching thickness values of 180 nm. Although the Furrial asphaltene adsorption behavior is similar to the Carabobo asphaltenes, the thickness of the layer in the third zone is noticeably lower and might be a consequence of the nature of the adsorption process in the sample.

At this point, it is necessary to consider the thickness of the layer, since it is well documented that the first aggregate has dimensions of the order of few nanometers [2,3,5,7,16,17] but the aggregation process forms colloids with larger size and a wider size distribution. The thickness of the films in both asphaltenes demonstrate an increase in the concentration near to the surface (Soret effect), allowing the formation of colloids and their deposition on to surfaces due to attractive forces, even in a very good solvent such as chloroform. The aggregation and adsorption of asphaltene dissolved in chloroform is reported in this work for the first time.

Subsequent experiments with asphaltene sub-fractions were carried out to study the influence of these sub-fractions on the adsorption behavior. Fig. 4A shows the SAA adsorption isotherm obtained for sub-fraction A1 from Carabobo asphaltene. It was observed that the adsorption increases in proportion to the concentration of asphaltenes in solution in the range 500–4000 mg/L. At this concentration, a plateau is clearly observed, corresponding to a thickness of approximately 60 nm, indicating apparent saturation, until the solution reaches a concentration close to 8000 mg/L. Then, an increase in the thickness of the adsorbed layer is observed, which is proportional to the concentration. At this point the thickness of the layer is approximately 220 nm. The high values of thickness and how these are revealed in the SAA isotherm corresponds to multi-layer aggregated adsorption processes, as highlighted. The behavior
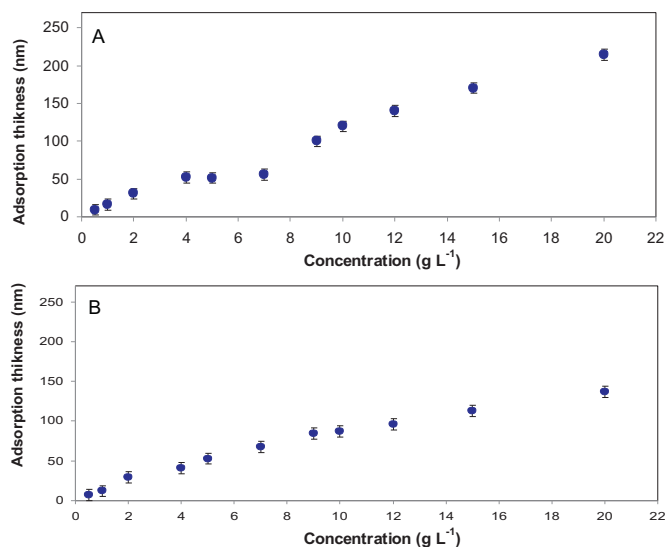

Fig. 4. Solute–solid adsorption isotherm for the Carabobo A1 sub-fraction (A) and A2 sub-fraction (B). Solvent: chloroform, $T = 26 °C$, $t = 96$ h.

of this asphaltene sub-fraction is clearly coincident with asphaltene including the layer thickness in each saturation step.

Fig. 4B shows the SAA isotherm obtained for the A2 asphaltene sub-fraction from Carabobo crude oil. The adsorption is proportional to the concentration over the entire range studied. For this fraction, thickness values around 140 nm were observed together with type I isotherm behavior. This behavior is significantly different from the total asphaltene and the A1 sub-fraction and is a direct consequence of the solubility of the sub-fraction in chloroform. The high solubility of the A2 fraction in chloroform reduces the tendency to form aggregates, producing a Langmuir type adsorption with a small layer thickness.

Fig. 5A shows the SAA isotherm obtained for the A1 sub-fraction of asphaltenes from Furrial crude oil. A linear increase of the thickness with solution concentration is observed up to 4000 mg/L, at which point the layer thickness is approximately 60 nm and remains constant up to about 7000 mg/L. Then an increase in thickness, related to an increase in the concentration up to 12,000 mg/L, was observed. Finally, there is an apparent saturation zone at concentrations of 20,000 mg/L. Values around 200 nm in thickness
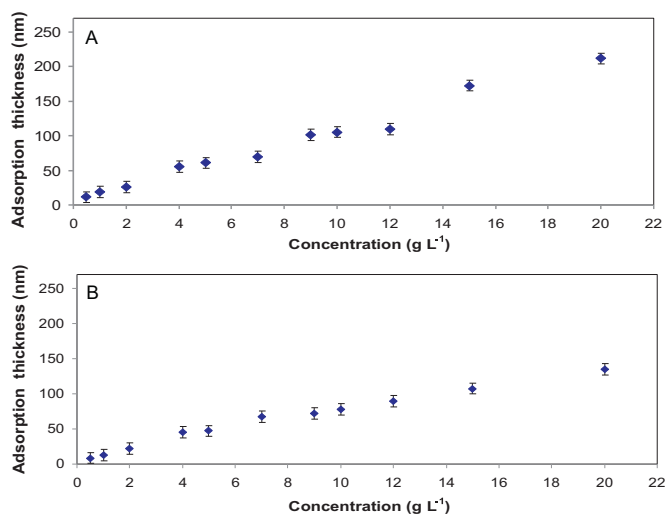

Fig. 5. Solute–solid adsorption isotherm for the Furrial A1 sub-fraction (A) and A2 sub-fraction (B). Solvent: chloroform, $T = 26 °C$, $t = 96$ h.
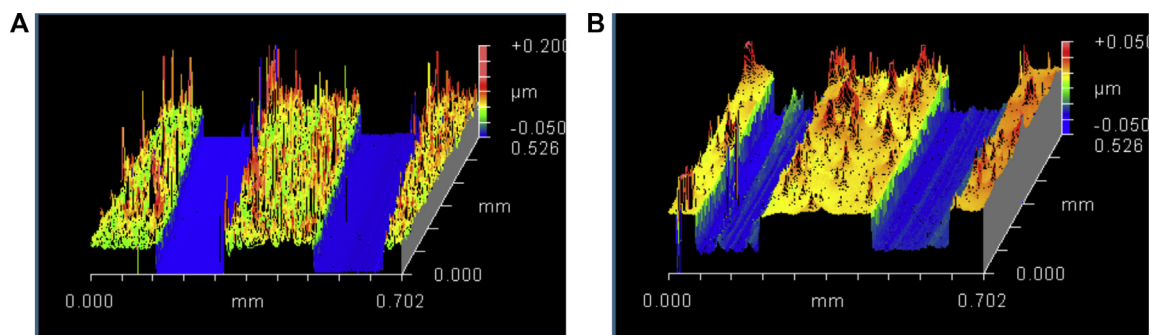
Fig. 6. Topographic interferometry images for adsorbed layers of asphaltene from crude oils: Furrial (A) and Carabobo (B). Solvent: chloroform, $T = 26\,°C$, $t = 96\,h$.
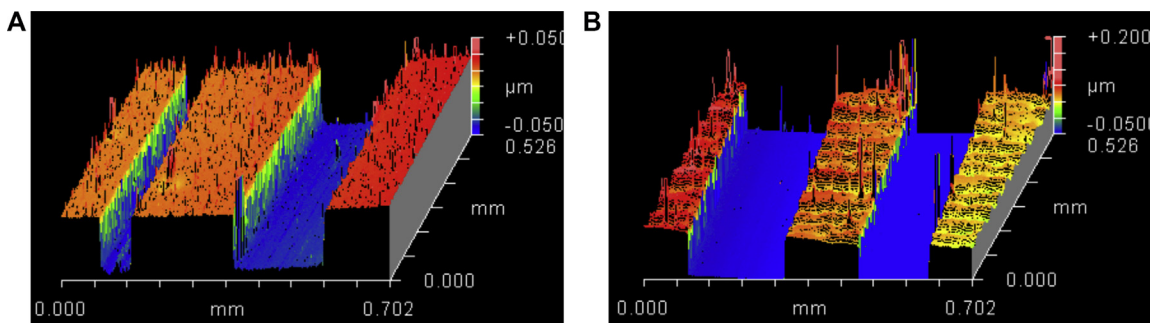

Fig. 7. Topographic interferometry images for adsorbed layers of A1 sub-fraction from crude oils: Furrial (A) and Carabobo (B). Solvent: chloroform, $T = 26\,°C$, $t = 96\,h$.

are reached, demonstrating the adsorption of aggregates over the entire concentration range studied. This sub-fraction shows similar behavior to that of the complete asphaltene, the same as the Carabobo A1 sub-fraction.

Fig. 5B illustrates the SAA isotherm obtained for the A2 sub-fraction from Furrial asphaltene where, as in the case of Carabobo A2, a linear dependence of adsorption with concentration is observed, with a maximum thickness of about 120 nm.

The observed differences in the A1 and A2 adsorption behavior support the model proposed by Acevedo et al. [1] where the A2 sub-fraction interacts with A1 forming small stable colloids in solution, and the solubility of A2 is higher than A1 in the solvent studied. Aggregate formation is promoted by the molecules of the A1 sub-fraction, producing the adsorption of aggregate on to the surfaces. This behavior supports previous experiments [23] and reinforces the idea of the coexistence of different molecular structures in the asphaltenes and the predominance of one type of structure that determines the aggregation and adsorption mechanism.

From the above results, it is clear that asphaltene aggregation is the main effect contributing to the thickness of the adsorbed layer on to the surface and the differences in the kind of colloid covering the surface. A difference in 100 nm in the thickness layer of A1 and A2 will be due to a different organization of the colloid on the surface.

The interferograms recorded for each sample were inspected in order to evaluate any differences in the surface topography associated with the adsorption behavior. Fig. 6 shows topographic images of the surface of the glass slide for adsorbed asphaltenes from Carabobo (A) and Furrial (B). The main difference between the samples is the cumulus formation in the Carabobo case, in which large aggregates of asphaltenes are adsorbed on to the surface. In contrast, the Furrial asphaltenes tend to form numerous small flocs which are then adsorbed.

Fig. 7 shows topographic images for adsorbed films of A1 sub-fractions for both crude oil. Images A and B correspond to the interferometric image, in two dimensions, of the asphaltenes

adsorbed, Furrial and Carabobo asphaltenes, respectively. An analysis of this figure shows that for the A1 Furrial plates, the surface is composed of a large number of small clusters. By comparison, the Carabobo asphaltenes produce a huge cluster which is adsorbed. In the case of A2, a similar image was observed. However, this differs from A1 sub-fractions from both Carabobo and Furrial, since a smooth surface with a few small peaks is observed, with a thickness of a few nanometers. This result is clear evidence that the A1 asphaltene sub-fraction is mainly responsible for the increase in the number of small aggregates.

4. Conclusions

Adsorption experiments were carried out on asphaltene and its sub-fractions A1 and A2 in chloroform as solvent. The high solubility of the samples has allowed us to detect the size of the first nanoaggregate, adsorbed at low concentrations of asphaltene, in solution. The experiments have given two remarkable results. First, the asphaltenes tend to form aggregates even in a good solvent like chloroform. Second, the A1 sub-fraction is the driving fraction, responsible for the aggregation tendency.

The white light interferometric microscopy technique provides a high precision measurement of the thickness of the asphaltene layer adsorbed on to the glass surface, allowing us to perform a detailed study of SSA asphaltenes and their sub-fractions in this context.

The topographic surface and thickness measurement of adsorbed asphaltene and A1 sub-fraction reveal differences in the form of aggregation of the adsorbed samples.

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