Revista Fuentes: El Reventón Energético
Vol. 15 Nº 1 de 2017 - Ene/Jun - pp 7/17

THE INFLUENCE OF CHEMICALS ON ASPHALTENES PRECIPITATION: A COMPARISON BETWEEN ATOMIC FORCE MICROSCOPY AND NEAR INFRARED TECHNIQUES

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ABSTRACT

Asphaltenes can cause serious problems to petroleum industry. Indication of asphaltenes stability can be obtained by precipitation induced by n-heptane, monitored by near-infrared (NIR). However, this technique does not provide information on the particles sizes. In this study, the precipitation onset of model systems (1wt% asphaltenes in toluene) was monitored by NIR, with and without adding additive. The particles sizes of the same systems were monitored by atomic force microscopy (AFM): Dispersions of asphaltenes in toluene, n-heptane and mixtures of these two solvents were analyzed by AFM. For the pure model system, the size of the asphaltenes aggregates clearly increased in function of rising n-heptane concentration in the solvent mixture, with this increase being much more pronounced for solubility parameter values below that corresponding to the precipitation onset. In the presence of additives, significantly smaller particles were obtained even when the precipitation onset showed only a slight shift.

Keywords: Asphaltenes, Precipitation, Near Infrared Spectroscopy, Particle Size, Atomic Force Microscopy.

LA INFLUENCIA DE LOS PRODUCTOS QUÍMICOS EN LA PRECIPITACIÓN DE ASFALTENOS: UNA COMPARACIÓN ENTRE LAS TÉCNICAS DE MICROSCOPÍA DE FUERZA ATÓMICA Y DE INFRARROJO CERCANO

RESUMEN

Los asfaltenos pueden causar serios problemas en la industria de petróleo. La evaluación de la estabilidad de los asfaltenos puede ser obtenida a través de la precipitación inducida por n-heptano, monitoreada por infrarrojo cercano (NIR). Sin embargo, esta técnica no provee información al respecto del tamaño de partículas. En este estudio, el onset de precipitación de sistemas modelo (asfaltenos en tolueno 1%p) fue monitoreado por NIR, con y sin la adición de aditivo. Los tamaños de partículas de los mismos sistemas fueron monitoreados por microscopía de fuerza atómica (AFM): dispersiones de asfaltenos en tolueno, n-heptano y mezclas de estos dos solventes fueron analizadas por AFM. Para el sistema modelo puro, el tamaño de los agregados de asfaltenos aumentó claramente en función del aumento de la concentración de n-heptano en la mezcla de solventes, siendo este aumento más marcado para valores de parámetros de solubilidad menor que el correspondiente al onset de precipitación. En la presencia de aditivos, partículas significativamente menores fueron obtenidas aun cuando el onset de precipitación mostró sólo un ligero cambio.

Palabras clave: Asfaltenos, Precipitación, Espectroscopia Infrarrojo Cercano, Tamaño de Partícula, Microscopía de Fuerza Atómica.

Cita: Figueira, J., Simão, R. Soares, B. & Lucas, E. (2017). The influence of chemicals on asphaltenes precipitation: a comparison between atomic force microscopy and near infrared techniques. *Revista Fuentes: El reventón energético, 15 (1), 7-17*.

DOI: http://dx.doi.org/10.18273/revfue.v15n1-2017001

1. INTRODUCTION

Asphaltenes are present in the heaviest fraction of crude oil and are one of the main sources of problems in the petroleum industry, because of their potential for precipitation and consequent deposition as solid particles. This deposition can occur in various stages, from the start or production, by impeding flow inside the reservoir rock formation, to the refining stage, by clogging lines and fouling equipment. Besides this, asphaltenes are indicated as the main reason for stabilization of water-in-oil emulsions. The characteristics of the asphaltenes extracted depend on the origin of the oil and quantity/quality of flocculant solvent added during the separation process (Gray, 1994), (Mullins, Sheu, Hammami & Marshall, 2007), (Ramalho, Lechuga & Lucas, 2010), (Honse, Ferreira, Mansur, Gonzalez & Lucas,2012), (Honse, Mansur & Lucas, 2012), (Marques, 2012).

The literature quotes two spectroscopic methods to study the potential for precipitation of asphaltenes, ultraviolet (UV) and near infrared (NIR). In both cases, the precipitation of the asphaltenes is induced by adding a flocculant solvent (an n-alkane with low molar mass, such as n-heptane). The absorbance of the system is measured at a constant wavelength in function of the quantity of flocculant added to the system, and the formation of asphaltenes aggregates can be detected by variation of the absorbance. Asphaltenes are considered to be more stable the greater the quantity of flocculant that is required to cause them to start precipitating. This point is called the precipitation onset (Lucas, Mansur, Spinelli & Queirós, 2009) (Garreto, Gonzalez, Ramos &Lucas, 2010) (Garreto, Mansur & Lucas, 2013) (Ferreira, Louzada, Gonzalez & Lucas, 2015) (Ferreira, et al., 2016). The performance of chemical additives to inhibit deposition of asphaltenes can also be evaluated by these techniques. A good additive should shift the precipitation onset to higher flocculant volumes, indicating their ability to increase the stability of asphaltenes in the petroleum sample (Ferreira, et al., 2015) (Lima, Mansur, Lucas & Gonzalez, 2010) (Lucas, Ferreira & Khalil, 2015) (Palermo & Lucas, 2016).

Of these two spectroscopic techniques, NIR is more comprehensive, because it allows analyzing model systems and the crude oil itself, while the UV technique is only able to analyze model systems of asphaltenes in toluene at low concentrations, because at high concentrations the system becomes too dark to read the absorption intensity (Garreto, et al., 2010) (Garreto, et al., 2013) (Ferreira, et al., 2015) (Moreira, Lucas & Gonzalez, 1999) (Sousa, Oliveira, Lucas, González, 2004). On the other hand, the NIR technique to monitor the absorption intensity of the system in function of flocculant concentration, although more versatile, only provides information about the point where the asphaltenes aggregates start to form, not the size of the particles formed.

It is known that the flow of crude oil is influenced by the formation of asphaltenes aggregates (Altoé, et al., 2014), and this influence depends on the size of the particles formed. In this case, the evaluation of the performance of additives to stabilize asphaltenes can produce false negatives, since the additive can present good performance in reducing the size of the asphaltenes aggregates without causing a significant shift in the precipitation onset.

The size of asphaltenes aggregates can be monitored by measuring the light scattered (Rajagopal & Silva, 2004) (Mansur, Melo & Lucas, 2012). However, this technique can only be applied to model systems with very low asphaltenes concentrations, which often does not allow studying model systems that reproduce the characteristics of the crude oil of interest.

Atomic force microscopy (AFM) is a technique that allows studying the morphology of materials with atomic or molecular resolution (Weinsenhorn, Maivald, Butt & Hansma, 1992) (Jagtap & Ambre, 2006), enabling its use to provide information about the aggregative character of asphaltenes molecules. Even though knowledge of the morphology of asphaltenes is scant and the AFM technique is a powerful tool for this type of study, few articles have been published in this respect (Toulhoat, Prayer & Rouquet, 1994) (Loeber, Muller, Morel & Sutton, 1998) (Long, Xu & Masliyah, 2007) (Madge & Garner, 2007) (Syunyaev, Balabin, Akhatov &Safieva, 2009) (Wang, Liu, Zhang, Masliyah &Xu, 2010) (Pizzorno, 2010) (Natarajan, 2011) (Wang, et al., 2012) (Natarajan, et al., 2014). The most important exceptions that can be mentioned are: (i) the formation of complex asphaltenes structures dispersed in the maltene matrix in asphaltic cement (Toulhoat, et al., 1994) (Pizzorno, 2010); (ii) the adsorption of asphaltenes on oil reservoir rocks, which can partially or totally block the oil's flow through the porous medium (Syunyaev, et al., 2009); and (iii) the characteristics of the asphaltenes aggregates formed in function of the interactions that occur with solvents having varied polarities (Madge & Garner,

2007) (Natarajan, 2011). Therefore, AFM is still little explored as a complementary technique to NIR or UV spectroscopy to assess the stability of asphaltenes and the performance of chemical additives, by monitoring the particle size in function of the solubility parameter (δ) of solvent mixtures, as is done through titration of n-heptane and monitoring the absorption by NIR. In this article, we report a systematic study to evaluate the particle sizes of asphaltenes by AFM in mixtures of solvents (solvent + non-solvent), mainly with solubility parameters near the precipitation onset as determined by NIR, to monitor the aggregative behavior of asphaltenes during the precipitation process, with and without the presence of a stabilizing additive.

2. EXPERIMENTAL

2.1. CHARACTERIZATION OF C7IP ASPHALTENES BY FOURIER-TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The C7IP asphaltenes sample, donated by Petrobras, was characterized by FTIR using the casting film technique in a KBr cell containing the dispersion of asphaltenes in toluene, in the region between 4000 and 400 cm^{-1}, with resolution of 4 cm^{-1}at room temperature, in a Varian Excalibur FTS 3100 spectrometer. This technique is very useful to identify the main functional groups, by obtaining the complete vibrational spectrum of the molecule of interest and confirming the asphaltenes fraction of the sample.

2.2. DETERMINATION OF THE ASPHALTENE PRECIPITATION ONSET BY NEAR INFRARED (NIR) SPECTROSCOPY

We first prepared a model dispersion of 1wt% asphaltenes in toluene in a round-bottom flask. When an additive was included, it was weighed and placed in the same beaker. Then the beaker was filled to the top with toluene, placed in an ultrasound bath for 15 minutes and left at rest for 24h. The asphaltenes precipitation onset was determined in a Bruker Matrix-F NIR spectrometer. The analysis was carried out by adding a non-solvent (n-heptane) to the system containing the asphaltenes. In this process, 10 mL of the model system was placed in a conical receptacle, into which the external probe of the spectrometer (optical path of 5 mm) was inserted. Then an isocratic pump was used to add n-heptane at a flow of 2 mL/min. The device was programmed to take absorbance readings at 1600 nm in function of the volume of n-heptane added to the system (Garreto, et al., 2010) (Garreto, et al., 2013). The initial addition of n-heptane causes dilution of the system, and thus reduction of the absorbance. When the n-heptane volume is large enough to cause the asphaltenes to precipitate, the formation of the resulting aggregates causes an increase in absorbance. Therefore, the volume of n-heptane added to 1 mL of the model system of asphaltenes necessary to increase the absorption is taken to be the precipitation onset (Syunyaev, et al., 2009) (Pizzorno, 2010. In practice, the volume of n-heptane at which the absorbance value is lowest is observed (Natarajan, 2011) (Henriques, Winter, Koroishi, Maciel & Bueno, 2011).

2.3. CHARACTERIZATION OF ASPHALTENE PARTICLE SIZE BY ATOMIC FORCE MICROSCOPY (AFM)

Unlike analysis of the precipitation onset by NIR, with AFM it is not possible to carry out a titration procedure, making it necessary to prepare various systems containing diverse toluene:heptane (solvent:flocculant) ratios. In a preliminary study, we prepared dispersions of asphaltenes in toluene and in heptane at a concentration of about 0.125 g/L. Two mica sheets, previously washed with isobutyl alcohol, were used, each one placed inside the dispersions. Then the mica sheets were left to dry in an exhaust hood and observed by AFM. For the other analyses, the dispersions were prepared with 1wt% of asphaltenes in the solvent for evaluation (toluene, heptane or a mixture of the two), placed in an ultrasound bath for 15 minutes and then left at rest for 24h in the dark. The previously cleaned mica sheets were immersed in the dispersions. The toluene:heptane ratios used were chosen in function of the precipitation onset determined by NIR, i.e., the ratios related to the precipitation onset point and just below and above it. Two mica sheets were prepared for each dispersion.

The mica sheets were analyzed under a JPK NanoWizard AFM, operating in non-contact mode at room temperature, using a Bruker RTESPA probe, with resonance frequency of 328 to 388 KHz and spring constant of 20-80 N/m, for imaging at a scan rate of 0.8 Hz. All the images had size of 10μm x 10μm. The images were analyzed using the JPK Image Processing program, by examining an average of five regions, and the results were expressed in tables presenting the maximum sizes indicated at the side of each figure, which corresponds to the maximum particle size in one of its dimensions.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF C7IP ASPHALTENES BY FTIR

In this work we used two types of asphaltenes samples, one extracted from petroleum and the other from refinery asphaltic residue, identified as C7IP and C7IR, respectively. Sample C7IP was characterized by FTIR to confirm the asphaltenes (**Figure 1**).

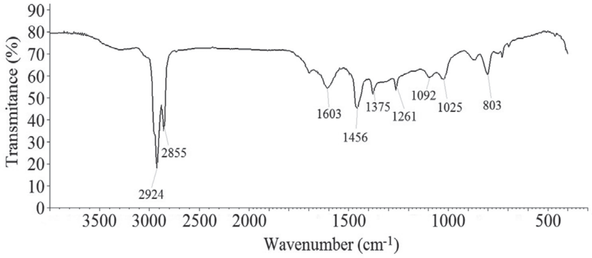

Figure 1. FTIR spectrum of asphaltenes C7IP

Absorption bands could be observed at 2924 and 2855 cm^{-1}, indicating axial stretching vibrations of CH_3 groups; a band at 1603cm^{-1}, characteristic of C=C stretching vibrations; C-H vibrations at 1456 cm^{-1} and 1375 cm^{-1}, attributed respectively to asymmetric and symmetric deformations of methyl groups; a band at 803 cm^{-1}, possibly related to the C-H deformation of aromatic groups; and absorption bands between 3472 and 3413 cm^{-1}, posibly corresponding to axial C-H vibrations of sp^2 carbons of the aromatic groups. These same bands were observed in a previous study involving the C7IR asphaltene sample (Palermo & Lucas, 2016).

3.2. DETERMINATION OF ASPHALTENE PRECIPITATION ONSET BY N-HEPTANE TITRATION USING NIR

In the precipitation onset test using NIR, the absorption intensity decreases by the effect of dilution caused by addition of n-heptane. When the quantity of n-heptane becomes sufficient to induce formation of molecular aggregates, the absorption intensity starts to increase. Therefore, the precipitation onset is identified as the minimum absorption intensity value, and can be reported in terms of mL of n-heptane/mL of asphaltenes dispersion.

We obtained precipitation onset results for the C7IP asphaltenes sample from absorbance curves in the near infrared (NIR) region in function of volume of n-heptane added to the model system (1 wt% asphaltenes in toluene), with and without a chemical additive. The purpose of these measurements was to observe the shift of the precipitation onset in function of the presence of a chemical additive and to establish the toluene:n-heptane ratios to be used in preparing the dispersions for analysis of the asphaltenes particle sizes by AFM.

Figure 2 presents the absorption intensity curves according to the volume of n-heptane added to 10 mL of the dispersion of C7IP asphaltenes in toluene. The test without the presence of stabilizer was performed in duplicate. It can be seen that the results were reproducible, with precipitation onset of asphaltenes in 1mL of n-heptane/mL of asphaltenes dispersion. This result also can be expressed in terms of a TOL:HEP ratio of 50:50 v/v. Based on an empirical scale, this model system could be considered unstable. The addition of 0.01 wt% of copolymer shifted the precipitation onset to a slightly higher value (1.1 mL of n-heptane/mL of asphaltenes dispersion). This result is the same as TOL:HEP ratio of 48:52 v/v. This indicates that the additive, at the concentration employed, did not perform satisfactorily in terms of shifting the precipitation onset. This is an interesting result, because it shows that an additive that has weak influence on the precipitation onset can affect the particle size of the aggregates formed. The tests were run in duplicate with an error of 0.05 mL of n-heptane/mL of model dispersion.

We also performed these tests for the model system at 1 wt% of C7IR asphaltenes in toluene, with and without addition of cardanol. The precipitation onset results are summarized in **Table 1** together with the results obtained previously for the C7IR asphaltenes model system, with and without addition of the selected copolymer (Palermo & Lucas, 2016).

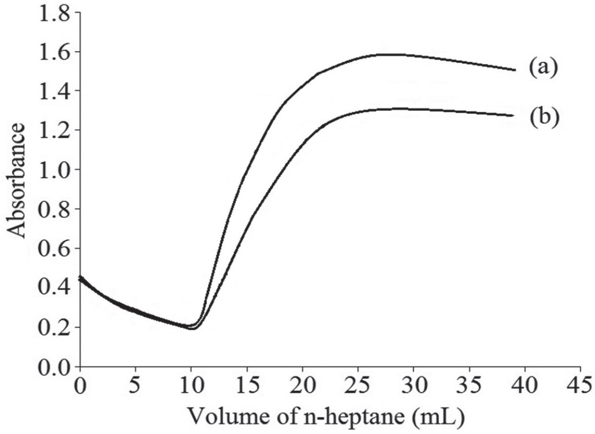

Figure 2. Absorbance at 1600 1600 cm^{-1}as a function of volume of n-heptane added to 10 mL of C7IP asphaltenes dispersion in toluene (a) and to the same dispersion containing 0.01 wt% of copolymer (b)

Table 1. Asphaltenes precipitation onset (mL of n-heptane/mL of asphaltenes dispersion) with and without additive (Palermo & Lucas, 2016).

Asphaltenes fraction	Asphaltenes precipitation onset (mL of n-heptane/mL of asphaltenes dispersion)			
		Copolymer (wt%)	Cardanol (wt%)	
	No additive	0.01	0.10	0.30
C7IP	1.00	1.10	-	-
C7IR	1.30*	1.80*	1.35	1.60

We also analyzed the effect of adding cardanol to the C7IR system on the change in the precipitation onset. The addition of 0.1 wt% of cardanol did not cause a significant variation in the onset value. However, adding 0.3 wt% of cardanol shifted the onset to 1.6 mL of n-heptane/mL of model dispersion, an increase of 15.4%. This result demonstrates the effectiveness of cardanol as a stabilizer, as previously reported (Moreira, et al., 1999). However, the copolymer presented similar results at significantly lower concentrations for the C7IR model system.

The results presented in Table1, some with and some without influence on the asphaltenes precipitation onset, are very interesting to investigate the asphaltenes particle sizes, in each case. This was done here by atomic force microscopy.

3.3. DETERMINATION OF ASPHALTENE PARTICLE SIZE BY ATOMIC FORCE MICROSCOPY (AFM)

As mentioned, information on the phase behavior of asphaltenes under different conditions of composition, temperature and pressure is very important to resolve problems found during the production, transport and refining of oil. The stability of asphaltenes can be inferred by spectroscopic tests with variable addition of a flocculant solvent, most commonly n-heptane. Spectroscopic techniques can indicate the volume of n-heptane necessary to start the precipitation of asphaltenes, but they do not provide information on the size of the particles formed. Therefore, relying only on these techniques alone to assess the performance of an additive can give misleading results, such as indicating total inefficiency for failing to shift the precipitation onset even when the additive induces the formation of smaller aggregates. AFM was used to observe the sizes of the asphaltenes particles formed in function of adding the flocculant (n-heptane) and the chemical additives. Since we did not find any description in the literature of tests employing AFM for this purpose, it was necessary to carry out preliminary assays to establish the methodology.

Mica is a standard substrate used in AFM because it has an extremely flat surface with high chemical stability and little influence on the film that forms on it (Liu & Wu, 2000). Therefore, the first images obtained were of mica sheets only washed in alcohol (**Figure 3a**) and sheets immersed in toluene (**Figure 3b**) and n-heptane (**Figure 3c**), since these were the two solvents used in the tests of the model systems containing asphaltenes. The maximum heights detected were around 30 nm, evidencing that values near or below this can be related to the mica sheet itself instead of the asphaltenes particles.

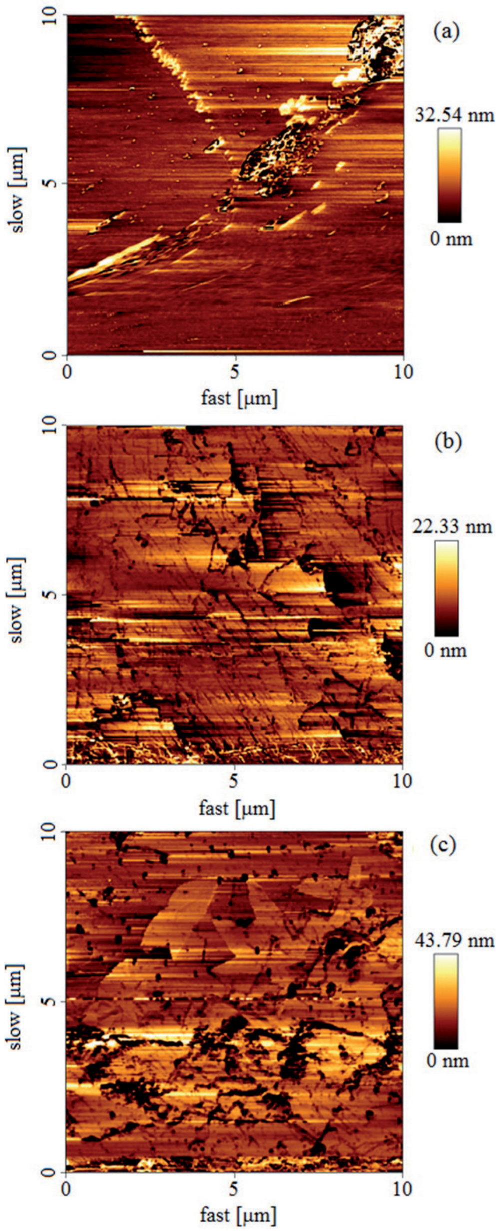

Figure 3. AFM images of pure mica washed with alcohol (a) and after being immersed in toluene (b) and n-heptane (c)

Then we obtained images of mica sheets submersed in the dispersion of C7IP asphaltenes in toluene (**Figure 4a**) and in n-heptane (**Figures 4b and 4c**), after leaving the dispersion to rest for 24 hours. By visual observation, the dispersion of asphaltenes in toluene was homogeneous and very dark, while that in n-heptane was heterogeneous, with sediment particles at the bottom of the beaker. The AFM images agreed with the visual inspection. The mica immersed in the dispersion of asphaltenes in toluene (**Figure 4a**) had the largest particle sizes on about 18 nm. This value is comparable with those observed for mica alone, indicating that the asphaltenes particle sizes were smaller than or equal to this value. Values on the order of 10 nm have been reported in the literature, obtained by light scattering measurements (Mansur, et al., 2012) for dispersions of asphaltenes in a good solvent (toluene), when there is good interaction between solute and solvent. This corroborates the result obtained by AFM for this system. On the other hand, in Figures 4b and 4c, since asphaltenes in n-heptane generate a heterogeneous dispersion, larger aggregates can be observed, respectively of 100 and 1000 nm, because n-heptane is not a solvent, so it was showed preferentially asphaltenes-asphaltenes interactions. The differences observed in these two figures are related to differences in the procedure for preparing the two mica sheets.

The image in **Figure 4b** was obtained after immersion of the mica in the dispersion allowed to rest for 24 h. In this case, the aggregates observed visually (those with sizes greater than 100 nm), were in the flask's bottom sediment, so those collected on the mica were not representative of the average particle sizes of the aggregates in this system. In contrast, in the image in **Figure 4c** the mica was immersed in the dispersion while under agitation to assure a representative range of particle sizes in the medium would be collected. The particle sizes observed are around 1,000 nm, in agreement with the values mentioned in the literature for model systems of asphaltenes in toluene:heptane mixtures (with high heptane content) with significantly lower asphaltenes concentrations, analyzed by light scattering (Mansur, et al., 2012). These results indicate the need to immerse the mica sheet in the dispersion while under agitation to obtain a representative particle size reading. These results also demonstrate that, even in heptane, less polar asphaltenes molecules formed relatively small aggregates (110 nm).

The proportions of the toluene-heptane mixtures (TOL:HEP) for preparing the asphaltenes dispersions at 1.0 wt% were chosen based on the precipitation onset results obtained by NIR. For the C7IP asphaltenes, the onset was 1.0 mL of n-heptane/mL of model system, corresponding to a TOL:HEP ratio of 50:50 v/v. Therefore, we established lower TOL:HEP ratios, near or above the precipitation onset, which were 71:29, 65:35, 60:40, 55:45, 50:50, 42:58 and 29:71 v/v.

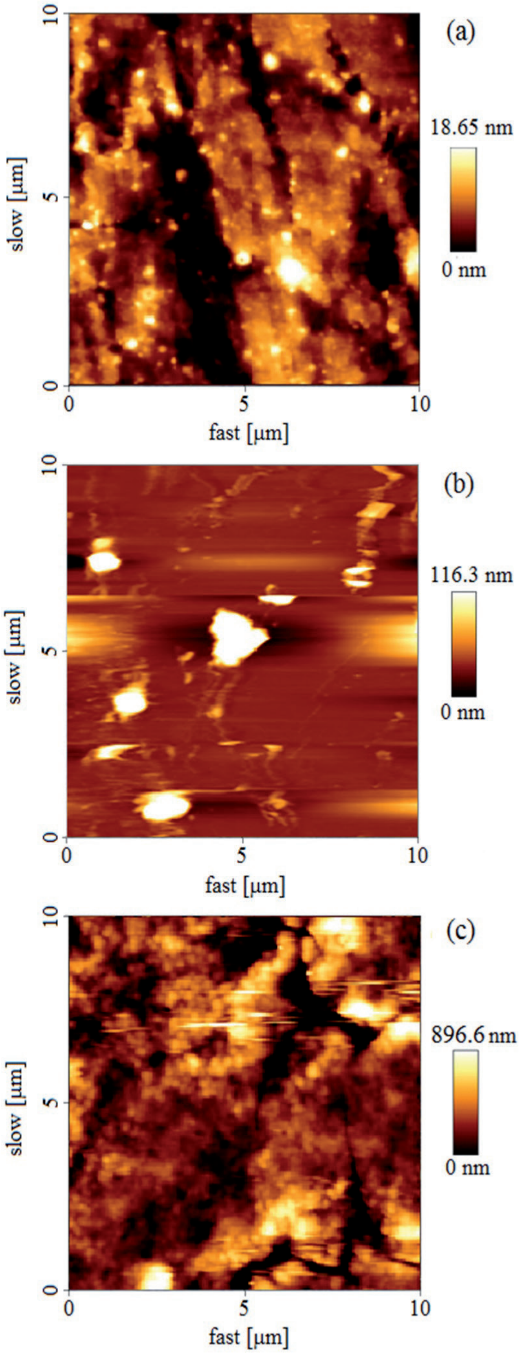

Figure 4. AFM images of the mica surface after being immersed into the C7IP asphaltenes dispersion in: (a) toluene, (b) n-heptane under resting and (c) n-heptane under stirring.

The results are summarized in **Table 2**, which presents the maximum size identified to the right of each image. The different values for the same system correspond to different observed areas. **Figure 5** presents some of the images captured during the experiment. A general analysis of the data in **Table 2** shows coherent results, since the particle sizes are considerably larger than those observed starting at the TOL:HEP ratio of 55:45 v/v, slightly lower than the precipitation onset identified by the NIR technique (TOLT:HEP of 50:50). In this respect, precipitation onset results of titration with n-heptane, obtained by optical microscopy (Garreto, et al., 2010) (Garreto, et al., 2013) (Ferreira, et al., 2015) (Ferreira, et al., 2016), indicate that the start of precipitation occurs with addition of a slightly lower volume of n-heptane than that identified by the minimum absorbance point. Therefore, it is coherent to observe a significant increase in the asphaltenes particle size, corresponding to the formation of asphaltenes aggregates, in lower n-heptane volumes than that of the onset determined by NIR.

Table 2. Maximum sizes of C7IP asphaltenes particles dispersed in different composition of toluene:n-heptane (TOL:HEP), in each area observed by AFM (values were taken from the indicator at the right side of each image)

TOL:HEP (v:v)	Maximum sizes in each observed area* (nm)		
100:0	18	37	22
71:29	21	44	-
65:35	54	30	-
60:40	34	42	-
55:45	355	119	-
50:50	**68**	**100**	
42:58	454	112	-
29:71	865	390	345

* Different values, for the same system, correspond to different observed areas

It is important to note that the interpretation of the analyses can vary according to the area chosen for observation, mainly for systems containing higher n-heptane content (above the precipitation onset of asphaltenes), as indicated by the size variation, for each system, presented in Table 2. This is due to the polydisperse nature in terms of polarity of the fractions extracted from the crude oil. The polydisperse nature can be observed in the AFM images (a single image shows a significant variation of particle sizes).

Besides this, for n-heptane concentrations higher than 45 vol%, the size of the aggregates tends to increase with rising n-heptane content. The results for the TOL:HEP ratio of 29:71 (223 – 865 nm) indicate the need for careful preparation of the mica sheets, since substantially smaller particles (150 nm) were obtained when the sheets were immersed in the system after sedimentation.

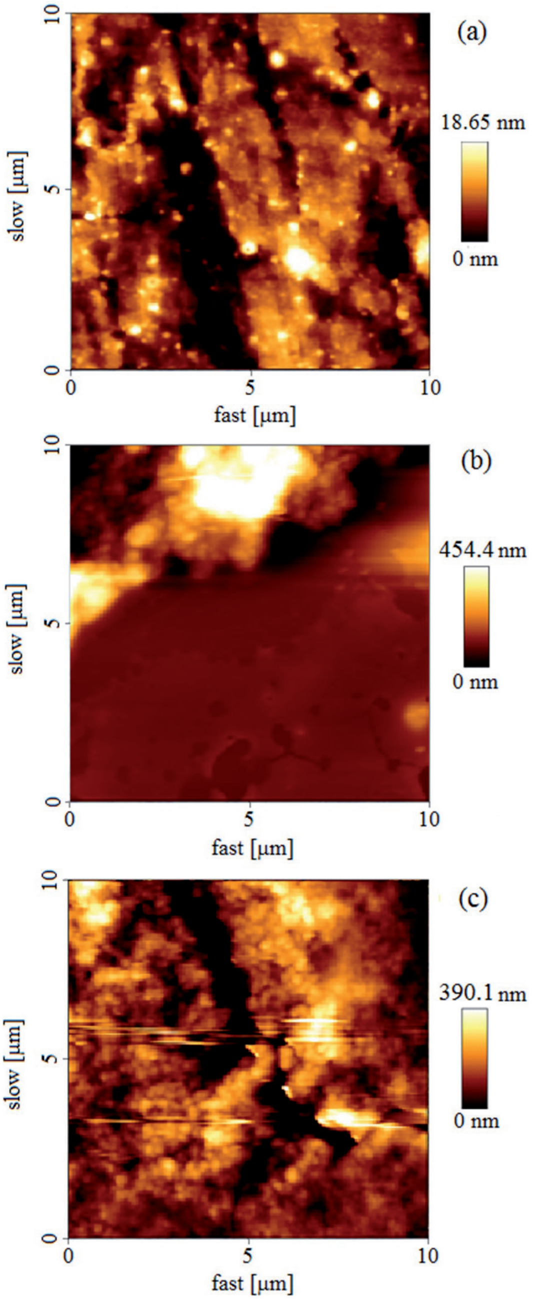

Figure 5. AFM images of the mica surface after being immersed into the C7IP asphaltenes dispersed in TOL:HEP mixture 100:0 (a), 42:58 (b) and 29:71 (c)

Comparing the results obtained for the TOL:HEP proportions of 100:0, 71:20, 65:35 and 60:40v/v, it is suggested that the particle sizes in these systems are equal, taking into consideration that the asphaltenes are also polydisperse in relation to their particle size.

Therefore, it would be necessary to observe different areas, a procedure that was not adopted for all the systems analyzed, such as that with asphaltenes in pure toluene, for which only one place on the mica sheet was observed. At the start of precipitation, there are still many asphaltenes particles with the same sizes as those dispersed in a good solvent (pure toluene).

Table 3 presents the compilation of the maximum sizes observed in each AFM image of the mica sheets immersed in the TOL:HEP 50:50, 45:55 and 42:58 v/v solvent systems, containing 1 wt% of asphaltenes, with copolymer addition of 0.01 wt%. The different values for the same system correspond to different observed areas. The precipitation onset identified by NIR for the system of C7IP asphaltenes in toluene containing 0.01 wt% of copolymer was 1.10 mL of n-heptane/ mL of asphaltenes dispersion, which corresponds to a TOL:HEP ratio of 48:52v/v. The shift of the onset caused by the additive's action was + 0.1 mL of n-heptane/mL of asphaltenes dispersion. The addition of 0.01 wt% of copolymer to the dispersion promoted the formation of particles with relatively small sizes due to the addition of higher n-heptane volumes, which is coherent with the slight shift in the precipitation onset to a higher value identified by the NIR technique. The AFM images show that even for heptane concentrations slightly higher than that corresponding to the precipitation onset, the particle sizes remain relatively small. A slightly more significant increase in particle sizes, characterizing the aggregation process, is observed for higher heptane concentrations.

Table 3. Maximum sizes of the C7IP asphaltenes particles dispersed in different compositions of toluene:n-heptane (TOL:HEP) in the presence of 0.01 wt% of copolymer, in each area observed by AFM (values were taken from the indicator at the right side of each image)

TOL:HEP (v:v)	Maximum sizes in each observed area* (nm)				
50:50	30	33	43	65	-
45:55	23	17	106	-	-
42:58	384	92	221	197	73

* Different values, for the same system, correspond to different observed areas

Continuing the particle size investigation by AFM of the systems previously evaluated by NIR (Table1), we performed tests with the C7IR asphaltenes without and with addition of 0.1 or 0.3 wt% of cardanol in solvent systems with TOL:HEP proportions of 100:0, 48:52, 43:57, 40:60 and 35:65 v/v and 1 wt% of asphaltenes. Table 4 reports the maximum particle sizes observed in each AFM image. **Figure 6** presents some AFM images from which the maximum sizes were obtained.

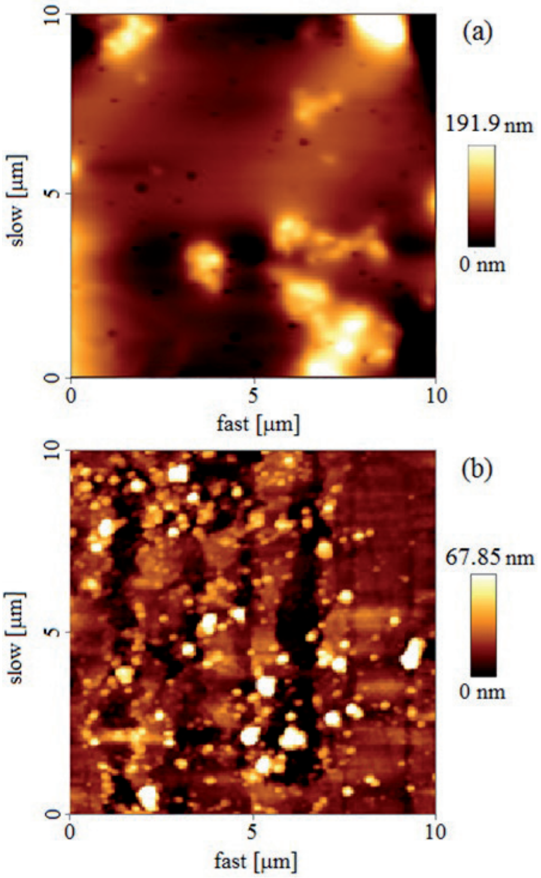

Figure 6. AFM images of the mica surface after being immersed into the C7IR asphaltenes dispersed in TOL:HEP (40:60) mixture: (a) without adding cardanol, and (b) with adding 0.3 wt% of cardanol.

It should be recalled that the TOL:HEP ratios for which the precipitation onset values were detected by NIR were 43:57, 43:57 and 38:62 v/v, respectively, for the C7IR asphaltenes without cardanol, with 0.1 wt% cardanol and 0.3 wt% cardanol, which correspond to the onset values presented in **Table 1**.

The results in **Table 4** show, for the system without additive, an increase in the particle size with increased n-heptane content that corresponds to points above the onset point, as expected. With addition of 0.1 wt% cardanol, the sizes remained relatively small, even for proportions above the onset level. These sizes continued being significantly smaller when using 0.3 wt% cardanol for the entire range of proportions analyzed. Therefore, specifically for the cardanol concentration of 0.1 wt%, we suggest that the additive acted to reduce the particle size, even though the precipitation onset (determined by using NIR to observe the variation of absorbance caused by titration with n-heptane) did not vary significantly in relation to the test with the additive's presence: from 1.30 to 1.35 mL of n-heptane/mL of asphaltenes dispersion in toluene.

These results suggest that the observation of the efficiency of additives by the NIR technique can, in some cases, lead to mistaken conclusions, since the problem of asphaltenes precipitation during production of petroleum is directly related to the size of the aggregates formed. Based on the AFM results, the additive in question would present better performance than that identified by NIR spectrometry.

Table 4. Maximum sizes of the C7IR asphaltenes particles dispersed in different compositions of toluene:n-heptane (TOL:HEP) in the presence of 0.1 and 0.3 wt% of cardanol, in each area observed by AFM (values were taken from the indicator at the right side of each image)

TOL:HEP v:v	Highest size at each AFM image (nm)								
	No additive			0.1 wt% of cardanol			0.3 wt% of cardanol		
100:0	2	3	23	27	104	134	31	13	5
48:52	74	147	16	15	314	188	53	86	73
43:57	12	37	24	47	77	-	5	9	3
40:60	205	192	-	19	28	18	68	77	106
35:65	272	254	300	173	129	135	31	7	8

4. CONCLUSIONS

Atomic force microscopy (AFM) is a promising tool to evaluate the size of asphaltenes particles in function of the characteristics of the solvent used, including identification of the formation of molecular aggregates, in systems with relatively high asphaltenes concentrations, overcoming a drawback of light scattering to determine particle sizes. The results provided by AFM are more realistic regarding the dispersion of asphaltenes in solvent media than those supplied by near infrared (NIR) spectrometry to monitor the precipitation onset. In the presence of additives, we found that significantly smaller particle sizes can occur even with a very small shift in the precipitation onset. Therefore, AFM can be used as a complementary technique to select the best type and concentration of stabilizing additives for application in the petroleum industry.

However, it is important in AFM to observe a large number of areas, to obtain more representative information on the system as a whole, and the interpretation of the shape of the aggregates requires varied magnification of the images, since the particles' size can vary from 10nm to 10000 nm. Finally, the use of a data treatment program is very useful in provide information on the particle size distribution, and further research is in progress taking in account this parameter.

5. ACKNOWLEDGEMENTS

The authors thank the Brazilian agencies (CNPq, CAPES, FAPERJ and ANP) for the financial support, and Petrobras for the donation of the asphaltic residue samples.

6. REFERENCES

1. Altoé, R., Oliveira, M. C. K., Lopes, H. E., Teixeira, C., Cirilo, L. C. M., Lucas, E. F., Gonzalez, G. (2014). Solution behavior of asphaltic residues and deasphalted oil prepared by extraction of heavy oil. *Colloid Surf* A, 445, 59-66.

2. Ferreira, S. R., Barreira, F. R., Spinelli, L., Seidl, P., Leal, K. Z., Lucas, E. F. (2016). Comparison between asphaltenes (sub)fractions extracted from two different asphaltic residues: chemical characterization and phase behavior. *Quim Nova*, 39, 26-31.

3. Ferreira, S. R., Louzada, H. F., Gonzalez, G., Lucas, E. F. (2015). Influence of the architecture of additives on the stabilization of asphaltenes and water-in-oil emulsions separation. *Energy Fuel;* 29: 7213-7220.

4. Garreto, M. S. E., Gonzalez, G., Ramos, A. C., Lucas, E. F. (2010). Looking for a model solvent to disperse asphaltenes. *Chem Chem Technol,* 4, 317-323.

5. Garreto, M. S. E., Mansur, C. R. E., Lucas, E. F. (2013). A model system to assess the phase behavior of asphaltenes in crude oil. *Fuel*, 113, 318-322.

6. Gray, M.R. (1994). *Upgrading Petroleum Residues and Heavy Oils*. New York: Marcel Dekker.

7. Henriques, C. B., Winter, A., Koroishi, A. T., Maciel

Filho, R., Bueno, M. I. M. S. (2011). Estudo da influência dos particulados no fenômeno de agregação dos asfaltenos por espectrometria de varredura óptica. *Quim Nova*, 34, 424-429.

8. Honse, S. O., Ferreira, S. R., Mansur, C. R. E., Gonzalez, G., Lucas, E. F. (2012). Separation and characterization of asphaltenic subfractions. *Quim Nova*, 35, 1991-1994.

9. Honse, S. O., Mansur, C. R. E., Lucas, E. F. (2012). The influence of asphaltenic subfractions on the stability of crude oil model emulsions. *J Braz Chem Soc,* 23, 2204-2210.

10. Jagtap, R. N., Ambre, A. H. (2006). Overview literature on atomic force microscopy (AFM): basics and its important applications for polymers characterization. *Ind J Eng Mat Sci,* 13, 368-384.

11. Lima, A. F., Mansur, C. R. E., Lucas, E. F., Gonzalez, G. (2010). Polycardanol or sulfonated polystyrene as flocculants for asphaltene dispersions. *Energy Fuels*, 24, 2369-2375.

12. Liu, A., Wu, R. C., Eschenazi, E., Papadopoulos, K. (2002). AFM on humic acid adsorption on mica. *Colloids Surf A*, 174, 245-252.

13. Loeber, L., Muller, G., Morel, J., Sutton, O. (1998). Bitumen in colloid science: a chemical, structural and rheological approach. *Fuel*, 77, 1443-1450.

14. Long, J., Xu, Z., Masliyah, J. H. (2007). Single Molecule Force Spectroscopy of Asphaltenes Aggregates. *Langmuir*; 23: 6182-6190.

15. Lucas, E.F., Ferreira, L. S., Khalil, C. N. (2015). *Polymers Applications in Petroleum Production, In Encyclopedia of Polymer Science and Technology*. Ed. H. F. Mark. New York:John Wiley & Sons.

16. Lucas EF, Mansur CR, Spinelli L, Queirós YGC. (2009). Polymer science applied to petroleum production. *Pure Appl Chem*, 81, 476-494.

17. Madge DN, Garner WN. (2007). Theory of asphaltene precipitation in a hydrocarbon cyclone. *Miner Eng*, 20, 387-394.

18. Mansur, C. R. E., Melo, A. R., Lucas, E. F. (2012). Determination of asphaltenes particles size: Influence of flocculant, additive and temperature. Energy Fuels 26, 4988.

19. Marques, L. C. C., Pereira, J.O., Bueno, A. D., Marques, V. S., Lucas, E. F., Mansur, C. R. E., Machado, A. L. C., González, G. (2012). A study of asphaltenes-resins interactions. *J Braz Chem Soc*, 23, 1880-1888

.

20. Moreira, L. F. B., Lucas, E. F., Gonzalez, G. (1999). Stabilization of asphaltenes by phenolic compounds extracted from cashew-nut shell liquid. *J Appl Polym Sci,* 73, 29-34.

21. Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G. (2007). *Asphaltenes, heavy oils, and petroliomics.* New York:Springer.

22. Natarajan, A., Kuznicki, N., Harbottle, D., Masliyah, J., Zeng, H., Xu, Z. H. (2014). Understanding Mechanisms of Asphaltene Adsorption from Organic Solvent on Mica. *Langmuir,* 30, 9370-9377.

23. Natarajan, A., Xie, J., Liu, S. W., Masliyah, J., Zeng, H., Xu, Z. (2011). Understanding Molecular Interactions of Asphaltenes in Organic Solvents Using a Surface Force Apparatus. *J Phys Chem*, 115, 16043-16051.

24. Palermo, L. C. M., Lucas, E. F. (2016). Asphaltene aggregation: influence of composition of copolymers based on styrene-stearyl methacrylate and styrene-stearylcinnamate containing sulfate groups. *Energy Fuels*, 30, 3941-3946.

25. Pizzorno, B. S. (2010). *Efeito do solvente e da temperatura na morfologia superficial do cimento asfáltico de petróleo.* Instituto Alberto Luiz Coimbra de Pós-Graduação e Pesquisa em Engenharia, Universidade Federal do Rio de Janeiro: Rio de Janeiro.

26. Rajagopal, K., Silva, S. M. C. (2004). An experimental study of asphaltene particle sizes in n-heptane-toluene mixtures by light scattering. *Braz J Chem Eng*, 21, 601-609.

27. Ramalho, J. B. V. S., Lechuga, F. C., Lucas, E. F. (2010). Effect of the structure of commercial

poly(ethylene oxide-b-propylene oxide) demulsifier bases on the demulsification of water-in-crude oil emulsions: Elucidation of the demulsification mechanism. *Quim Nova*, 33, 1664-1670.

28. Sousa, M. A., Oliveira, G. E., Lucas, E. F., González, G. (2004). The onset of precipitation of asphaltenes in solvents of different solubility parameters. *Progr Colloid Polym Sci*, 128, 283-287.

29. Syunyaev, R. Z., Balabin, R. M., Akhatov, I. S., Safieva, J. O. (2009). Adsorption of petroleum asphaltenes onto reservoir rock sands by near-infrared (NIR) spectroscopy. *Energy Fuels*, 23, 1230-1238.
30. Toulhoat, H., Prayer, C., Rouquet, G. (1994). Characterization by atomic force microscopy of adsorbed asphaltene. *Colloids Surf A,* 91, 267-283.

31. Wang, S., Liu, J., Zhang, L., Masliyah, J., Xu, Z. (2010). Interaction Forces between Asphaltene Surfaces in Organic Solvent. *Langmuir,* 26, 183-190.

32. Wang, J., Opedal, N., Lu, Q., Xu, Z., Zeng, H., Sjoblom, J. (2012). Probing Molecular Interactions of an Asphaltene Model Compound in Organic Solvents Using a Surface Forces Apparatus (SFA). *Energy Fuels*, 26, 2591-2599.

33. Weinsenhorn, A. L., Maivald, P., Butt, H–J., Hansma, P. K. (1992). Measuring adhesion, attraction, and repulsion between surfaces in liquids with an atomic-force microscope. *Phys Rev* B, 45, 11226-11232.

Recepción: 12 de febrero de 2017
Aceptación: 25 de abril de 2017