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# Aggregation Behavior of Two Asphaltenic Fractions in Aromatic Solvents

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Data on the behavior of crude oil *n*-pentane- and *n*-heptane-insoluble fractions in aromatic solvent systems were obtained. Surface and interfacial tensions in systems formed by Brazilian crude oil *n*-pentane insolubles (C5I) and *n*-heptane insolubles (C7I) in the aromatic solvents toluene, pyridine, and nitrobenzene were measured at room temperature using the ring method and employing an automatic tensiometer. The results indicated possible asphaltene aggregation as well as the probable existence of critical micelle concentrations for both C5I and C7I fractions in each of the three solvents considered. Critical micelle concentrations measured for the C5I fraction in toluene and pyridine solutions were consistently higher than those in systems containing the C7I fraction, indicating a lower association tendency in the C5I fraction. Average molecular areas for asphaltenes adsorbed at different interfaces estimated from surface tension measurements were found to be in agreement with literature values and appeared to suggest a planewise surface adsorption of asphaltene molecules, which is consistent with currently accepted stacking aggregation mechanism of asphaltenes. The presence of a discontinuous point for the kinematic viscosity of asphaltene/toluene solutions as a function of asphaltene concentration suggested yet another type of aggregation of asphaltenes at concentrations higher than the observed cmc in toluene.

## Introduction

The major constituents in the heavy and polar fractions of petroleum fluids, asphaltenes, and resins have condensed polyaromatic structures containing alkyl chains and heteroatoms (such as O, S, and N) and some metals. The deposition of asphaltenes is responsible for serious problems during production, transport, and refining of petroleum fluids, causing production losses and large increases in maintenance costs.<sup>1–4</sup> Considering the ever increasing demand for enhanced oil recovery, the study of the behavior of asphaltenes in crude oils and the comprehensive understanding of the complex aggregation/deposition processes are fundamental for the development of preventive and curative solutions with the accurate prediction of asphaltene deposition conditions as well as the formulation of inhibitors and dispersants.

As a complete characterization of the molecular nature of these polar fractions remains elusive, asphaltenes and resins continue to be described in terms of their solubility behavior in *n*-alkanes. The *n*-alkane

insolubles, frequently denominated asphalts and asphaltenes, are fractionated further using several analytical methods. Schwager and Yen<sup>5</sup> used the solvent fraction method to fractionate *n*-alkane insolubles to saturates, aromatics, resins, and asphaltenes. The saturates–aromatics–resins–asphaltenes (SARA) method was used by Acevedo et al.,<sup>6</sup> while Wang and Yen<sup>7</sup> employed a thin-layer chromatography method.

It is now recognized that asphaltenes are formed by aromatic compounds with  $\pi$ – $\pi$  interactions, undergo acid–base interactions, and self-associate through hydrogen bonding.<sup>8</sup> Current tendencies point to the mechanism suggested by Ho and Briggs<sup>9</sup> and Andersen and Birdi<sup>10</sup> to describe the behavior of asphaltenes in crude oil:

dissolved monomer  $\rightarrow$  micelle (aggregate)  $\rightarrow$   
particulate  $\rightarrow$  precipitate

In this mechanism, we have the presence of asphaltene monomers, the association of monomers to generate

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intermediate products, and the ultimate formation of a precipitate through the continuing association of intermediate products. It is widely accepted that at low concentrations, asphaltenes appear as nonassociated molecules (monomers). With changes in temperature, pressure, or concentration, monomers associate to form aggregates or micelles. These two terms "aggregate" and "micelle" are often used interchangeably in the literature, even though they define two different processes. A micelle is an aggregate that remains constant in size and aggregation number for a given set of environmental constraints. As we have no proof of the existence of such a micelle in crude oils, we believe that the term "aggregate" is more appropriate to describe asphaltene association. To keep in line with the literature, we, nevertheless, shall use in this paper the expression critical micelle concentration (cmc) for the concentration at which asphaltene molecules start to aggregate. At higher concentrations, asphaltenes aggregate and form nondissolved larger particles that, at a later stage, agglomerate and precipitate, forming the undesirable deposits.

This proposed mechanism has been supported by several experimental observations including those of Dwiggins,<sup>11</sup> Ho and Briggs,<sup>9</sup> and Xu et al.,<sup>12</sup> who used small-angle X-ray scattering (SAXS) to demonstrate the existence of particles with sizes ranging from 30 to 150 Å in crude oils diluted in aromatic solvents. Small-angle neutron scattering (SANS), used by Ravey et al.,<sup>13</sup> revealed particle sizes in this same size range. Sheu et al.<sup>14</sup> used surface tension measurements in solutions of oil heptane-insoluble (C7I) and pentane-soluble (C5S) fractions in pyridine and nitrobenzene and observed a break in the surface tension vs concentration curve, which they attributed to the attainment of an asphaltene cmc in these solvents. The nonpersistence of such a break for nitrobenzene solutions when presented on a surface tension vs the logarithm of concentration (log C) plot,<sup>15</sup> in accordance with the Gibbs isotherm, raised serious doubts about the existence of a cmc in these solutions. Andersen and Birdi<sup>10</sup> have used calorimetric titration to investigate the behavior of asphaltenes in different organic solvents and revealed the existence of a distinct break in the enthalpies of dilution vs concentration curve, which was also used to identify the critical micelle concentrations.

While there seems to be a general agreement on the micellization phenomenon and on the existence of a cmc for asphaltenes in organic solvents, doubts raised with regard to some of the data presented thus far in the literature suggest the need for more systematic and methodical studies that can generate reliable data and solid and indisputable evidence for the existence of such phenomenon. Andersen and Speight<sup>16</sup> have stressed the need for a more systematic work on this subject.

Later steps in this proposed mechanism have been characterized using other experimental techniques, such as scattering techniques<sup>9</sup> or viscosity measurements.<sup>17</sup>

In this paper, we present surface and interfacial tension measurements in solutions formed by Brazilian crude oil pentane-insoluble (C5I) and heptane-insoluble (C7I) fractions in pyridine, nitrobenzene, and toluene. The C5I and C7I asphaltenes are characterized using vapor pressure osmometry (VPO) and fractionated into saturates, aromatics, resin, and asphaltene using the SARA method. Viscosity measurements of asphaltene solutions were also carried out and used to characterize potential asphaltene aggregation at concentrations higher than those used in surface tension measurements.

## Experimental Section

Asphaltenes used in this study were extracted from a Brazilian offshore crude oil according to the IP 143/84<sup>18</sup> standard method. Briefly described, these asphaltenes were precipitated with *n*-heptane (Extra Pure, >99%) or *n*-pentane (ACS, 99%) at a dilution ratio of 40 mL of *n*-alkane/(g of oil). The solids were washed with the *n*-alkane for 4 h, redissolved in toluene, filtered, and recovered as a solid phase following toluene evaporation and labeled *n*-heptane insolubles (C7I) and *n*-pentane insolubles (C5I), depending on the *n*-alkane used. The complete behavior of asphaltenes as a function of the amount of *n*-pentane or *n*-heptane added is also determined.

Nitrobenzene (>99%), toluene (ACS 99.5%), and pyridine (ACS 99%) were acquired from Merck S. A. (Rio de Janeiro, Brazil). Surface-chemical purity of these solvents was verified using the criterion of the stability of surface tension over time as proposed by Goebel and Lukenheimer.<sup>19</sup> While nitrobenzene and pyridine showed acceptable purity and were subsequently used as supplied, toluene had to be further purified using an alumina-packed chromatographic column before use. Water used in interfacial tension measurements was Milli-Q quality, with a purity verified by a measured surface tension that is stable with time and in agreement with the literature value.

Surface and interfacial measurements were performed using an automatic tensiometer, KSV model Sigma 701 (Helsinki, Finland), and employing the ring method. Some experiments were repeated using the Wilhelmy plate method and led to essentially the same results. All the measurements were conducted in a temperature-controlled cell at 25 °C.

The C5I and C7I fractions were characterized by the determination of their average molecular weights using VPO and fractionation using the SARA analytical method. Average molecular weights for asphaltene fractions were determined using an osmometer purchased from Knauer (Berlin, Germany). Measurements were carried out in asphaltene/toluene solutions at 65 °C using benzil (C<sub>6</sub>H<sub>5</sub>COCOC<sub>6</sub>H<sub>5</sub>) as a primary standard and poly(ethylene glycol) (PEG 3350), obtained from Sigma Chemical Co. (St. Louis, MO), as a secondary standard.

The SARA method used to fractionate the crude oil into saturates, aromatics, resin, and asphaltenes was carried out using liquid chromatography. The thin-layer chromatography apparatus used included a rack of 10 columns, each being 50 cm long and 4.6 mm in diameter, with silica and neutral alumina as the adsorbing solid and UV and refraction index detectors. The mobile phases were *n*-hexane, dichloromethane, methanol, and toluene, all supplied in chromatographic purity.

Viscosity measurements in asphaltene/toluene solutions were obtained using glass capillary viscometers (Cannon—Fenske Opaque) convenient for working with dark fluids. The viscometers were calibrated according to ASTM D2162. The measurements were carried out in triplicate, and the solubility of the asphaltenes was verified in each sample by visual observation using an optical microscope. All measurements were carried out at 25 °C.

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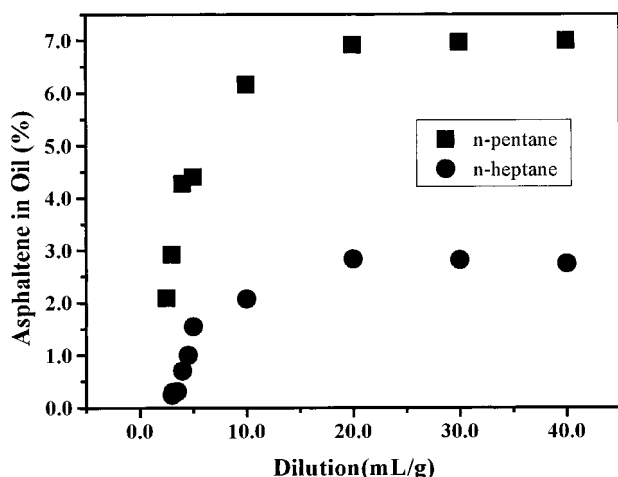
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**Figure 1.** Amount of *n*-pentane and *n*-heptane insolubles as a function of the *n*-alkane/oil dilution ratio.

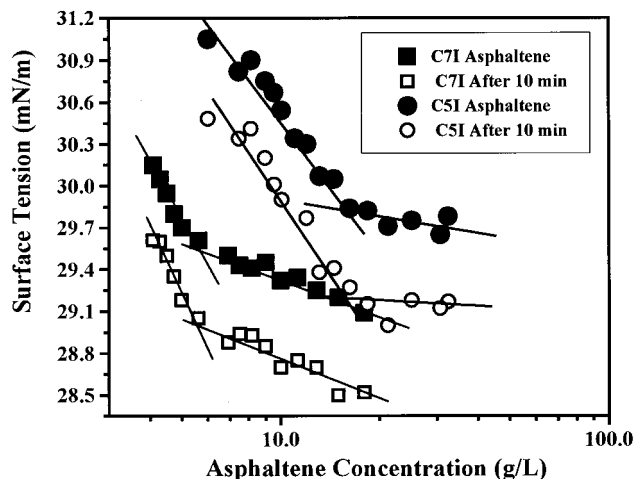
### Results and Discussion

Figure 1 shows the amount of asphaltenes precipitated following the addition of a flocculant, namely, *n*-heptane and *n*-pentane, according to the IP 143/84 standard method.

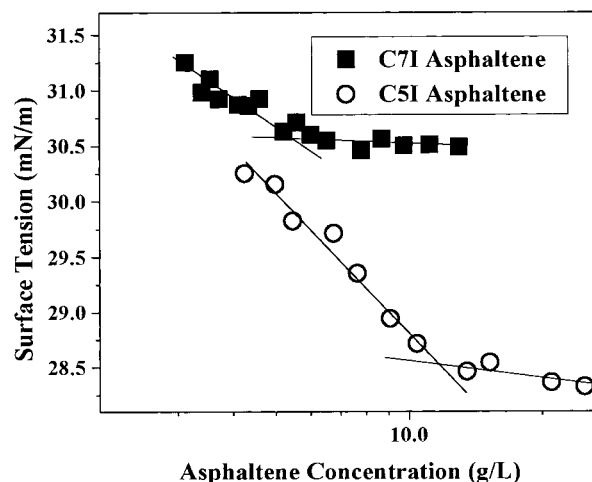
In Figure 1, we observe that the fraction insoluble in *n*-pentane (C5I) is larger than that insoluble in *n*-heptane (C7I) and contains a wider range of molecules, including the fraction of C5I that is soluble in *n*-heptane. This fraction is sometimes referred to as 'resins' due to its larger solubility with regard to alkane addition.

Characteristics for the crude oil samples, the fractions C5I and C7I, and the *n*-heptane-soluble portion of the C5I fraction were obtained through vapor pressure osmometry and liquid chromatography using the SARA analytical method. Distinct differences in the asphaltene content, defined as the fraction eluted by toluene in a thin layer-method, and resins, the methanol eluted fraction for the two fractions, C5I and C7I, were identified from chemical composition data. The C7I fraction was formed by mostly asphaltenes, more than 95%, while the C5I fraction was concentrated in resins. The average molecular weight of these fractions differ significantly, with C7I possessing a value of  $5430 \pm 270 \text{ g mol}^{-1}$  and C5I a value of  $3250 \pm 150 \text{ g mol}^{-1}$ . These values are in the range of reported molecular weights for asphaltenic fractions.<sup>20,21</sup> The C5I *n*-heptane-soluble portion is found to be rich in aromatic and resin content.

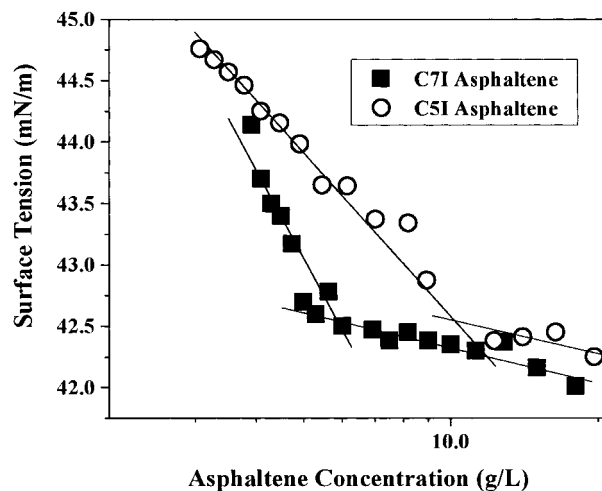
The behavior of the surface tension with an increase in asphaltene concentration in toluene solutions is shown in Figure 2. The observed small decrease in the surface tension (less than 10%) with an increase in asphaltene concentration is evidence of the weak surface-active character of these asphaltenes due to their high solubility in this solvent. Similar results were obtained for solutions in asphaltene/pyridine and asphaltene/nitrobenzene as shown in Figures 3 and 4. Close examination of these figures also reveals the existence of a distinct break in surface tension vs log(concentration) curve, similar to that observed in surfactant solutions and in accordance with the Gibbs equation.



**Figure 2.** Surface tension measurements vs log(C5I and C7I concentration) in toluene taken immediately and 10 min following dilution.



**Figure 3.** Surface tension vs log(C5I and C7I concentrations) in pyridine.



**Figure 4.** Surface tension vs log(C5I and C7I concentrations) in nitrobenzene.

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Due to this similarity, the break is used to define a critical micelle concentration of asphaltenes in each solvent. While the surface tension of asphaltene solutions was found to decrease with time, as shown in Figure 2 for measurements taken immediately and after 10 min following sample dilution, the concentration at



**Table 1. Critical Micelle Concentration Values for the Two Fractions in Toluene, Pyridine, and Nitrobenzene**

fraction	solvent	method <sup>a</sup>	cmc (g/L)
C5I	toluene	ST	15.4
C5I	toluene	IT	14.8
C5I	pyridine	ST	12.1
C5I	nitrobenzene	ST	9.0
C5I	nitrobenzene	IT	8.2
C7I	toluene	ST	6.5
C7I	pyridine	ST	5.6
C7I	nitrobenzene	ST	6.1

<sup>a</sup> ST and IT refer to surface and interfacial tensions, respectively.

which a break, ascribed as their cmc, is observed remained unaltered with solution aging. In this work, all the cmc measurements were taken immediately following sample dilution. The cmc values obtained in toluene, pyridine, and nitrobenzene solutions are presented in Table 1 and represent mean values of at least two independent experiments with an average deviation of  $\pm 1.0$  g/L.

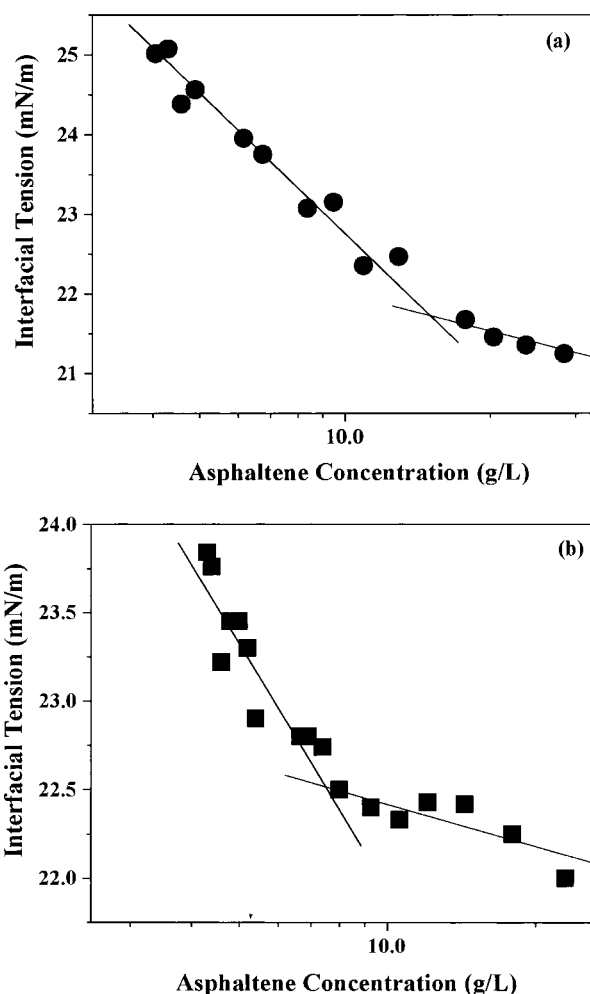
Interfacial tensions vs C5I and C7I concentrations were also obtained for toluene and nitrobenzene (Table 1). Data also show a break in the interfacial tension vs log(concentration) curve and result in critical micelle concentrations similar to those obtained from surface tension measurements. A typical example is presented in Figure 5.

The fact that both surface and interfacial tension measurements led to the same cmc for a given fraction (C5I or C7I) in each solvent indicates that the observed break reflects a phenomenon occurring in the bulk organic phase. As we have no other data on the solubilities of these two asphaltenic fractions, the only conclusion one can reach, based on our experimental data, is that any solubility differences and, therefore, different tendencies to self-association between these two fractions would be too small to be reflected in the cmc values.

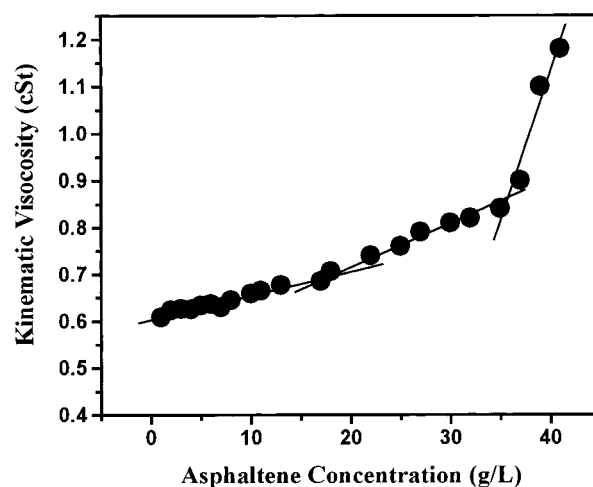
A comparison of Figures 2, 3, and 4 reveals different surface activities for C5I and C7I when present in the three solvents studied. In toluene, C7I is more effective than C5I in reducing the solution surface tension, while an opposite behavior is observed in pyridine, where C5I shows the larger decrease in the surface tension. In nitrobenzene, both fractions display a similar surface activity at concentrations larger than the cmc of C7I. As the surface activity is related to the solubility of each fraction in a specific solvent, these results can be attributed to the different chemical composition of the fractions, as previously discussed. Any attempt to correlate these trends in surface activity with solvent polarity should take into account the inherent complexity of these phenomena.

The cmc values obtained in this study are in the upper limit of the broad range of  $0\text{--}15\text{ g L}^{-1}$  reported in the literature,<sup>16</sup> which indicates, perhaps, a smaller tendency of self-association for asphaltenes used in this work as compared to those represented in the literature.

Viscosity measurements for C5I in toluene (Figure 6) show two distinct breaks as the asphaltene concentration increases, the first is slightly above the cmc and the second is at higher concentrations. This anomalous behavior represents a deviation from the monotonic viscosity increase expected for solutions with small



**Figure 5.** Interfacial tension vs log(C5I concentration): (a) in toluene, (b) in nitrobenzene.



**Figure 6.** Kinematic viscosity vs C5I concentration in toluene at 25 °C.

dissolved polymers where no phase transition is observed. The first discontinuity is less pronounced and consistent with the appearance of small aggregates. The second, much steeper, change reflects the appearance of larger particles, as predicted by the aggregation/deposition model of Andersen and Birdi<sup>10</sup> previously described. Similar viscosity changes caused by asphaltene flocculation have been reported to occur in oil samples with *n*-alkane addition.<sup>17</sup> Investigation of these

more concentrated samples with optical microscopy (up to 1000 times magnification) revealed no detectable entities, ruling out the presence of particles in the micrometer range. Therefore, it is expected that these small particles should form, yet, larger particles, eventually leading to precipitation.

It is still unclear whether these aggregation/flocculation steps, observed to occur with an asphaltene concentration increase in aromatic solvents, would also occur in oil samples, prompted by composition changes or other perturbations. This central question confirms the importance of studies in simple model systems as a way of understanding the more complex phenomena occurring in oil samples.

The observed higher cmc values encountered for C5I when compared to those for the C7I fraction in the same solvent can be attributed to the portion of C5I that is soluble in *n*-heptane, as shown in Figure 1. This portion of C5I can form mixed micelles with the C7I molecules, consequently, leading to smaller cmc values due to the higher stability of these micelles, as in the case of mixtures of ionic surfactants and alcohols. This portion of C5I can also interact with the C7I monomers, leading to higher solubility, a weaker tendency of association, and consequently higher cmc values. If the molecules of this portion of C5I neither associate nor affect the aggregation of the other fraction (C7I), the cmc value calculated assuming the whole C5I fraction would be larger due to the relatively smaller amount of C7I present in the samples.

The concentrations of the heptane-insoluble portion within C5I at the cmc of the C5I fraction calculated considering C7I to be about 43% of the C5I fraction (Figure 1) were 6.5, 5.2, and 3.9 g L<sup>-1</sup>, for toluene, pyridine, and nitrobenzene solutions, respectively, while those obtained for the pure C7I fractions were 6.5, 5.6, and 6.1 g L<sup>-1</sup>. This suggests that the heptane-soluble portion in C5I has a negligible effect on the association of the C7I fraction in the case of toluene and pyridine solutions. On the other hand, this portion seems to facilitate association in nitrobenzene solutions, indicating perhaps the formation of mixed micelles. While, this would obviously need experimental verification, a similar observation was reported by Andersen and Birdi<sup>16</sup> to explain the decreases in the reduced cmc values observed in toluene solutions formed with asphaltenes collected at different fractionation stages.

Surface tension data were also used to estimate the average area occupied by each asphaltene molecule at the organic solvent interface assuming the applicability of the Gibbs equation to the adsorption of asphaltenes in the organic solvent interface.<sup>15</sup> Estimated average radii are presented in Table 2 and found to be within the range of values reported by Ho and Briggs<sup>9</sup> and

**Table 2. Molecular Areas and Radii of Asphaltenes Adsorbed at the Interface**

fraction	solvent	area (Å <sup>2</sup> )	radius (Å) <sup>a</sup>
C5I	toluene	252	9.0
C5I	pyridine	307	9.9
C5I	nitrobenzene	255	10.6
C7I	toluene	279	9.4
C7I	pyridine	487	12.5
C7I	nitrobenzene	176	7.6

<sup>a</sup> Average radii estimated assuming circular cross-sectional geometry.

Zajac et al.<sup>22</sup> using small-angle X-ray scattering and scanning microscopy techniques, respectively. These results suggest that asphaltene molecules adsorb plane-wise at the interface, as any other conformation would produce smaller areas. This is consistent with the view that asphaltene aggregation occurs as stacking, a different way to what occurs in the case of normal surfactants, therefore comparable in solution behavior to that exhibited by bile salts and other so-called facial amphiphiles.<sup>23,24</sup>

## Conclusions

Surface and interfacial tension data reported in this work suggested aggregation of asphaltenes in toluene, pyridine, and nitrobenzene and allowed the determination of cmc values for *n*-pentane- and *n*-heptane-insoluble asphaltenes. In toluene and pyridine solutions, the C5I fraction consistently showed higher cmc values, suggesting perhaps a much lower tendency of association of the *n*-heptane-soluble portion in the C5I fraction. This *n*-heptane-soluble portion, however, seems to facilitate association in nitrobenzene solutions, due to the possible formation of mixed aggregates. Average molecular areas for these C5I and C7I asphaltenes estimated from surface tension measurements are comparable to literature values and indicate a planewise adsorption of asphaltene molecules at the interface, which is in line with the currently accepted stacking aggregation mechanism.

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