# Asphaltenes and Other Natural Surfactants from Cerro Negro Crude Oil. Stepwise Adsorption at the Water/ Toluene Interface:  Film Formation and Hydrophobic Effects

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The adsorption of asphaltenes and other natural surfactants at the water/toluene interface has been studied here, using both the ring and pendant drop method to measure the interfacial tension ($\gamma$). The dependence of $\gamma$ on the logarithm of the sample concentration ($\ln C$) (represented as the $\gamma(\ln C)$ isotherm) leads to a stepwise isotherm similar to that corresponding to the adsorption of asphaltenes at the toluene/silica interface. As is the case for the toluene/silica interface, the stepwise $\gamma(\ln C)$ isotherm seems to be the result of adsorption at the toluene/water interface of molecules, as well as aggregates formed in solution. Once adsorbed, these aggregates flocculate at the interface, leading to the well-known three-dimensional asphaltene films. In agreement with previous evidence from thermal lens experiments, the onset of asphaltene aggregation was observed near a sample concentration of $C = 60$ mg/L. Although the presence of aliphatic (acid fraction soluble in heptane, AFSH) and other types of acidic components in the asphaltene mixture increases the interfacial activity of asphaltenes, the removal of these components does not prevent the adsorption and leads to a film with an interfacial tension of $\gamma = 26$ mJ/m$^2$. This shows that such asphaltene films are less hydrophobic than what might be expected. As suggested by the detailed description of the results given in this paper, the asphaltene interfacial film is a mixed film formed by both AFSH and asphaltenes, where the role of AFSH is to reduce the value of $\gamma$ and the role of asphaltenes is to reduce hydrophobic effects by forming a film that effectively separates oil from water.

## Introduction

Water in crude oil emulsions is a serious problem that the oil industry faces every day. They may be formed during oil production by natural or artificial contact with water or during spillage in natural waters such as seas, lakes, and rivers. It has been known for a long time that asphaltenes have a central role in these emulsions, and so many investigations have been dedicated to their study and to the influence of the asphaltenes in them.[1-19]

Film-forming asphaltenes and resins have been studied for quite some time.[1,2] Several studies have reported the isolation of these natural surfactants from the oil.[3-5,10,13] Rheological behavior,[6,8,11,14,16] emulsion stability,[6-8,11-19] and chemical and interfacial characterization of interfacial components[1,3,4] are among the properties that are studied in this field.

Asphaltenes are a complex mixture of high-molecular-weight compounds, where 90% or more of the mass is composed of carbon and hydrogen; the sulfur, oxygen, and nitrogen contents in asphaltenes are ~5%, 2%, and 1%, respectively, and trace quantities of other heteroatoms are present.[20] Hence, a highly hydrophobic

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material could be anticipated and a modest (if any at all) interfacial activity should be expected for such a material.

Actually, the opposite is true: they adsorb at any water/oil interface, albeit slowly. Moreover, according to interfacial rheology reports,[6,8] they form thick multilayers or three-dimensional (3-D) networks with a viscoelastic consistency.

In this paper, we have tried to account for these somehow unexpected properties, and, in so doing, we consider two main factors: (i) the presence in crude oils of the AFSH, which is a fraction of acidic compounds with a prevalent aliphatic structure, soluble in heptane, and having a relatively low molecular weight (MW);[10] and (ii) the very well-known aggregation tendency of asphaltenes in organic solvents.[21]

As suggested by the detailed description of results presented below, the interfacial film (at the toluene/water interface) is a mixed film that is formed by both AFSH and asphaltenes, where the role of AFSH is to reduce the interfacial tension ($\gamma$) and the role of asphaltenes is to reduce the hydrophobic effects by forming a film that effectively separates the oil from the water.

As expected, film properties are dependent on the concentration of asphaltenes in the oil phase. As is very well-known, asphaltenes do aggregate in organic solvents and they do so even at very low concentrations in aromatic solvents such as toluene, where aggregation at concentrations of ~50 mg/L has been reported.[21,22]

Stepwise adsorption at the toluene/silica interface has been reported for asphaltene solutions.[23,24] In other words, isotherms that resemble multilayer adsorption have been observed for several asphaltenes. These have been accounted for in terms of the adsorption of aggregates at the interface.[24] Aggregates of increasing size are formed when the solute concentration in solution $C$ increases. These then are adsorbed at the interface, yielding a step with a "high" proportional to the size of the aggregate.[24] Somewhat similar stepwise adsorption has been observed at the toluene/water interface for $C_5$ and $C_7$ asphaltenes[25] (see below). Apparent increases in aggregate size with $C$ have also been reported by other authors.[26]

The Results and Discussion sections given later in this paper suggest that, in general terms, the toluene/water isotherms reported here are the outcome of a similar aggregation−adsorption mechanism, which, in the present case, is followed by flocculation, leading to film formation. Although some adsorption of "free" molecules is expected, most of the material at the interface arrives there as aggregates of AFSH and asphaltenes.

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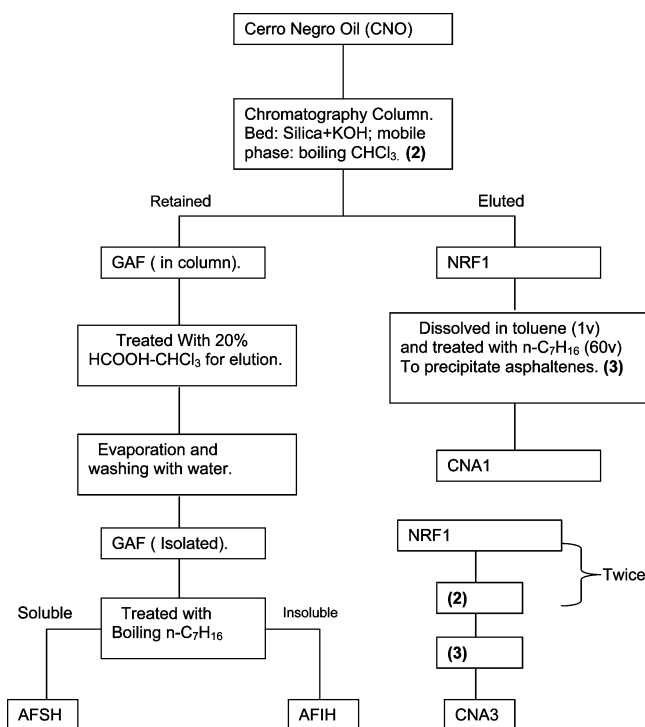
**Figure 1.** Separation scheme used for isolation of the samples studied. See the Glossary for sample identification.

## Materials

Asphaltenes were isolated from a 1:1 (v/v) mixture of Cerro Negro crude oil and toluene after the addition of 60 *n*-heptane volumes, as reported earlier.[27] Coprecipitated resins were thoroughly extracted using boiling *n*-heptane. The asphaltene yield was 13% (w/w). Maltenes were obtained from the supernatant after evaporation of the *n*-heptane.

**Acidic and Non-retained Fractions.** The acidic fraction and the non-retained fraction (NRF1, which is probably composed of neutral and basic compounds) were isolated from the oil, using a modification of the reported chromatography procedure.[4] Briefly, in this procedure, the stationary phase (bed) is comprised of silica that has been treated with potassium hydroxide dissolved in a mixture of water and 2-propanol; the bed is then washed with chloroform and used to charge a chromatography column fitted with a recycling solvent system. After recycling some boiling chloroform volumes, a solution of the Cerro Negro oil (CNO) sample in chloroform is fed into the bed (see Figure 1). The NRF1 fraction was collected with several columns of chloroform, whereas the general acid fraction (GAF, which is retained in the column) was collected using a mixture (20% v/v) of formic acid in chloroform. The GAF was recovered after evaporation of 90% of the solvents, washed with water to remove formic acid, dried with magnesium sulfate, and evaporated under vacuum to obtain 3% of acids, with respect to crude oil.

The GAF (1 g) was treated with *n*-heptane (50 mL) and refluxed for 3 h. The suspended solid (the acidic fraction that is insoluble in heptane, AFIH) that remained was filtrated, dried, weighed (to 1%, with respect to crude oil), and saved for analysis. The filtrate was evaporated to dryness under vacuum to obtain the AFSH fraction. The yield was 2%, with respect to crude oil.

The NRF1 fraction was dissolved in toluene (1:1 v/v), and asphaltenes (CNA1) were precipitated as described previously for the crude oil. The yield was 11%, with respect to crude oil.

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Using the aforementioned chromatography technique, a sample of the aforementioned NRF1 fraction was passed through the column twice more, to remove as much of the acidic components as possible. The triple-extracted sample then was treated as previously described to obtain the triple-extracted asphaltenes (denoted as CNA3).

**Equipment.** A homemade pendant drop system was used. As usual, the oil drop was produced from a syringe that was provided with a U-shaped needle imbedded in 0.1 N HCl aqueous solution. The aqueous solution was placed within a chamber provided with two glass windows. The chamber was illuminated with a lamp (ordinary white light), and drop images were focused with two lenses and beamed into a video camera. Images were then analyzed using a computer program to obtain the interfacial tension $\gamma$.

The equipment used for the ring detachment method was a commercial TE 1C Lauda tensiometer.

## Methods

Two methods were applied to measure $\gamma$. The ring detachment method was used when high accuracy was desired. For the present system, where equilibrium is expected to be obtained after a long time, this method has the disadvantage of being slow. Usually, measurements were performed after 24 or 48 h. In the present case, we conducted our measurements after 48 h. Measurements were performed as follows: The measurement ring was pushed through the interface, where it contacted the water phase. Thus, during this process, the film was broken. The film was allowed to mend itself, and the measurement was performed by pulling the ring from the water to the toluene phase.

The pendant-drop method has the advantage of being fast, even for the present slow system, where equilibrium was usually apparent after 5 min. Of course, this is due to the very small size of the oil phase. However, the pendant-drop method that we used was unreliable at concentrations of $C < 100$ mg/L and, therefore, was not used for these concentrations. Otherwise, the method gives reliable values and is very convenient when a large amount of measurements is required.

Pendant-drop measurements were performed by filling the syringe with the solution of samples in toluene. The syringe was then placed in the holder, between the lamp and the optical system.. The upside-down drop was then produced in the U-shaped needle, and the image was recorded using the video camera. Measurements were taken after 5 min of contact between the toluene solution and water. The interfacial tension $\gamma$ was then obtained using the software provided.

Both pendant-drop and ring-detaching measurements were performed at room temperature, using doubly distilled water that was presaturated with toluene. Using the ring method, readings were performed after 48 h. Trial measurement with the pendant-drop apparatus, taken after 5 min, were within 5% (or better) of those measured by the ring method. The pendant-drop method was validated by comparison with literature values for several pure compounds. The agreement was good (within 5% or better) in all cases.

Vapor-phase osmometry (VPO) measurements were measured in nitrobenzene at 100 °C, using the Jupiter Model 833 equipment and a procedure that has been described elsewhere.[27] Four solutions were measured in

**Table 1. Yields and Molecular Mass of Samples Studied**

| sample | yield (%) | molecular mass, MM |
|---|---|---|
| CNA | 13 | 1370 |
| CNA 1 | 12 | 1330 |
| CNA 3 | 10 | 1400 |
| GAF | 3.2 | 510 |
| AFSH | 2 | 400 |

the concentration range of $C = 1-5$ g/L range, and the molecular mass (MM) was determined by extrapolation to zero concentration.

## Results

The yield and MM values of some samples are shown in Table 1. Differences in MM for the various asphaltene from CNO (CNA) samples are not significant, because the expected errors in the VPO measurements are ∼10%. Figure 1 shows the scheme used for separation of acidic fractions. According to ^{13}C nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, all these fractions presented carbonyl signals that are characteristic of carboxylic acids. As reported previously, AFSH was a mostly aliphatic, low-molecular-weight acidic fraction.[10] The GAF and AFIH fractions produced ^{13}C NMR spectra that were similar to that of asphaltenes.

In Figure 2, the $\gamma$ results for the water/toluene, CNA, and CNA3 asphaltene systems are shown in a semilogarithmic plot ($\gamma$ vs ln $C$, where $C$ is the concentration (in mg/L)). These values were obtained using the ring method, whereby highly accurate values could be obtained, regardless of sample concentration. Here, the values for the CNA and CNA3 samples are compared. These were obtained in the $C = 0-4000$ mg/L range, at the doubly distilled water (pH ∼6.5)/toluene interface, using the ring-detachment method, after 48 h. These values are the average of four determinations, with a standard deviation in each point of ±0.05 mJ/m². As shown here, a big step (second from left to right) was observed for the extracted sample at <60 mg/L (ln $C \approx$ 4). A smaller step, common to both samples, was observed at $C < 20$ mg/L (ln $C < 2.9$). The formation of an interfacial film could easily be seen for $C > 100$ mg/L, when the film could be stretched downward with the measuring ring. In this test, a stretching of the film, similar to that expected for an elastic membrane, could be observed with the naked eye.

Figure 3 show a semilogarithmic plot ($\gamma$ vs ln $C$) measured for several samples using the pendant-drop method. Although the values of $\gamma$ are pH-dependent, we were interested only in relative $\gamma$ values of the samples in Figure 3. Because these relative $\gamma$ values were weakly dependent on pH, we decided that it was convenient to measure these systems at pH 1, where a wider range of $\gamma$ values could be measured. The concentration range from 100 mg/L to 110 g/L was studied. This last concentration corresponds to the solubility of CNA in toluene. With the pendant-drop method that was used, $\gamma$ values obtained at $C < 100$ mg/L were unreliable. The remaining $\gamma$ values are averages of five or more determinations, with standard deviations of ±0.2% or better for each point. All samples but AFSH and maltenes (denoted as M in Figure 3) show the up-and-down behavior observed for the asphaltenes in Figure 2. In
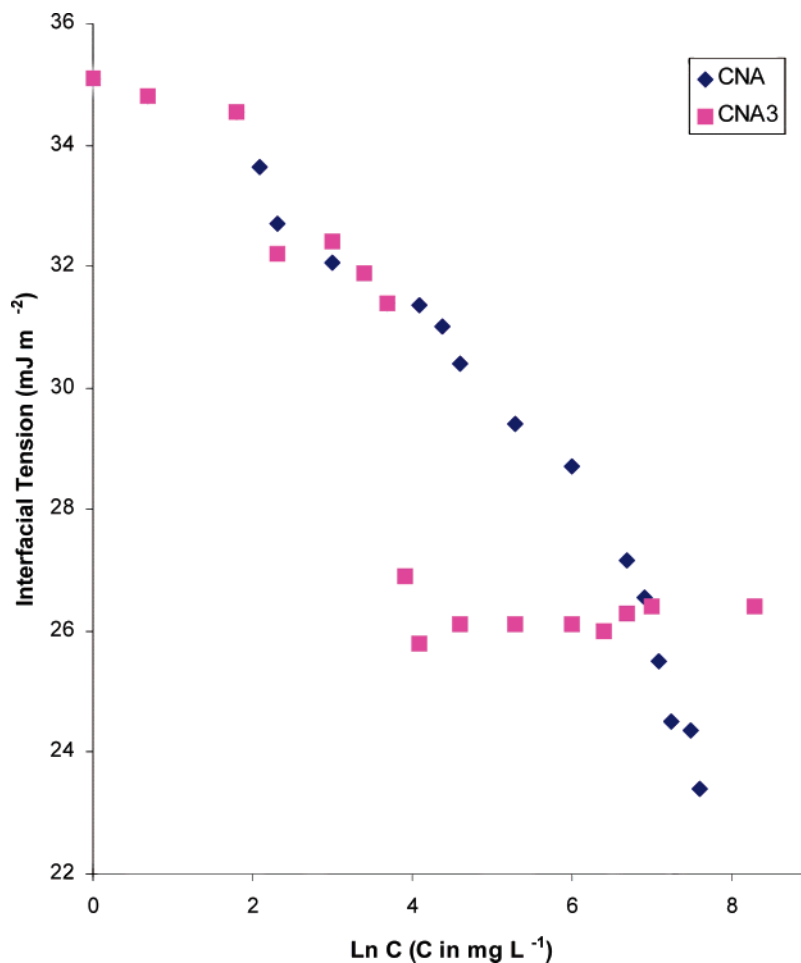
**Figure 2.** Adsorption isotherms for the water/toluene interface of the CNA and CNA3 asphaltene samples, measured at room temperature and neutral pH using the ring-detachment method (see text).

Figure 3, the $\gamma$ values are bracketed by those of the maltenes at the top and those of AFSH at the bottom. Being an acidic and low-molecular-weight fraction, the lower $\gamma$ values observed for AFSH are expected. Similarly, being a general acidic fraction, low $\gamma$ values were expected and observed for the GAF fraction. Being a fraction where acids have been extracted once, the CNA1 fraction was expected and observed to provide $\gamma$ values that were higher than those found for CNA (see Figure 3). However, as shown in Figure 3, the difference in $\gamma$ values between CNA and CNA1 was observed to be rather small.

Plots for other samples (GAF, CNA, and CNA1) follow the same trend, with general slopes similar to that observed for AFSH with GAF shifted by a small $\Delta\gamma$ value from AFSH.

**Discussion**

There are two interesting aspects related to the measurements in Figure 2; one is the stepwise nature of the isotherm corresponding to the CNA sample, which is also observed for the GAF and CNA1 fractions in Figure 3, and the other is the large step corresponding to the measurements of the CNA3 sample. We will first discuss the nature of the isotherms.

As described in the Introduction section, toluene solutions of asphaltene do adsorb at some inorganic surfaces (for instance, glass[22] and silica[23]), leading to

stepwise adsorption isotherms. Such adsorption has been taken into account, in terms of the adsorption of aggregates formed as the solute concentration in solution increases.

Somewhat similar phenomena may be occurring for some systems described in Figures 2 and 3. In other words, depending on concentration, single molecules, aggregates, or both would adsorb at the water/toluene interface. However, because of the liquidlike nature of the present interface, these molecules or aggregates, after adsorption, would condense, leading to different types of liquid films. This would account for the stepwise nature of some isotherms in Figures 2 and 3. Thus, the same property (aggregation in toluene) could be used to account for the nature of isotherms in the two very different adsorption phenomena.

It is noteworthy that the first two steps in the isotherms of Figure 2 occur at very low concentration ($C \approx 10$ and $60$ mg/L, respectively). The first step could be related to the formation of an expanded liquidlike film, of the type known for ordinary surfactants.[28] The second step is clearly visible in the case of the CNA3 sample. When compared to the onset concentration for aggregate formation in the bulk[21] ($<100$ mg/L; see Introduction), then the second step should be related to adsorption of aggregates formed in the bulk. Thus,

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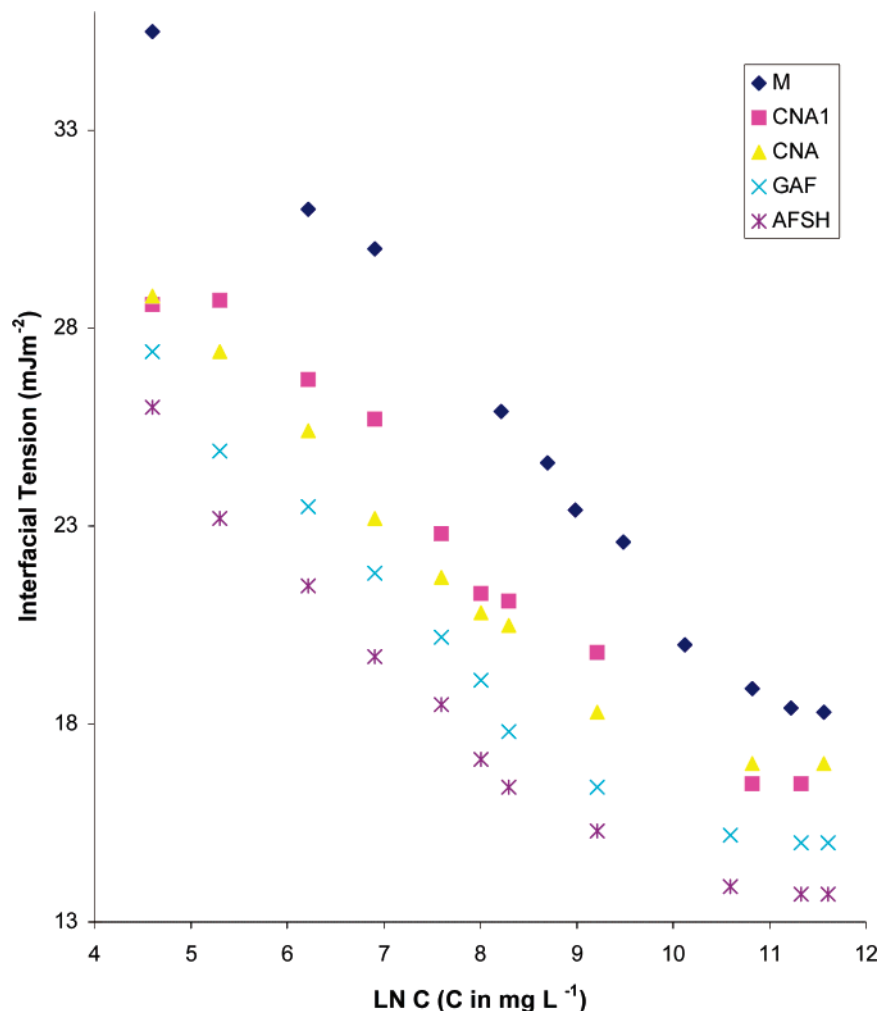
**Figure 3.** Adsorption isotherms for the water/toluene interface of AFSH, maltenes (M), and other asphaltene and asphaltene-derivate fractions. Measurements were performed at room temperature, using the pendant-drop method at pH 1 (see text).

from two very different types of experiments (thermal lens[21] and interfacial tension), the onset of aggregation in toluene could be placed near 60 mg/L.

As shown in Figures 2 and 3, the interfacial tension for CNA (Figure 2), and that for CNA, CNA1, and GAF (Figure 3), decrease continuously, without any sudden change or break in the slope. In other words, no critical micelle concentration (CMC)-like behavior is apparent in these results. In fact, the interfacial tension for CNA decreases all the way up to the saturated solution (see Figure 3). Again, the multistage type of adsorption that is apparent in Figures 2 and 3 for these samples resembles the adsorption at mineral surfaces. These results are better accounted for in terms of adsorption of aggregates, which increase in size as the bulk concentration increases.

The adsorption of aggregates formed in solution, followed by interface flocculation and film formation, account nicely for the films described previously and for the thick films formed at the water/oil interface for several crude oil and asphaltene solution systems. The strong dependence of rheological properties of these films with salt and pH clearly show that these films are charged,[6,8] probably negatively (as a consequence of carboxylic acid ionization at the interface).

The big step near $C = 60$ mg/L and the flat $\gamma(\ln C)$ curve obtained after the step observed for the isotherm

of the CNA3 sample are likely to be due to the adsorption of aggregates, followed by film formation combined with hydrophobic effects (see the CNA3 curve in Figure 2). As described in the Materials section of this paper, this sample was extracted three times to remove acidic components. Hence, a sample with less interfacial activity was expected. Actually, in a significant concentration range, the sample has a higher-than-expected interfacial activity. A similar result was observed for the CNA and CNA1 samples (see Figure 3); the interfacial activity for the CNA1 sample was higher than expected.

Hydrophobic effects, combined with film formation leading to highly condensed, solidlike films, could be a reasonable hypothesis to account for these somewhat-unexpected results. Thus, the sharp change in the $\gamma$ value observed for the CNA3 sample near $\ln C \approx 4$ ($C = 60$ mg/L; see Figure 2) should be due to film formation after aggregate flocculation. The driving force for this would be a drastic reduction of unfavorable water/toluene contacts after film formation (in other words, a reduction of hydrophobic effects). Apparently, the number of unfavorable water contacts is largely reduced after film formation.

Note that the CNA3 sample was the only sample that showed a relation of $\partial\gamma/\partial(\ln C) \approx 0$ in any concentration range (see Figures 2 and 3). In this case, $\gamma$ remained

almost constant, $\sim$26 mJ/m$^2$, after $C = 60$ mg/L. This strongly suggest that acids were effectively removed from this sample and that the *asphaltenes*, as such, should not reduce $\gamma$ to a value below 26 mN/m. However, when compared to the toluene/water interfacial tension (35 mJ/m$^2$), this is a very significant reduction of the $\gamma$ value, which strongly suggests that the interface formed is not as hydrophobic as might be expected.

It is important to note that the interfacial activity of the CNA3 sample, displayed after $C = 60$ mg/L, is not due to the presence of any single polar group, as is the case for ordinary surfactants. In this case, it is because the film that is formed is less hydrophobic than that prevailing for $C < 60$ mg/L.

Simple inspection of Figure 3 shows that average slopes are similar to that for AFSH. This suggest that AFSH is present in all these samples in different concentrations. Thus, the GAF and maltenes are the oil fractions that contain the highest and lowest amounts of AFSH, respectively. This shows that acids fractions do concentrate in asphaltenes or asphaltene-containing fractions. This could be explained because when in the oil, carboxylic acids would form hydrogen bonding to basic functionalities that should be abundant in asphaltenes.

The results in Figure 3 for the GAF, CNA, and CNA1 fractions are then consistent with mixed films of AFSH and asphaltenes. Because of the presence of the AFSH, interfacial tension of $\gamma < 26$ mJ/m$^2$ could be measured for these samples.

Stepwise isotherms have been observed for $C_7$ and $C_5$ asphaltenes by Ramos et al.[24] In this case, much-higher (10 g/L and higher) concentrations were examined and several "breaks" were observed in the isotherms. Although those authors emphasized only one of these breaks and attributed this to a CMC, in our view, these data could be analyzed using the aforementioned arguments: adsorption of aggregates, which increase in size as the bulk concentration increases. It should be mentioned that the lowest interfacial tension measured by Ramos et al. was always >26 mJ/m$^2$, which suggests the absence of AFSH in their samples.

## Conclusions

The evidence presented here is consistent with a stepwise adsorption of aggregates at the oil/water interface as the solution concentration ($C$) is increased. After adsorption, flocculation of these aggregates leads to three-dimensional films, which effectively separate the oil (toluene) from the water. For the present asphaltene sample, these films are mixed films that contain aliphatic-like, low-molecular-weight acids (AFSH) and asphaltene fractions. However, asphaltenes alone are capable of reducing the interfacial tension by 9 mJ/m$^2$. It is proposed that such reduction could be due to the reduction of hydrophobic effects after film formation at the oil/water interface.

## Nomenclature

CNA: asphaltene sample from CNO

CNA1: asphaltene obtained from the NRF1

CNA3: asphaltene obtained after two column extractions of NRF1 sample

AFSH: acidic fraction soluble in heptane (obtained from the filtrate after treating GAF with heptane; mainly comprised of low-molecular-weight ($\sim$400) aliphatic-type acids

AFIH: acidic fraction insoluble in heptane (obtained from the residue after treating GAF with heptane); an asphaltene-like sample

$C$: sample concentration (mg/L)

CNO: Cerro Negro oil

GAF: general acid fraction obtained from CNO; an asphaltene-like sample

NRF1: CNO fraction that was not retained after one pass through the chromatographic column (probably composed of neutral and basic compounds)

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