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Zeta Potential and Langmuir Films of Asphaltene Polar Fractions

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In this work, we study the surface and electrokinetic properties of asphaltenes and some of their polar fractions. Using different mixtures of pentane/methylene chloride as a precipitant, we obtain four fractions (F1−F4), which contain different proportions of iron, nickel, copper, cobalt, aluminum, and vanadium. Modifications of asphaltenes and fractions F1 and F2 are performed by treatment with the salt form of ethylenediamine tetraacetic acid (EDTA) and, after this, with aqueous solutions of copper sulfate. The results indicate differences in the metal content between fractions before and after the treatments. Besides these differences, we observed differences in the zeta potential measurements and differences in the isotherms at the air/water interface. Our results show that, after the EDTA treatment, asphaltenes and fractions F1 and F2 can retain copper (>200% of the original copper content of the samples). This high copper content of the treated asphaltenes and the F1 and F2 samples is reflected in a change of the electrical charge from a negative charge to a positive charge. The hydrophobic behavior of the samples was analyzed with a Langmuir balance. The results show that the asphaltenes and the F1 fractions are more hydrophilic, with a smaller molecular area, and the F4 fractions are more hydrophobic, with a larger molecular area, before and after EDTA and copper sulfate treatments. Both the zeta potential measurements and Langmuir films of the samples indicate the possibility that EDTA molecules remain attached to the asphaltene molecules.

Introduction

The decline of the oil production with conventional methods, has obligated producers to exploit heavy oil reservoirs, and, at the same time, the corresponding problems that are associated with the deposition of the asphaltenes have been increased. Asphaltenes, which are defined as the heaviest fraction of the crude, are obtained by precipitation with *n*-heptane or *n*-pentane, among other compounds.[1] Many methods to obtain asphaltenes have been described in the literature,[2,3] and it has been shown that the physicochemical properties of asphaltenes are sensitive to the separation techniques and solvents that are used.

Different attempts have been realized to investigate the physical and chemical properties of the different fractions of asphaltenes. Groenzin and Mullins[4] have investigated the molecular size of different asphaltenes fractions obtained via precipitation by modifying the toluene/*n*-pentane proportions and determined that different subfractions have the same type of molecules but different molecular population distributions. Another interesting procedure to separate the soluble and insoluble fractions of asphaltenes was used by Acevedo et al.,[5] who used the PNP (*p*-nitrophenol) method. They found interesting results in the composition of the subfractions. The resulting toluene-insoluble fraction had poor hydrogen aromaticity and rich carbon aromaticity, which is consistent with a more rigid and planar structure; in addition, both soluble and insoluble fractions contained a high content of hydrogen bound to aliphatic carbons that were joined to aromatic compounds. The fraction that was soluble in toluene was rich in hydrogen that was bound to aliphatic chains, which is consistent with a more flexible structure. Similar results of the behavior of asphaltenes treated using PNP were obtained by Gutierrez et al.[6]

Recently, Douda et al.[7] analyzed the asphaltene fractions by the Soxhlet method and found, by different techniques, a series of maltenes fractions with different aromatic proportions and showed that the original asphaltenes contained a greater amount of heterocyclic molecules and ketones than the maltenes subfractions.

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(1) Zhang, L. Y.; Lawrence, S.; Xu, Z.; Masliyah, J. H. *J. Colloid Interface Sci.* **2003**, *264*, 128−140.
(2) Parra-Barraza, H.; Hernández-Montiel, D.; Lizardi, J.; Hernández, J.; Herrera-Urbina, R.; Valdez, M. A. *Fuel* **2003**, *82*, 869−874.
(3) Alboudwarej, H.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. *Energy Fuels* **2002**, *16*, 462−469.
(4) Groenzin, H.; Mullins, O. C. *Energy Fuels* **2003**, *17*, 498−503.

(5) Acevedo, S.; Escobar, O.; Echavarría, L.; Gutiérrez, L. B.; Méndez, B. *Energy Fuels* **2004**, *18*, 305−311.
(6) Gutiérrez, L. B.; Ranaudo, M. A.; Méndez, B.; Acevedo, S. *Energy Fuels* **2001**, *15*, 624−628.
(7) Douda, J.; Llanos, M. E.; Alvarez, R.; Navarrete-Bolaños, J. *Energy Fuels* **2004**, *18*, 736−742.

In contrast, the maltenes contain more alkyl side chains, which contribute to the solubility of the asphaltenes.

Asphaltenes precipitated with both polar (acetone) and nonpolar (*n*-heptane) solvents have been analyzed by Buenrostro-González et al.,[8] and interesting differences in solubility and molecular weight distributions were obtained, depending on the toluene/*n*-heptane and toluene/acetone proportions used to precipitate the asphaltene fractions of the solvent. Boukir et al.[9] observed important differences in the constituents of resins and asphaltenes. Resins have more-aliphatic and less-aromatic compounds, and they are composed of polar end groups with O, S, and N heteroatoms and nonpolar paraffinic groups. Their proposed model of resin/asphaltene interaction suggests that resins are attached to asphaltene micelles through their polar end groups (hydrogen bonding, dipole−dipole interactions). Kaminski et al.[10] have classified asphaltenes according to the polarity of the solvent to precipitate asphaltenes. Using a mixture of pentane/methylene chloride, they obtained different fractions with different solubility properties, as a consequence of their polarity properties.

On the other hand, surface properties of asphaltenes have been shown to be very important in the absorption process on different rocks,[11] and, recently, Jada and Salou[12] used the zeta potential to demonstrate that the proportion of resins to asphaltenes determines the charge of the bitumens and this proportion contributes to maintain the stability in the crude oil. In a recent paper,[2] we have used zeta potential measurements on different asphaltenes samples, obtained with different *n*-heptane/crude proportions, and demonstrated the influence of the precipitation method on the electrical behavior of asphaltenes.

In this work, we investigate different asphaltene fractions, using the method of Kaminski et al.[10] to obtain different polar fractions. We modify the asphaltenes and the fractions by treatment with the salt form of ethylenediamine tetraacetic acid (EDTA) and with aqueous solutions of copper sulfate and perform zeta potential measurements and Langmuir isotherms for the asphaltenes and some fractions. Our aim is to understand the influence of polarity and metal content of asphaltenes and the fractions with the corresponding surface electrical charge and the behavior of their monolayers on the air/water interface.

Experimental Section

Asphaltenes were obtained by precipitation with *n*-heptene with a modified procedure contained in ASTM 2007D.[13] Asphaltenes samples were obtained from a crude oil (Maya) from the Instituto Mexicano del Petróleo, México. Briefly, one volume of crude oil was mixed with 40 volumes of *n*-heptane for 1 h at room temperature and kept sealed for 2 days at room temperature. The mixture was filtered with Whatman #4 filter

(8) Buenrostro-González, E.; Andersen, S. I.; García-Martínez, J. A.; Lira-Galeana, C. *Energy Fuels* **2002**, *16*, 732−741.

(9) Boukir, A.; Aries, E.; Guiliano, M.; Asia, L.; Doumenq, P.; Mille, G. *Chemosphere* **2001**, *43*, 279−286.

(10) Kaminski, T. J.; Folger, H. S.; Wolf, N.; Wattana, P.; Mairal, A. *Energy Fuels* **2000**, *14*, 25−30.

(11) Kokal, S.; Tang, T.; Schramm, L.; Sayegh, S. *Colloids Surf. A* **1995**, *94*, 253−265.

(12) Jada, A.; Salou, M. *J. Pet. Sci. Eng.* **2002**, *33*, 185.

(13) *ASTM Annual Book of ASTM Standards*, Vol. 5.0; American Society for Testing and Materials (ASTM): Philadelphia, PA; 1983; p 158.
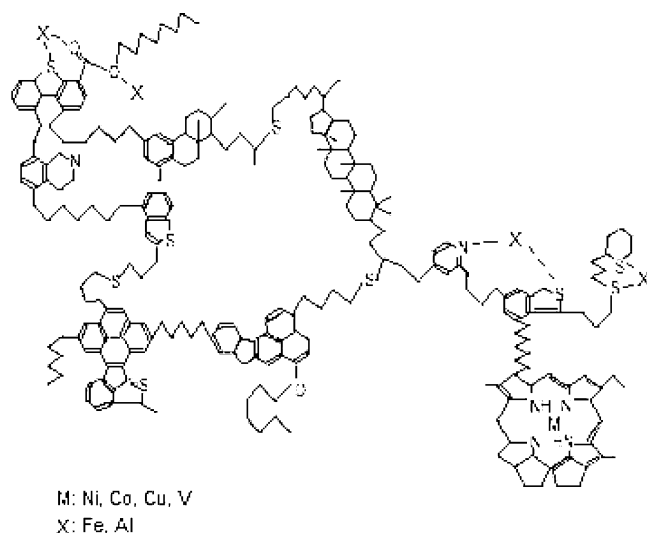
paper (10−15 µm). The asphaltenes were dried at room temperature.

Fractionation. The asphaltene sample obtained was dissolved in methylene chloride (10% w/w). Pentane then was added until a 3/7 methylene chloride/pentane ratio was obtained. The precipitate is termed the F1 fraction. This fraction was collected by filtration with a Millipore 0.45 µm filter and was allowed to dry at room temperature. The F2 fraction was precipitated using the supernatant and adding enough pentane to obtain a ratio of 1:3. Other fractions were obtained by continuing with the method.[10]

Metal Chelation. We used 1.5 g of asphaltenes, F1 fraction, and F2 fraction, respectively, and separately mixed with 500 mL of a 0.15 M of EDTA in deionized water at pH 9. The solutions were agitated for 3 h at room temperature. The precipitates then were filtered and vacuum-dried for 4 h.

The effect of a copper sulfate solution on the samples treated with EDTA was investigated by mixing the samples with a 0.2 M $CuSO_4 \cdot 5H_2O$ solutions. The solutions were agitated for 3 h at room temperature and twice washed with deionized water and filtered. Samples then were vacuum-dried for 3 h.

Aqueous suspensions of asphaltenes for zeta potential measurements were prepared as follows. First, 50 mg of asphaltenes were dispersed in 15 mL of ethanol under ultrasound during 20 min. A quantity (1.5 mL) of this suspension was added to 100 mL of triply distilled water containing 0.001 M $NaNO_3$ to fix the ionic strength. The pH then was adjusted, using nitric acid or sodium hydroxide diluted solutions, to the desired value and the suspension was conditioned for 20 min under magnetic agitation. During the conditioning time, if the pH changed, it was readjusted to the desired value.

Zeta potentials were measured with a Zeta Meter 3.0+ unit (manufactured by Zeta-Meter, Inc., New York). This apparatus includes a microprocessor that first measures the electrophoretic mobility of colloidal particles dispersed in aqueous solutions, and then automatically calculates the zeta potential (in millivolts) using the Smoluchowski equation. This is the most elementary expression for zeta potential (ζ) calculations from electrophoretic mobility (U_e) measurements. The equation can be written as

$$\zeta = \left(\frac{\eta}{\epsilon}\right) U_e$$

where η and ϵ represent the viscosity and the permittivity of the aqueous medium. Zeta potentials reported here are the average values obtained by tracking at least 20 different particles.

A Langmuir balance (Nima, Langmuir Blodgett through, model type 611), whose surface tension precision is 0.1 mN/m, was used to determine two-dimensional isotherms of asphaltenes at the air/water interface. Each asphaltene sample was dissolved in toluene, and then 100 µL of a 1 mg/mL solution was deposited at the clean water surface (using Milli-Q water, Millipore) with a Hamilton microsyringe. The temperature was maintained at 25 ± 0.1 °C.

Sample preparation for atomic adsorption spectroscopy (AAS) was conducted as follows. We prepared 1.25 g of an equimolar mixture of Na_2CO_3 and K_2CO_3, then mixed them with 250 mg of the sample in a mortar with a pestle. The mixture was fused at 900 C, then 5 mL of nitric acid (HNO_3) and 1 mL of hydrochloric acid (HCl) were added at room temperature. The solution is boiled with deionized water. Finally, deionized water was added to bring the sample volume to 100 mL. Sample analysis was performed using a Perkin−Elmer instrument (model 2380).

Results

Metal Content of Samples. The results of the content of some metals (iron, nickel, copper, cobalt,

Figure 1. Proposed asphaltene structure with incorporated metal ions. The asphaltene structure without metal ions has been proposed in an earlier publication. [Strausz, P. O.; Mojelesky, W. T.; Faraji, F.; Louren, M. E.; Perg, P. Additional Structural Details on Athabasca Asphaltene and Their Ramifications. *Energy Fuels* **1999**, *13*, 207−227.]

Table 1. Metal Content of the Asphaltenes and the First Two Fractions (F1 and F2) before and after Treatment with Ethylenediamine Tetraacetic Acid (EDTA)

	Metal Content (mg/mL)					
	Before EDTA Treatment			After EDTA Treatment		
metal	asphaltene	F1	F2	asphaltene	F1	F2
iron	713	905	865	421	520	514
nickel	267	329	285	264	325	277
copper	220	80	59	131	76	50
cobalt	43	50	50	31	44	44
vanadium	1462	1778	1680	1141	1752	1654
aluminum	440	560	396	290	427	268

vanadium, and aluminum) in the aqueous phase of the digestion of the samples of asphaltenes and two fractions (F1 and F2) before and after treatment with EDTA at pH 9, as described previously, are shown in Table 1. The results are in accordance with those observed by Kaminski et al.[10] Taking into account the effect of the EDTA treatment, we can identify two groups of metals: one group is formed by iron and aluminum, which are removed considerably (>40%). The other group is formed with nickel, copper, cobalt, and vanadium, which practically retain their original concentrations. This could be explained by considering that nickel, copper, cobalt, and vanadium are being sequestered in central porphyrin-like structures, where these metal ions show a strong stability. In Figure 1 (extracted from ref 14), these metal ions are represented by the symbol M in the porphyrin ring. We consider that one important fraction of Fe and Al must be joined to the asphaltene molecules in a different form (represented by the symbol X in Figure 1). We suggest that the fraction of Fe and Al extracted with EDTA could be ions joined with other heteroatoms such as sulfur and oxygen, which are present in the asphaltenes structures and, therefore, the interactions between metal X and the asphaltenes could be weaker than the interactions between metal X and the EDTA.
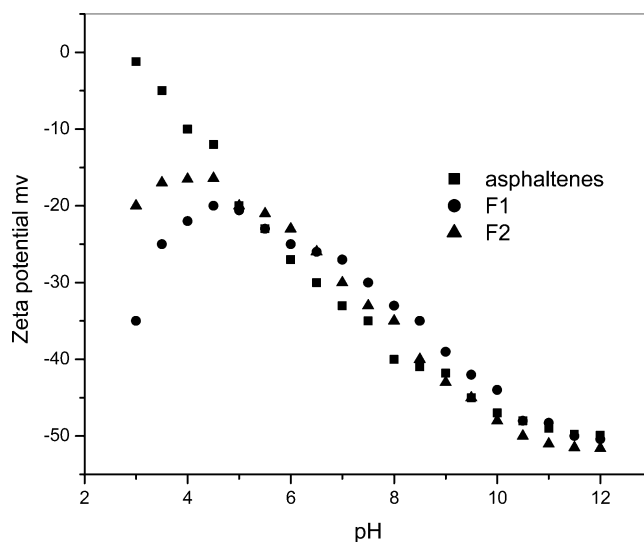
(14) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Edition; Wiley: New York, 1999.

Figure 2. Zeta potential measurements of the asphaltenes and fractions F1 and F2, for different pH in triply distilled water and 0.001 M $NaNO_3$ to fix the ionic stregnth.

The effect of the treatment of asphaltenes and the F1 and F2 fractions with a $CuSO_4$ solution showed that the amount of copper was increased by >200%, in comparison with the copper present in the original samples (527 mg/mL for asphaltenes, 340 mg/mL for the F1 fraction, and 165 mg/mL for the F2 fraction after the treatment).

Zeta Potential Results. Zeta potential measurements have been proven to be a good reference to detect the presence of resins in the bitumens composition, as demonstrated by Jada and Salou.[12] Bitumens with a high resins/asphaltenes ratio show a higher positive zeta potential at low pH, compared with samples with a low resins/asphaltenes ratio. This behavior was demonstrated earlier[2] with different asphaltenes samples by precipitating asphaltenes with different crude/*n*-heptane proportions. The same behavior has been observed by González et al.[15] for asphaltenes from different Brazilian crude oils. The pH at which the zeta potential is zero defines the isoelectric point (IEP) of the material; at pH values smaller than the IEP, the zeta potential is positive whereas at pH values higher than the IEP, the zeta potential is negative. The pH effect on the zeta potential of asphaltenes is explained if one considers that the surfaces of these materials contain pH-dependent ionizable functional groups, acidic and basic, that can undergo dissociation and protonation.[16] A negative surface charge on asphaltenes results upon dissociation of acidic surface functional groups such as carboxylic, which exhibit pK_a values of ≤ 4,[12,14] and phenolic groups, which exhibit pK_a values of $4 < pK_a < 9$.[17] The positive surface charge results upon protonation of basic nitrogen-containing functional groups, such as pyridine.[12]

In Figure 2, we show the behavior of the zeta potential for the asphaltene sample and the two fractions F1 and F2 for different pH. We observe that the behavior of the complete asphaltenes is similar to that which has previously been observed.[2] We notice a different behavior for the fractions at low pH. The zeta potential value

(15) González, G.; Neves, G. B. M.; Saraiva, S. M.; Lucas, E. F.; dos Anjos de Sousa, M. *Energy Fuels* **2003**, *17*, 879−886.
(16) Abraham, T.; Christendat, D.; Karan, K.; Xu, Z.; Masliyah, J. *Ind. Eng. Chem. Res.* **2002**, *41*, 2170.
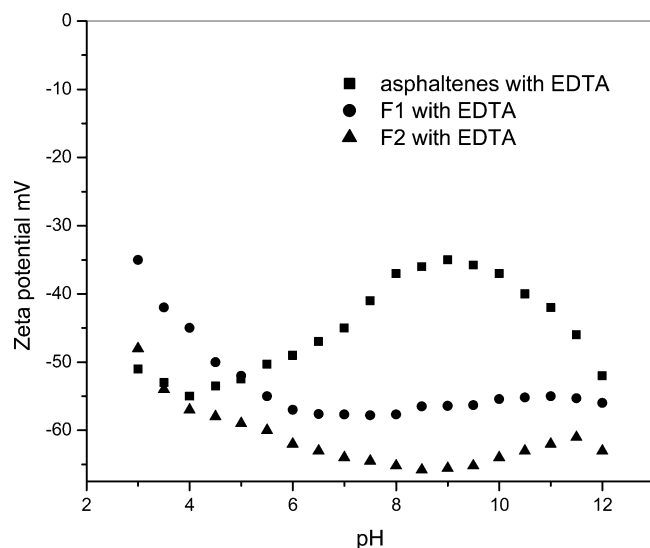(17) Jada, A.; Chau, A. A. *J. Pet. Sci. Eng.* **2003**, *39*, 287−296.

Figure 3. Zeta potential measurements of the asphaltenes and fractions F1 and (▲) F2 treated with EDTA, for different pH in triply distilled water and 0.001 M NaNO₃ to fix the ionic strength.

Figure 4. Zeta potential measurements of the asphaltenes and fractions F1 and F2 treated with CuSO₄ after treatment with EDTA, for different pH in triply distilled water and 0.001 M NaNO₃ to fix the ionic strength.

is slightly higher (in magnitude) for the F1 fraction than for the F2 fraction and the asphaltenes. This could be a consequence of the higher polarity of the F1 fraction, because of its lower resins proportion, which leaves free more carboxylic or phenolic groups at the interface. The polarity of the F1 fraction is probably increased with the higher metal content (10% more than fraction F2 and 15% more than asphaltenes). We notice that, for the lowest pH used, asphaltenes particles find their IEP.

As long as we increase the OH⁻ concentration, we observe a decrease in the zeta potential values of the F1 and F2 fractions. This phenomenon could be understood if we assume that, for the F1 and F2 frations, asphaltene molecules and resins could be joined by hydrogen or dipole−dipole bondings[9] and when OH⁻ radicals are added to the water, they neutralize the protons or the metal ions, destroying these bonds and leaving free negatively charged resin molecules. This would leave F1 and F2 particles less negative charged until this process ends and a relative maximum around pH 4 and 4.5 is reached as observed in Figure 2. Up to this pH, the behavior is similar for the three samples, and for pH >10, it seems that the surface charge of the particles of the three samples is saturated with the OH⁻ radicals from the solution.

The effect of the EDTA, as shown in Table 1, is to eliminate a great proportion of some metals from asphaltenes and both fractions. These changes in the metal composition of asphaltenes and fractions produce variations on the zeta potential measurements of the same three samples, as can be observed in Figure 3. We notice that, for low pH, the behavior of asphaltenes is very different, in comparison to that shown in Figure 2. At low pH, the zeta potential value of the asphaltenes and F2 samples is higher in magnitude (≥40 mV) comparing with the values without the EDTA treatment. This probably happens because EDTA molecules remove some cations outside of the kernel of the asphaltene molecules and the two fractions and probably some type of EDTA−resin bonds are formed at the surface of the particles. Observe that the zeta potential value at low pH for F1 is almost the same as that shown
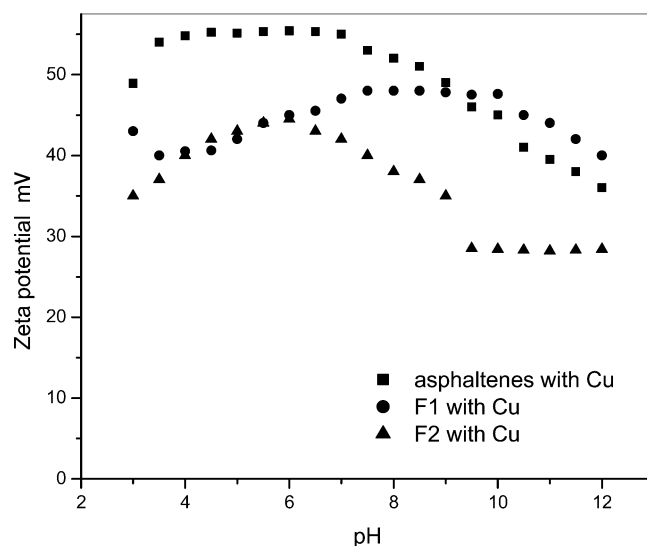
for the F1 fraction without EDTA treatment and is not very sensitive to the increasing pH. This could mean that this fraction, when reduced of cations and resins, is not significantly affected by EDTA molecules and is now completely saturated by negative charges at lower pH, and additional OH⁻ radicals in solution do not contribute significantly to the net charge of the particles. A similar effect is produced in the F2 sample. However, it seems that the charge saturation is produced at higher pH (∼9), which was indicative that EDTA strongly modified the F2 structure and charge sites. At higher pH, there is a slight increase of the zeta potential values; however, this variation can be considered as a fluctuation inside the error bars. The asphaltene particles showed a decrease in the zeta potential values as the pH was increased, and, for pH ∼9, we observed a relative maximum. This could mean, again, that, first, at low pH, the OH⁻ radicals break hydrogen bonds between asphaltenes and negatively charged resins and/ or negatively charged EDTA−resin complexes, leaving less negatively charged asphaltene molecules at the interface of asphaltene particles. Thus, with the addition of more OH⁻ radicals, a partial neutralization was produced and less-negative zeta potential values were obtained. For higher pH values, the behavior of asphaltenes is similar to that observed in Figure 2.

Finally, we show the results of zeta potential measurements for the three samples after they were treated with the copper sulfate solution, as described in the Experimental Section. As can be observed in Figure 4, we notice that the sign of the charge is inverted for all the pH range for both fractions and asphaltenes. From the results obtained of the copper content of the samples with the copper sulfate treatment (527 mg/mL for asphaltenes, 340 mg/mL for F1 and 165 mg/mL for F2) and the corresponding values shown in Table 1, we conclude that samples treated with the copper solution contain ∼3−4 times the amount of copper than the samples treated only with EDTA. This effect suggests that copper is included in the particles of asphaltenes and both fractions, producing a positive zeta potential. The small changes of the zeta potential values with the

increasing pH suggests that very few charges are added to the particles from the solution in the entire range of pH analyzed, and the added OH^- radicals are not enough to change the sign of the particles. Another possible effect of the copper treatments on the asphaltenes and the two fractions could be that most of resins were absent in the samples, increasing the positive sign of the charge. This possibility will be discussed by analyzing the corresponding monolayers at the air/water interface.

Langmuir Isotherms. The molecular behavior of monolayers of asphaltenes and fractions F1−F4 were investigated at the air/water interface, using a Langmuir balance. The two-dimensional isotherms are obtained by measuring the pressure, which is defined as

$$\pi = \gamma_0 - \gamma$$

where γ_0 is the surface tension of pure water and γ is the surface tension when some hydrophobic molecules are adhered at the air/water interface and varies depending of the molecular concentration and the exposed area in the balance. One of the most important parameters to characterize isotherms is the compressibility of the films at the interface. This is defined as[18]

$$C^s = -\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}\pi} \qquad (1)$$

where A is the cross-sectional area and π is the surface pressure. This parameter is the inverse of the film elasticity ϵ that has been used by other authors.[19]

The shape of the $\pi-A$ isotherms is similar to that reported by Zhong et al.[1] and Mohammed et al.[20] The monolayers behave as a two-dimensional gas phase, where the molecules are far apart. In this phase, the surface pressure is very low and when the area is further compressed, molecules are closer, creating the liquid expanded (LE) phase (at a pressure of ∼5 mN/m when the curves begin to rise). Under further compression, asphaltene molecules are closely packed and the resins or alkyl chains are assumed to be in the air and more-ordered, building the liquid-condensed (LC) phase (at a pressure of ∼30 mN/m in Figure 5). After this phase, we find the critical area (A_c), where molecules start overlapping and folding, which leads to a new three-dimensional phase. No abrupt collapse is observed for any sample, as in the case of simple lipids such as arachidic or stearic acid monolayers.[21] Of course, no specific phase transition points were observed in any case that was analyzed, because of the wide molecular distribution of the samples.

In Figure 5, where the results of the isotherms for the asphaltenes and the four fractions are shown, we observe that only fractions F3 and F4 show the presence of A_c, which is obtained by intersecting tangent lines of the isotherms from the LC phase and from the three-
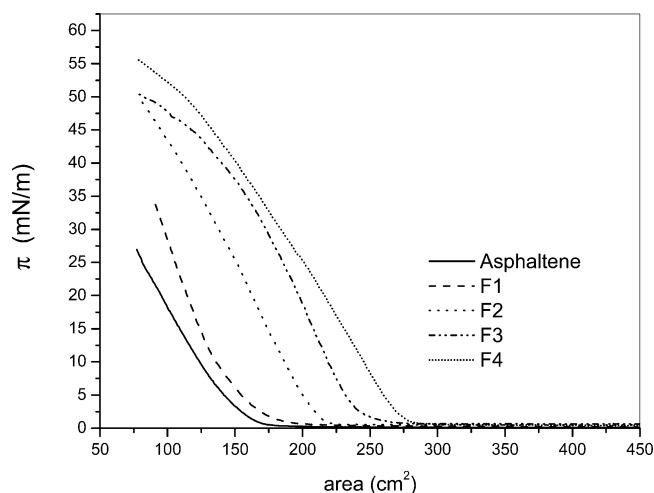

Figure 5. Isotherms in the air/water interface of the asphaltene sample and the four fractions at 25 °C. Samples of 0.1 mg/100 μL in toluene were deposited at the interface.

dimensional-like phase. This behavior is not observed for the F1 and F2 samples, probably because the F1 and F2 molecules are less extended and cannot be overlapped or folded at the minimum area reached by the balance.

Another important parameter of isotherms is the limiting area (A_0), which is obtained by extrapolation at the intersection of the abscissa axis with the tangent at the $\pi-A$ isotherm at $\pi = 2$ mN/m. We observe a regular behavior of A_0 for asphaltenes and the four fractions: 170 cm^2 for asphaltenes, 185 cm^2 for the F1 fraction, 225 cm^2 for the F2 fraction, 260 cm^2 for the F3 fraction, and 280 cm^2 for the F4 fraction. These values indicate the monolayer expansion of the films, and, from these results, we conclude that the F4 molecules occupy the largest surface area at the air/water interface and, as suggested by Fauconnier et al.,[19] this order could correspond to the corresponding order of the hydrodynamic radius of the molecules. In contrast, the original asphaltenes sample seems to occupy the smallest area at the interface, compared to the area of the fractions, probably because of the influence of the more polar and abundant F1 fraction at the air/water interface. We should remember that asphaltenes are built as a mixture of different proportions of molecules, and the small average molecular area at the air/water interface indicates that small polar molecules dominate, producing a more condensed and rigid structure. The hydrophobic properties of the asphaltenes and the fractions can be compared by observing the corresponding pressure at small areas. We notice that the pressure of the films increases according to the following order: asphaltenes < F1 < F2 < F3 < F4. This sequence corresponds to the same order in the limiting area as a consequence of the increasing hydrophobicity from asphaltenes to fraction F4. These results are in correspondence with the results of solubility obtained by Kaminski et al.,[10] showing that fraction F1 and unfractionated asphaltene are less toluene soluble than fraction F4, probably because more resin molecules remain attached to fraction F4.

From the isotherms, we evaluated the compressibility of the samples in the entire range of measured pressures, according to the definition and procedure ex-

(18) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid−Gas Interfaces*; Wiley−Interscience: New York, 1966.

(19) Fauconnier, M. L.; Blecker, C.; Gryone, J.; Razamindralmbo, H.; Vanzerven, E.; Marlier, M.; Paquot, M, *J. Agric. Food Chem.* **2000**, *48*, 2709−2712.

(20) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. *Colloids Surf. A* **1993**, *80* (2−3), 237−242.

(21) Valdes-Covarrubias, M. A.; Cadena-Nava, R. D.; Vásquez-Martinez, E.; Valdes-Pérez, D.; Ruiz-García, J. *J. Phys. Condens. Matter* **2004**, *16*, 2097−2017.
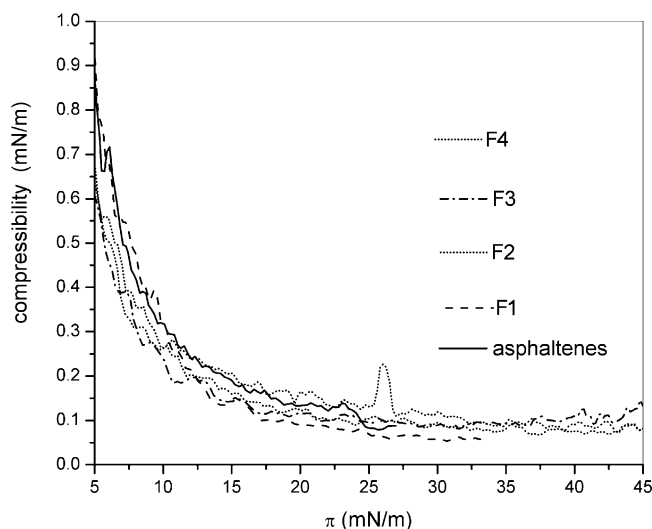
Figure 6. Compressibility of the asphaltenes and the four fractions (F1−F4) for different pressures. Curves were obtained from eq 1 directly from Figure 4.

Figure 7. Isotherms in the air/water interface of the asphaltene sample and the four fractions treated with EDTA at 25 C. Samples of 0.1 mg/100 μL in toluene were deposited at the interface.

plained in eq 1. The results are shown in Figure 6 and Table 2. We found that, for low π, the compressibility values for the asphaltenes and fraction F1 seems to be higher than that for fractions F2, F3, and F4. For higher pressures ($\sim$30 mN/m), the compressibility of fraction F4 takes the largest value ($\sim$0.11 m/mN) and that of fraction F1 is $\sim$0.05 m/mN. The compressibility values of asphaltenes and fractions F2 and F3 are almost the same at this pressure. These values are larger, compared to the values obtained by Zhang et al.[22] using asphaltenes extracted from Athabasca oil sands bitumen. The compressibility values that they determined at the pressure of π = 30 mN/m were <0.02 m/mN, which means that our asphaltenes and fractions films are more flexible than those used by Zhang et al.[22] This can be due to the method that they used for extracting and purifying asphaltenes. We assume they obtained asphaltenes that were almost free of resins, producing more-rigid films at the air/water interface.

These results are expected because, at larger areas (low π), small hydrophilic molecules of fraction F1 do not touch each other enough, contrary to the expanded molecules of fraction F4, which contribute to a more relatively rigid monolayer. At larger π values, small and rigid molecules of fraction F1 are closer and interact strongly to produce a more rigid and compact monolayer than molecules of fraction F4, which probably contain more-flexible resin residues.

The effect of EDTA on the asphaltenes and fractions F1−F4 is observed in Figure 7. The behaviors of all of the isotherms are similar to those before treatment with EDTA. The sequence of the corresponding limiting area
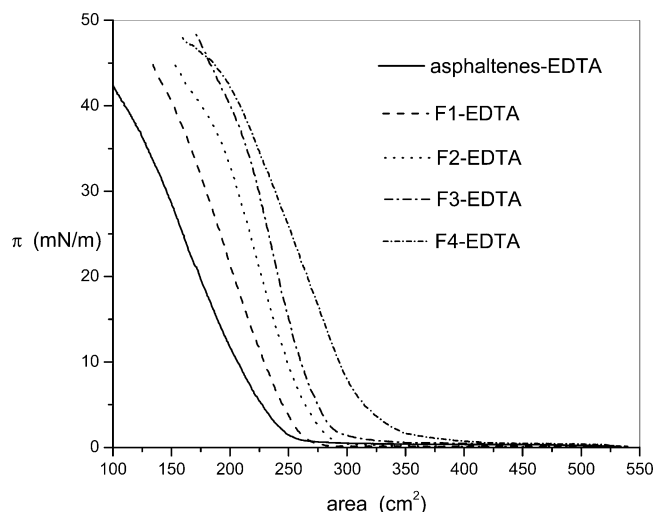
is the same as that shown in Figure 5. However, the values of A_0 are larger for each sample: 255 cm^2 for asphaltenes, 260 cm^2 for F1, 280 cm^2 for F2, 290 cm^2 for F3, and 360 cm^2 for F4. The tendency of the curves show that, at 100 cm^2, the pressure is higher, compared with the pressure reached for the samples at the same area before using EDTA. This means that EDTA modifies the samples, thereby increasing the hydrophobic properties of the asphaltenes and fractions monolayers at the air/water interface. It seems that the molecular area of the samples is larger or bigger aggregates are formed as a consequence of eliminating metal atoms from asphaltenes and its fractions. Another reason could be that asphaltenes and EDTA form a complex molecular system with a larger area. Kaminski et al.[10] did not find any evidence of such interaction via Fourier transform infrared spectroscopy; however, a weak interaction could be responsible for such an increase in molecular area, as we have already demonstrated while investigating the interaction of cholesterol and chitosans at the air/water interface.[23]

It is important to mention that the collapse like phase is now present in all samples, indicating the presence of folded or overlapped large molecules, which is due to the influence of EDTA molecules.

The compressibility values at 30 mN/m are almost the same as those shown in Figure 6, except for fraction F1, which, at this pressure, now shows a larger value (0.08 m/mN). This result is consistent with the fact that the average molecular area has grown due to the influence of EDTA, producing more-flexible films. At low pressure (π = 2 mN/m), the compressibility values are different,

Table 2. Compressibility for the Monolayers of the Asphaltenes and the Four Fractions Obtained by Different Methods (F1−F4) at the Air/Water Interface at 25 °C

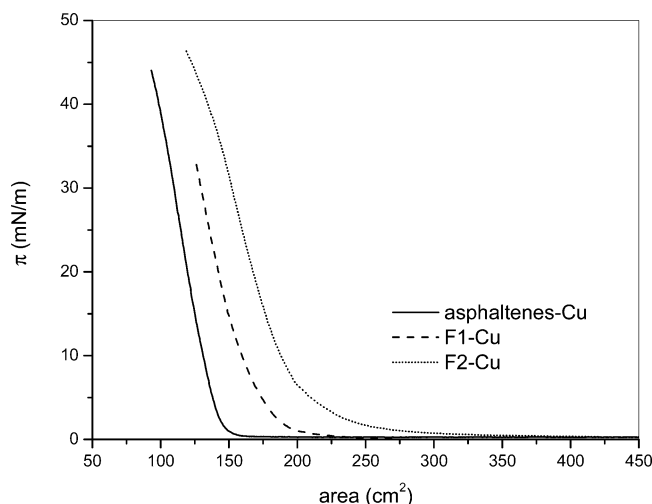| sample	pressure (mN/m)	Compressibility (m/mN)				
		asphaltenes	F1	F2	F3	F4
untreated sample	2	3.10	4.57	2.1	4.03	3.12
untreated sample	30	0.08	0.05	0.08	0.09	0.11
sample with EDTA	2	4.2	2.97	2.78	4.9	7
sample with EDTA	30	0.09	0.08	0.07	0.07	0.09
sample with CuSO$_4$·5H$_2$O	2	1.64	3.96	4.8		
sample with CuSO$_4$·5H$_2$O	30	0.03	0.04	0.05		

Figure 8. Isotherms in the air/water interface of the asphaltene sample and the four fractions treated first with EDTA and then with $CuSO_4$ at 25 C. Samples of 0.1 mg/100 μL in toluene were deposited at the interface.

compared to the values of the samples without EDTA. All samples, except fraction F1, showed larger compressibility values, as can be observed in Table 2. This is reasonable for larger areas, in the sense that bigger or more hydrophobic molecules at the air/water interface remain closer than smaller or hydrophilic ones.

Finally, we discuss the isotherms for the asphaltenes and fractions F1 and F2 that have been treated with copper sulfate. In Figure 8, we show the isotherms of the asphaltenes and fractions F1 and F2. As observed, the limiting area A_0 does not show important variations, compared to the areas of the monolayers obtained with the original asphaltenes and fractions. On the contrary, they now appear smaller than the limiting areas shown for the samples treated with EDTA. The largest difference in limiting area is shown by the isotherm that corresponds to asphaltenes ($\sim$100 cm^2). This is a very important difference in the hydrophobicity of the samples and the molecular structure at the air/water interface. The size of the aggregates of asphaltenes and the fractions now seem to be reduced or/and the influence of the electrical charge of the asphaltene−copper and fraction−copper complexes become the molecules in relatively more hydrophilic solutions. The compressibility values shown for the isotherms at $\pi = 30$ mN/m are shown in Table 2. All these values were smaller, compared to those derived from Figures 5 and 7. Observe that now our asphaltenes monolayer has almost the same compressibility as that observed by Zhang et al.[22] It is also noticeable that the buckling (the zone of three-dimensional domains) disappears at higher π, as a consequence of the increasing rigidity of the monolayers, because of the effect of the copper addition and the partial elimination of resins.

(22) Zhang, L. Y.; Xu, Z.; Masliyah, J. H. *Langmuir* **2003**, *19*, 9730−9741.
(23) Parra-Barraza, H.; Burboa, M. G.; Sánchez-Vázquez, M.; Juárez, J.; Goycoolea, F. M.; Valdez, M. A. *Biomacromolecules* **2005**, in press.

Conclusions

In this work, we have analyzed the effect of ethylenediamine tetraacetic acid (EDTA) and copper sulfate treatments on the asphaltenes and some of its polar fractions. Differences in the metal content of the asphaltenes and fractions were observed, with a predominance of iron and vanadium. After the EDTA treatment, we observed that the proportions of vanadium, cobalt, copper, and nickel did not change appreciably. In contrast, iron and aluminum showed a significantly decrement in the samples. This difference suggests that the former metals are being located in central porphyrin-like structures, where these metal ions show strong stability, whereas iron and aluminum are metals that could be joined with other heteroatoms such as sulfur and oxygen, showing weaker interactions than the metal−EDTA interactions. These differences in metal composition and the method of precipitation created differences in the zeta potential measurements and Langmuir films at the air/water interface. Our zeta potential measurement results, and the behavior of the asphaltenes and the four fractions at the air/water interface, indicate the possibility that EDTA molecules remain attached to the different samples. One of the most interesting results was the fact that, when samples are treated with copper sulfate, the zeta potential values changes sign and becomes positive for all pH analyzed, indicating the effect of the metal content. The isotherms of the asphaltenes and the four fractions showed differences in hydrophobicity and compressibility. The hydrophobicity (limiting area) increased in the sequence of asphaltenes < F1 < F2 < F3 < F4 before the EDTA treatment; after the EDTA treatment, the same sequence was preserved but with larger limiting area values, indicating the formation of complexes between the samples and EDTA molecules and an enhancement of the hydrophobic character of the samples. The effect of the copper sulfate on the isotherms, as expected, showed a decreasing effect on the limiting area of asphaltenes and both fractions F1 and F2, because of the larger amount of copper in the samples. Other effects of the copper on the monolayers was the enhancement of the monolayer rigidity, in comparison with that observed in samples that were treated with EDTA.

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