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Role of asphaltene origin in their adsorption at oil-water interfaces

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Abstract

We have studied the interfacial properties of oil-water interfaces in the presence of asphaltenes from different sources, crude oil, bitumen and coal. The study includes dynamic interfacial tension (DIFT) and interfacial compression rheology measurements. By comparing DIFT for different concentrations, we show that the kinetics is dominated by interfacial reorganization. Some of the asphaltenes are found more interfacially active than others, but adsorption is irreversible for all. The interfacial rheological behavior is also varied: asphaltenes from petroleum with equal aliphatic and aromatic fractions, and immature bitumen with a large aliphatic fraction and small aromatic fraction, form flexible interfacial layers, whereas coal asphaltenes, with a large aromatic fraction and small aliphatic fraction, form rigid layers. As other asphaltenes, the petroleum and coal asphaltenes of the present study form layers that equilibrate rapidly below the CNAC. The immature shale asphaltenes behave differently as the other asphaltenes studied above the CNAC. The interfacial layers have a marked non-linear behavior, particularly pronounced for the coal asphaltenes, which complex Lissajous' diagrams indicate stacking upon compression. We discuss the overall interfacial behavior in terms of molecular differences between asphaltenes.

1. Introduction

The name crude oil is used for natural and unprocessed oil. Crude oils are mixtures of many components, hydrocarbons (mainly alkanes, cycloalkanes and aromatics) and other organic compounds, containing nitrogen, oxygen, sulfur and traces of metals. Asphaltenes are the components of crude oils with the highest molecular weight ¹. They are also among the most polar and consist of polycyclic aromatic rings surrounded by hydrocarbon chains at their periphery ².

The amount of asphaltenes in crude oil varies widely: it is negligible in volatile oils, small in condensates, a few wt% in fluid black oils and up to tens of wt% in heavy crude oils and in asphalt. Their quantity largely determines the oil viscosity which influences oil recovery, transport and processing in refineries. Asphaltenes can precipitate when the temperature or pressure is lowered and be a problem during operation, storage and processing. Asphaltenes adsorb to solid surfaces and can alter the wettability of oil reservoirs, thus affecting the oil recovery process. They also adsorb at oil-air interfaces and oil-water interfaces in foams and emulsions made with petroleum, respectively: during the exploitation of reservoirs, the rapid depressurization caused by production leads to the formation of foams, sometimes called 'chocolate mousses'. Emulsions may form when water is injected into the reservoir to displace the oil. These foams and emulsions are very stable when asphaltenes are present, they are very difficult to destabilize. Asphaltenes are generally removed from oil during refining processes. However, bitumen or asphaltene-rich residues from refining processes are used in road surfaces. These processes are based on the great temperature dependence of their viscosity: spread hot, they solidify on cooling. This use has been known since antiquity. Asphaltenes are also found in coal and oil sands, both solid and mined.

Asphaltene molecules have extremely varied chemical formulas, in number of aromatic rings, carbon chain length, atoms other than carbon and hydrogen. They are generally obtained by definition by precipitating the crude oil with the addition of paraffinic solvents, most often pentane or heptane. Depending on the solvent, different classes of molecules are thus obtained and asphaltenes are defined as a solubility class. The non-precipitated fraction of crude oil is called maltene. The constituents of maltene have a lower molecular weight than those of asphaltenes. Among them, compounds called resins also adsorb at interfaces. The resins are extracted from the maltenes by liquid chromatography. Above a concentration called CNAC, of the order of 100 mg/L ³, asphaltenes self-associate into different types of aggregates and their exact structure has remained unclear for many years. Less than 20 years ago, the molecular weights reported in the literature varied between 500 and 10⁹ Daltons. It was only very recently that a consensus was reached with the Yen-Mullins model and that a better description of asphaltene molecules became available ⁴. This model describes the molecular structure of asphaltene molecules and the hierarchical structures that form within assemblages of these molecules, from nano-aggregates to nano-aggregate clusters. The molecular weight of asphaltenes typically varies between 500 and 1000, the high weights reported in the literature are those of aggregates. However, there is still a lot of

debate about how asphaltenes adsorb to surfaces.

Knowledge of the structure of asphaltenes has, however, made it possible to begin to understand their influence on the stability of foams and emulsions. Above the CNAC, asphaltene molecules are thought to aggregate first, then the aggregates adsorb at the interface and slowly form interfacial gels. It is now admitted that the oil-air or water-oil interfacial tension is not directly correlated with the stability of emulsions and foams. As in many other systems, the stability of emulsions and foams depends on the interfacial rheological properties⁵. For example, high interfacial elastic moduli promote the stability of emulsions. A characterization of these moduli is therefore useful for modeling the stability of the emulsion and to develop strategies to destabilize them and recover the oil.

The present work is focused on water-crude oil emulsions and on the determination of interfacial properties. We are beginning to understand the role of asphaltenes in stabilizing emulsions, but this understanding does not yet cover their detailed molecular structure. It was shown recently that measurements of interfacial properties can give information on the interactions between asphaltene molecules at the interface⁶. Interested in this result, we then decided to study different asphaltenes, in order to highlight the differences in the behavior of these molecules at the interface. Three different asphaltene molecules were used, extracted from different sources: crude oil, immature source rocks bitumen and coal. In the literature, a single source of asphaltenes is generally used and a comparison of the interfacial properties measured under the same conditions is therefore lacking.

2. Materials and methods

Three different asphaltene samples were supplied by Schlumberger-Doll Research

- Petroleum Asphaltenes (PA), UG8 C7
- Immature Shale Asphaltenes (ISA), EF Asph C7
- Coal-derived Asphaltenes (CDA), Adaro C7. The CDAs are obtained from the resid of distillation of coal after hydrogenation and liquefaction.

These three asphaltenes have the same nanoaggregate aggregation number⁷. The CNAC was measured for PAs and CDAs and found similar, of the order of 100 mg/L⁸. It was not measured for ISAs, but it is expected to be also similar (the measured CNACs of asphaltenes are all of the same order). Their molecular structure is represented in Figure 1.

These asphaltenes were selected in order to exhibit different molecular interactions at the oil-water interface. CDAs have a small alkane content (~20%) and no flexible aliphatic chains, just rigid polycyclic aromatic hydrocarbons (PAH) with some methyl groups attached. The repulsion between adsorbed CDAs should differ from that between PAs that have a much larger alkane content (50%). The ISAs have a still larger alkane content (~75%), and in addition sulfoxide groups, probably alkyl-sulfoxide groups, that might bring differences with respect to PAs. Essentially, the ISAs correspond to the heavy ends prior to kerogen catagenesis, a disproportionation reaction, which yields heavy ends that have reduced

alkane content (with oil formation) and have larger PAHs ⁹.

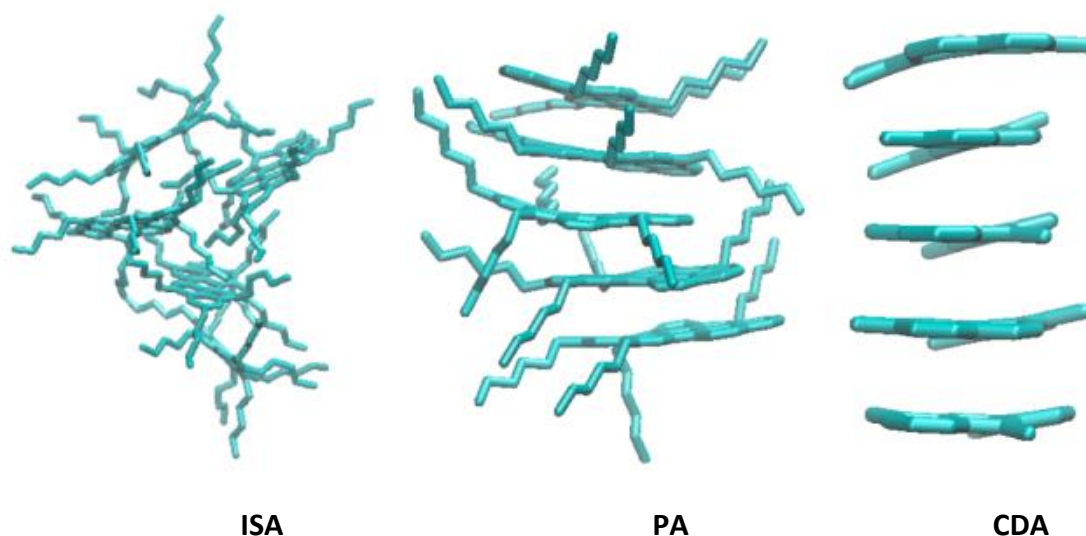


Figure 1. Molecular structure of the different asphaltenes of this study. Reprinted with permission from ref ⁷, copyright {2017} American Chemical Society.

Figure 1 shows results of molecular dynamics calculations for nanoaggregate structures of these three types of asphaltenes. All three types of asphaltenes are dominated by the ‘island’ molecular structure with a single polycyclic aromatic hydrocarbon (PAH) per molecule ^{2 10}. The role of aliphatic to aromatic fraction was clearly demonstrated ⁹. Immature source rock asphaltenes (ISAs) with their large (~75%) aliphatic fraction do not exhibit any PAH stacking. Petroleum asphaltenes with half aliphatic, half aromatic fractions exhibit disordered PAH stacking. Coal-derived asphaltenes with their large aromatic fraction (~75%) exhibit excellent PAH stacking. ⁹

We chose to use toluene as common solvent. We have dissolved the asphaltenes in toluene (Sigma, HPLC grade 99.9% purity) with concentrations below the CNAC (down to 0.01 g/L) and above (up to 5 g/L). The water was demineralized and 5 g/L of sodium chloride was added for the purpose of comparison with former works. The salt was roasted overnight at 500 °C to remove organic impurities. The interfacial tension between pure toluene and brine was found equal to (36 ± 1) mN/m, confirming the absence of interfacial contamination.

In this work, the interfacial properties are determined from the shape of a drop, either at rest for the measurement of the interfacial tension γ , or undergoing periodic extensions and contractions for the measurement of the interfacial compression properties. The device used is the Tracker by Teclis ¹¹. Experiments were repeated 3 times, the interfacial tensions varied typically by ± 1 mN/m between measurements. The drop volume was 30 μ L for PAs and CDAs, and 15 μ L for ISAs (larger drops detached from syringes). Upon small oscillations of the drop volume at a frequency ω , the interfacial tension varies sinusoidally at the same frequency (in the linear regime) but there is a phase shift ϕ due to dissipation. The measurement of the amplitude of the tension variation $\Delta\gamma$ and of the phase shift ϕ allows the determination of the real and imaginary parts of the compression modulus E at the frequency used E' and E'' ,

also called storage and loss moduli. In the following we will sometime use instead of the tension γ the surface pressure π , which is the difference between the tension with and without asphaltenes. Non linearities have been investigated using large amplitude compressions, and Lissajous curves were recorded.

3. Results

3.1 Dynamic surface tension

We show in Figure 2 the variation of the interfacial tension γ between the brine and 1g/L solutions of the three different asphaltenes in toluene.

As usual in these systems, there is a first fast decay followed by a slower one over typically one hour, after which the interfacial tension decreases very slowly. It is generally considered that this large span of characteristic times reflects the reorganization of the asphaltenes in the interfacial layer. One sees that the ISA are the most interfacially active and the PAs, the less interfacially active. The higher surface pressures of CDAs with respect to PAs are possibly due to their lack of alkane to interfere with surface adsorption. This is consistent with SFG work on asphaltenes showing that the PAHs of PAs lie in the surface plane and their alkane chains are out of plane¹². The ISAs have some sulfoxide groups that are expected to be in contact with water at the interface, possibly explaining why the surface pressure is the largest for these asphaltenes.

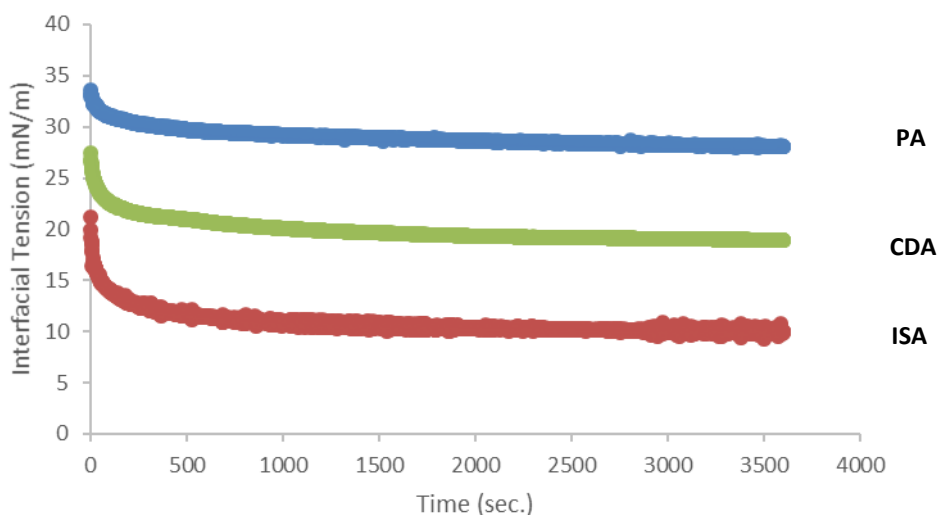


Figure 2. Time variation of the interfacial tension between the brine and 1g/L solutions of the three different asphaltenes in toluene. The data shown is an average over measurement repetitions, the corresponding error bars are not shown, being comparable to the size of the points.

Several authors claimed that the long-time decay is due to less abundant asphaltene species that adsorb more slowly^{13 14}. This can be excluded for the asphaltenes of this study, because experiments performed at different asphaltene concentrations show similar time dependences, as it can be seen in Figure 3.

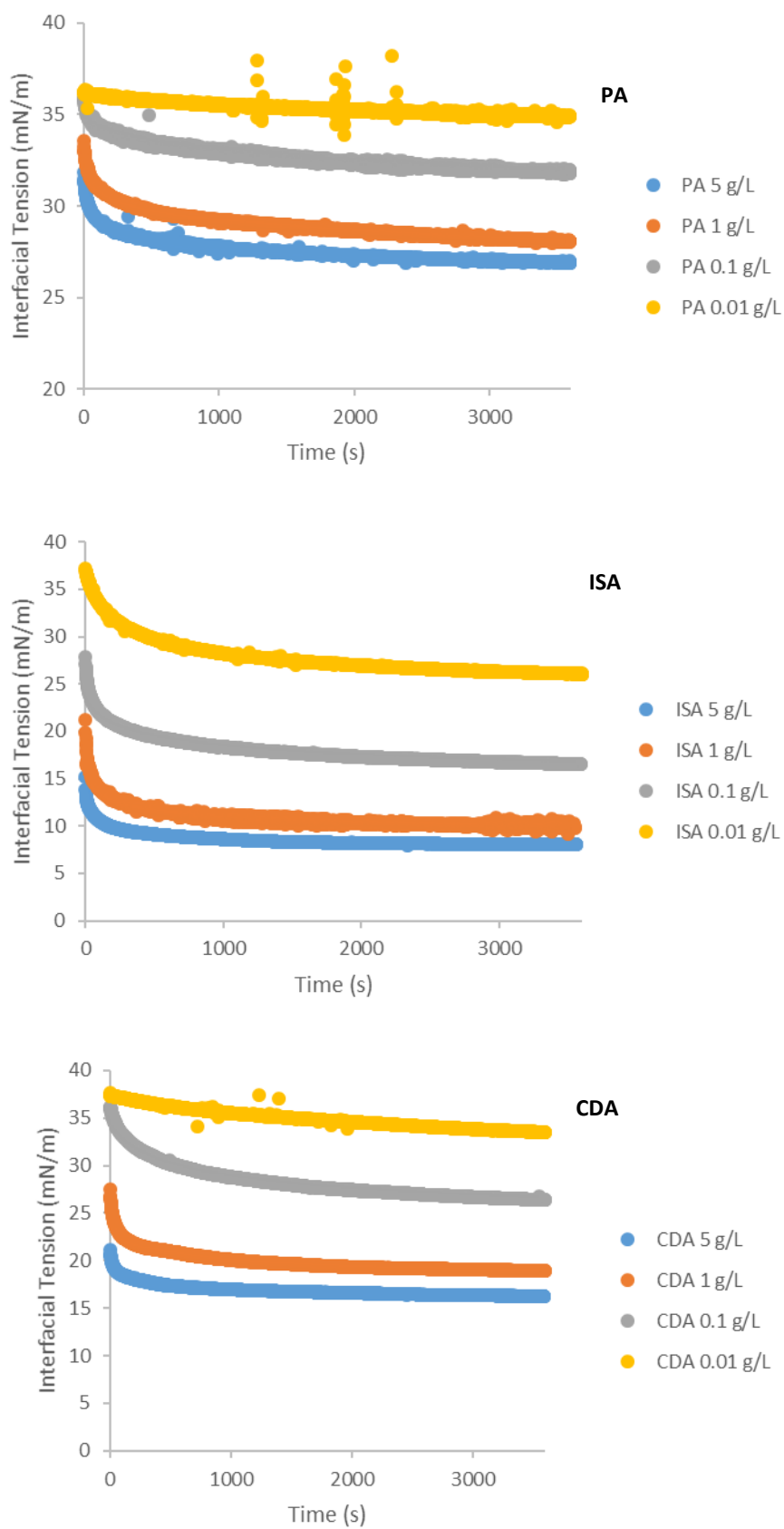


Figure 3. Interfacial tension evolution with time for the different asphaltene solutions at different bulk concentrations.

If adsorption were diffusion controlled, the characteristic time would vary as the square of the concentration, whatever the number of species. This confirms that the interfacial tension changes are not related to asphaltene diffusion towards the oil-water interface, but rather to asphaltene reorganization in this interfacial region. Additional arguments can be found in the discussion section (4.1).

Experiments were performed with drops at rest and undergoing sinusoidal variations of volume and are also shown in Figure S1. The time variation of the tensions was similar for PAs and ISAs. In the case of CDAs, the decrease was faster with oscillations, as reported in other systems, such as polymer-surfactant mixed solutions¹⁵. This may arise when the homogenization of the layer is accelerated by the successive expansions and contractions of the interface.

3.2 Compression modulus

Figure 4 shows the variation of the real part of the compression modulus E' (storage modulus) with surface pressure during equilibration (from $t = 0$ up to 3600 s). Let us recall that surface pressure π is the difference between interfacial tension γ and bare oil-water tension γ_0 .

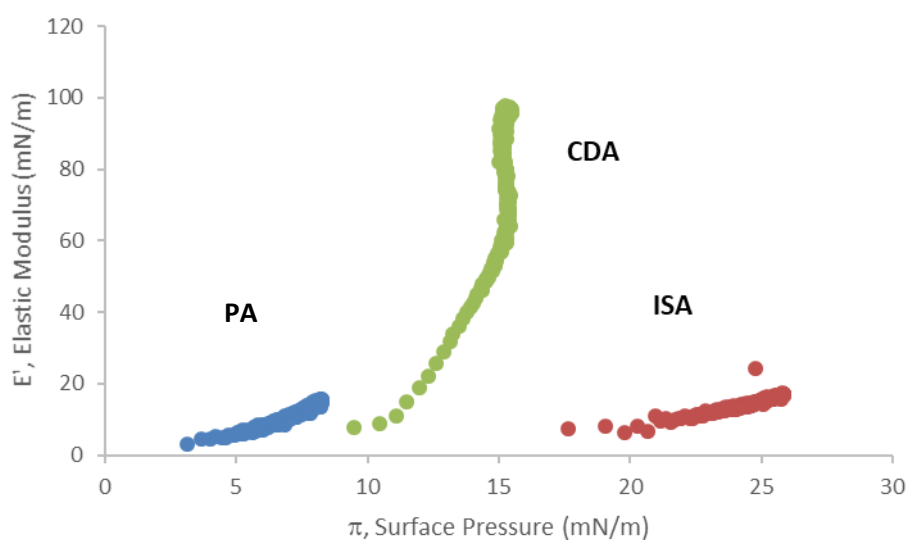


Figure 4. Variation with surface pressure of the real part of the interfacial compression modulus between the brine and 1g/L solutions of the three different asphaltenes in toluene during equilibration (from $t = 0$ up to 3600 s). Frequency 0.1Hz

The slope of the curves $E'(\pi)$ is larger if the interactions in the surface layer are more repulsive. This can be easily demonstrated by expanding the surface pressure in powers of the surface concentration. The case of an expansion limited to the second power of Γ is described in ref⁶. In the present case, E'' is not zero, and equations of state $\pi(\Gamma)$ cannot be identified, but the general trend between the slope of $E'(\pi)$ and the interactions is intuitive and should hold. CDA layers exhibit much more important repulsion than PA and ISA layers. This appears consistent with the large quantity of rigid PAH rings in CDAs and the large

quantity of flexible alkane chains in both PAs and ISAs. Smaller differences are observed between PAs and ISAs, ISAs having more alkane chains than PAs exhibit slightly smaller repulsion (slope ~ 1.5 instead of ~ 2 for PAs).

In previous studies, using asphaltenes from Athabasca bitumen¹⁴, crude oil asphaltenes from the Norwegian continental shelf¹⁶, fractionated asphaltenes from a Middle Eastern heavy crude oil^{6,14} and coal asphaltenes¹⁷, it was shown that for a given π , the compression moduli were the same, independently of bulk concentration. It was argued that even if there is no thermodynamic equilibrium between surface and bulk, equilibrium is achieved within the surface layers and the surface pressure only depends on surface concentration. We checked if the asphaltenes of this study behave similarly, by plotting E' versus π for asphaltene solutions with different bulk concentrations in Figure 5.

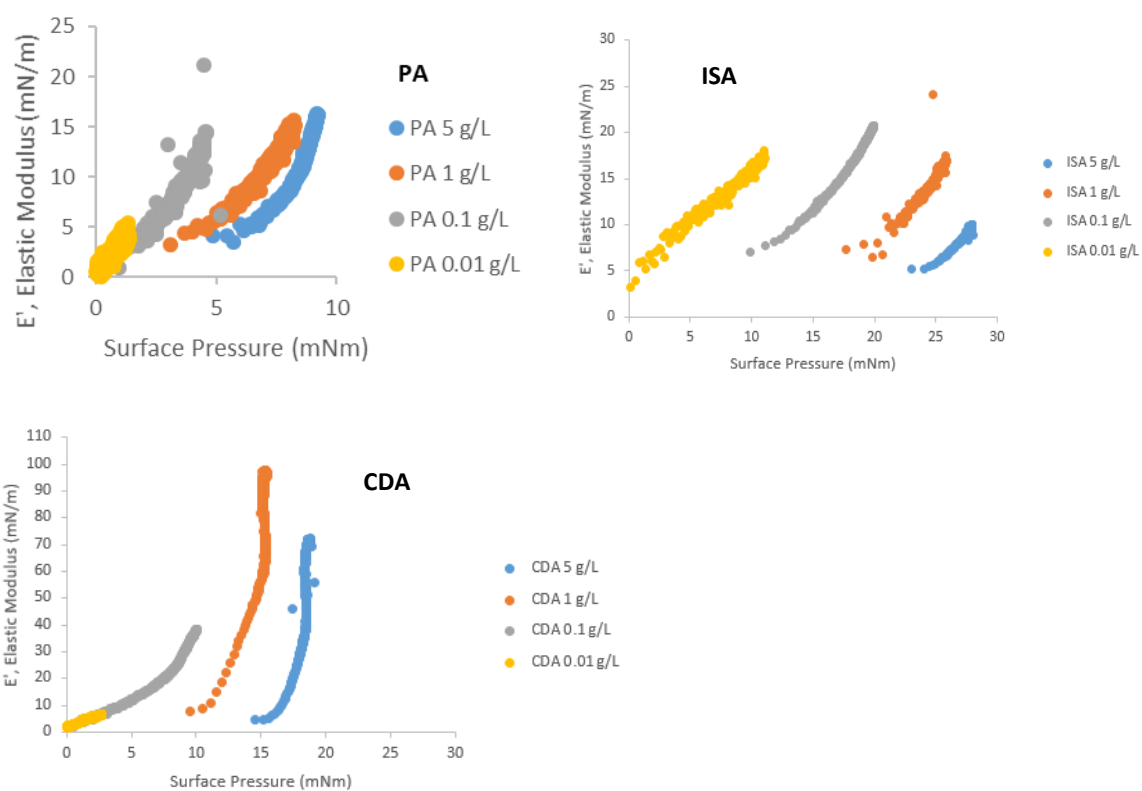


Figure 5. Variation with surface pressure of the real part of the interfacial compression modulus between the brine and solutions of the three different asphaltenes in toluene with different bulk concentrations as indicated during equilibration (from $t=0$ up to 3600 s). Frequency 0.1 Hz

Figure 5 shows that only PAs and CDAs below CNAC behave in this way. ISAs for all concentrations, and PAs and CDAs above CNAC do not behave as in of previous studies. In the study of⁶ the imaginary part of the compression modulus (loss modulus) E'' was negligible compared to the storage modulus. In other studies^{16,17}, the concentrations used were small (up to 0.5 g/L) and the frequencies used such that E'' was also negligible. In the study of¹⁴, E'' was not small; the authors calculated a high frequency modulus, assuming that bulk-surface exchanges were diffusion controlled, in which case the high frequency loss

modulus is zero. For the asphaltenes of this study, the loss modulus E'' is not as small, especially for the CDAs as shown in Figure 6.

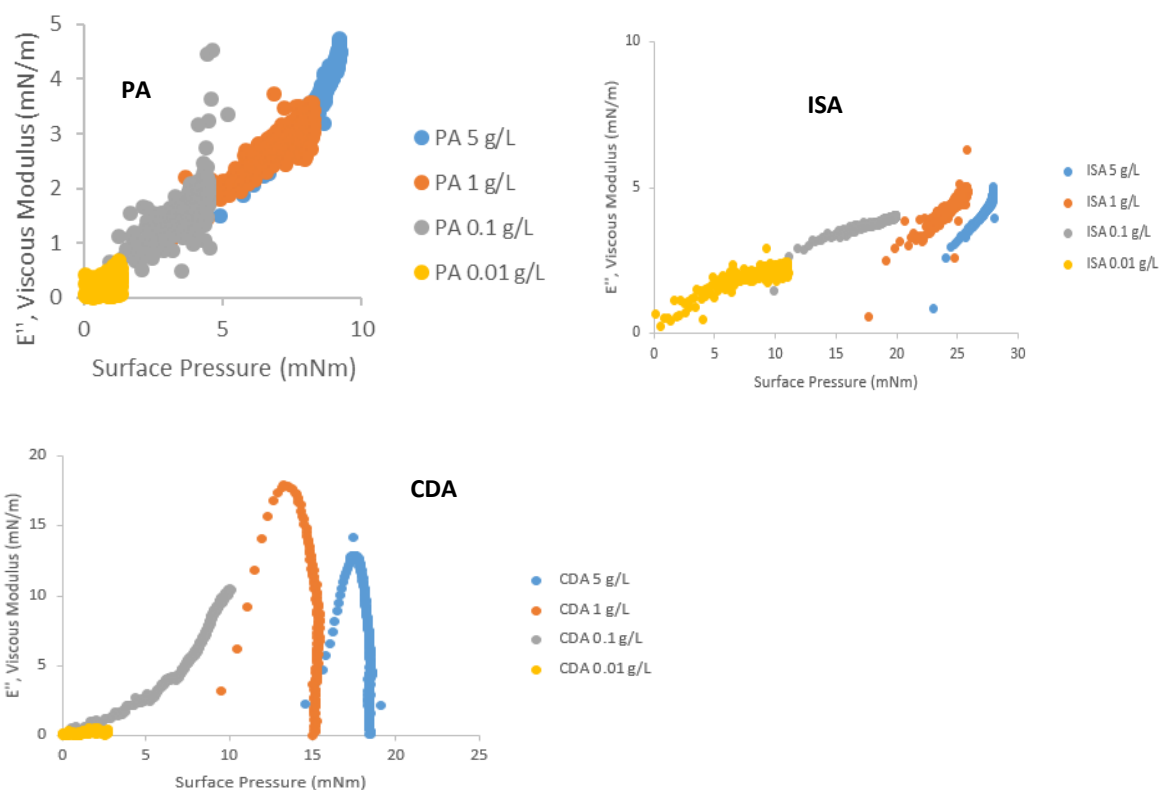


Figure 6. Loss interfacial compression modulus versus surface pressure between the brine and solutions of the three different asphaltenes in toluene with different bulk concentrations as indicated during equilibration (from $t=0$ up to 3600 s). Frequency 0.1 Hz

The curves $E''(\pi)$ for different bulk concentrations coincide for PA layers and only below CNAC for ISA and CDA layers. Note that the curves $E'(\pi)$ and $E''(\pi)$ approximately coincide below the CNAC, E' for ISA being an exception.

The fact that E'' is not zero means that relaxations occur in the layer, which therefore is not in equilibrium. This explains why there is no universal relation between E and π . Because adsorption is not diffusion controlled, we could not calculate the high frequency modulus as in ref ¹⁴. CDAs and ISAs behave differently than PAs, their molecular structures being significantly different.

Frequency scans were performed and the results are shown in the Supporting Information (SI, Figures S2 and S3). As in other asphaltene systems, the frequency variations observed are moderate (factors of about 2) and mostly important below 1 rad/s. They were attributed to gel behavior ¹⁸. The frequency variation increases with asphaltene concentration, suggesting that the gels stiffen.

We show in Figure S4 the data obtained during measurements performed a few months apart are shown. One can see that the reproducibility is reasonably good, except perhaps at the largest PA concentration (5g/L) and for CDA at the lowest concentrations.

3.3 Behavior upon continuous compression

The amplitude variations of the moduli are small for PA and ISA, at least below a deformation amplitude of 10% (Figure S5). The response deviates from linearity for PAs above 10%, whereas it remains quite linear for ISAs even up to 25%. In turn, the response is nonlinear for CDAs, even at small amplitudes.

We investigated the behavior upon larger compression. Figure 7 shows the interfacial tension evolution with compression amplitude for 1 g/L PA asphaltenes aged 1 hour. The variation is linear for small compression amplitude as already mentioned (see Figure S5). At compression amplitudes above 40%, non-linearities are seen and are accompanied above 50% by increasing deviations of the drop shape from Laplacian. Above 80%, wrinkles appear on the drop as shown in the bottom of the Figure 7. Remarkably, the wrinkles disappear rapidly during decompression.

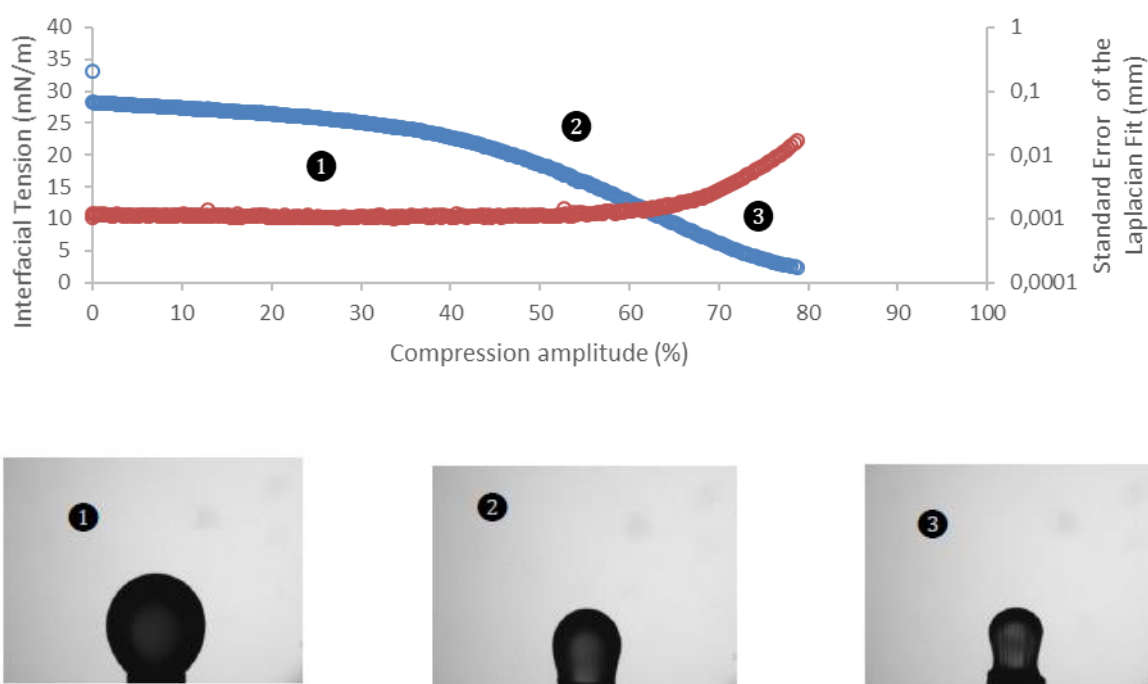


Figure 7. Top: interfacial tension versus compression amplitude (blue curve) and standard error of the Laplacian fit (red curve). PA asphaltenes, 1g/L, aged 1 hour. Compression velocity: 0.1 $\mu\text{L/s}$.

The nonlinearities appear earlier at smaller compression rates as aging time increases. They also appear at smaller amplitudes for ISA and still at smaller amplitudes for CDAs. More complete results are shown in the SI (Figures S6, S7 and S8). In Table 1, we give the limit compression rate R1 above which non linearities are seen and R2 above which wrinkles are observed

Table 1. Limit compression amplitude R1 above which non-linear responses are seen and R2 above which wrinkles are observed on the drops for the different asphaltenes (1 g/L) at different aging times

	PA 10s	PA 600s	PA 3600s	ISA 10s	ISA 600s	ISA 3600s	CDA 10s	CDA 600s	CDA 3600s
R1 (%)	55	45	40	60	40	40	20	40	10
R2 (%)	90	90	80	90	80	85	60	40	15

Non linearities can also be observed when cyclic deformations are performed and the variation of interfacial tension is plotted versus the amplitude of the deformation (Lissajous curves). The duration of each cycle was 100 s and complete data is shown in the SI. We show in Figure 8 typical examples for the three asphaltenes and similar compression rates

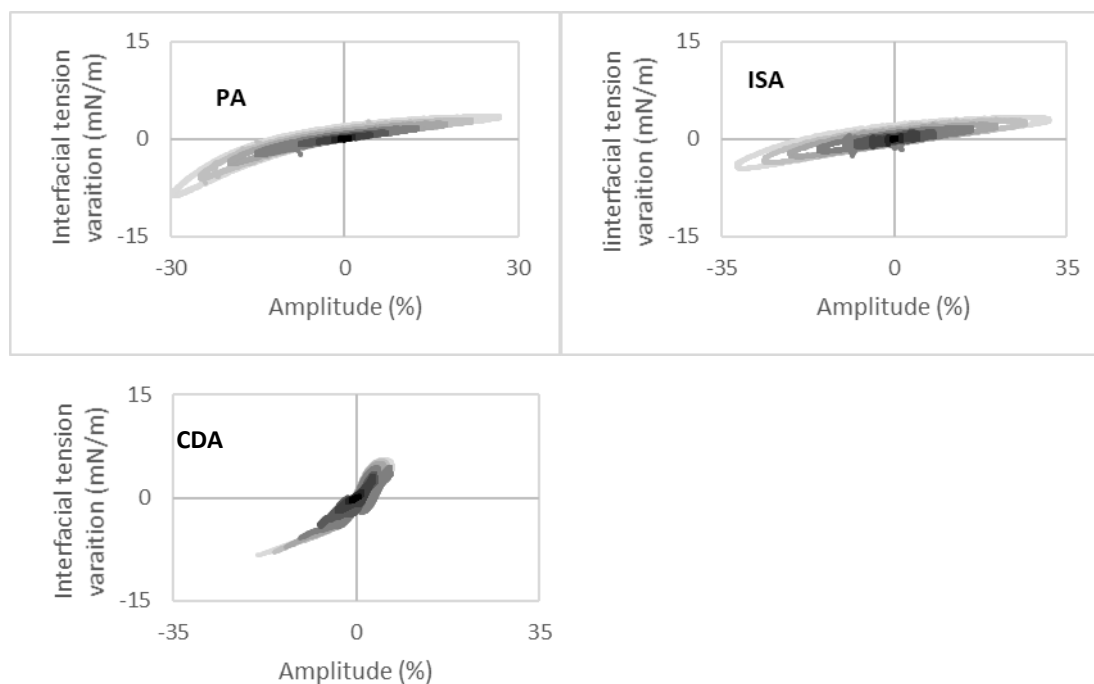


Figure 8. Interfacial tension change versus relative area change during cyclic compression/expansion cycles for the three different asphaltenes with concentration 1g/L. Duration of each cycle: 100 s. Measurements performed after an equilibrium time of 1 hour. The darker the grey, the smaller the amplitude.

The fact that for small amplitudes, the Lissajous curves are not straight lines confirms that there are long relaxation times, already evidenced by the non-zero values of the loss modulus E'' , and that arise from internal relaxation in the interfacial zone. Although the curves do not deviate too much from lines for PA and ISA, the tension variation during compression and expansion do not coincide. However, the curves remain the same when

several cycles are performed. This interfacial behavior is similar to that of several plant proteins (pea and whey)¹⁹. It proves unambiguously that PA and ISA adsorption is irreversible. Lissajous curves cannot indeed be obtained with surfactants that desorb when compressed and the surface tension remains constant. Note that the duration of the cycles (100 s) is long enough to allow for substantial re-adsorption of species eventually desorbed (see Figure 2).

Lissajous' curves of PAs and ISAs show strain softening in extension and strain hardening upon compression, the behavior being less marked for ISAs. This is consistent with Figure 4 that reveals stronger in-plane interaction in PA layers.

The behavior of CDAs is more complex, highly nonlinear, and the different cycles do not superimpose (Figure S10). However, the amplitude of tension variations is not significantly shifted, still consistent with adsorption irreversibility. Such an interfacial behavior is similar to that of several saponins which are natural surfactants²⁰ (Figure 9). It was attributed to multilayer formation, that could correspond to stacking for asphaltenes, accounting for the softening observed upon compression. Upon expansion, the surface pressure is nearly constant (see Figure 9 showing a cycle of smaller amplitude). Adsorption of new asphaltene molecules could occur if some degree of stacking persists. This could explain why cycles do not superimpose exactly.

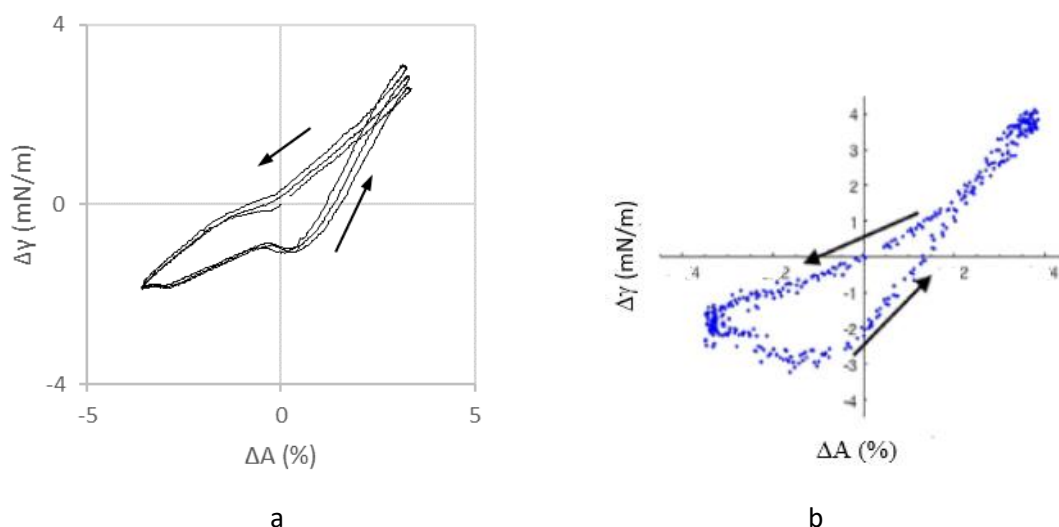


Figure 9. Lissajous curves for small amplitudes; a) CDA 1g/L; b) escin solution 5 g/L in water; reprinted from²⁰.

The striking difference between the Lissajous curves of CDA and those of PA and ISA could be due to stacking. Indeed, the in-plane interactions include the much softer aliphatic interactions for PA and ISA, precluding facile stacking whereas for CDA, the much stiffer aromatic interaction edgewise might allow stacking like graphite. Another indication of facile stacking of CDAs is the fact that Langmuir Blodgett films were obtained with PAs and several model compounds, but not with CDAs²¹.

4. Discussion

Although it is generally considered that asphaltenes behave similarly at oil-water interface, the three types of asphaltenes studied have clearly different behavior. In particular, CDAs have a much more pronounced non-linear behavior. For a given value of the interfacial tension, the elastic modulus depends on the bulk concentration of the asphaltenes above the CNAC (and even below for ISAs). This is different from reported earlier by several authors^{14, 6, 16} who showed that there is a universal curve $E(\pi)$. In the study of⁶, the imaginary part of the compression modulus (loss modulus) E'' was negligible compared to the storage modulus. In other studies^{16 17}, the concentrations used were small (up to 0.5 g/L) and the frequencies used such that E'' was also negligible. This means that despite the adsorption process being long, once adsorbed, the molecules equilibrate fast in the interfacial layer. This is not the case for the asphaltenes studied here, meaning that surface equilibration is much longer above CNAC (and below for ISAs).

In the study of ref⁶, the asphaltenes were fractionated and their molecular distribution was significantly narrower than in other studies; the loss modulus E'' was found negligible compared to the storage modulus E' . It is possible that the relaxation of interfacial stresses is easier if the molecules are more similar. In the case of the asphaltenes of this study, the loss modulus E'' is not small, especially for the CDAs (see Figure 5). In the study of ref¹⁴, the loss modulus was important in some cases and a limit modulus was calculated assuming that bulk-surface exchanges were diffusion controlled. This is clearly not the case for the asphaltenes of the present study. In turn, the fact that the loss modulus is large possibly accounts for longer equilibration times of the interfacial concentration. In the studies of ref^{16 17}, the asphaltene concentrations were small, close to the CNAC, and we have seen that only ISAs have a compression modulus that is not a unique function of surface pressure at these low concentrations.

At concentrations close and below the CNAC, the curves $E'(\pi)$ (ISAs excepted) and $E''(\pi)$ coincide roughly as shown in Figures 4 and 5. Equilibrium in the surface layers is therefore reasonably achieved for asphaltene solutions below the CNAC. Likely, the reorganization of asphaltene aggregates at the interface occurring above CNAC is difficult and long. Note that it was shown that these aggregates, once formed, no longer disassemble²².

4.1 Dynamic interfacial tension

Let us focus on the dynamic interfacial tension data (Figure 1). The interfacial tension γ decreases with time t reflecting the adsorption kinetics process. If we assume that adsorption is diffusion controlled, at early times²³:

$$\gamma \sim \gamma_0 - 2k_B T C \sqrt{\frac{Dt}{\pi}} \quad (1)$$

where γ_0 is the interfacial tension of the bare interface (brine-toluene) and C the asphaltene concentration expressed in number of molecules per unit volume, T the absolute temperature and k_B , the Boltzmann constant.

For PAs below the CNAC, adsorption is slower than at higher concentrations, and tensions close to γ_0 can be measured at short times. Good fits with equation 1 can be obtained for the concentration of 0.01 g/L, but only for times less than 150 s for 0.1 g/L (Figure S10). The slopes of the curve γ versus \sqrt{t} are respectively 0.032 and 0.13 mN.m⁻¹s^{-1/2}, which leads according to Equation 1 to diffusion coefficients D of 6 10⁻¹³ and 1.2 10⁻¹⁴ m²/s respectively. Similar diffusion coefficients, together with concentrations variations, were reported by other authors^{24 25}. They also depend on the solvent (D in toluene is about 10 times smaller than in heptol 75/25, whereas the viscosities of these solvents are similar)²⁵. The diffusion coefficient is much smaller than the actual value: about 5 10⁻¹⁰m²/s as estimated in⁶ or 3.6 10⁻¹⁰m²/s using the Stokes relation and assuming a hydrodynamic radius of 1 nm as in²⁶. Note that the diffusion coefficient closest to these estimations has been measured in mixtures of toluene and decane oligomers²⁶. However, the proportion of toluene was small and the asphaltenes could have flocculated during the course of experiments. In the present study, toluene is used and the asphaltenes remain well dispersed. One may also wonder if the eventual presence of nano-aggregates could affect the diffusion coefficient, because the concentration of 0.1 g/L is close to the CNAC. However, the nanoaggregates are quite small, their dimensions are of the order of 2nm⁴, so the estimated diffusion coefficient will be only lower than that of individual asphaltenes by a factor 2.

Liu et al argued that a small proportion of asphaltene is more interfacially active than the others; they adsorb more slowly and populate the interface at long times¹⁴. The relative concentration of these species could possibly depend on the solvent used, but not on the total bulk concentration. If adsorption were diffusion controlled, the measured diffusion coefficients should not vary with the overall bulk concentration. The large variations observed suggest that adsorption is not fully diffusion controlled.

At longer times, most authors recognize that the kinetics is independent of bulk concentration as in the present study, hence that the kinetics is no longer diffusion controlled. Some authors report linear variations with $t^{-1/2}$ as in the late stages of diffusion-controlled adsorption^{27 13}. In the present experiments, a logarithmic variation was observed instead (see Figure S9), slower than $t^{-1/2}$, and incompatible with diffusion-controlled adsorption. Because the initial kinetics is much slower than expected, asphaltenes arrive very rapidly at the interface, and the dynamic interfacial tension is controlled by reorganization in the interfacial region. This may include molecular exchanges with what is sometimes called the sub-surface region, for instance, adsorption barriers. For instance, as postulated²⁸, less abundant but more interfacially active asphaltenes progressively replace the asphaltenes which adsorb first (random sequential adsorption).

Adsorption controlled by energy barriers can be analyzed using the Langmuir adsorption equation:

$$\frac{d\Gamma}{dt} = k_a C_s (\Gamma_\infty - \Gamma) - k_d \Gamma \quad (2)$$

denoting the surface concentration by Γ , the surface concentration at saturation by Γ_{∞} and the sub-surface concentration by C_s ; k_a and k_d are respectively the adsorption and desorption constants, related to the adsorption and desorption energy barriers E_a and E_d by : $k_{a,d} = k_{a,d}^0 \exp(-E_{a,d}/k_B T)$ ²³. Here, the asphaltenes are irreversibly adsorbed, so $k_d = 0$. If we assume that k_a and C_s are independent of Γ , Equation 2 predicts an exponential variation of the surface concentration Γ with time.

Assuming that once the surface concentration reaches a given value Γ , the surface layer is equilibrated, the interfacial tension γ will be a unique function of Γ . The Langmuir equation of state which relates γ and Γ , is frequently used to describe asphaltene monolayers¹⁶:

$$\gamma = \gamma_0 + k_B T \Gamma_{\infty} \ln(1 - \Gamma/\Gamma_{\infty}) \quad (3)$$

This equation assumes that there are no interactions between adsorption sites. For the asphaltene solutions studied here, the tension rather varies logarithmically with time, (Figure S11). If adsorption was barrier-controlled, the product $k_a C_s$ in Equation 2 should vary as the inverse of $\Gamma_{\infty} - \Gamma$. Note that in the work with fractionated asphaltenes, the tension was rather varying exponentially with time, so the reorganization process may depend on the type of asphaltenes. Note also that the use of Equation 3 is questionable, because there are clearly important lateral interactions between asphaltenes in the interfacial layers.

4.2 Compression modulus

Above the CNAC, reorganization could include modifications of aggregate structures. Because aggregate PAHs are partially hidden from the solvent by their alkane chains, it is likely that an asphaltene monolayer forms first and that aggregates later attach through the pending alkane chains of this monolayer. The aggregate structure may then change with time in order to expose PAHs groups to water. Note that the nano-aggregate and nano-aggregate clusters concentration is small since there are about 6-8 asphaltene monomers per nano-aggregate and 200 per cluster⁴ and their diffusion coefficient is also small (only about ten times smaller than for monomers for the clusters). Despite these small numbers, aggregates are expected to arrive at the interface at times shorter than those of the tension measurements.

For a given value of the interfacial tension, the elastic modulus depends on the bulk concentration of the asphaltenes. This is because surface equilibration is long. Only at concentrations below the CNAC, the curves $E(\pi)$ approximately coincide (despite small but systematic deviations at the largest pressures for the concentration of 0.01 g/L, as seen in Figure 3).

The Lissajous plots show that the ISA layers are quite soft and very elastic. Their alkane content is the largest and compression/expansion should involve mainly these aliphatic groups. A slight softening is observed in expansion. The ISAs have one or fewer sulfoxide groups per molecule. These groups are likely in contact with water and contribute to the surface pressure, as suggested by the fact that this pressure is the largest for ISAs (Figure 1).

They should therefore not contribute much to the modulus, because they will not be available for lateral interaction with other ISA molecules.

The PA asphaltenes are stiffer, especially in compression. This could be due to a larger fraction of aromatic carbon and larger PAHs compared to the ISAs, these PAHs could be responsible for stiff, short range interactions. They are not very different than ISAs in expansion where one might argue that longer range interactions between aliphatic groups will dominate.

A series of molecular dynamics simulations were performed by Bhattacharjee et al ²⁹ to investigate the effect of aliphatic side-chain length of a model asphaltene in water. They found that asphaltene molecules with very short or very long side chains can form dense aggregates, whereas those with intermediate chain lengths cannot. Long side chains hinder the formation of parallel stacking structures of the polyaromatic cores while also favoring aggregation through hydrophobic association. The CDAs have a much more pronounced non-linear behavior than PA and ISA. The CDAs do not form Langmuir Blodgett films, probably due to stacking upon compression. As for saponin layers, the Lissajous plots are a multilayer signature where significant strain occurs without much change in stress. That is, the PAHs in CDAs evidently can slide over each other much as in the lubricant graphite. In addition, the layers are very stiff. The molecules have no flexible aliphatic chains, just rigid PAHs with some methyl groups which are also rigid.

It can be concluded that interactions between asphaltenes are predominant in explaining their interfacial behavior, as already noted in the comment ³⁰ published by Bouriat about ref.¹⁴

5. Conclusions

The present work demonstrates that the behavior of asphaltenes depends appreciably on their molecular structure, which varies with their origin. Asphaltenes with many alkane chains and small PAH form flexible layers, whereas asphaltene with less alkane chains and larger PAH form rigid layers. All the asphaltenes layers of this study have a marked non-linear behavior, particularly pronounced for the coal asphaltenes. At large concentrations (and ISAs at all concentrations), they do not exhibit a universal relation between compression modulus and surface pressure, as reported for in other asphaltenes studies, performed in conditions where the loss moduli were very small. The adsorption kinetics does not appear controlled by diffusive transfer of asphaltenes from the bulk to the interface, which is much faster. More work will be needed to clarify this issue and to better predict interfacial behavior of asphaltenes. This would help the evaluation of the properties of emulsions stabilized by different types of asphaltenes.

6. Supporting Information.

The supporting information provides various additional measurements : comparisons between interfacial tensions measured with and without oscillations, frequency and

amplitude variations of the compression modulus, reproducibility of measurements after a few months, behavior of the modulus upon large compression, together with aging, Lissajous curves. Fits of the dynamic interfacial tension with various models are also presented.

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TOC Graphic

