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Role of Asphaltene Origin in Its 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 comparison of 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 critical nanoaggregate concentration (CNAC). The immature shale asphaltenes behave differently as the other asphaltenes studied above the CNAC. The interfacial layers have a marked nonlinear behavior, particularly pronounced for the coal asphaltenes, in 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, such as 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 weight percentages in fluid black oils, and up to tens of weight percentages in heavy crude oils and 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 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, and 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 upon 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, and 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. Dependent upon the solvent, different classes of molecules are thus obtained, and asphaltenes are defined as a solubility class.

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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 the critical nanoaggregate concentration (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 Da. 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 nanoaggregates to nanoaggregate clusters. The molecular weight of asphaltenes typically varies between 500 and 1000, and 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, and 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 upon the interfacial rheological properties.⁵ 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 developing strategies to destabilize them and recover the oil.

The present work is focused on water—crude oil emulsions and 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 interface.⁶ Interested in this result, we then decided to study different asphaltenes, 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 rock 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: (1) petroleum asphaltenes (PAs), UG8 C7; (2) immature shale asphaltenes (ISAs), EF Asph C7; and (3) coal-derived asphaltenes (CDAs), Adaro C7. The CDAs are obtained from the residue of distillation of coal after hydrogenation and liquefaction.

These three asphaltenes have the same nanoaggregate aggregation number.⁷ The CNAC was measured for PAs and CDAs and found similar, on the order of 100 mg/L.⁸ It was not measured for ISAs but is expected to also be similar (the measured CNACs of asphaltenes are all of the same order).

These asphaltenes were selected to exhibit different molecular interactions at the oil–water interface. CDAs have a small alkane content (\sim 20%) and no flexible aliphatic chains, just rigid polycyclic aromatic hydrocarbons (PAHs) 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 (\sim 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 a reduced alkane content (with oil formation) and larger PAHs.⁹

Figure 1 shows results of molecular dynamics calculations for nanoaggregate structures of these three types of asphaltenes. All three



Figure 1. Nanoaggregate structure of the different asphaltenes of this study. This figure was reprinted with permission from ref 7. Copyright 2017 American Chemical Society.

types of asphaltenes are dominated by the "island" molecular structure with a single PAH per molecule.^{2,10} The role of aliphatic to aromatic fraction was clearly demonstrated.⁹ ISAs with their large (~75%) aliphatic fraction do not exhibit any PAH stacking. Petroleum asphaltenes with half aliphatic and 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, high-performance liquid chromatography (HPLC) grade, 99.9% purity] with concentrations below the CNAC (down to 0.01 g/L) and above the CNAC (up to 5 g/L). The water was demineralized, and 5 g/L of sodium chloride was added for the purpose of comparison to 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 $36 \pm 1 \text{ mN/m}$, 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, and the interfacial tensions varied typically by $\pm 1 \text{ mN/m}$ 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 as a result of dissipation. The measurement of the amplitude of the tension variation $\Delta \gamma$ and the phase shift φ allows for 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. Nonlinearities 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 1 g/L solutions of the three different asphaltenes in toluene.





As usual in these systems, there is a first fast decay followed by a slower decay over typically 1 h, 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 ISAs are the most interfacially active and the PAs are 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 sum frequency generation (SFG) work on asphaltenes showing that the PAHs of PAs lie in the surface plane and their alkane chains are out of plane.¹² 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.

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 seen in Figure 3. If adsorption was 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 toward the oil– water interface but rather to asphaltene reorganization in this interfacial region. Additional arguments can be found in the Discussion in section 4.1.

Experiments were performed with drops at rest and undergoing sinusoidal variations of volume and are shown in Figure S1 of the Supporting Information. 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 solutions.¹⁵ 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 .

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 ref 6. 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, with ISAs having more alkane chains than PAs exhibiting slightly smaller repulsion (slope ~1.5 instead of ~2 for PAs).

In previous studies, using asphaltenes from Athabasca bitumen,¹⁴ crude oil asphaltenes from the Norwegian continental shelf,¹⁶ fractionated asphaltenes from a Middle Eastern heavy crude oil,^{6,14} and coal asphaltenes,¹⁷ it was shown that, for a given π , the compression moduli were the same, independent of the bulk concentration. It was argued that, even if there is no thermodynamic equilibrium between the surface and bulk, equilibrium is achieved within the surface layers and the surface pressure only depends upon the 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 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 previous studies. In the study of ref 6, 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 were used such that E'' was also negligible. In the study of ref 14, 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.

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, with 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



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

adsorption is not diffusion-controlled, we could not calculate the high-frequency modulus as in ref 14. CDAs and ISAs behave differently than PAs, with their molecular structures being significantly different.

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

We show in Figure S4 of the Supporting Information the data obtained during measurements performed a few months apart. On can see that the reproducibility is reasonably good,



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



Figure 5. Variation with the 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.

except perhaps at the largest PA concentration (5 g/L) and for CDAs 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 of the Supporting Information). 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 the compression amplitude for 1 g/L PA asphaltenes aged 1 h. The variation is linear for a small compression amplitude, as already mentioned (see Figure S5 of the Supporting Information). At compression amplitudes above 40%, nonlinearities are seen



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.



Figure 7. (Top) Interfacial tension versus compression amplitude (blue curve) and standard error of the Laplacian fit (red curve). (Bottom) Images of oil drops with PA asphaltenes, 1 g/L, aged 1 h. Compression velocity = $0.1 \mu L/s$.

and are accompanied above 50% by increasing deviations of the drop shape from the Laplacian fit. Above 80%, wrinkles appear on the drop, as shown in the bottom of Figure 7. Remarkably, the wrinkles disappear rapidly during decompression. The nonlinearities appear at smaller compression amplitudes as aging time increases. They also appear at smaller amplitudes for ISAs and still at smaller amplitudes for CDAs. More complete results are shown in Figures S6-S8 of the Supporting Information. In Table 1, we give the limit compression pubs.acs.org/EF

Table 1. Limit Compression Amplitude R1 above Which Nonlinear Responses Are Seen and R2 above Which Wrinkles Are Observed on the Drops for the Different Asphaltenes (1 g/L) at Different Aging Times



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



Figure 9. Lissajous curves for small amplitudes: (a) CDA at 1 g/L and (b) escin solution at 5 g/L in water. This figure was reprinted with permission from ref 20. Copyright 2020 Elsevier.

amplitude R1 above which nonlinearities are seen and R2 above which wrinkles are observed.

Nonlinearities 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 are shown in the Supporting Information. We show in Figure 8 typical examples for the three asphaltenes and similar compression rates.

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 does 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 readsorption of species eventually desorbed (see Figure 2).

The Lissajous curves of PAs and ISAs show strain softening in extension and strain hardening upon compression, with 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 and highly nonlinear, and the different cycles do not superimpose (Figure

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S10 of the Supporting Information). 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.

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 for 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 CDAs.²¹

4. DISCUSSION

Although it is generally considered that asphaltenes behave similarly at the oil-water interface, the three types of asphaltenes studied have clearly different behaviors. In particular, CDAs have a much more pronounced nonlinear behavior. For a given value of the interfacial tension, the elastic modulus depends upon the bulk concentration of the asphaltenes above the CNAC (and even below for ISAs). This is different from what was reported earlier by several authors, ^{14,6,16} who showed that there is a universal curve $E(\pi)$. In the study of ref 6, 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 were 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 ref 6, 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 ref 14, 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 refs 16 and 17, the asphaltene concentrations were small and close to the CNAC, and we have seen that only ISAs have a compression modulus that is not a unique function of the surface pressure at these low concentrations.

At concentrations close and below the CNAC, the curves $E'(\pi)$ (ISAs excluded) 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 disassemble.²²

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

$$\gamma \sim \gamma_0 - 2k_{\rm B}TC\sqrt{\frac{Dt}{\pi}} \tag{1}$$

where γ_0 is the interfacial tension of the bare interface (brine-toluene), *C* is the asphaltene concentration expressed in the number of molecules per unit volume, *T* is the absolute temperature, and $k_{\rm B}$ is 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 eq 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 of the Supporting Information). The slopes of the curve γ versus \sqrt{t} are 0.032 and 0.13 mN m^{-1} s^{-1/2}, respectively, which accordingly lead to eq 1 with 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 upon 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 \times $10^{-10}~m^2/s$ as estimated in ref 6 or 3.6×10^{-10} m²/s using the Stokes relation and assuming a hydrodynamic radius of 1 nm as in ref 26. Note that the diffusion coefficient closest to these estimations has been measured in mixtures of toluene and decane oligomers.²⁶ 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 nanoaggregates could affect the diffusion coefficient, because the concentration of 0.1 g/L is close to the CNAC. However, the nanoaggregates are quite small, with their dimensions on the order of 2 nm;⁴ therefore, the estimated diffusion coefficient will be only lower than that of individual asphaltenes by a factor of 2.

Liu et al. argued that a small proportion of asphaltenes is more interfacially active than the others; they adsorb more slowly and populate the interface at long times.¹⁴ The relative concentration of these species could possibly depend upon the solvent used but not 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 the bulk concentration, as in the present study; hence, 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 of the Supporting Information), 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 subsurface region, for instance, adsorption barriers. For instance, as postulated,²⁸ less abundant but more interfacially active asphaltenes progressively replace the asphaltenes that adsorb first (random sequential adsorption).

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

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = k_{\mathrm{a}}C_{\mathrm{s}}(\Gamma_{\infty} - \Gamma) - k_{\mathrm{d}}\Gamma \tag{2}$$

denoting the surface concentration by Γ , the surface concentration at saturation by Γ_{∞} , and the subsurface concentration by $C_{s'}$ and k_a and k_d are the adsorption and desorption constants, respectively, related to the adsorption and desorption energy barriers E_a and E_d by $k_{a,d} = k_{a,d}^{0} \exp(-E_{a,d}/k_{\rm B}T)$.²³ Here, the asphaltenes are irreversibly adsorbed; therefore, $k_d = 0$. If we assume that k_a and C_s are independent of Γ , eq 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 monolayers.¹⁶

$$\gamma = \gamma_0 + k_{\rm B} T \Gamma_\infty \ln(1 - \Gamma/\Gamma_\infty) \tag{3}$$

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 of the Supporting Information). If adsorption was barrier-controlled, the product k_aC_s in eq 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; therefore, the reorganization process may depend upon the type of asphaltenes. Note also that the use of eq 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 to expose PAH groups to water. Note that the nanoaggregate and nanoaggregate cluster concentration is small because there are about 6-8 asphaltene monomers per nanoaggregate and 200 per cluster,⁴ and their diffusion coefficient is also small (only about 10 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 upon 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 mainly involve 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, and these PAHs could be responsible for stiff, short-range interactions. They are not very different from 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 the 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 nonlinear behavior than PAs and ISAs. The CDAs do not form Langmuir-Blodgett films, probably as a result of 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 comment³⁰ published by Bouriat about ref 14.

5. CONCLUSION

The present work demonstrates that the behavior of asphaltenes depends appreciably upon their molecular structure, which varies with their origin. Asphaltenes with many alkane chains and small PAHs form flexible layers, whereas asphaltene with less alkane chains and larger PAHs form rigid layers. All of the asphaltene layers of this study have a marked nonlinear behavior, particularly pronounced for the coal asphaltenes. At large concentrations (and ISAs at all concentrations), they do not exhibit a universal relation between the compression modulus and surface pressure, as reported in other asphaltene 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 the interfacial behavior of asphaltenes. This would help the evaluation of the properties of emulsions stabilized by different types of asphaltenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c00966.

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, and fits of the dynamic interfacial tension with various models (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Asphaltenes, Heavy Oils, and Petroleomics; Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G., Eds.; Springer Science & Business Media: New York, 2007; DOI: 10.1007/0-387-68903-6.

(2) Schuler, B.; Meyer, G.; Peña, D.; Mullins, O. C.; Gross, L. Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy. *J. Am. Chem. Soc.* **2015**, *137* (31), 9870–9876.

(3) Andreatta, G.; Bostrom, N.; Mullins, O. C. High-Q Ultrasonic Determination of the Critical Nanoaggregate Concentration of Asphaltenes and the Critical Micelle Concentration of Standard Surfactants. *Langmuir* **2005**, *21* (7), 2728–2736.

(4) Mullins, O. C. The Modified Yen Model. *Energy Fuels* **2010**, *24*, 2179–2207.

(5) Langevin, D.; Argillier, J. F. Interfacial Behavior of Asphaltenes. *Adv. Colloid Interface Sci.* **2016**, 233, 83–93.

(6) Cagna, A.; Esposito, G.; Quinquis, A. S.; Langevin, D. On the Reversibility of Asphaltene Adsorption at Oil–Water Interfaces. *Colloids Surf., A* **2018**, *548*, 46–53.

(7) Wang, W.; Taylor, C.; Hu, H.; Humphries, K. L.; Jaini, A.; Kitimet, M.; Scott, T.; Stewart, Z.; Ulep, K. J.; Houck, S.; Luxon, A.; Zhang, B.; Miller, B.; Parish, C. A.; Pomerantz, A. E.; Mullins, O. C.; Zare, R. N. Nanoaggregates of Diverse Asphaltenes by Mass Spectrometry and Molecular Dynamics. *Energy Fuels* **2017**, *31* (9), 9140–9151.

(8) Andreatta, G.; Goncalves, C. C.; Buffin, G.; Bostrom, N.; Quintella, C. M.; Arteaga-Larios, F.; Pérez, E.; Mullins, O. C. Nanoaggregates and Structure-Function Relations in Asphaltenes. *Energy Fuels* **2005**, *19* (4), 1282–1289.

(9) Bake, K. D.; Craddock, P. R.; Bolin, T. B.; Abdallah, W.; Mitra-Kirtley, S.; Andrews, A. B.; Mullins, O. C.; Pomerantz, A. E. Structure-Solubility Relationships in Coal, Petroleum, and Immature Source-Rock-Derived Asphaltenes. *Energy Fuels* **2020**, *34* (9), 10825–10836. (10) Schuler, B.; Zhang, Y.; Collazos, S.; Fatayer, S.; Meyer, G.; Pérez, D.; Guitián, E.; Harper, M. R.; Kushnerick, J. D.; Peña, D.; Gross, L. Characterizing Aliphatic Moieties in Hydrocarbons with Atomic Force Microscopy. *Chem. Sci.* **2017**, *8* (3), 2315–2320.

(11) Lucassen-Reynders, E. H.; Cagna, A.; Lucassen, J. Gibbs Elasticity, Surface Dilational Modulus and Diffusional Relaxation in Nonionic Surfactant Monolayers. *Colloids Surf., A* **2001**, *186* (1–2), 63–72.

(12) Andrews, A. B.; McClelland, A.; Korkeila, O.; Demidov, A.; Krummel, A.; Mullins, O. C.; Chen, Z. Molecular Orientation of Asphaltenes and PAH Model Compounds in Langmuir-Blodgett Films Using Sum Frequency Generation Spectroscopy. *Langmuir* **2011**, 27 (10), 6049–6058.

(13) Chaverot, P.; Cagna, A.; Glita, S.; Rondelez, F. Interfacial Tension of Bitumen–Water Interfaces. Part 1: Influence of Endogenous Surfactants at Acidic PH. *Energy Fuels* **2008**, *22* (2), 790–798.

(14) Liu, F.; Darjani, S.; Akhmetkhanova, N.; Maldarelli, C.; Banerjee, S.; Pauchard, V. Mixture Effect on the Dilatation Rheology of Asphaltenes-Laden Interfaces. *Langmuir* **2017**, *33* (8), 1927–1942.

(15) Ritacco, H.; Cagna, A.; Langevin, D. Oscillating Bubble Measurements of the Compression Viscoelasticity of Mixed Surfactant-Polyelectrolyte Surface Layers. *Colloids Surf., A* 2006, 282–283, 203–209.

(16) Rane, J. P.; Pauchard, V.; Couzis, A.; Banerjee, S. Interfacial Rheology of Asphaltenes at Oil–Water Interfaces and Interpretation of the Equation of State. *Langmuir* **2013**, *29* (15), 4750–4759.

(17) Rane, J. P.; Zarkar, S.; Pauchard, V.; Mullins, O. C.; Christie, D.; Andrews, A. B.; Pomerantz, A. E.; Banerjee, S. Applicability of the Langmuir Equation of State for Asphaltene Adsorption at the Oil–Water Interface: Coal-Derived, Petroleum, and Synthetic Asphaltenes. *Energy Fuels* **2015**, *29* (6), 3584–3590.

(18) Anton, N.; Vandamme, T. F.; Bouriat, P. Dilatational Rheology of a Gel Point Network Formed by Nonionic Soluble Surfactants at the Oil–Water Interface. *Soft Matter* **2013**, *9* (4), 1310–1318.

(19) Hinderink, E. B. A.; Sagis, L.; Schroën, K.; Berton-Carabin, C. C. Behavior of Plant-Dairy Protein Blends at Air–Water and Oil–Water Interfaces. *Colloids Surf., B* **2020**, *192*, 111015.

(20) Giménez-Ribes, G.; Habibi, M.; Sagis, L. M. C. Interfacial Rheology and Relaxation Behavior of Adsorption Layers of the Triterpenoid Saponin Escin. *J. Colloid Interface Sci.* **2020**, *563*, 281–290.

(21) Andrews, A. B. Private Communication, 2022.

(22) Dechaine, G. P.; Gray, M. R. Membrane Diffusion Measurements Do Not Detect Exchange between Asphaltene Aggregates and Solution Phase. *Energy Fuels* **2011**, *25*, 509–523.

(23) He, Y.; Yazhgur, P.; Salonen, A.; Langevin, D. Adsorption-Desorption Kinetics of Surfactants at Liquid Surfaces. *Adv. Colloid Interface Sci.* 2015, 222, 377–384.

(24) Zhang, S.; Zhang, L.; Lu, X.; Shi, C.; Tang, T.; Wang, X.; Huang, Q.; Zeng, H. Adsorption Kinetics of Asphaltenes at Oil/Water Interface: Effects of Concentration and Temperature. *Fuel* **2018**, *212*, 387–394.

(25) Mohammadi, M.; Zirrahi, M.; Hassanzadeh, H. Adsorption Kinetics of Asphaltenes at the Heptol–Water Interface. *Energy Fuels* **2020**, 34 (3), 3144–3152.

(26) Rane, J. P.; Harbottle, D.; Pauchard, V.; Couzis, A.; Banerjee, S. Adsorption Kinetics of Asphaltenes at the Oil–Water Interface and Nanoaggregation in the Bulk. *Langmuir* **2012**, *28* (26), 9986–9995.

(27) Zarkar, S.; Pauchard, V.; Farooq, U.; Couzis, A.; Banerjee, S. Interfacial Properties of Asphaltenes at Toluene - Water Interfaces. *Langmuir* 2015, 31 (17), 4878–4886.

(28) Pauchard, V.; Rane, J. P.; Zarkar, S.; Couzis, A.; Banerjee, S. Long-Term Adsorption Kinetics of Asphaltenes at the Oil–Water Interface: A Random Sequential Adsorption Perspective. *Langmuir* **2014**, *30* (28), 8381–8390.

(29) Jian, C.; Tang, T.; Bhattacharjee, S. Probing the Effect of Side-Chain Length on the Aggregation of a Model Asphaltene Using Molecular Dynamics Simulations. Energy Fuels 2013, 27 (4), 2057–2067.

(30) Bouriat, P. Comment on "Mixture Effect on the Dilatation Rheology of Asphaltenes-Laden Interfaces". *Langmuir* **2019**, 35 (6), 2451–2453.

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