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Heavy Oil−Water Interfacial Properties and Emulsion Stability: Influence of Dilution

Gabriela Alvarez,*,†,‡ Sandrine Poteau,†,‡ Jean-François Argillier,† Dominique Langevin,‡
and Jean-Louis Salager§

*Institut Français du Pétrole, 1-4 avenue de Bois Préau, 92852 Rueil-Malmaison Cedex, France,
Laboratoire de Physique des Solides, Université Paris-Sud, CNRS UMR8502, Bâtiment 510,
91405 Orsay Cedex, France, and Laboratorio FIRP, Ingeniería Química, Universidad de los Andes,
Mérida, Venezuela*

We have performed a study of dynamic interfacial tension and rheology of interfaces between water and either crude oil diluted in toluene or in a model oil consisting of toluene, in which pentane-extracted asphaltenes were redissolved. We show that the break point of the curve interfacial tension versus asphaltene concentration is not related to an eventual critical aggregation concentration but rather to the collapse of the asphaltene surface layer. As for other amphiphilic species that adsorb irreversibly at an oil−water interface, the corresponding emulsion stability increases with the amphiphile concentration, even above the collapse point. The behavior of diluted crude oil and model oil are quite similar. However, the surface layers evolve over longer time scales in the case of diluted crude oil, probably because of the contribution of resins that form less polar aggregates with asphaltenes. This results in less stable emulsions, especially before the collapse point.

1. Introduction

Nowadays, there is an increasing interest for alternative energy resources, because of the growing world energy demand and high price of conventional oils. Heavy and extra heavy oils are strategic reserves but pose new challenges to the oil industry. One major problem is their high viscosity (100−10 000 mPa s at room temperature),[1] which makes them difficult to transport. One method used to reduce their viscosity is dilution by less viscous oil (condensate, naphtha, kerosene, or light crude oil). In the oil sand (bitumen) industry, because of the similar density of water and bitumen, dilution is also required to improve the separation of water and solids from the bitumen.[2] Besides, these oils frequently form dispersed systems, such as emulsions or foams during production, transportation, and processing. These dispersions can be very stable and difficult to break, which increases treatment costs. The breaking methods are not well-controlled yet because of the complex oil chemistry, which contains surface-active molecules, such as asphaltenes and resins.

Asphaltenes are considered by most researchers[3−5] as the amphiphilic compounds responsible of the high stability of water-in-crude oil emulsions, mainly because of their capacity to form a stable thick network at the interface.[5] However, several studies have established the importance of other components of crude oils, such as resins,[4,6] waxes,[7] solids,[8,9] and naphtenic acids.[10]

The influence of dilution on bulk and interfacial properties of water−crude oil systems is not well-understood yet. Several studies have been made with systems, such as bitumen,[2,8,10,11] heavy oils,[12] and model oils, such as asphaltene solutions in hydrocarbon solvents;[13−16] correlations between emulsion stability and surface compression moduli have been highlighted.[15,16] Czarnecki et al.[2,10] have observed the existence of a critical dilution ratio: diluent/bitumen (D/B), at which the rigidity of the interface changes. This evolution was explained in a model, where a change in the surface layer composition[10,17] results in a reorganization of the amphiphilic species at the interface.

In the present study, our aim was to improve the understanding of the influence of dilution on the interface structural changes and its relationship with emulsion instability/stability. We have studied both the surface viscoelastic properties and the emulsion

* To whom correspondence should be addressed. Telephone: +33-1-47-52-68-62. Fax: +33-1-47-52-70-58. E-mail: gabriela.alvarez-jurgenson@ifp.fr.
† Institut Français du Pétrole.
‡ Université Paris-Sud.
§ Universidad de los Andes.

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Table 1. SARA Analysis of the Crude Oil and Elementary Composition of the Pentane-Extracted Asphaltene Fraction

components	% weight
asphaltenes	17
resins	33
aromatics	37
saturates	12

asphaltenes	% weight
C	83.2
H	8
N	2.7
O	1.4
S	5.1

stability with a diluted crude oil. For the sake of comparison, we have also performed the same type of study with model oil (pentane-extracted asphaltenes diluted in toluene).

2. Experimental Section

2.1. Water and Oil Phases. In all experiments, 5 g/L NaCl aqueous solutions prepared from MilliQ distilled water were used. A Venezuelan heavy crude oil [9° American Petroleum Institute (API)] was diluted in ultrapure-grade toluene to obtain the oil phase.

Asphaltenes were extracted using American Society for Testing and Materials (ASTM) 863-69 norm: a sample of crude oil was first poured in an excess of *n*-pentane (1 g of oil and 30 mL of pentane), then submitted to stirring for 1 h at 50 °C, and allowed to rest at ambient temperature for 2 h to facilitate asphaltene precipitation. The precipitated asphaltene fraction was filtered; the residue was abundantly washed with pentane until a colorless solution was obtained; next the solid fraction of asphaltene was dried and grinded. The remaining solution is a mixture of pentane and oil without asphaltenes, so-called maltenes. The saturates, aromatics, resins, and asphaltenes (SARA) analysis and elementary composition are given in Table 1. These asphaltenes were diluted in toluene to obtain the model oil phase.

The different oils were pre-equilibrated during 24 h with the aqueous phase prior to measurements.

2.2. Dynamic Interfacial Tension and Rheology Measurements. The dynamic interfacial tension and dilational viscoelastic properties have been measured with a commercial pendant drop tensiometer (Tracker from IT Concept, now Teclis).

2.2.1. Interfacial Tension. A fresh oil drop was formed and maintained vertically at the end of an inverted needle in a transparent thermostatted cell (25 ± 1 °C) containing the aqueous phase. Dynamic interfacial tension was obtained by fitting the drop shape with the Laplace equation coupled with the hydrostatic equation. We used the oil densities measured with a densimeter Anton Paar DMA 5000.

2.2.2. Viscoelastic Properties. The drop area can be varied sinusoidally at a low amplitude with a syringe and a pump. This deformation leads to a sinusoidal change in surface tension (dγ). The dilational modulus, ε^*, is given by

$$\varepsilon^* = \frac{d\gamma}{d \ln A} = A\frac{d\gamma}{dA}$$

This parameter measures the interface response to a compression or an expansion. For viscoelastic interfaces, the change in surface area and change in surface tension are out of phase, so that the dilational modulus is a complex quantity, with real and imaginary components defined as follows:

$$\varepsilon^* = \varepsilon' + i\varepsilon''$$

where ε' is the interfacial storage dilational modulus (or elastic modulus), which measures the energy stored during a periodic deformation of the interface and ε'' is the loss dilational modulus (viscous modulus), accounting for energy dissipation through different relaxation processes, such as diffusion of surface-active species from the bulk or subsurface, as well as interfacial reorganization of adsorbed species.

The absolute value of the complex dilational modulus $|\varepsilon^*|$ is related to the storage and loss moduli by

$$\varepsilon' = |\varepsilon^*|\cos \phi$$
$$\varepsilon'' = |\varepsilon^*|\sin \phi$$

where ϕ is the phase angle: $\phi = 0°$ corresponds to an elastic response, while $\phi = 90°$ corresponds to a viscous response.

The dilational viscoelasticity measurements were performed with a relative area variation of 10% (to remain in the linear regime) and an oscillation period of 10 s.

2.2.3. Crumpling Ratio. When the drop area is reduced by larger amounts, a "crumpling" phenomenon can be observed: the drop surface becomes rough because of an apparent buckling. This effect was attributed to the presence of a rigid "skin" at the surface and occurs above a certain reduction of area, called "crumpling point", with the relative area reduction at this point being defined as the crumpling ratio.[18]

Our experiments were performed with the Tracker: an oil drop of radius of 30 μL is compressed after a given aging time, at a constant volume rate (0.1 μL/s). Images are recorded, during the drop contraction and if a skin is observed, and the corresponding crumpling ratio is calculated using the apparatus software.

2.3. Emulsification and Emulsion Stability Measurement. Model emulsions, of 30 mL total volume, were made by mixing equal volumes of an aqueous solution and a solution of crude oil or of asphaltenes in toluene. Emulsification was carried out with an Ultra Turrax turbine blender, at 13 000 rpm during 1 min at 25 ± 2 °C.

The emulsion stability against coalescence was studied by measuring the volume of water resolved at the bottom of the tube. To accelerate the separation process, emulsions were centrifuged at 6000 rpm (40 g) for different time intervals of 5 min each.

The time (in minutes) necessary to separate half the total volume of water was taken as a measurement of the emulsion stability.

All of the measurements performed with the different techniques were repeated at least 3 times, to check for reproducibility. The results presented afterward are averages over the measurements performed.

## 3. Results and Discussion

3.1. Structure. Three regions could be differentiated as for conventional surfactant systems. At low crude oil content, the surface tension does not vary appreciably. In the range of 10−100 g/L (equivalent to an asphaltene concentration of 2−20 g/L), a fast tension decrease is observed, followed by a plateau above a break point at C* (∼80 g/L, equivalent to an asphaltene concentration of 16 g/L), which likely indicates interface saturation.

Even if this is similar to the behavior of classical surfactant systems, a word of caution is necessary before extending the comparison to the "critical micelle concentration (cmc)" because the aggregation of asphaltenes, i.e. the major amphiphiles in crude oils, is not yet well-understood. Recent studies[19] suggest that asphaltenes are already associated at concentrations lower than the break point observed in the interfacial tension curve (around 100 mg/L of asphaltenes). On another hand, adsorption is essentially irreversible. The break point could therefore rather signal a collapse phenomenon as in classical insoluble monolayers[20]: above collapse, the layer is in equilibrium with a three-

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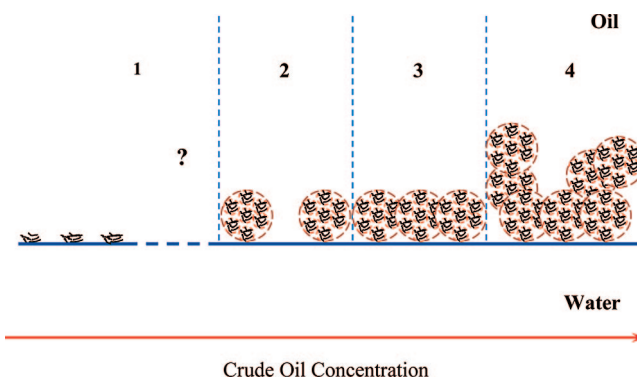(20) Gaines, G. L. *Insoluble Monolayers at Liquid−Gas Interfaces*; Interscience: New York, 1966.
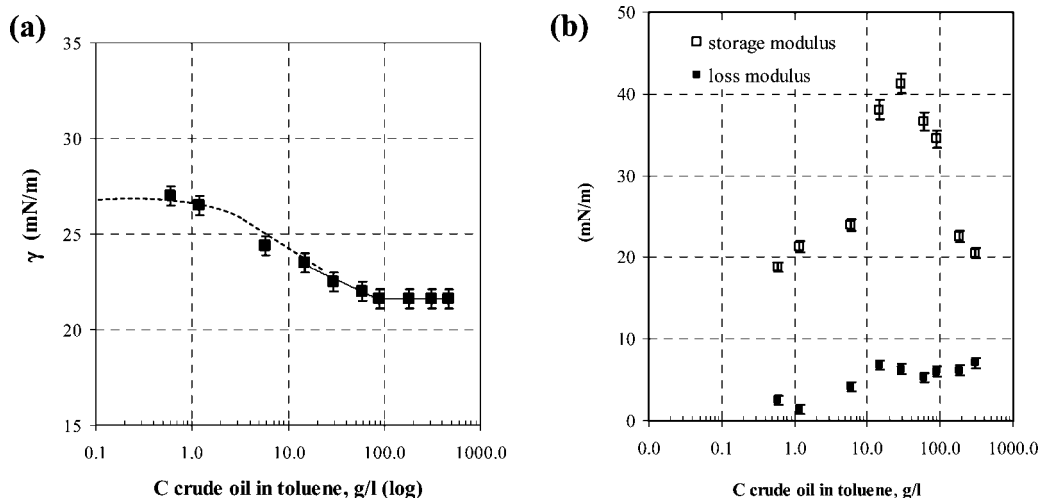
Figure 1. (a) Oil−water equilibrium interfacial tension versus crude oil concentration in toluene and (b) storage and loss modulus.

dimensional bulk phase. Here, we propose that a similar phenomenon happens: upon adsorption, the asphaltenes form a surface layer; once the surface is saturated, the additional asphaltenes cannot incorporate and remain in a configuration closer to that of the bulk because they have little contact with water. A very similar behavior occurs with proteins adsorbed from aqueous solutions, either at air−water or oil−water interfaces.[21] This is also consistent with the fact that asphaltenes are mixtures of molecules with a wide range of shapes and molecular weights; no clear break point should be visible at the concentration where bulk aggregates start to form.

The storage elastic surface modulus exhibits a pronounced maximum before C^* (Figure 1b), and afterward, the layer becomes less rigid. This is accompanied by an increase in the loss modulus (see Figure 1b), which indicates that more energy is dissipated when the interface is deformed, likely because of the increasing amount of adsorbed species.

Note that it has been recently reported that the asphaltene aggregates change in nature between 1 and 10 g/L,[22] a phenomenon that could also affect the surface behavior, as will be discussed in the following.

In order to account for the observations, we propose the following evolution of the organization and structure of the adsorbed layer: (1) when $C < 5$ g/L ($C_{asph} < 1$ g/L), small variations in the IFT and viscoelastic properties are found, because there are not enough amphiphilic molecules in the bulk to completely cover the interfacial area. (2) For concentrations between 5 and 15 g/L (C_{asph} between 1 and 3 g/L), the IFT begins to diminish and the elastic modulus increases, because of the stronger adsorption of amphiphilic species at the interface, which end up forming a denser layer. (3) Close to C^* (15−60 g/L; 3−10 g/L asphaltenes), the elastic modulus reaches a maximum: the monolayer becomes compact and rigid. This is the same as in insoluble monolayers: the surface tension decreases with the surface concentration Γ and saturates at the collapse point Γ^*; as a result, the curve $\gamma(\Gamma)$ has an inflection point at $\Gamma = \Gamma_i < \Gamma^*$ and the elastic modulus, which is equal to $-\Gamma d\gamma/d\Gamma$ is maximum at Γ_i. This explains why this maximum is shifted with respect to C^*. Again, this is quite different from soluble surfactant solutions, for which there is thermodynamic

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Figure 2. Schematic representation of possible structural changes at the interface with an increasing crude oil bulk concentration.

equilibrium between interface and bulk: the elastic modulus increases up to the cmc and remains constant above the cmc. A behavior similar to those of asphaltenes is observed with proteins.[21] (4) Beyond C^*, the surface tension saturates, suggesting that the surface layer collapses and builds up structures in the third dimension. It exhibits little resistance to compression, because the surface tension is now independent of the surface concentration.

Earlier studies[15,23] have shown that the characteristic times of evolution of interfacial tension are very long and cannot be accounted for by diffusion of species toward the newly formed surface. This suggests that the evolution observed here is accompanied by a molecular reorganization at the interface. As for proteins at interfaces, when multilayers are formed, the layer closer to the interface is the one where the conformation of the protein is changed the most.

It has been shown in neutron scattering experiments performed with asphaltene solutions in xylene that the layer thickness was comparable to the diameter of the bulk aggregates,[24] suggesting that the adsorbed layers are constituted by bulk aggregates packed side by side. As mentioned above, a reorganization occurs in the layer, which does not seem to affect significantly the dimensions of the adsorbed aggregates. This leads us to propose a tentative scheme of the evolution of the surface layer with the asphaltene concentration in Figure 2. We should point out that this representation is oversimplified

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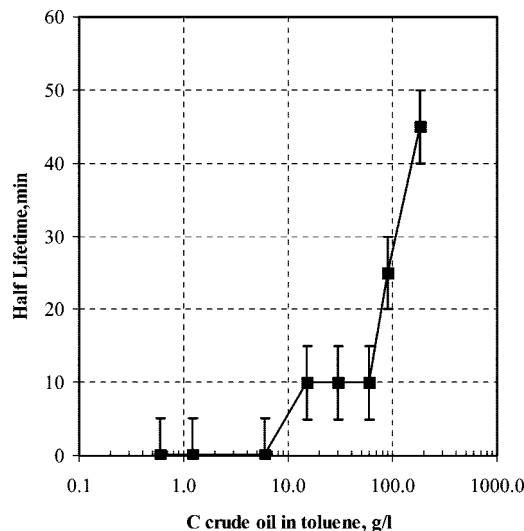
Figure 3. Emulsion stability as a function of the crude oil concentration.

Figure 4. Comparison of the interfacial tension between diluted crude oil (−) and dissolved asphaltenes (□).

Figure 5. Characteristic times for the dynamic interfacial tension with diluted crude oil (■) and dissolved asphaltenes (□).

and might not be fully accurate. We omitted the layer in the dilute range (from 100 mg/L to 1 g/L asphaltenes), because the size of the aggregates has not be measured in this concentration range. It has been postulated that the asphaltene aggregates change above 1 g/L, and those represented Figure 2 correspond to the aggregates formed in the high-concentration range.

The results obtained for the emulsion stability are shown in Figure 3 and can be correlated with those of the interfacial properties for the four concentration ranges: (1) At low concentrations, emulsions are completely unstable: there are not enough amphiphiles to cover the interface, a surface layer begins to form, but its rigidity is insignificant. (2) In the 5−15 g/L range (1−3 g/L asphaltenes), stabilization occurs because of the formation of a tighter monolayer, with more adsorbed species and stronger interparticle interactions. (3) After 15 g/L (3 g/L asphaltenes), a stability plateau, which coincides with the region of the maximum in elastic modulus, is seen, where the monolayer is highly compact and extremely rigid. (4) Finally, for concentrated solutions, emulsions are even more stable. This behavior corresponds to the change in the interfacial layer structure from 2D to 3D configuration and, hence, provides a more efficient protection against coalescence of emulsion droplets.

We do not think that a change of the aggregates could explain the maximum of elastic modulus, although both phenomena occur in the same range. Indeed, one could argue that the adsorbed bulk aggregates are more compressible than at low asphaltene concentration, but it will be difficult to explain the increased stability of emulsions and the saturation of the surface tension at higher concentrations. However, the change in nature of the aggregates above 1 g/L asphaltenes coincides with the surface tension decrease: the aggregates might then be more surface-active than those formed at lower concentrations.

3.2. Composition. The existence of changes in interfacial rigidity and composition has been reported in several studies on bitumen[10,16,25] by using other techniques, such as the micropipette and the quartz microbalance. These changes have been attributed to a modification of the interfacial structure, with asphaltenes being displaced from the interface by naphtenic acids below a "critical bitumen/diluent ratio". In the high dilution range, the interfaces are mostly covered by asphaltenes, the
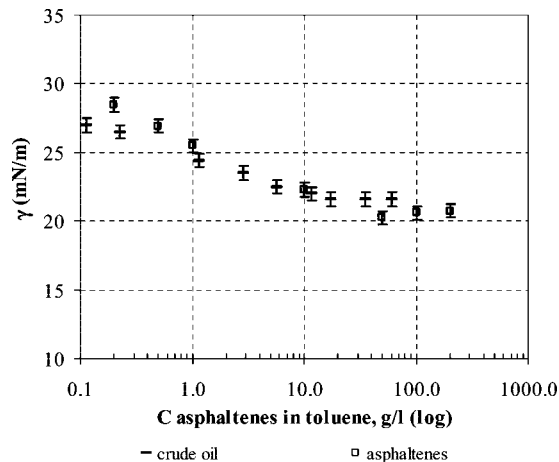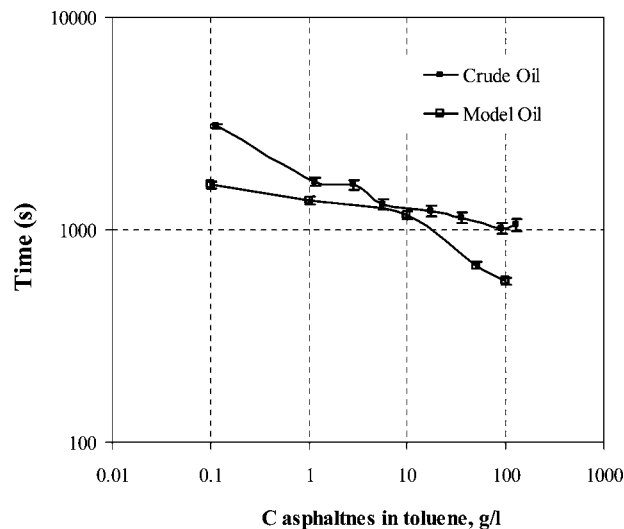
interfaces are rigid (crumpling is seen upon compression), whereas in the low dilution range, the H/C ratio is similar to that of resins and the interfaces are fluid.

To confirm this picture, we performed a comparative study of the interfacial properties of toluene-diluted heavy crude oil (its concentration now expressed as a function of its asphaltene content) and pentane-extracted asphaltenes dissolved in toluene. The comparison should allow for the evaluation of the influence of the amphiphilic species other than asphaltenes present in the oil.

As may be seen in Figure 4, the interfacial tensions for both solutions are similar at all concentrations. This result suggests that the interface is governed by the pentane-extracted asphaltenes and not by the resins.

The time variation of the interfacial tension curves has been analyzed assuming single-exponential decay. The characteristic times are shown in Figure 5.

In both cases, the characteristic times decrease with an increasing asphaltene concentration. The times are slightly larger for the diluted crude oil. It should be noted that the fits are of better quality if a distribution of relaxation times is used, but all of these times decrease with an increasing asphaltene concentration. This means that the surface reorganization becomes faster at higher asphaltene concentrations. This may

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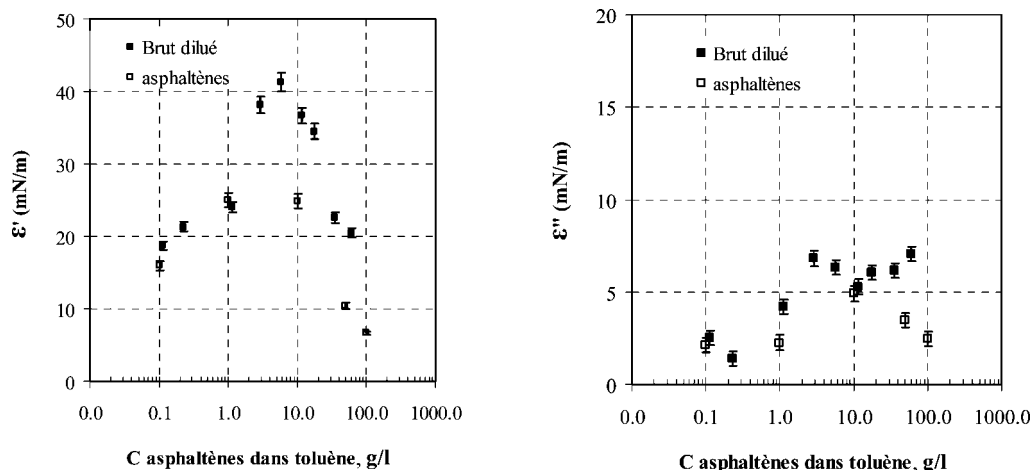
Figure 6. Comparison of the elastic and viscous moduli between diluted crude oil (■) and dissolved asphaltenes (□), after 2.5 h.
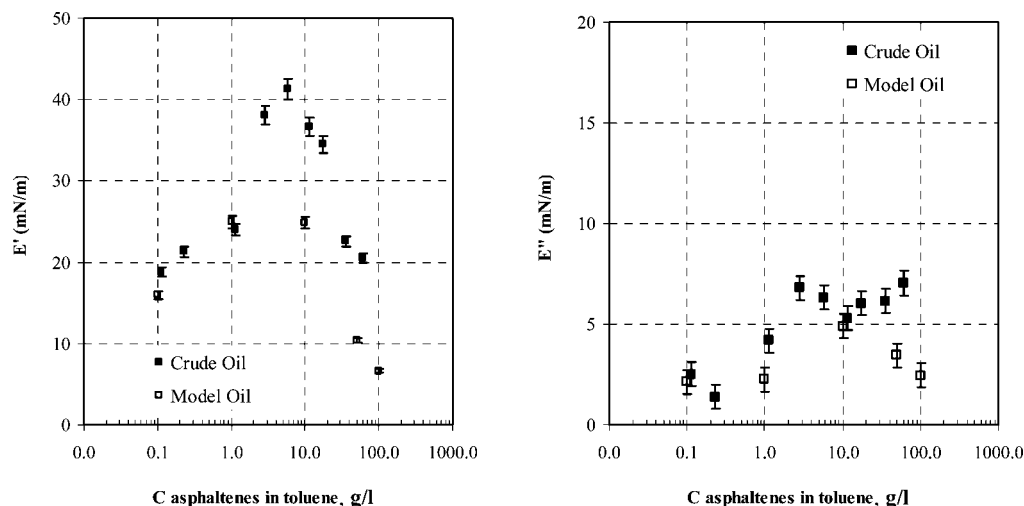
Figure 7. Comparison of the elastic and viscous moduli between diluted crude oil (■) and dissolved asphaltenes (□), after 12 h.

be associated with the fact that the bulk aggregates adsorb without much deformation at these concentrations as mentioned earlier.

For short aging times, the viscoelastic moduli are similar, confirming that the water/crude oil interface is dominated by asphaltenes (Figure 6).

At longer times, appreciable differences are observed in the range of $1 < C < 15$ g/L, with the elastic and viscous moduli for crude oil/water interfaces being higher (Figure 7). It seems that the heavy crude oil/water interface is constituted of amphiphilic species that are less polar (possibly asphaltenes aggregates peptized by resins) than those found in the pentane-extracted asphaltene solution.

The longer equilibration times seen in Figure 5 and the long time increase of the elastic and viscous moduli (Figures 6 and 7) in the case of crude oil show that the formation of the surface layer is slowed down, in comparison to the behavior observed for the solutions of pentane-extracted asphaltenes.

It was proposed by Masliyah and co-workers[10] that the maximum of the surface modulus was due to a structural transition and a change in composition of the adsorbed layer. One of the arguments given was that, at low asphaltene concentrations, a "crumpling" of the layer was seen upon compression, whereas the layer remained smooth above the transition whatever the degree of reduction in the surface area.

We show in Figure 8 the crumpling ratio (defined in section 2.2) measured with the systems studied here at long times. It correlates well with the compression modulus as found by
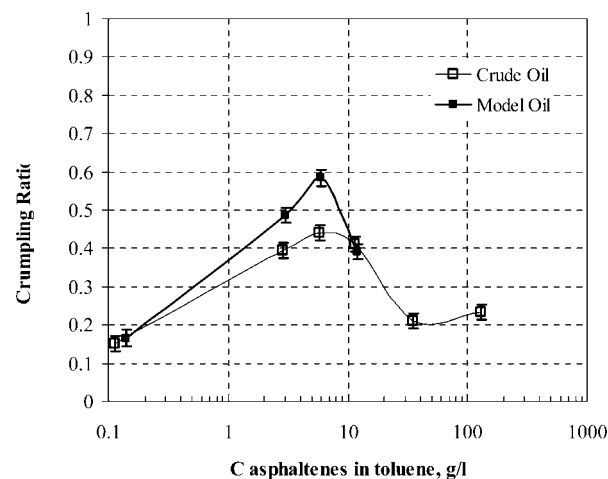

Figure 8. Crumpling ratio as a function of dilution for diluted crude oil (■) and dissolved asphaltenes (□), after 12 h.

Masliyah et al. At short aging times, the crumpling ratios are lower, as also seen in their experiments.

However, because the diluted crude oil and asphaltene solutions behave similarly, it is difficult to attribute the change in crumpling behavior to a change of the chemical composition of the surface layers. It is more likely due to a change of layer organization, such as that proposed in Figure 2.

As for the viscoelastic properties for long aging times, the emulsion stability (Figure 9) variations exhibit three regions
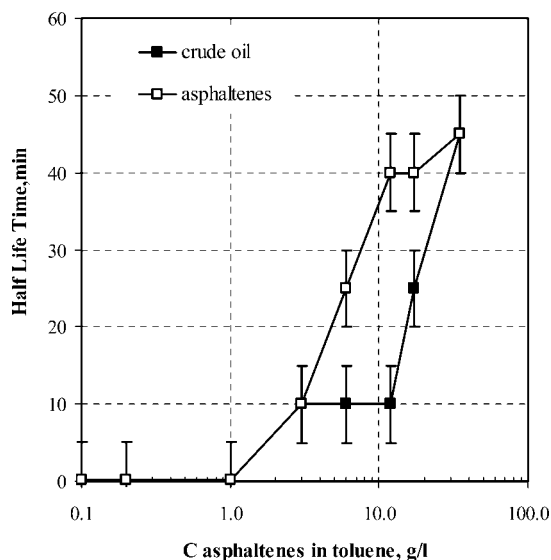
Figure 9. Comparison of the stability of emulsions made with diluted crude oil (■) and diluted asphaltenes (□) (non-aged emulsions).

depending upon the concentration: (1) Emulsions are unstable for asphaltene concentrations below 1 g/L. (2) Between 3 and 15 g/L, emulsions made with asphaltenes solutions are more stable. (3) For concentrations beyond 15 g/L, the emulsion stability is the same in both cases, which suggests that the composition and structure of both interfaces are similar.

Before C^*, the emulsion stability is well-correlated with the increase in both elastic and viscous moduli. Close to C^*, the moduli decrease and the stability increases further. This is the same as in other emulsions stabilized by irreversibly adsorbed species: after the surface layer collapse, the surface tension remains constant, so that the compression modulus $Ad\gamma/dA$ becomes zero. This is because the compressed monolayer can expel material in the region above the surface layer without energy cost (see Figure 2). However, the surface layer is still present and able to protect the emulsion droplets against coalescence. It is therefore not necessary to invoke a change in chemical composition of the interface to account for the emulsion behavior. It is however possible that, beyond collapse, the layer contains more oil: indeed, it is likely made of a compact first layer to which bulk aggregates are sticking. With

these bulk aggregates being less compacted, the average H/C ratio of the surface layer increases. It is possible that the change in surface layer composition seen by Wu[17] is also due to the trapped oil.

The difference in stability between diluted crude oil and diluted asphaltenes is difficult to explain. We have seen that the surface layers evolve over longer time scales in the case of diluted crude oil, probably because of the contribution of resins that form less polar (more oil-soluble) aggregates with asphaltenes. Although the measured moduli are higher, the layers might be less able to resist to a rapid expansion during a coalescence process. Let us recall that the time scales of the surface rheological measurements are quite long, e.g. 10 s, whereas coalescence events are believed to occur from milli- to microseconds. The surface moduli might well be different at these frequencies. There is unfortunately no instrument able to determine the surface compression rheology at such high frequencies at oil−water interfaces.[26]

Conclusions

We have shown that the break point of the curve interfacial tension versus the degree of crude oil dilution concentration is not related to an eventual critical aggregation concentration but rather to the collapse of the asphaltene surface layer. As for other amphiphilic species that adsorb irreversibly at an oil−water interface, the corresponding emulsion stability increases with the amphiphile concentration, even above the collapse point. The behavior of diluted crude oil and model oil are quite similar. However, the surface layers evolve over longer time scales in the case of diluted crude oil, probably because of the contribution of resins that form less polar (more oil-soluble) aggregates with asphaltenes. This results in less stable emulsions, especially before the collapse point.

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