

# Influence of pH on Stability and Dynamic Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil–Water Interface<sup>†</sup>

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Oil-in-water emulsions are currently being investigated to facilitate the transport of viscous heavy oils. The behavior of these emulsions is largely controlled by the interfaces between oil drops and water. The surface-active components of crude oil, such as asphaltenes and naphthenic acids, compete among themselves at these interfaces and also with possibly added synthetic surfactant emulsifier. Here, we present a study of dynamic interfacial tension of interfaces between water and a model oil (toluene) in which variable amounts of asphaltenes are solubilized. We show that pH has a strong influence on interfacial properties of asphaltenes at the oil/water interface. At high or low pH, asphaltenes functional groups become charged, enhancing its surface activity. The influence of lower-molecular-weight surface-active species, such as the natural naphthenic acids contained in maltenes (crude oil without asphaltenes), has been investigated, and an interaction between asphaltenes and maltenes that facilitates molecular arrangement at the interface was detected. Several micropipette experiments, in which micrometric drops have been manipulated, are also described and indicate that very little coalescence of water droplets is observed at high or low pH. The microscopic properties of the interface and the macroscopic behavior of the emulsion are determined to be correlated.

## Introduction

Asphaltenes are defined as the crude oil fraction that is insoluble in alkanes such as pentane or heptane and constitute the heaviest and the most polar components of a crude oil. This fraction, which is composed of various compounds of high molecular weight (in the range of 700–2000 g/mol), is observed in important quantities in heavy oils.<sup>1</sup> They include a large variety of chemical species, with functional groups including acids or bases. They are responsible for the very large viscosities of heavy oils that are presently of great interest in view of the existence of important reserves.<sup>2</sup> Because of their large viscosities, new extraction procedures must be

found for these oils. One of the possibly methodologies is emulsification in the form of more-fluid oil-in-water emulsions. Because asphaltenes are surface-active, water-in-oil emulsions are formed when oil and water are stirred together, for instance, during the production processes. Many studies of these emulsions can be found in the literature.<sup>3–8</sup> Very early, the oil–water interfacial properties in the presence of asphaltenes have been shown to be very peculiar, with long adsorption times and formation of rigid skins at the interface.<sup>9–11</sup> The

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**Table 1. Saturates, Aromatics, Resins, and Asphaltenes (SARA) Analysis of the Crude and Elementary Composition of the Different Fractions**

component	SARA Analysis (wt %)		Composition of C20+ Heptane SARA Fraction (wt %)				
	pentane	heptane C20+	C	H	N	O	S
asphaltenes	17	14.1	83.8	7.5	1.3	1.7	4.8
resins	33	37.3	82.8	8.9	1.5	2.0	4.3
aromatics	37	37.2	84.3	10	<0.3	1.1	4.0
saturates	12	11.4	86.6	13	<0.3	<0.2	<0.1

influence of pH has been studied on model emulsions with asphaltenes<sup>12</sup> or on water–crude oil emulsions.<sup>9,10,13–16</sup> There are basically two ways to obtain oil-in-water emulsions: through the addition of water-soluble surfactants and/or the addition of bases to saponify amphiphilic molecules contained in the oil, making their compounds (such as naphthenic acids, asphaltenes, ...) more hydrophilic. The aim of the present study is to investigate, in more detail, the role of pH on interfacial properties of asphaltenes and asphaltene/surfactant mixtures at the oil/water interface and to study the relationship between interfacial properties and the stability of model emulsions as a function of pH.

### Experimental Section

Samples were prepared from a 9° API Venezuelan heavy crude oil. Asphaltene extraction has been performed using the ASTM 863–69 standard: the crude oil was first stirred with an excess of *n*-pentane (1 g of oil and 30 mL of pentane). The precipitated fraction was filtered, dried, and ground. The remaining solution is a mixture of pentane and oil without asphaltenes; these are called maltenes. Maltenes were separated from the excess pentane using a rotovapor. The SARA (saturates, aromatics, resins, asphaltenes) analysis and elementary composition are given in Table 1.

Ultrapure-grade toluene was used as the solvent for the asphaltenes. In all experiments, NaCl (5 g/L) aqueous solutions prepared from Milli-Q distilled water (Millipore Corp.) were used to reduce the sensitivity to changes in ionic strength. The pH of the aqueous solution was adjusted to the desired value with NaOH or HCl.

Dynamic interfacial tensions and dilatational viscoelastic properties have been measured with a commercial dynamic surface tension instrument (IT Concept).<sup>17</sup> In this technique, an oil drop is formed at the end of a syringe tip in a glass cell filled with the second fluid, and the drop is imaged with a video camera. The drop shape is analyzed with a computer program that solves the Laplace equation describing mechanical equilibrium under capillary and gravity forces and allows monitoring of the interfacial tension variation with time. All experiments were performed at room temperature (25 °C) and atmospheric pressure. The drop volume can be varied sinusoidally with a low amplitude. The dilatational viscoelasticity measurements were performed with a relative volume variation of 10% and oscillation periods of 10 s.

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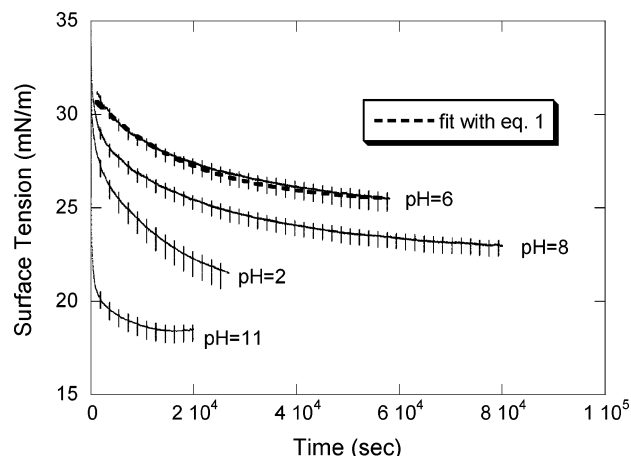
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Model emulsions were produced by mixing equal volumes of an aqueous solution and of an asphaltene solution in toluene (ultraturrax 19000 rpm for 2 min at 25 °C). The emulsions were characterized by optical microscopy. The emulsion stability against coalescence was studied by measuring the volume of water resolved at the bottom of the tube after 30 min of centrifugation at 4000 rpm.

### Results and Discussion

**1. Interfacial Properties of Model Asphaltene Systems.** The time variation of the oil–water interfacial tension for different pH is represented in Figure 1. As



**Figure 1.** Oil–water interfacial tension versus time for different pH; the dotted line is the fit with eq 1.

noted earlier,<sup>18</sup> the characteristic evolution times are very long and cannot be explained by the diffusion of the surface-active molecules toward the newly formed surface. The process observed here is rather a molecular reorganization at the interface. This is very similar to what one observes during protein adsorption,<sup>19</sup> where this process can be described by an exponential function:

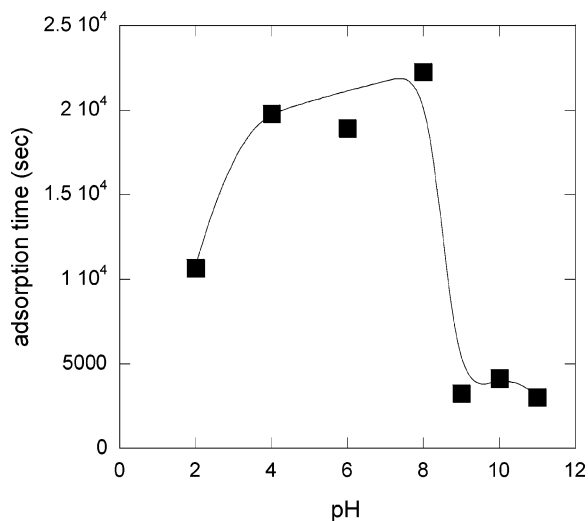
$$\gamma = \gamma_{\text{eq}} + (\gamma_0 - \gamma_{\text{eq}})e^{-t/\tau} \quad (1)$$

where  $\gamma$  is the surface tension,  $\gamma_0$  the initial surface tension,  $\gamma_{\text{eq}}$  its equilibrium value, and  $\tau$  the characteristic time for the reorganization process.<sup>20</sup> The quality of the fit (shown for pH 6 in Figure 1) is good, although small deviations are observed, indicating that the relaxation process is not purely monoexponential. However, the value of  $\tau$  gives a good idea of the characteristic time scale of the surface tension variation.

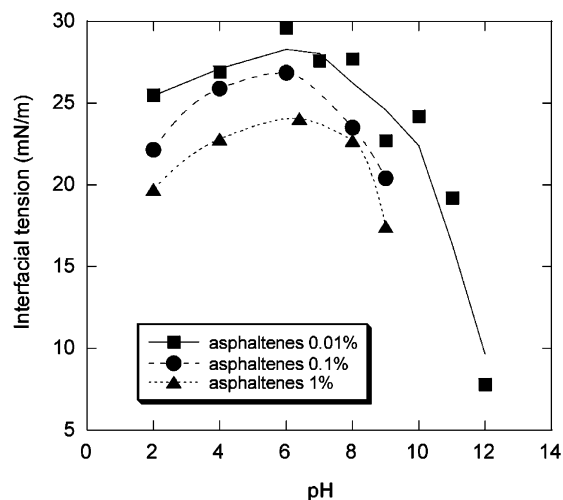
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**Figure 2.** Characteristic time ( $\tau$ ) of the oil–water interfacial tension variation versus pH.

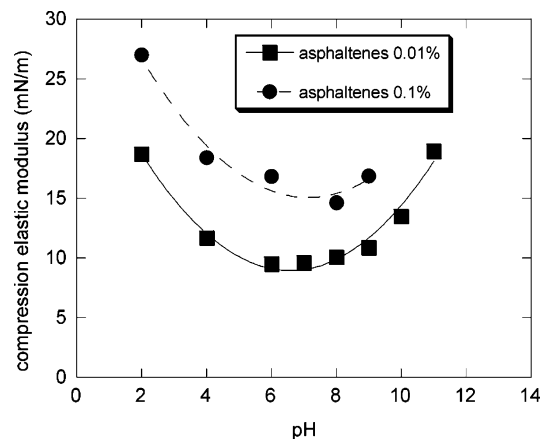


**Figure 3.** Oil–water interfacial tension measured after 5400 s (1 h, 30 min) versus pH for three different asphaltene concentrations in toluene.

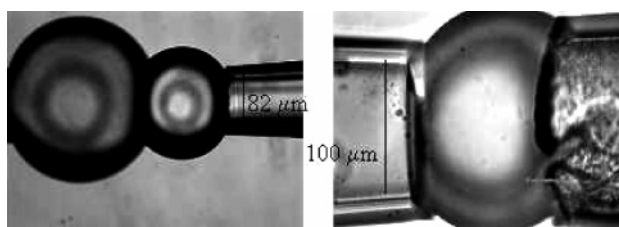
Figure 2 shows the pH variation of  $\tau$  (as deduced from fits with eq 1). The variations observed are large enough to be above experimental uncertainties (typically 5%).

The influence of pH on the oil–water interfacial tension measured after 5400 s (1 h, 30 min) is shown for three asphaltene concentrations (0.01%, 0.1%, and 1%) in Figure 3.

Because asphaltenes are amphoteric materials, the charge acquired at low pH (cationic) and high pH (anionic) increases their hydrophilic behavior and makes them more surface-active. They accumulate more easily at the interface when they are charged. Figure 3 shows that the interfacial tension  $\gamma$  decreases when the asphaltene concentration increases, as expected. The effect of asphaltene concentration seems more important when the functional groups are ionized, i.e., at very low or high pH. When the asphaltene concentration is high, the interfacial tension decreases rapidly; above a certain pH, it becomes impossible to make measurements because the drop detaches from the capillary immediately after formation. For 0.1% and 1% asphaltenes, we were limited to pH values below 10. Let us note that we have sometimes observed a transfer of asphalt-



**Figure 4.** Compression elastic modulus for oil–water interfaces after 5400 s (1 h, 30 min) and two asphaltene solutions in toluene versus water pH.



**Figure 5.** Two aqueous drops held by the tip of a micropipette immersed in an asphaltene solution in toluene. In panel a, the two drops do not coalesce; panel b shows two drops that have fused.

enes toward the water phase, in particular at high pH. All the results presented have been obtained after equilibration of the different phases together.

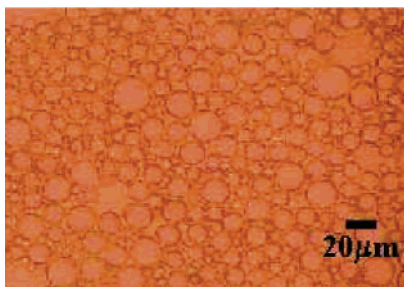
The variation of the elastic surface compression modulus, as a function of pH, is shown in Figure 4. The modulus is minimum at neutral pH and increases when the pH decreases or increases. These results show that the interface is more rigid and should be more stable at high or low pH.

Several micropipette experiments have been performed, in which two droplets are being pushed against each other.<sup>21</sup> The cell was filled with toluene containing 0.5% asphaltene. Micropipettes were filled with aqueous solutions of different pH. Each experiment was repeated 10 times. Droplets were kept in contact for 1 min, during which we watched for an eventual coalescence. Figure 5a (left) shows a case where coalescence is not observed, whereas the two droplets have fused in Figure 5b (right).

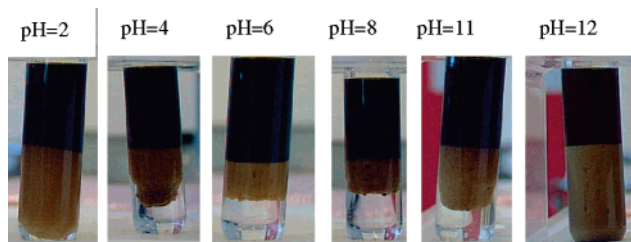
Qualitative results for different pH and asphaltene concentrations are gathered in Table 2. These results

**Table 2. Influence of pH and Asphaltene Concentration on Coalescence of Two Water Droplets Immersed in Asphaltene Solutions in Toluene**

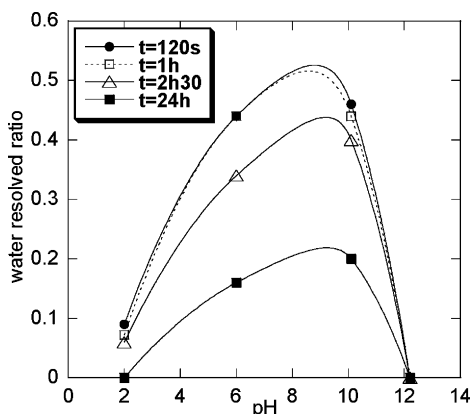
asphaltene concentration in toluene (%)	pH	coalescence
0.01	2	immediate
0.01	12.5	rapid
0.1	2	rapid
0.5	2	occurs within 2 min
0.5	6	rapid
0.5	12.5	not observed within 2 min
1	2	solution too dark



**Figure 6.** Microscope image of a water-in-oil emulsion (1% asphaltenes, pH 2).



**Figure 7.** Pictures of the emulsions after centrifugation (4000 rpm, for 30 min); the pH varies from 2 to 10, and the asphaltene concentration is 0.1 wt %.

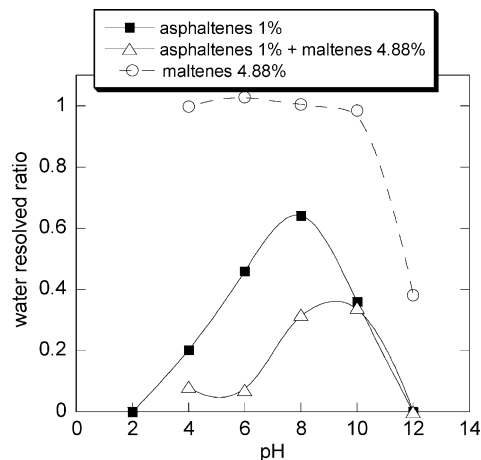


**Figure 8.** Stability of water-in-oil emulsions, as a function of the initial pH of water, expressed as the ratio of water resolved after centrifugation at different aging times.

are consistent with interfacial tension and elastic modulus results. At high or low pH, we observe a stronger affinity of the asphaltenes for the interface: the interfacial tension is smaller, the modulus higher, and coalescence is hindered. At a given pH, the stability against coalescence is stronger when the asphaltene concentration is higher, and the interfacial film is more rigid.

**2. Stability of Model Asphaltenes Oil–Water Emulsions.** Emulsions have been prepared at different pHs and centrifuged to study their stability. For all pHs, water-in-oil emulsions were obtained. A typical microscope image of an emulsion is shown in Figure 6. Pictures of the tubes after centrifugation are shown in Figure 7 for different pH values.

The emulsion stability is quantified by the percentage of water resolved after centrifugation. The results are plotted in Figure 8 and clearly show that coalescence is more important at intermediate pH and that the emulsion is much more stable in the high- or low-pH range.



**Figure 9.** Stability of three different emulsions, as a function of the initial pH of water, expressed as the ratio of water resolved after centrifugation.

Influence of aging of the emulsion has been studied. For all emulsions, we observe an increase in emulsion stability with time. Note that this is typical of petroleum emulsion, whereas classical surfactant emulsions become less stable when they age. This behavior is probably linked to the very long reorganization time of asphaltene molecules at the interface. These results are also in agreement with an increase of the elastic modulus with time, as measured with the dynamic drop tensiometer.

**3. Influence of Addition of Maltenes.** The addition of maltenes (crude oil without asphaltenes) to the asphaltene solutions in toluene has been studied to investigate the influence on emulsion stability of the smaller surface-active molecules present in maltenes, such as natural naphthenic acids.

Emulsions were prepared with water at different pHs and toluene containing 1% asphaltenes and 4.88% maltenes. These emulsions were also centrifuged to study their stability. The maltenes/asphaltenes ratio in these model emulsions was chosen to be the same than in the original crude (83%/17%). In this case, as well as for asphaltenes emulsions, only water-in-oil emulsions were obtained.

The stability of the emulsion is quantified by the percentage of water resolved after centrifugation. The stability results obtained at  $t = 120$  s are presented in Figure 9. The emulsion stability is increased, with respect to that of asphaltenes emulsions. Therefore, there is a stabilizing interaction between asphaltenes and smaller amphiphilic molecules found in maltenes, different from resins, because it is known that resins render the asphaltenes less interfacially active and reduce emulsion stability.<sup>22</sup> We have observed that the stability of these emulsions increases with time, as for asphaltenes emulsions.

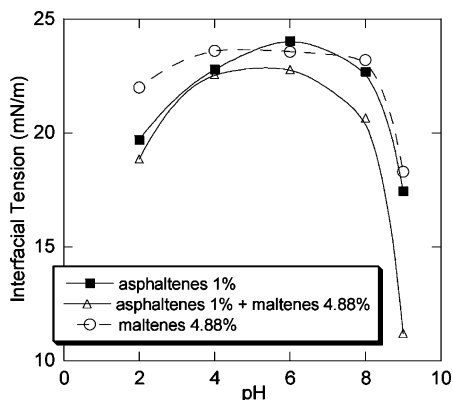
The emulsions made with maltenes alone are not very stable, excepted at pH 12, where enough carboxylic groups are ionized. In this case, no increase of the emulsion stability is observed with time.

The influence of pH on the oil–water interfacial tension, measured after 1 h, 30 min, is shown in Figure

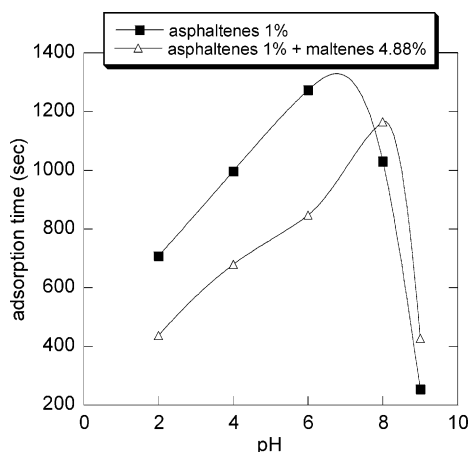
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**Figure 10.** Oil–water interfacial tension measured, after 5400 s (1 h, 30 min), versus pH for three different oils.



**Figure 11.** Characteristic time ( $\tau$ ) of the oil–water interfacial tension variation versus pH for different oils.

10 for the three toluene solutions studied previously (1% asphaltenes, 4.88% maltenes, 1% asphaltenes + 4.88% maltenes).

The behavior of the mixture of asphaltenes and maltenes is similar to the behavior of the asphaltenes: the charges acquired at low pH (cationic) and high pH (anionic) increase the hydrophilic behavior of the surface-active molecules and their surface concentration increases. The phenomenon is more marked at high pH for the mixture. At this pH, there is a coadsorption of the asphaltenes and of the surface-active molecules coming from the maltenes; these molecules carry primarily carboxylic functional groups, which are ionized

at high pH. This result is consistent with the stability of emulsions. Note that this effect is less visible at intermediate pH, whereas the stability of the emulsions is different. Therefore, interfacial tension data cannot fully explain the different behaviors observed.

Figure 11 shows the variation of  $\tau$  (as deduced from fits with eq 1) with pH for the asphaltenes and for the mixed asphaltenes/maltenes system.

In all cases, the surface-active molecules accumulate more rapidly at the interface when they are charged. In the case of the mixture of asphaltenes and maltenes, the characteristic time  $\tau$  for the reorganization process is smaller than that for asphaltenes only. This confirms the existence of interactions between asphaltenes and maltenes, which facilitate the arrangement of the molecules at the interface.

Although maltenes alone do not stabilize oil-in-water emulsions at these concentrations, when mixed with asphaltenes, they do enhance emulsion stability.

## Conclusions

Our results show that the pH has a strong influence on the interfacial properties of asphaltenes at the oil/water interface. At high or low pH, the functional groups carried by asphaltene molecules become charged (at least partly), increasing their hydrophilic behavior and enhancing their surface activity. The interfacial tension decreases and the elastic modulus increases. Asphaltene molecules accumulate more easily at the interface when they are charged. This effect is stronger in the high-pH range, because asphaltenes contain more acidic groups than basic groups. At high pH, we observe very little coalescence of water droplets and the emulsion is stable. When maltenes (crude oil without asphaltenes) are added to the asphaltenes, the stability of the emulsions is larger. There is an interaction between asphaltenes and maltenes that facilitates molecular arrangement at the interface. The results obtained at the microscopic level (interfacial tension, viscoelastic modulus, micro-pipette experiments) and the results obtained at the macroscopic level on model emulsions are well-correlated.

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