Supporting Information for

Surface and Interface Characterization of Asphaltenic Fractions Obtained with Different Alkanes: A study by Atomic Force Microscopy and Pendant Drop Tensiometry

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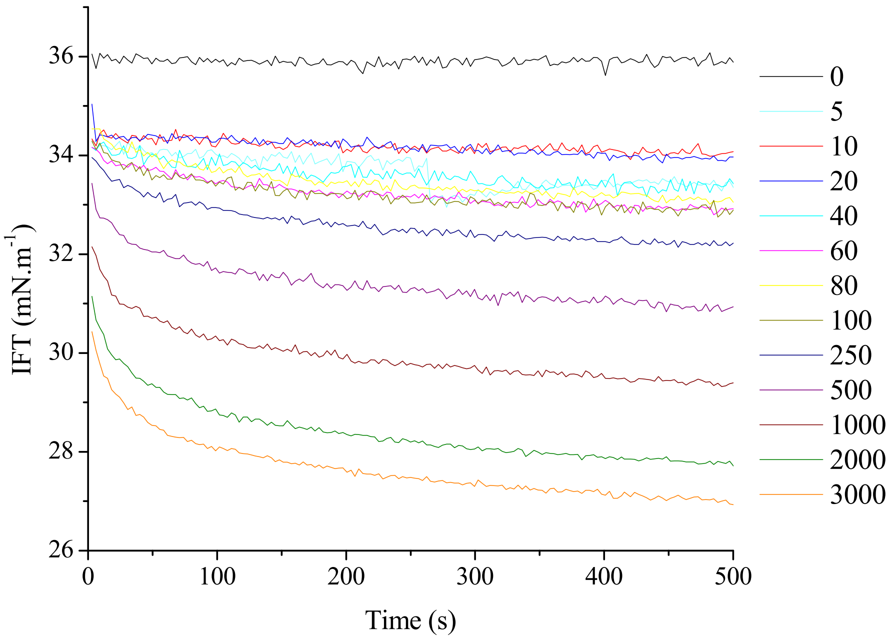

Figure S1. Interfacial tension (IFT) by time for AH concentrations from 0 to 3000 mg.L^{-1}.

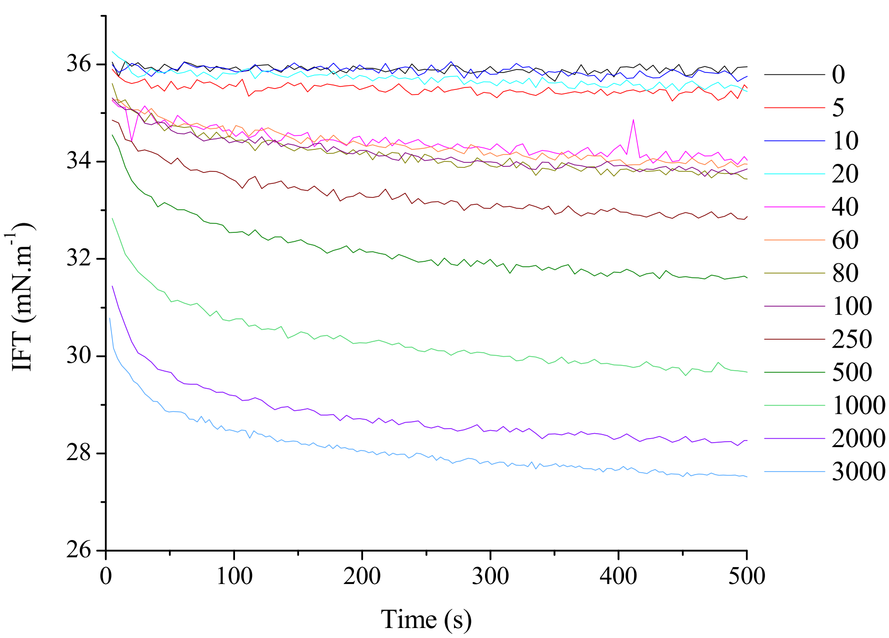

Figure S2. Interfacial tension (IFT) by time for AP concentrations from 0 to 3000 mg.L^{-1}.

Study of initial parameters for interfacial characterization

1. Experimental Section

1.1. Interfacial characterization

Static measurements

To perform tests on the pending drop tensiometer, some initial care needs to be taken to ensure the best results and the absence of errors during the tests. Regarding the volume of the drop to be used for each system under study, one of the main concerns is with the possible detachment of gout, especially in the trials that require long execution times. These detachments are affected by the volume and area of the drop used, by the temperature conditions and addition of surfactants to the system. In order to select the ideal drop volume and area for each system, specific analyzes are performed to avoid dropping and noise generation in the systems being studied.

Initially, the maximum volume provided by the capillary used for the system under study was verified. The maximum volume of the drop was defined as the largest volume of the drop before it was peeled off. Interfacial tension measurements with aging time of 30 min were performed for drops with maximum defined volume and 80%; 60%; 40%, 30% and 25% of this volume. The choice is made through the volume that does not have a sharp size to the point of detachment, but that presents a low noise in the measures of interfacial tension.

Once the initial parameter studies were carried out, static tests were performed to obtain interfacial tension versus time curves at different concentrations of AH and AP fractions (from 0 to 3000 $mg.L^{-1}$) in toluene. The purpose of these tests is to evaluate the influence of fractions on interfacial tension.

Dilatational rheological experiments

The total dilatation modulus measurements are influenced by some experimental parameters including the volume of the formed droplet, the amplitude and the oscillation frequency[1]. Therefore, it is necessary to study these parameters in advance.

According to Covis et al.[2], the oscillation amplitude directly influences the values of the modules. Then the area amplitude is selected in a region where there is no variation of the values of the dilatational models, presenting a linear behavior. To select the ideal amplitude, oscillatory dynamic tests were performed with some amplitude values (10; 8; 7; 6; 5; 4 and 2%) and then the total dilatation modulus were measured.

According to Yarranton et al.[3], the drop oscillation frequency also directly influences the dilatation modulus measurements (total modulus and its elastic and viscous components). High oscillation frequencies are more indicated to obtain more precise values of the modules, because at low frequencies the surfactants would have enough time to rearrange in the newly created interfacial film due to the oscillation of the drop. On the other hand, for high frequencies some systems can cause negative values of dilatational modules generating results that do not correspond to the reality of the system studied. The influence of different frequencies on the total dilatation modules was evaluated. To this, measurements of the total dilatational module were performed through oscillatory dynamic tests with frequency values of: 0.1; 0.05; 0.03 and 0.02Hz.

After determination of the initial parameters, the dilatation modules were obtained by forming a drop which remained at rest for 30 min and then the oscillation procedure was performed and repeated every 30 min during the experiment time. Four oscillations were conducted in a total time of 2 h for each experiment.

2. Results and discussion

2.1. Interfacial characterization

All measurements of the interfacial properties were determined using the pendant drop tensiometry. In this work, the interfacial properties were obtained through two different methodologies: the static tests where the interfacial tension measurements are obtained as a function of time and the dynamic oscillatory tests where the total viscoelastic modulus and its elastic and viscous components are obtained as a function of interfacial film aging time. The properties were determined at room temperature.

Static experiments

To determine the ideal parameters for conduction of static experiments both fractions AH and AP with concentrations of 1000 $mg.L^{-1}$ were used.

The maximum volume is the highest volume obtained before dropping, for the studied system the area and maximum volume were 49.5 mm^2 and 33.9 mm^3, respectively. Once the maximum volume was reached, static tests of 30 min were performed, where the area is kept constant to observe the behavior of the Interfacial tension (IFT) over time. Tests were performed with the maximum area and another five fractions corresponding to 80, 60, 40, 30 and 25% of the maximum area. Results indicate a small variation in interfacial tension with reduction of interfacial areas. This may be related to experimental error caused by the reduction of this area. Figure S1 shows the stress curves by time of all areas studied.

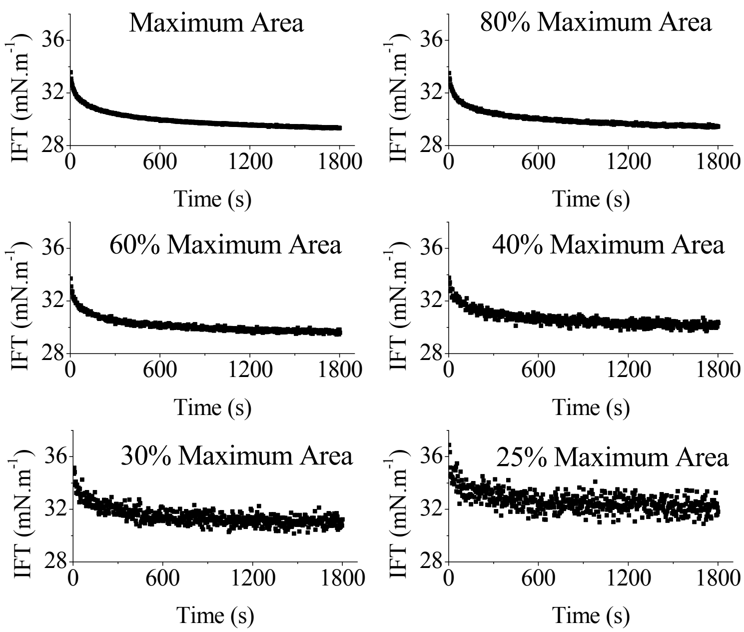

Figure S3. Behavior of the interfacial tension versus time for fractions of the interfacial area of the 1000 mg.L^{-1} sample of AH fraction in toluene at a temperature of 25º C.

It is observed that very small areas, as those corresponding to fractions of 30 and 25%, present larger spreads of the data in the IFT curve, increasing the variation of voltage values over time. Very small area should be avoided to reduce experimental errors. As indicated in previous studies by our group[4], usually the ideal volume for testing varies between 60% and 80% of the maximum volume, since in this region usually a low estimation error is obtained and enables oscillations in the drop area.

From the volume study, the area and volume of 39.6 mm^2 and 24.8 mm^3, respectively, were selected. The maximum volume was not used in order to avoid drop detachment during oscillations. Small areas were not used as well to reduce experimental errors. The same interfacial area was used for the AP fraction and tensile tests in fractions of 100, 80, 60, 40, 30 and 25% were repeated for this fraction, with similar results being found. Thus, all tests performed in this work used the same interfacial area for both asphaltenic fractions: 39.6 mm^2.

Dilatational rheological experiments

After the determination of the ideal interfacial area, the ideal oscillation amplitude value should be defined. This parameter intends to evaluate the region where the viscoelastic properties remain constant with the oscillation amplitude variation. Figure S2 shows the total dilatational modulus values as a function of the different oscillation amplitude fractions of sample AH. The tests were performed with aging time of 30 minutes and frequency of 0.1 Hz at the concentration of 1000 mg.L^{-1} of asphaltenic fraction in toluene at 25º C.

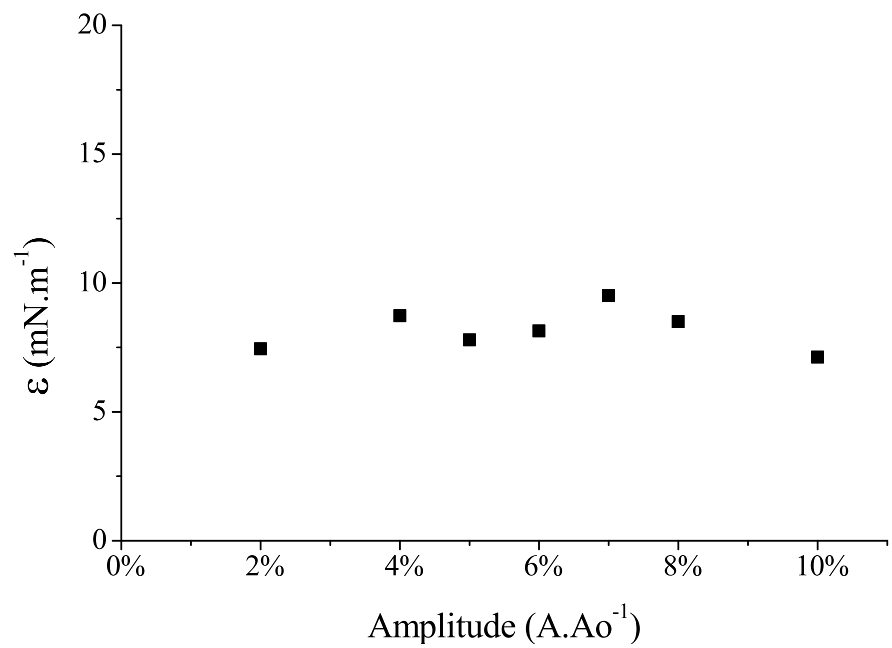

Figure S4. Total dilatational modulus values as a function of oscillation amplitude fractions.

Figure S2 suggests that oscillation amplitude between 4% and 8% did not lead to pronounced variations in total dilatational modulus values. Similar results were observed for AP fractions. According to Covis et al.[2] this property should not be dependent on oscillation amplitude values and amplitude is more favorable to be used when the total dilatational modulus remains constant. Thus, the value of 6% of the interfacial area was chosen, taking into account tests with this amplitude in previous works[4–6].

Based on previous literature studies and the group's experience with oil studies, the frequency of 0.1 Hz was initially adopted for dilatational rheological tests. Four concentrations were selected for the tests, being 10, 250, 1000 and 3000 mg.L^{-1}. Table S1 shows the values of total dilatational modules and their components for this frequency in 30 min.

Table S1. Variation of the total dilatation modules and their elastic and viscous components for the frequency of 0.1 Hz in the oscillatory tests with the fractions AH and AP.

Concentration (mg L^{-1})	AH				AP			
	E	E'	E"	IFT (mN m^{-1})	E	E'	E"	IFT (mN m^{-1})
3000	8.9	6.4	6.4	26.6	9.0	7.5	4.8	26.9
1000	7.3	3.2	3.2	28.7	7.2	7.2	0.4	29.0
250	7.0	-4.9	-4.9	31.6	6.7	4.7	-4.8	32.2
10	2.7	-0.9	-0.9	33.7	8.5	-3.4	-7.8	35.4

From Table S1 it is possible to observe disordered variations in the modules at different concentrations. In addition, negative values of the viscous modules suggest an incompatibility of this frequency (0.1 Hz) with tests in these systems, especially at low concentrations of asphaltenic fractions. Consequently, it was necessary to evaluate oscillations over longer periods of time. Table S2 shows the values of total dilatation modulus and its components for the concentration of 250 mg.L^{-1} of asphaltenic fraction in toluene for different frequencies of oscillation in 30 min. This concentration was selected because the negative values of the modules occur mainly at low concentrations.

Table S2. Total dilatational modules and their components for the concentration of 250 mg L^{-1} of fractions AH and AP in toluene in the frequencies of 0.1; 0.05; 0.03 and 0.02 Hz.

Frequencies (Hz)	AH				AP			
	E	E'	E"	IFT (mN m^{-1})	E	E'	E"	IFT (mN m^{-1})
0.1	7.0	-4.9	-4.9	31.6	6.7	4.7	-4.8	32.2
0.05	7.2	6.8	-2.3	31.8	5.7	5.6	-1.0	32.6
0.03	6.8	6.7	-1.0	31.7	6.0	5.8	-1.6	32.5
0.02	6.7	6.7	0.1	31.6	5.5	5.5	0.4	32.4

As observed in Table S2, the increase in the oscillation period allowed a better reorganization of asphaltenic fractions at the interface during adsorption and desorption of these surfactants during the oscillation, resulting in better values of interfacial modules. Based on these results, oscillation frequencies less than 0.02 Hz are recommended for this system.

References

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