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Effect of Fumed Silica Particles on Water-in-Crude Oil Emulsion: Emulsion Stability, Interfacial Properties, and Contribution of Crude Oil Fractions

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ABSTRACT: The effect of fumed silica particles on water-in-crude oil emulsions was analyzed by stability tests, interfacial tension measurements, dilatational rheology of the interface, rheology of the particles dispersions, and Cryo-SEM analysis. The crude oil studied is a paraffinic one and was separated by distillation in three fractions containing mainly saturate, aromatic, and resin compounds. The stability of emulsions formed from these oil fractions was also studied with or without silica particles. Experiments without particles performed with oil or its fractions underline that the most stable emulsion is formed with the heavy fraction which corresponds to the highest elastic modulus of the interface. Different mechanisms of emulsion stability in the presence of particles were discussed according to the particle wettability. Whatever the oil phase composition, it is obviously noticed that hydrophilic particles destabilize water-in-oil emulsions, whereas hydrophobic particles stabilize them. For hydrophilic particles, the "solid-like" behavior of the interfacial film revealed by the high value of the elastic modulus, IFT measurements and the observations by Cryo-SEM, supports the presence of A200 particles at the oil/water interface. The highest stability of the emulsions in the presence of hydrophobic particles results from the addition of several effects: the tendency to form a structured organization in the oil continuous phase and the influence of the attached particles at the interface. This study underlined that no direct relation is observed between the stability of water-in-oil petroleum emulsions and the interfacial tension measurements particularly in the presence of particles. Otherwise the viscoelastic measurements by the dilatational drop technique corroborate the relation between a high emulsion stability and a high viscoelastic modulus in the case of emulsions without particles. In the presence of particles, the elastic behavior of the interface is less affected by the hydrophobic than by the hydrophilic particles.

1. INTRODUCTION

As crude oil is often extracted with water, the formation of undesired water-in-oil emulsions is favored by high shear conditions encountered at the production wellhead. Consequently problems in production and processing of crude oil increase drastically.

The high stability of these petroleum emulsions is generally attributed to the presence of naturally occurring surface-active molecules, such as resins and asphaltenes, respectively classified as the low and high molecular weight polar fraction of crude oil.[1] Asphaltenes are the most aromatic components of crude oils. In relation with the numerous chemical species that compose asphaltenes class, advanced techniques were recently used to determine their chemical composition and associated structure.[2,3] Asphaltenes have the tendency to self-associate from nanoaggregates up to larger scale clusters in solution.[4,5] Moreover, they are able to form a structured film that surrounds water droplets.[6−8] It has been observed that the kinetics of reorganization of such molecules at the interface are quite slow i.e. some hours depending on the crude oil origin and solvent conditions.[9,10] Some studies underlined that the mechanism of formation of the interfacial film from asphaltenes is not purely controlled by a molecular diffusion process from the bulk as it is observed for small surfactant molecules.[11,12] These surface-active molecules or aggregates with high molecular weight form a mechanical barrier that prevents droplets from coalescence. Resins are often presented as a solvent of asphaltenes components, and most of the studies focused on the behavior of the asphaltenes/resins mixture and not on resins alone.[13]

Rheological studies on water−oil interfaces have been performed with the aim to predict the stability of these petroleum emulsions. Whatever the techniques used, Langmuir trough,[14,15] oscillatory drop technique,[5,16] or shear rheology,[17−19] the behavior of the interfacial film may be characterized as "solid-like" according to the magnitude of the elastic part in the viscoelastic modulus.

Organic or inorganic small solids are also known to stabilize emulsions[20,21] and specifically water-in-oil petroleum emulsions[22,23] in the case of particles such as waxes and silica. Among the different parameters influencing the emulsion stability in the presence of particles, the wettability and the size of the particles have been extensively studied. Thus, hydrophilic particles tend to stabilize oil-in-water emulsions, whereas hydrophobic particles tend to stabilize water-in-oil emulsions.[24−27] The size of solids able to stabilize emulsions are between a few nanometers and several micrometers.[28−30] The mechanism of stabilization by the particles seems to be different, depending on the size of the particles. According to Sztukowski et al., for the smallest particles, less than 500 nm, solids are attached on the droplets interface, whereas particles with a size larger than 1 μm act as bridges between droplets.[31] Furthermore, the stabilization due to the presence of a particle network in the bulk has been noticed by several authors.[32−34]

The studies dealing with silica particles/model oil interactions are extensively described,[35,36] but the mechanism of interactions

with crude oil is more difficult to analyze, mainly due to the complex composition of crude oils. Moreover, most of the studies focused on the interactions between particles and surface-active components extracted from crude oil as asphaltenes and resins.[37]

In the present study, we focused on the analysis of the stability of petroleum emulsion in the presence of fumed silica particles having different wettabilities in relation with the interfacial film properties. One of the silicas employed is highly hydrophilic, one is hydrophobic, and one is expected to possess intermediate hydrophobicity. Experiments have been performed not only with the original crude oil but also with the different fractions issued from distillation in order to determine the role of each fraction in the process of stabilization. The experimental procedure included the systematic measurement of dynamic oil–water interfacial tension and interfacial rheological measurements by the oscillating pendant drop method as well as rheological measurements of particles dispersions with a cone–plate geometry. Complementary Cryo-SEM analysis were also performed to visualize the location of the particles in the emulsions.

2. EXPERIMENTAL SECTION

2.1. Materials. Experiments were performed with a crude oil directly sampled from a French oil field. Cautions for sampling were taken in order to avoid the presence of chemicals frequently used in oil production. It is considered that the oil sample was free of surfactants chemicals added during production i.e. corrosion inhibitor, biocide, and demulsifier.

Crude oil was separated in three cuts by successive distillations at two temperatures 375 and 520 °C (final boiling point at atmospheric pressure). The heaviest cut (>520 °C) was the residue of the second distillation. The choice of the distillation temperature was made according to a previous work[7] which noticed that most of the crude oil acidic compounds are present in the intermediate cut (375–520 °C). The main characteristics as well as SARA (Saturates, Aromatics, Resins, and Asphaltenes) analysis[38] of the crude oil and the different cuts A, B, and C are given in Table 1. It is interesting to notice that the crude oil

Table 1. Analysis of Crude Oil and A, B, and C Cuts

distillation cut	crude oil	A (<375 °C)	B (375–520 °C)	C (>520 °C)
weight ratio-%w/w	100%	53%	26%	21%
density@15 °C-kg/m³	860	813	898	956
SARA-%w/w				
saturates	69.9	93.2	56.7	26.7
aromatics	22.6	6.8	35.7	46.7
resins	6.5	-	3.8	26.3
asphaltenes[a]	<1	-	-	<1

[a] n C7 precipitate.

acidity referred to the TAN (Total Acid Number) analysis[39] was not possible to determine due to its too low value (<0.1) in all cases. For verification purposes, the crude oil density @ 15 °C and the total amount of each component (Saturates, Aromatics, Resins) were recalculated from the appropriate values of each cut. The recalculated density value of 865 kg/m³ is close to the measured one of 860 kg/m³. Moreover, the total mass balance of each compound is correct with an accuracy of less than 1% w/w indicating that no significant component loss occurred during the distillation process.

Differential Scanning Calorimetry (DSC) performed on the A, B, and C cuts showed a paraffin crystallization temperature around −13 °C, 31 °C, and 45 °C, respectively. Paraffin crystallization was measured at 23 °C for the crude oil. To avoid any problem of solubility, the B and C cuts were diluted in the light A cut in the same proportion than in the crude oil (Table 1), in order to reconstitute three fractions of increasing viscosity. The light fraction (LF) is composed of A solely and contains

mainly saturated hydrocarbons. The intermediate fraction (IF) is composed of a mixture of A and B (67/33%w/w) in order to respect the B/A ratio encountered in the original crude oil. It contains saturates, aromatics, and a few resins but no asphaltenes. Finally, the heavy fraction (HF) is composed of a mixture of A and C (72/28%w/w) so that the C/A ratio in the crude oil is kept. This last fraction contains saturates, aromatics, resins, and a very small amount of asphaltenes. Density, viscosity, SARA analysis, and wax appearance temperature are given in Table 2 for the original crude oil and the three reconstituted fractions.

Table 2. Analysis of Crude Oil and Light, Intermediate, and Heavy Fractions

	crude oil	light fraction (100% A)	intermediate fraction (67%A + 33%B)	heavy fraction (72%A + 28%C)
density @30 °C-kg/m³	839	803	834	856
viscosity @30 °C-mPa·s	12.0	2.0	8.3	17.2
WAT[a]-°C	22.5	−13.4	22.6	28
SARA-%w/w				
saturates	69.9	93.2	81.2[c]	74.6[c]
aromatics	22.6	6.8	16.3[c]	18.0[c]
resins	6.5	-	1.3[c]	7.4[c]
asphaltenes[b]	<1	-	-	<1

[a] Wax appearance temperature. [b] n C7 precipitate. [c] Calculated values.

When referring to the analysis presented in Table 2, a very rough classification between oil fractions could be the following:

The LF oil mainly contains saturated hydrocarbons (low molecular weight),

the IF oil mainly contains saturated and aromatic hydrocarbons (medium molecular weight),

and the HF oil contains the heaviest molecular weight compounds, mainly saturated and aromatic hydrocarbons and a significant amount of resins.

Oils and brine (NaCl 5g/L) were stored at 30 °C, which corresponds to the reference temperature of the study. This temperature was chosen to avoid the appearance of paraffin crystals, which could disturb the analysis.[40]

The particles were fumed silica supplied by Evonik Industries AG (Rheinfelden, Germany). Three types of particles with various hydrophobicities were used: hydrophilic (Aerosil A200), hydrophobic (Aerosil R972), and intermediate (Aerosil R711). Aerosil A200 is produced by hydrolysis of chlorosilane in a combustion process and contains silanol groups. Aerosil R711 and Aerosil R972 are made more hydrophobic by the substitution of silanol (4.5–5.5%) by methacrylsilane and dimethyldichlorosilane (0.6–1.2%), respectively.[41,42] Fumed silica consist of small primary particles (diameter around 15 nm) which are fused together to furnish very stable aggregates during the combustion process. For hydrophilic particles, the contact angle is less than 90°, and particles are mainly wetted by the aqueous phase. For hydrophobic particles, the contact angle is higher than 90°, and the particles are mainly wetted by the oil phase.

Some demulsification tests were performed with a demulsifier D, a polysiloxane base surfactant with a structure of block copolymer, provided by Momentive, Switzerland.

2.2. Particle Dispersion, Emulsion Preparation, and Demulsification Tests. The particles dispersions were prepared in their most suitable solvent: brine for A200 and oil for R711 and R972. Then they were dispersed by mixing with an Ultra-Turax T25 homogenizer at 10000 rpm for 30 min. The water-in-oil emulsions (30% water/70% oil v/v) were prepared by slowly adding the water phase to the oil phase while mixing with the same homogenizer at 10000 rpm for 1 min. Then, the emulsion was mixed again at 14000 rpm for 7 min at room temperature. For all the studied emulsions, the percentage of brine was 30 vol % and the percentage of particles was 0.35 wt % of the total mass
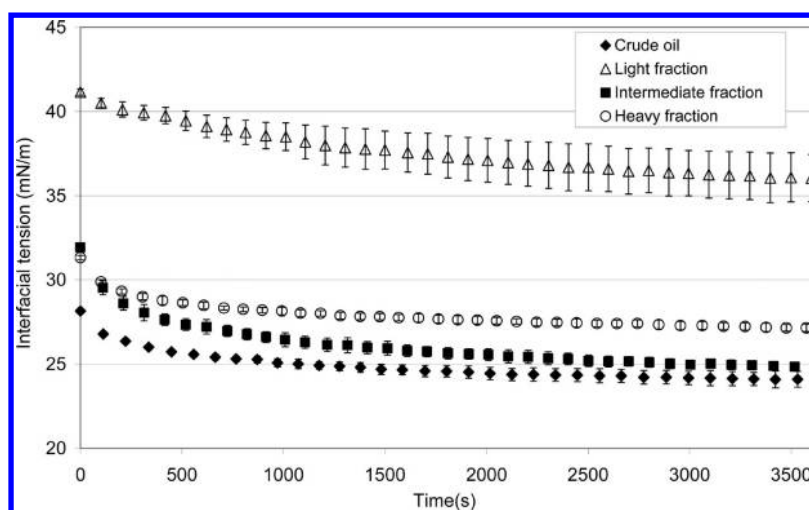
Figure 1. Interfacial tension of freshly formed droplets of crude oil or oil fractions in brine, T = 30 °C.

of emulsion (i.e. 1 wt % of A200 dispersed in brine, 0.5 wt % of R711 or R972 dispersed in oil before emulsification).

It should be noted that a reference emulsion was systematically made without particles.

Some demulsification tests were conducted by adding a fixed concentration of demulsifier D to the emulsion, with respect to the total volume of the emulsion. A mother solution of demulsifier at a concentration of 2 wt % was done in a mixture of xylene/methanol (75/25 vol.%). Then, the required volume of this demulsifier mother solution was injected with a precision Hamilton syringe in 15 mL of emulsion poured in a test tube. Finally, the tube was gently homogenized on an agitation table for one minute at 300 returns/min.

After preparation, the emulsion, with or without demulsifier, was kept at 30 °C for 24 h before being centrifuged at 6000 rpm for 30 min. The amount of separated water at the bottom of the tube was measured to determine the stability of the emulsion. Each experiment was repeated three times.

2.3. Interfacial Tension Measurements. Interfacial measurements were performed with a dynamic interfacial oscillatory drop tensiometer, Tracker, from Teclis France. The principle of the measure is to form an oil drop which is vertically maintained at the end of an inverted needle located in a transparent thermostatted cell containing the aqueous solution.[43] The drop profile is recorded in real time with a CDD digital camera. The interfacial tension is calculated from the Laplace's equation and the balance between capillarity and gravity forces. The interfacial tension between the crude oil and the aqueous phase was monitored for fresh drops for 1 h at 30 °C. The volume of each fresh drop was 20 μL in order to reach a Bond number of 0.15−0.2, which indicates that surface tension dominates gravity effects. Indeed, the bond number is calculated as Bo = $(\Delta\rho g R^2)/\gamma$, where $\Delta\rho$ is the density difference between the two phases; g is the gravitational acceleration; R is the drop radius; and γ is the interfacial tension between the immiscible phases.[44] The validity of the measurement was checked by recording the standard error on the Laplacian drop at the beginning and at the end of each experiment.

2.4. Dilatational Rheological Measurements. The surface dilatational elastic modulus or complex modulus (E^*) was measured with the same oscillatory drop tensiometer. The syringe is connected to an electromechanical system controlled by software which allows for the application of sinusoidal variations of the drop volume. The user can then fix the amplitude and the frequency of the sinusoidal profile. The software can determine both the absolute value of the complex modulus $E = |E^*|$ and the phase angle ϕ, which is the phase difference between the surface profile and the tension profile during the sinusoidal deformation. In the case of small area variation, the absolute value E can be calculated from the changes in interfacial tension $\Delta\gamma$ and the interfacial area ΔA:

$$E = A\frac{\Delta\gamma}{\Delta A}$$

In this case, the response of the interfacial tension must be sinusoidal. Dilatational elastic modulus E can also be expressed as the summation of an elastic and a viscous contribution

$$E = |E|e^{i\phi} = |E|\cos\phi + i|E|\sin\phi = E' + iE''$$

where E' is the elastic modulus, and E'' is the viscous modulus.

In order to study the viscoelastic properties in a linear regime, a surface deformation less than 10% was applied for all the measurements. A pulsation frequency of 0.1 Hz was used, and the tests were carried out at 30 °C. Due to the difficulty to perform this type of experimentation each experiment was repeated at least three times for each studied system. The reported values are presented as the average of three measurements ± the standard deviation.

2.5. Rheological Measurements. Rheological measurements of crude oil and oil fractions containing R711 and R972 particles were performed by creep tests. Measurements were carried out at 30 °C by using a AR2000 TA-Instruments (Waters) with a cone−plate geometry. The diameter of the cone was 60 mm, and the cone angle was 1°. The temperature regulation was performed with a Peltier system to maintain the sample temperature at 30 °C. According to a published procedure,[34] samples were allowed to equilibrate for 900 s. Then, shear stresses were regularly increased from 0.01 to 10 Pa, and at each step, shear strain value was measured at equilibrium i.e after a waiting time of one minute. The presence of a flow threshold, associated with a flow regime transition could be estimated by the observation of the evolution of the shear strain (ε) versus the applied shear stress (τ). When the curves present a very fast jump zone which separates two flow regimes, this transition can be associated with the existence of a yield stress. It should be observed that the slopes of these two zones are close to unity, as the theory for viscoplastic behavior predicts. A critical stress τ_c can be defined as the value of the shear stress at the transition.

2.6. Cryo-Scanning Electron Microscopy Analysis (Cryo-SEM). Cryo-SEM was performed on a Carl Zeiss SUPRA 40 SEM equipped with an OXFORD (Gatan) CT 1500 cryo system at an acceleration voltage of 15 kV. A sample of the emulsion was placed on a sample stub and was plunged into slush liquid nitrogen (−200 °C). The frozen sample was put in the cold chamber linked to the microscope (−170 °C) and then fractured with a knife. The sample was then coated with a fine layer of chromium and inserted in the observation chamber of the microscope, where the temperature was kept constant at −180 °C. Imaging was performed with the backscattered electrons detector at an acceleration voltage of 15 kV. The droplet size distribution was determined from visual observation by measuring at least 200 droplet diameters on different zones of the sample. Even if caution has been taken to point out enough droplets to statistically determine an average

droplet size, the accuracy on this value is very broad. The values presented in this study have to be considered as an order of magnitude. Energy Dispersive X-ray spectroscopy (EDX) was allowed to locate the silicon and the oxygen elements in the sample. Due to the low intensity of the signal corresponding to the silicon element, this intensity was magnified by 14 regarding the oxygen element in all the figures.

3. RESULTS

3.1. Study of Crude Oil and Fractions without Particles.

The stability of the emulsions made with crude oil and its fractions was compared to determine what molecules may contribute to emulsion stability. No free water is observed with the crude oil and the heavy fraction HF, showing their high stability. On the contrary, a total separation of oil and water is observed with the light fraction LF (highly unstable emulsion). With the intermediate fraction IF, 72% of water is released indicating that the emulsion is weakly stable. As expected, the fraction which mainly contributes to the emulsion stabilization is the heaviest fraction HF. Indeed, even if this crude oil contains very few asphaltenes, the resins present in the heavy fraction seem able to favor the formation of stable water-in-crude oil emulsions.

To highlight a difference of stability between emulsions made with the crude oil or the heavy fraction, 10 ppm of demulsifier D was added after the emulsification step.[45] The volume of separated water was 24% with the crude oil emulsion, whereas absolutely no free water was observed with HF fraction. Thus, the emulsion made with HF seems more stable than with crude oil and is much more stable than with other fractions, which supports the specific effect of resins on emulsion stability.

The pendant drop method was used to follow the interfacial tension (IFT) between the different oil phases and brine during one hour (Figure 1).

For all oils, a rapid decrease of the interfacial tension (IFT) is observed during the first minutes. Then, the IFT slowly decreases, but no plateau value is reached. This behavior has previously been observed with crude oil components. The literature suggests that after a first step of attachment to the interface, the slow evolution of the IFT is rather due to a reorganization of surface active materials at the interface than to a diffusion control process.[11,12]

After one hour, the highest value of IFT is obtained with the light fraction (36 mN/m) and the smallest one with the intermediate fraction (25 mN/m, similar to crude oil 24 mN/m). The heavy fraction presents an intermediate IFT value (27 mN/m). These IFT values measured after one hour are not directly representative of a "surface activity", which is more related to the IFT decrease. However, it is interesting to note that if the less stable emulsion formed with LF corresponds to the highest IFT, the most stable with HF is not characterized by the smallest IFT. As a matter of fact, there is not direct relation between emulsion stability and IFT, as reported in various publications.[7,21] A low IFT facilitates the formation of small droplets in the emulsion but does not ensure a high stability.

The interfacial properties of each fraction were then studied by interfacial rheological measurements. The viscoelastic modulus E versus time was measured for the different oil phases during 5 h. The final values of the elastic E' and viscous E'' moduli are strongly dependent on the type of oil (Figure 2).

It is observed that the viscoelastic modulus slowly increases even after 5 h for the crude oil, the LF and IF oils. This increase is more pronounced for the heavy fraction, and the values do not seem to stabilize after 5 h. As previously mentioned in the case of IFT measurements, this behavior seems to be more related to a molecular rearrangement in the interfacial film than to the diffusion
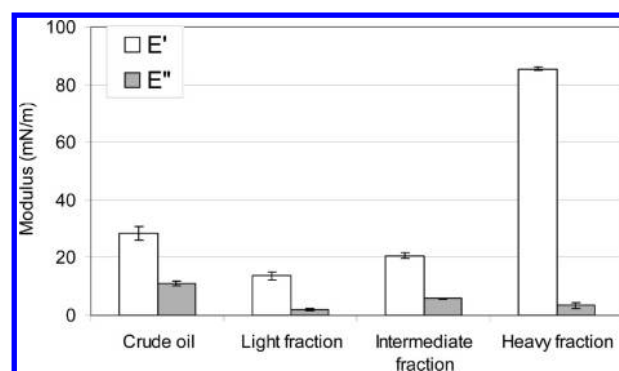

Figure 2. Elastic E' and viscous E'' moduli for interfaces between the crude oil or oil fractions/brine after 5 h. Frequency 0.1 Hz, $T = 30\ °C$.

of surfactants (i.e., resins or asphaltenes) to the interface.[12] A quite slow kinetic of reorganization over several hours has been already observed.[6,8,46]

With the heavy fraction, the high value of the elastic modulus E' (86 mN/m) indicates that the interfacial film becomes very structured over time thanks to the presence of resins. In comparison with crude oil (29 mN/m), the high value of E' observed with the heavy fraction can be related to the presence of resins and eventually to asphaltenes, even if their quantity is quite low (<1%). Indeed, numerous studies highlighted that a high elastic modulus for dispersions of asphaltenes in model oils make the interfacial film organized and rigid.[47] Consequently, the amplitude of the elastic dilatational modulus seems to be correlated with the stability of the corresponding emulsion: the higher the elastic modulus is, the more stable the emulsion is.

3.2. Study of Crude Oil with Particles.

The stability of crude oil emulsions was studied in the presence of the different types of silica particles (Table 3).

Table 3. Results Summary of Crude Oil with the Different Particles

crude oil	without particles	+ A200	+ R711	+ R972
emulsion stability[a]	0	55	0	0
IFT mN/m	24	26	29	28
elastic modulus-mN/m	29	117	10	30

[a]Expressed as the % vol of resolved water.

Even after centrifugation, crude oil emulsions without particles or in the presence of the most hydrophobic (R972) and the intermediate (R711) particles are highly stable, i.e. no free water was observed. On the contrary the hydrophilic particles (A200) destabilize the emulsion and 55% of separated free water was measured. These preliminary bottle tests showed that the initial water-in-oil emulsion was too stable to demonstrate the influence of hydrophobic particles on emulsion stabilization. Consequently, experiments were performed with demulsifier D within the objective to point out the effect of particles on the emulsion stability. Several concentrations of demulsifier were tested to establish a difference of stabilization between the three types of particles. To differentiate R711 and R972 particles, it was necessary to add up to 200 ppm of demulsifier. In this case, the percentage of resolved water was 17% in the presence of hydrophobic particles (R972), while no separation was observed with intermediate hydrophobic particles (R711). These results indicate that particles with an intermediate hydrophobicity have a more stabilizing effect than totally hydrophobic particles.
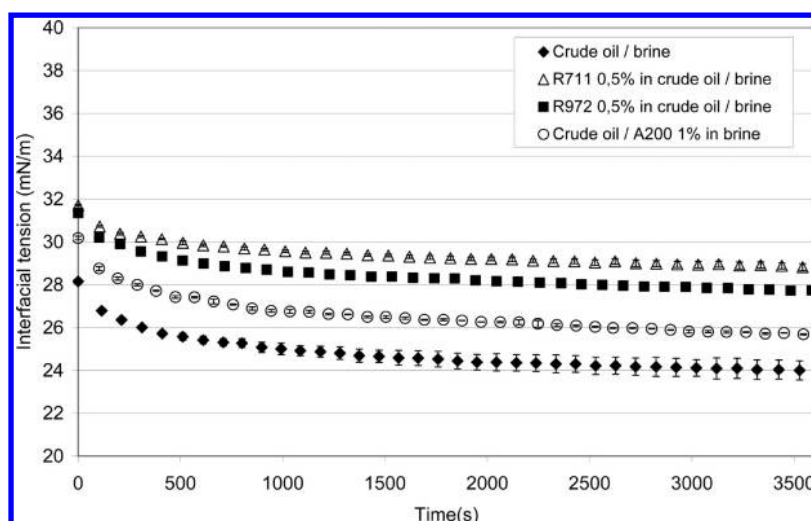
Figure 3. Interfacial tension of freshly formed droplets of crude oil in brine, with or without particles, $T = 30$ °C.
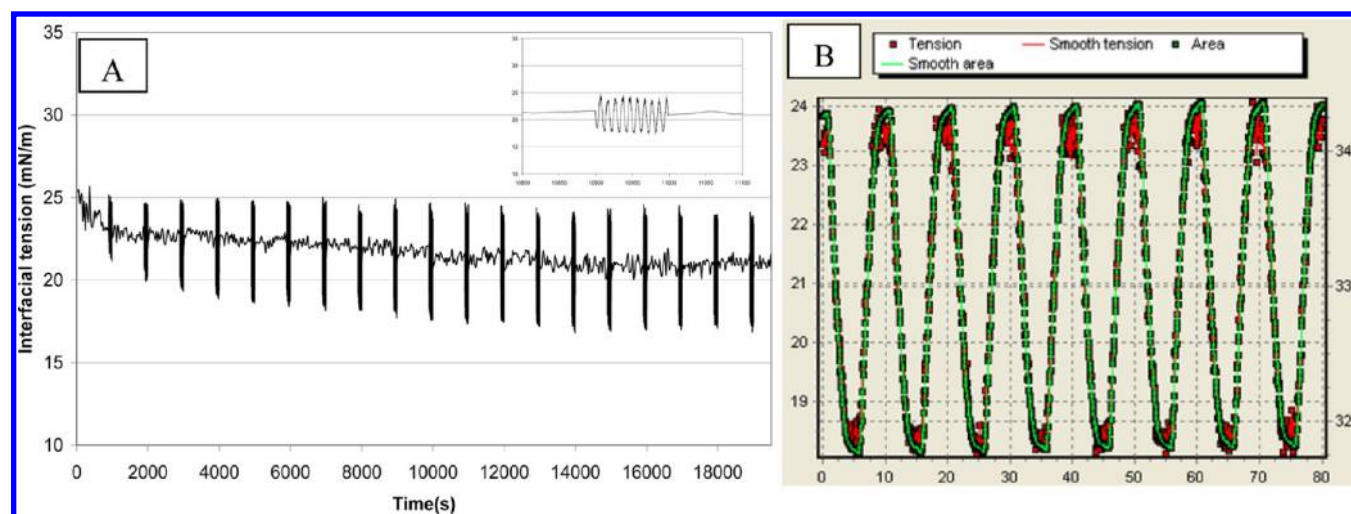

Figure 4. A: Interfacial tension oscillations every 15 min for the interface A200 in brine/crude oil: B: Sinusoidal response of the IFT during the application of a sinusoidal variation of the drop area.

The pendant drop method was used to follow the interfacial tension between the crude oil and brine in the presence of particles during one hour (Figure 3).

IFT measurements after one hour show higher values in the presence of particles mainly with intermediate and hydrophobic particles (24 mN/m up to 29 mN/m).

Concerning fumed silica particles, Hannisdal et al. showed that contact angles of hydrophilic and hydrophobic particles increase after contact with resins and asphaltenes, especially with hydrophilic particles, proving that active compounds of the crude oil are able to adsorb on the particles surface.[37] In the case of the hydrophilic particles dispersed in the water phase, crude oil surfactants and particles can only interact at the oil−water interface.

Whitby et al. reported similar experiments of pendant drop with hydrophilic colloidal particles dispersed in the water droplet in contact with a surfactant solubilized in hexane.[48] After contact with surfactants that occurred only at the interface, particles were made more hydrophobic due to a wettability change by adsorption. The attachment of particles at the liquid−liquid interface was then enhanced, consequently inducing some surfactants displacement from the interface to the oil phase and an increase of the IFT. Competition at the oil/water interface was also underlined

by Pichot et al. with fumed silica particles A200 in the presence of surfactants. The IFT variation depends on surfactant's type and concentration.[36]

In the present study, the slight IFT increase in the case of the hydrophilic particles A200 is assumed to be due to interactions at the interface between particles and active compounds of the crude oil.

The IFT increase is slightly higher with hydrophobic than with hydrophilic particles. R711 and R972 particles are first dispersed in crude oil before emulsion formation. The particles have therefore a previous contact with the crude oil surfactants which could induce the adsorption with time of surface active oil components on particles, prior to the formation of the interface.

The pendant drop method has already been used to determine the viscoelasticity of the interface in the presence of particle dispersions in model oil or in aqueous phase.[35,48,49] In this study, the validity of this technique for crude oil/brine interface has been checked in the presence of particles. We have previously verified that the viscosities of particles dispersions were not too high, so that the calculation of the viscoelastic modulus may be correctly performed.[50]

To measure the viscoelastic properties of the interface, sinusoidal variations of the drop area were imposed. The responses of the interfacial tension have to be sinusoidal to supply valid results. In this purpose, we recorded the oscillations every 15 min during 5 h. Figure 4A gives an example of records. Furthermore, the oscillations of the interfacial tension and of the drop area were superimposed (Figure 4B), the delay between the two curves corresponding to the phase angle ϕ.

The oscillations of the interfacial tension are effectively sinusoids at the same frequency as the drop area variation. The determination of the viscoelastic properties is then possible and valid in the presence of fumed silica particles dispersed in crude oil or brine.

The complex viscoelastic modulus E for the crude oil/brine interface was measured as a function of time with the different particles, and the calculated elastic modulus E' are compared in Figure 5.
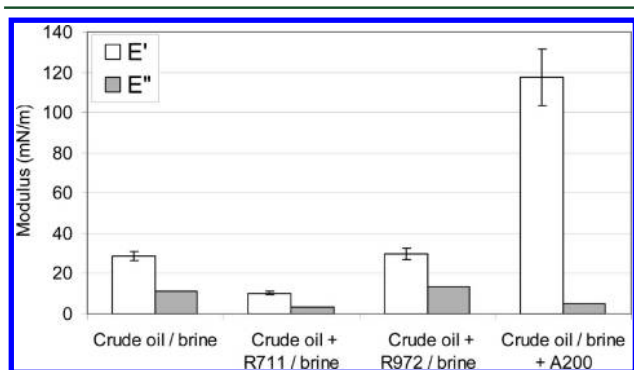

Figure 5. Elastic E' and viscous E'' moduli for interface between crude oil and brine with or without particles after 5 h. Frequency 0.1 Hz, $T = 30$ °C.

The addition of particles having different wetting properties modifies the elastic moduli E' according to their interfacial activity. The most hydrophilic A200 particles induce higher E' value (117 mN/m) than crude oil alone (29 mN/m). R972 particles do not change the moduli E' (30m/Nm), while intermediate wetting R711 particles induce a decrease of modulus E' (10 mN/m). In addition, the values of viscous modulus E'' are always much lower than the elastic part E', for all types of particles. The high value of E' compared to E'' confirms the "solid-like" properties of the crude oil/water interface i.e. a large amount of energy will be required for its deformation.

The highest value of E' (117 mN/m) and the lowest value of E'' (5 mN/m) are observed in the presence of hydrophilic particles A200 which induce a more easy emulsion destabilization than other particles. These observations may appear in contradiction with our previous observations on the oil fractions and with the behavior of asphaltenes which induce a structured film at liquid—liquid interfaces but are well-known to stabilize emulsions.[7,47]

But, if we consider, as previously suggested from IFT measurements, that some A200 particles are localized at the interface after contact with crude oil surfactants through the interface, it is reasonable to assume that these attached particles could participate in the interface organization, which is evidenced by an increase of the elastic dilatational modulus. Similar observations were performed with simple surfactants in model oil after contact with hydrophilic colloidal particles dispersed in water.[51] Of course, the presence of hydrophilic A200 particles at the interface does not automatically imply the formation of a stable emulsion. Indeed, before contact with the crude oil, A200 particles are mainly hydrophilic. After contact through the interface with the polar compounds of oil, their contact angle should increase but not sufficiently. Thus, the hydrophilic particles localized at the interface can destabilize the emulsion, probably because of their still low contact angle even in the presence of resins.[37]

Compared to crude oil, the modulus E' is nearly constant with R972 particles and decreases with R711 particles. These results are consistent with IFT measurements previously discussed.

To analyze the complex role of particles in the process of emulsion stabilization, the rheological properties of the dispersions of hydrophobic particles in crude oil were measured. Evolutions of the shear strain as a function of the shear stress are plotted in Figure 6A for the dispersions with 1% R711 and R972 particles and in Figure 6B for the dispersions with 0.1, 0.5, and 1% R972 particles.

The crude oil shows a Newtonian flow behavior with a viscosity of 12 mPa·s. This type of graphical representation of the creep experiments results, i.e. shear strain versus shear stress, may be used to identify the existence of a yield stress through the jump in the curve.[34] The intensity of the jump depends on particles concentration. In the presence of 1% particles, the dispersion of R972 particles shows a higher yield stress (around 0.1 Pa) than R711 particles (around 0.08 Pa), but both present low values. The presence of yield stresses has already been described for silica particles dispersions. With the same R711 particles dispersed in paraffin oil, Drelich et al. noticed yield stresses for particles concentrations varying between 0.4% and 2.4%.[34]

Moreover, experiments were performed with 0.1% and 0.5% of R972 particles dispersed in the crude oil phase. Shear strain measurements with 0.5% of R972 indicated also a quite rapid jump at a shear stress value around 0.08 Pa. The dispersion with
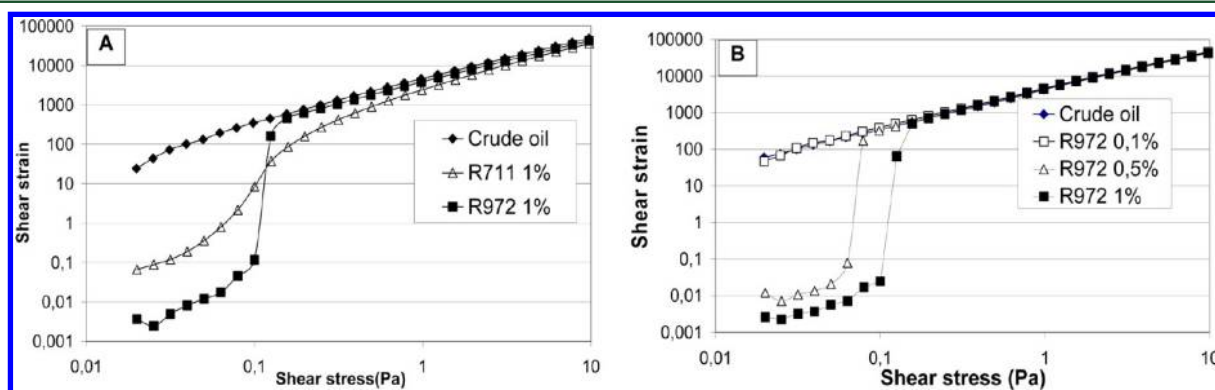

Figure 6. Stress—strain curves of crude oil with or without R711 or R972 particles, $T = 30$ °C.

0.1% particles presented the same Newtonian flow behavior than the crude oil alone.

These rheological measurements are in agreement with previous literature observations showing that these hydrophobic silica particles have a tendency to form an organized structure in an organic solvent with the formation of a gel—type solution.[52] Moreover, the presence of particles slightly increases the viscosity of crude oil. The viscosities of the dispersions with 1% R711 and R972 are respectively 17 mPa·s and 14 mPa·s. For emulsion stability purposes, the viscosity and the organization of the continuous phase will reinforce the stability by limiting the contact between droplets. In this way, as petroleum emulsions are water-in-oil emulsions, we focused the rheological part on the behavior of the oil phase containing hydrophobic particles.

3.3. Study of Oil Fractions with Particles.
Tables 4, 5, and 6 summarize all the results concerning the stability of water-in-oil

Table 4. Results Summary of Light Fraction LF with the Different Particles

light fraction	without particles	+ A200	+ R711	+ R972
emulsion stability[a]	100	100	65	<5
IFT mN/m	36	37	39	39
elastic modulus- mN/m	14	83	14	9

[a]Expressed as the % vol of resolved water.

Table 5. Results Summary of Intermediate Fraction IF with the Different Particles

intermediate fraction	without particles	+ A200	+ R711	+ R972
emulsion stability[a]	72	90	36	53
IFT mN/m	25	25	31	31
elastic modulus- mN/m	21	48	10	14

[a]Expressed as the % vol of resolved water.

Table 6. Results Summary of Heavy Fraction HF with the Different Particles

heavy fraction	without particles	+ A200	+ R711	+ R972
emulsion stability[a]	0	0	0	0
IFT mN/m	27	26	27	27
elastic modulus- mN/m	86	92	52	66

[a]Expressed as the % vol of resolved water.

emulsions formed with or without particles, with the different crude oil fractions LF, IF, and HF, respectively.

As previously mentioned, the light fraction did not allow the formation of a stable emulsion. Similarly, hydrophilic particles did not lead to the formation of an emulsion, whereas the more hydrophobic particles, R711 and R972, tend to increase the emulsion stability (65% and 5% resolved water, respectively). As LF contains very few interfacially active compounds and mainly saturated hydrocarbons, its behavior can be compared with a model oil such as hexane. Thus, these results are in agreement with numerous previous studies, where an increase of particle hydrophobicity stabilizes water-in-oil emulsions.[18,20]

Concerning the intermediate fraction, the hydrophilic particles (A200) tend to destabilize the emulsion (90% resolved water), while hydrophobic particles (R711) stabilize it more (36% resolved water) than the most hydrophobic particles (R972) (53% resolved water). The intermediate fraction contains more aromatic molecules than the light fraction. These aromatic components at higher content seem to be able to modify the wettability of

particles by adsorption and consequently to change their interfacial behavior.

For the heavy fraction, particles do not affect the emulsion stability, whatever their wettabilities. To try to underline the particles effect, 50 ppm of demulsifier D was added in all the HF emulsions with particles. Then, some separated water was observed only for the reference emulsion (HF alone) and in the presence of hydrophilic particles (A200). The demulsifier action alone or in combination with A200 particles induces some emulsion destabilization, whereas R711 and R972 particles stabilize it totally.

IFT measurements were performed in order to evaluate which fraction of the crude oil has the greatest interactions with the three types of particles. The evolution of the interfacial tensions between the different oil fractions and brine in the presence of particles are presented in Figure 7A, 7B, and 7C for LF, IF, and HF, respectively.

As already noticed and presented in Figure 1, an error bar of 2 mN/m on IFT values is estimated for the LF/brine interface. Considering this error on the measurements, the IFTs of the light fraction with hydrophobic particles is slightly higher (39 mN/m) than without particles (37 mN/m) or with hydrophilic particles (36 mN/m) (Figure 7A).

Similarly to the crude oil/brine interface, as shown in Figure 3, the presence of hydrophobic particles in intermediate fraction oil increases the IFT (from 25 mN/m up to 31 mN/m), while the presence of hydrophilic particles has few or no effect (25 mN/m) (Figure 7B). Thus, surfactants (aromatics and resins) of the intermediate fraction interact more with R711 and R972 particles than with A200 particles.

The IFTs obtained with the heavy fraction show a different behavior: the addition of hydrophobic particles in the oil phase has no effect, while hydrophilic particles in the water phase slightly decrease the IFT (Figure 7C). It seems that the main surfactants of the heavy fraction (resins) do not desorb from the interface to adsorb on the hydrophobic particles. These results are different from previous work that measured resins adsorption on particles whatever their hydrophobicity.[37] However in our study, experiments were performed with crude oil having a huge amount of resins that mainly concentrated in the heavy fraction. Thus, the resins may be partially desorbed from the interface by the particles but in a likely insufficient amount.

The viscoelastic moduli E' and E'' of the different oil fractions were measured with or without particles and presented in Figure 8A, 8B, and 8C for LF, IF, and HF, respectively.

For the light fraction, the values of the elastic modulus with A200 particles were difficult to determine as shown by the error bars in Figure 8A. Nevertheless, the high value of the elastic modulus E' with A200 (83mN/) is difficult to analyze without assuming interactions at the interface between some LF oil compounds and particles. On the contrary, elastic modulus E' is very close to the reference interface (LF/brine 14 mN/m) for R711 particles (14 mN/m) and slightly lower for R972 particles (9 mN/m).

For the intermediate fraction the viscoelastic properties of the interfaces with particles are quite similar to the ones of crude oil/brine: the complex modulus increases with hydrophilic particles and decreases with hydrophobic particles (Figure 8B). However, the main difference is observed with the relatively smallest value of the elastic modulus E' with hydrophilic particles (48 mN/m) in comparison with the high value (117 mN/m) in the case of crude oil. The viscoelastic behavior of the heavy fraction interfaces is quite different in the presence of hydrophobic
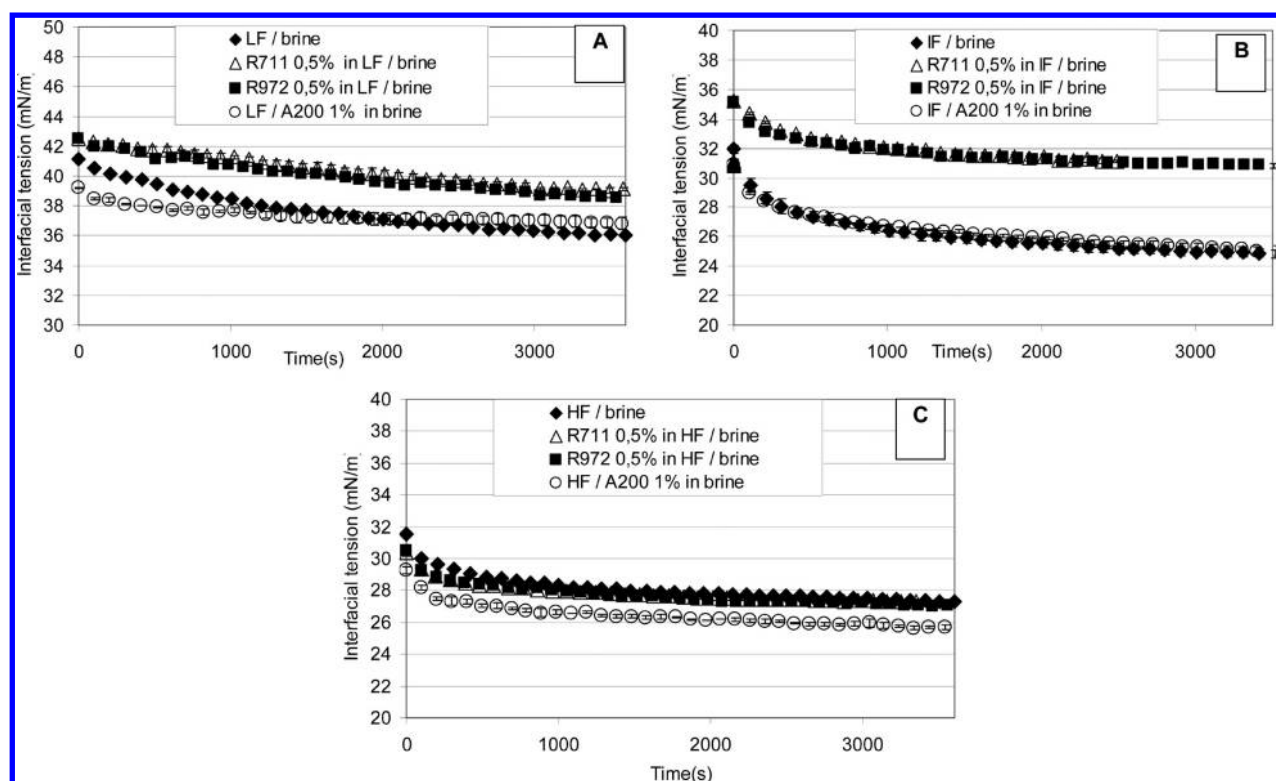
Figure 7. Interfacial tension of freshly formed droplets of oil fractions (LF, IF, HF) in brine, with or without particles, $T = 30\ ^\circ C$.
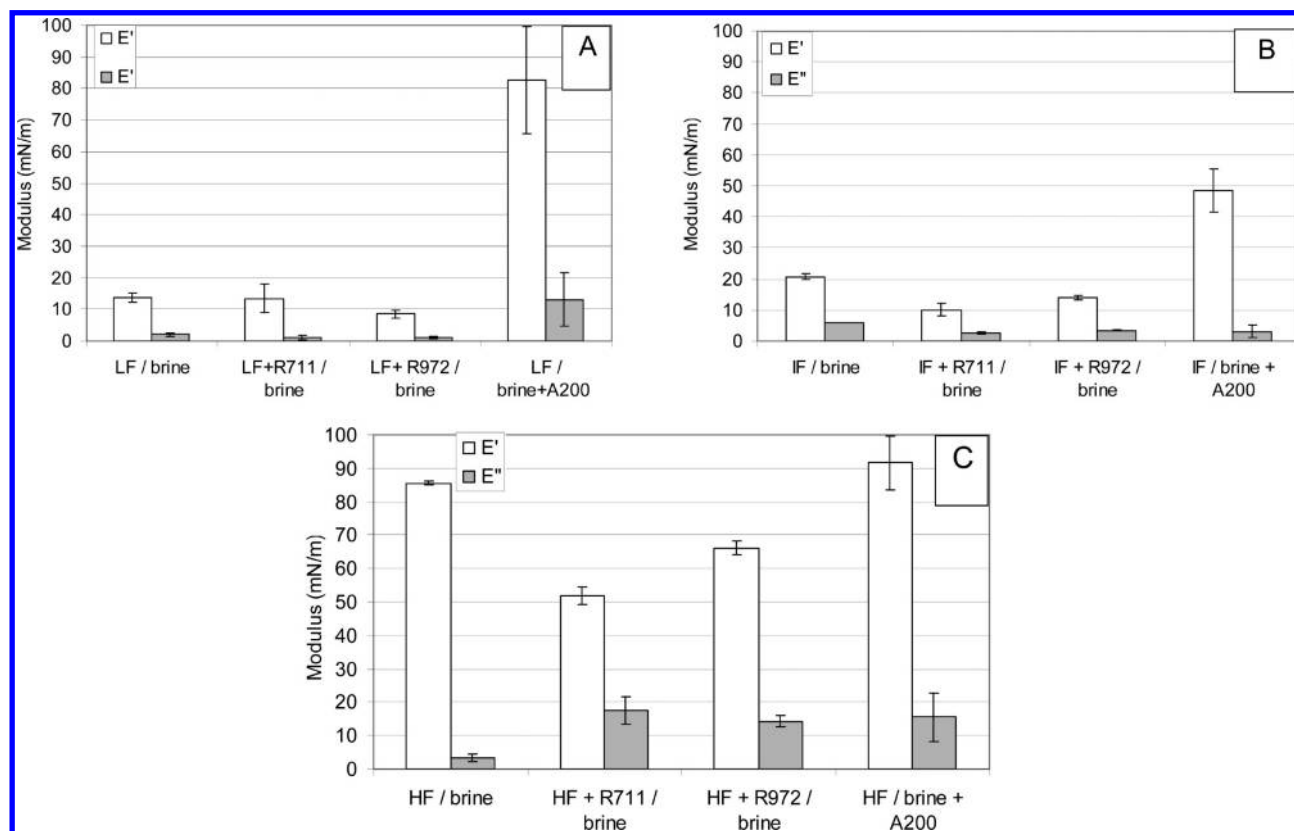

Figure 8. Elastic E' and viscous E'' moduli for interfaces between oil fractions (LF, IF, HF) and brine with or without particles after 5 h. Frequency 0.1 Hz, $T = 30\ ^\circ C$.

particles (Figure 8C). The elastic moduli exhibit high values (52 mN/m and 66 mN/m for R711 and R972, respectively) in comparison with the ones of crude oil and LF and IF oils

(9 to 30 mN/m). Moreover, the elastic modulus of the reference HF/brine interface significantly decreases in the presence of hydrophobic particles in comparison to the other interfaces,
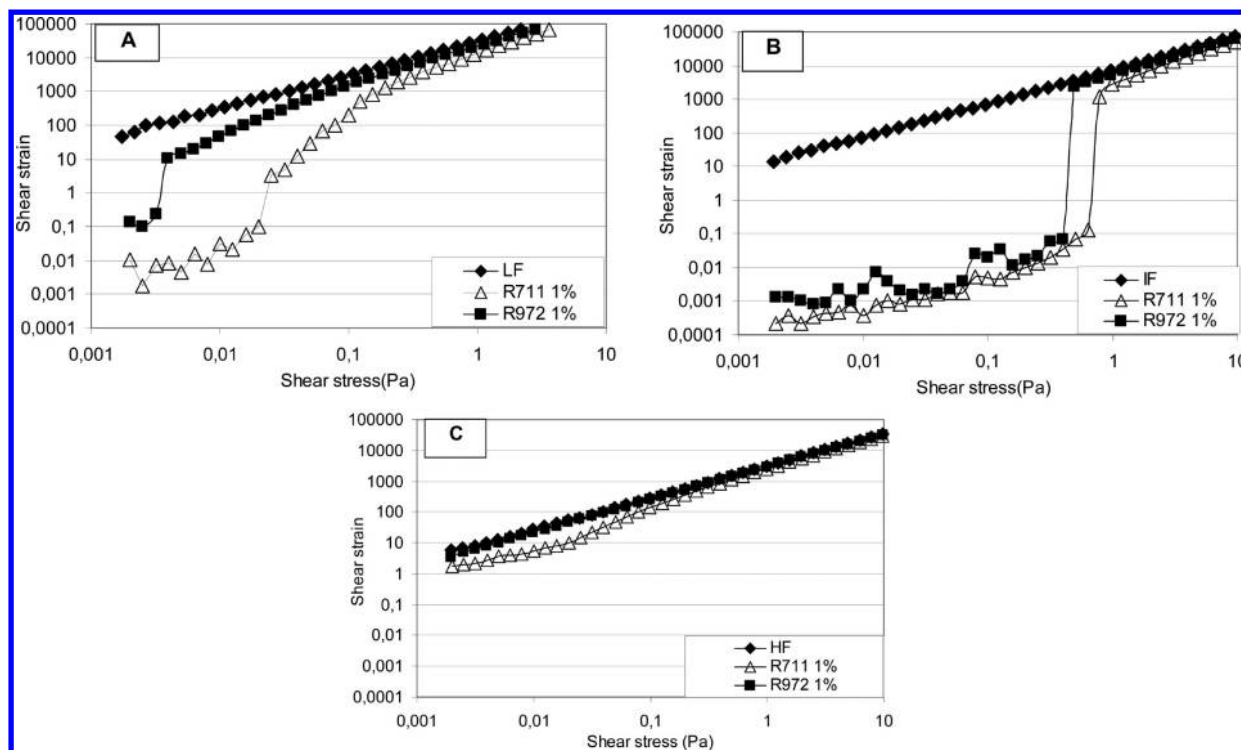
Figure 9. Stress−strain curves of oil fractions (LF, IF, HF) with or without R711 or R972 particles, $T = 30$ °C.

indicating that interface properties are more affected by these particles. Thus, even if IFT measurements do not show a particular adsorption of surfactants on particles, the viscoelastic measurements show that this adsorption certainly occurs. On the contrary, no significant change is observed with the hydrophilic particles that still exhibit a high value of E' (92 mN/m), close to the one measured with the heavy fraction alone (86 mN/m).

The particles dispersions present very different rheological behaviors, depending on the crude oil fractions. Results are summarized in Figure 9A, 9B, and 9C for LF, IF, and HF, respectively.

In the light fraction, very low values of yield stresses are measured at 1% particles concentration: less than 0.1 Pa with R711 particles and less than 0.01 Pa for R972 particles (Figure 9A). These low values do not allow for conclusion that networks of particles are formed in the light fraction. Similar observations are made with the heavy fraction because no clear yield stresses are detected (Figure 9C). On the contrary, yield stresses are more easily measured with the intermediate fraction (Figure 9B). The yield stress values are even higher than those in the crude oil: 0.71 Pa ± 0.08 and 0.44 Pa ± 0.01 Pa for R711 and R972 particles, respectively, and confirm the tendency to the formation of a particles network in the bulk of the intermediate oil phase.

3.4. Cryo-SEM Analysis. All the emulsions were analyzed by Cryo-SEM to try to determine the morphology of emulsions, and EDX analysis was performed on images to locate the silicon and the oxygen elements in the sample.

For the reference emulsion (crude oil/brine), the image analysis indicates a droplet size distribution centered around 4 μm, with a range of size from 1.5 to 13 μm (Figure 10). It is noteworthy that the droplet size distribution is rather homogeneous.

In the case of emulsions containing hydrophilic particles (1% A200 in brine), the Cryo-SEM images and EDX analysis were only recorded with the crude oil and the heavy fraction (Figure 11) because other fractions did not form stable emulsions.
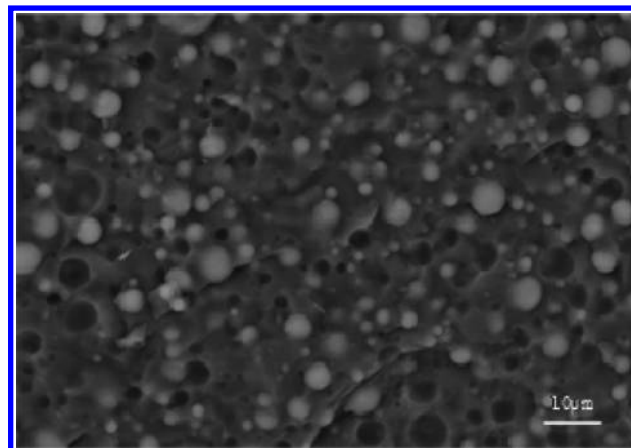

Figure 10. Cryo-SEM images of crude oil/brine emulsion scale bar = 10 μm.

In the crude oil, the droplet size varies between 1 and 90 μm, with a droplet size distribution centered around 5 μm. Even if the average size of the droplets is not very different from this of the reference emulsion, much larger droplets are present, suggesting that some droplets have coalesced. These observations confirm the tendency of A200 particles to destabilize emulsions as measured in the previous stability tests. In the heavy fraction, the image analysis shows a droplet size distribution centered around 2 μm, with a range of size from 500 nm to 4 μm. Contrary to the emulsion formed with crude oil, the presence of hydrophilic particles A200 does not increase the droplet size.

A mapping of the images allowed for detection of the location of silicon in the samples. As expected, hydrophilic A200 particles seems more present on the surface or inside water droplets than in the oil bulk phase (Figure 11) .

Qualitative analysis of the silicon and oxygen elements on the profile of several water droplets was then performed (Figure 12).
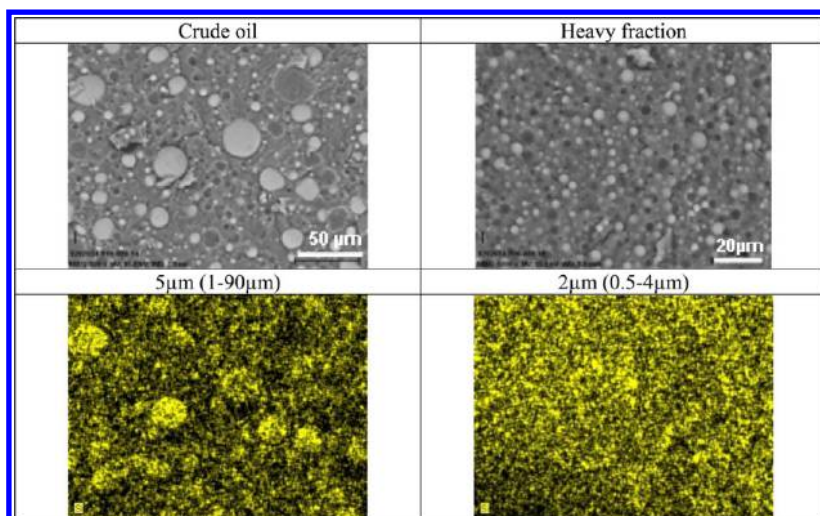
Figure 11. Cryo-SEM images (up) and EDX silicon cartography (bottom) from emulsions with A200 particles in brine/crude oil or heavy fraction.
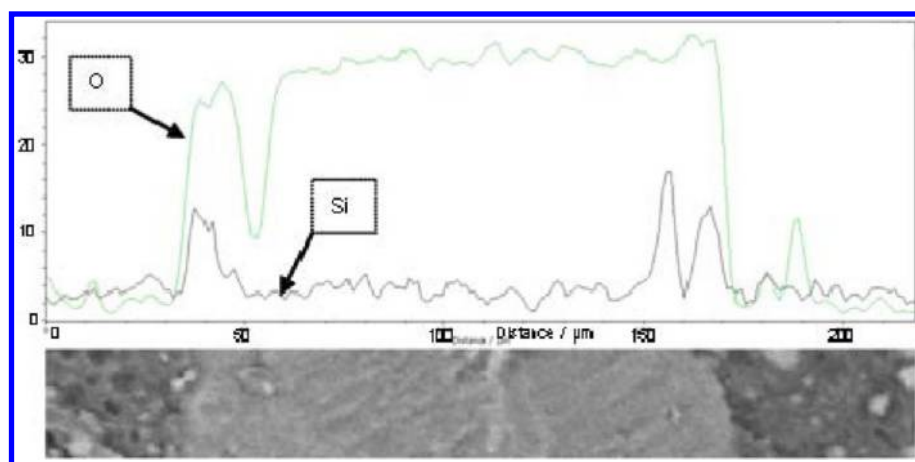

Figure 12. Analysis of droplet profiles in emulsion with A200 particles in brine/crude oil. EDX detection of oxygen and silicon.
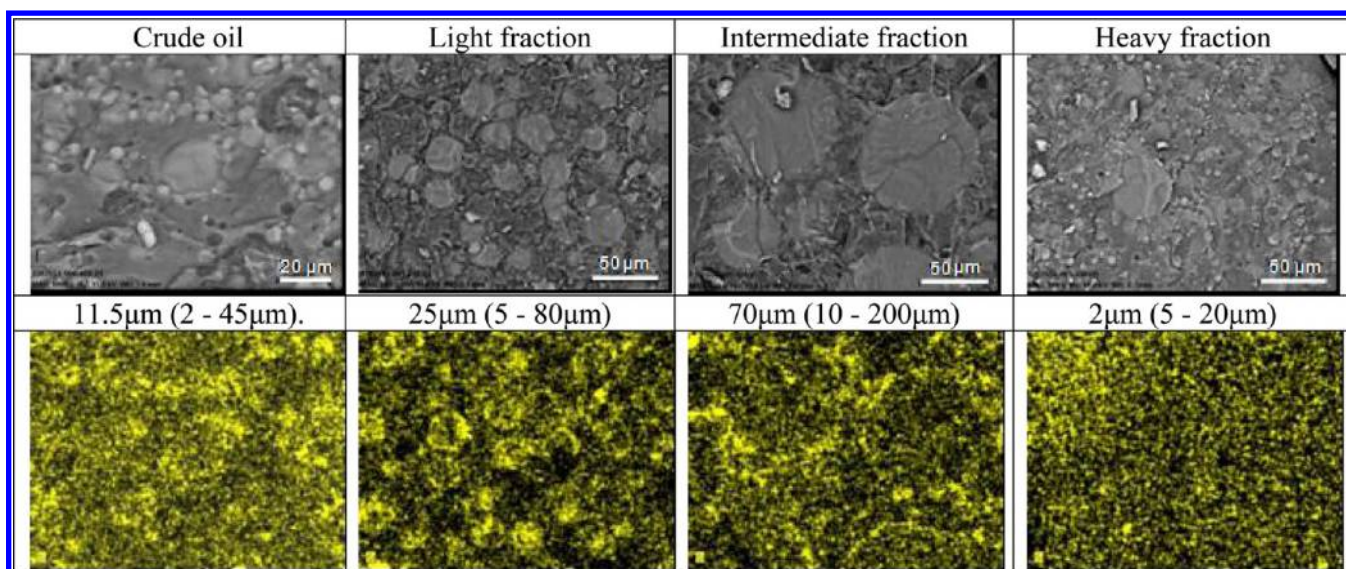

Figure 13. Cryo-SEM images (up) and EDX silicon cartography (bottom) from emulsions with R711 particles in crude oil or its fractions.

The presence of oxygen indicates the location of water droplet. The silicon element signal was magnified to facilitate the interpretation because it was in very low quantity in comparison with oxygen. This element analysis shows that silica particles are located close to the water/oil interface confirming the tendency of the hydrophilic particles A200 to concentrate at the interface.
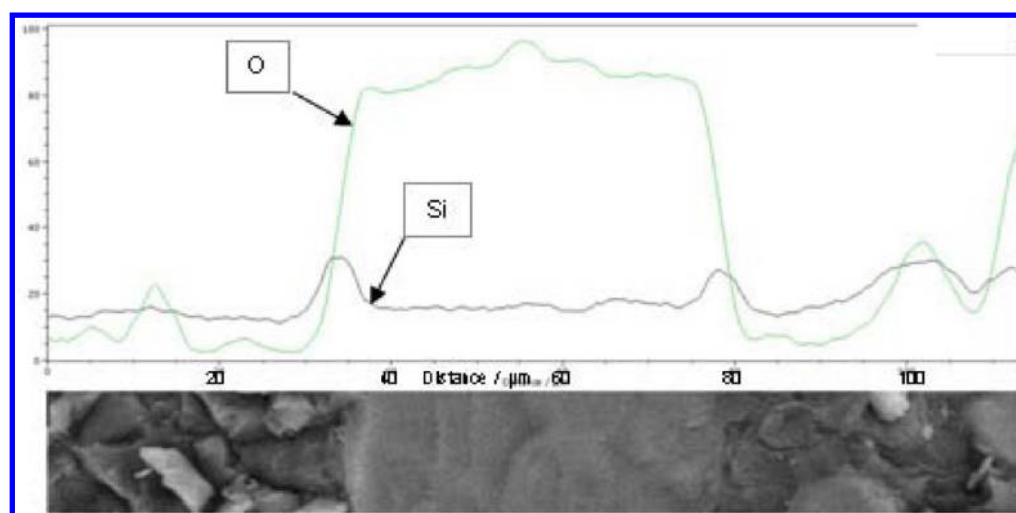
Figure 14. Analysis of brine droplet profiles in emulsion with R711 particles in light fraction. EDX detection of oxygen and silicon.
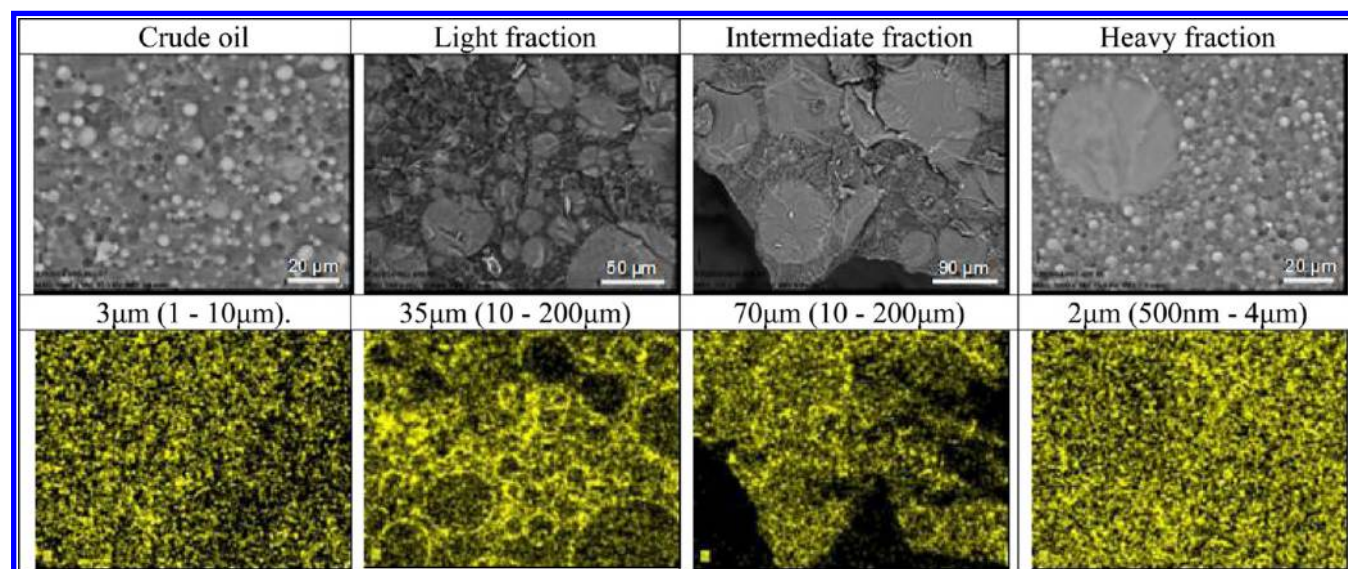

Figure 15. Cryo-SEM images (up) and EDX silicon cartography (bottom) from emulsions with R972 particles in crude oil or its fractions.

Cryo-SEM images and silicon cartographies of emulsions with 0.5% R711 particles in the different oil fractions are presented in Figure 13.

An indication of the average droplet size is also given below the pictures, and the distribution range is noted into brackets. It is first observed that the droplet size in the emulsion and the particle location depend on the nature of the oil phase.

The smallest droplet size distributions are measured with the heavy fraction and the crude oil. It becomes broader with the light fraction and even broader with the intermediate fraction. As expected, the most stable emulsions correspond to the smallest droplets (i.e., crude oil or heavy fraction). The less stable emulsions (i.e., light or intermediate fraction) correspond to the biggest droplets. But, the biggest droplets are observed for the intermediate fraction emulsion which is more stable than the light fraction one. This unexpected result has to be modulated in respect to the accuracy of the technique used for the droplet average size determination. As noticed in paragraph 2.6, microscopy analysis should be only used as an indication of the droplet size repartition and an estimation of the average size.

The mapping of the pictures allows for the distinguishing of different silicon distributions in the emulsions (Figure 13). The greater the amount of heavy molecules in the oil is, the better the dispersion of particles in the bulk oil is, implying less particles at the water−oil interface. The detection of particles at the interface is consistent with the steric barrier described by Binks for colloidal particles.[53]

This distribution of the silicon in the light fraction emulsion is confirmed by the profile of a water droplet, where the silicon is magnified (Figure 14). The profile with the intermediate fraction does not show clear silicon peaks close to the interface.

In the same way, Cryo-SEM images and silicon cartographies of emulsions with 0.5% R972 particles in the different oil fractions are presented in Figure 15.

As for emulsions with R711 particles, the smallest droplet size distributions are obtained with the heavy fraction and the crude oil. Then, the size distribution increases with the light and intermediate fractions. In comparison with R711 particles, R972 particles seem to be better dispersed in the oil phases, certainly because of their more hydrophobic properties. However, the emulsion with light fraction shows an accumulation of R972
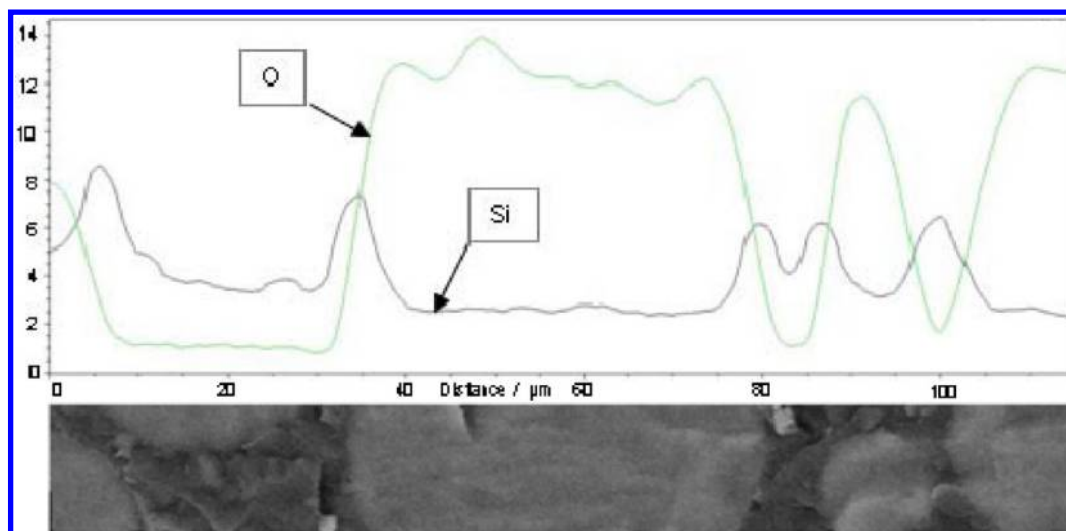
Figure 16. Analysis of brine droplet profiles in emulsion with R972 particles in light fraction. EDX detection of oxygen and silicon.

particles at the interface. In the profile of a water droplet, the silicon concentration significantly increases at the interface (Figure 16) .

4. DISCUSSION

The main results obtained with the crude oil and the LF, IF, and HF fractions are summarized in Tables 3, 4, 5, and 6, respectively.

General trends can be pointed out on the contribution of each fraction to the water-in-crude oil emulsion behavior with or without particles:

Whatever the oil composition, hydrophilic particles destabilize water-in-oil emulsions, whereas hydrophobic particles tend to stabilize them.

The viscoelastic properties of the interfacial film may be analyzed regarding the emulsion behavior. Two situations have to be considered:

Without particles, the emulsion stability increases with the corresponding elastic modulus value due to the presence at the interface of the heavy molecular weight oil compounds which are also the most polar ones, i.e. the resins in the studied crude oil.

In the presence of particles, whatever the oil fraction composition, no direct relation could be established between the emulsion stability and the elastic moduli measured values. Different behaviors are observed depending on the particles wettabilities.

Hydrophobic particles R711 and R972 have the tendency to form an organized structure in the case of crude oil and intermediate fraction, and it is only slightly detectable in the light fraction and not detectable in the heavy fraction. However, the formation of a particle network in the oil continuous phase is not a sufficient condition to explain the formation of stable emulsions.

Whatever the oil phase composition, a slight increase of the interfacial tension is observed with particles related to the adsorption of surface active compounds on particles that modifies their wettability. The emulsion stability is related to the number of collisions between droplets and then to droplet coalescence efficiency. The presence of heavy molecular weight compounds in the oil phase and of a network of particles in the oil continuous phase limits the possibility of a contact between droplets. Thus, a structural organization of the interfacial film (i.e., "solid-like" behavior) affects the mobility of the surface active molecules and hinders film breakage and coalescence.

Whereas no direct relation between emulsion stability and interfacial tension is noticed, the presence of particles at the oil/water interface modifies the interfacial film properties:

For hydrophilic particles, IFT measurements and Cryo-SEM observations suggest that interactions at the interface are not excluded. Due to their possible attachment at the interface, the viscoelastic interfacial properties are modified leading to an increase of the droplet coalescence phenomena, hence to emulsion destabilization. When comparing IF and HF fractions, the higher the amount of aromatics and resins compounds is, the less the effect of A200 particles on the elastic modulus is. Moreover, with these hydrophilic particles in HF oil, no emulsion destabilization was observed.

- Concerning the hydrophobic particles, the emulsion stability seems to be reinforced by the addition of two complementary effects: the attachment of particles at the water droplet interface and the tendency to form an organized structure in the oil. However, each fraction contributes more or less to these effects. For the light fraction, mainly composed of saturated hydrocarbons, the particles attachment at the interface is enhanced. This accumulation of particles does not lead to an important variation of the elastic modulus even if an increase of the emulsion stability was observed. For the intermediate fraction, the aromatic compounds seem to favor the dispersion of particles, so few particles are attached to the interface, which could explain the slight variation of the elastic modulus. Both types of hydrophobic particles form a network in the oil continuous phase that limits droplet coalescence and reinforces emulsion stability. For the heavy fraction (i.e. aromatic and resins compounds), particles seem to be totally dispersed in the bulk. It was not possible to detect the tendency to form an organized structure through the rheological procedure used.

A demulsifier was added only to underline the stabilization brought by the hydrophobic particles in the case of crude oil and IF and HF fractions. Further studies are needed to understand the interactions between particles, demulsifier, and crude oil compounds.

4. CONCLUSION

In the present paper, the potential effect of fumed silica particles with various hydrophobicities on the stabilization of water-in-crude oil emulsions was studied regarding the interfacial properties.

The studied oil was mostly paraffinic and contained only a very few amount of asphaltenes. It was separated by distillation in three fractions containing mainly saturate, aromatic, and resin compounds. The stability of emulsions formed from these oil fractions was also studied with or without silica particles. Various techniques were used to analyze the particles effect: interfacial tension measurements, dilatational rheology of the interface, rheological measurements of the particles dispersions, and Cryo-SEM analysis.

As a first point, experiments without particles performed with the oil or its fractions underline that the most stable emulsions are formed with the heavy fraction which corresponds to the highest elastic modulus of the interface. It is also observed that the IFT value is not the lowest in that case.

Different mechanisms of emulsion stabilization in the presence of particles were discussed according to the particles wettability.

Whatever the oil phase composition, it is obviously noticed that hydrophilic particles destabilize water-in-oil emulsions, whereas hydrophobic particles stabilize them.

For hydrophilic particles, the "solid-like" behavior of the interfacial film revealed by the high value of the elastic modulus, the IFT measurements and the observations by Cryo-SEM indicates the presence of A200 particles at the oil/water interface. Despite this, water-in-oil emulsion destabilization is systematically observed, certainly due to the hydrophilic nature of particles.

The higher stability of emulsions observed in the presence of hydrophobic particles results from the addition of several effects: the tendency to form a structure in the oil dispersed phase and the influence of the attached particles at the interface.

This study underlines that no direct relation is observed between the emulsion stability and the interfacial tension measurements particularly in the presence of particles. Otherwise the viscoelastic measurements by the oscillating drop technique corroborate the relation between a higher emulsion stability and a higher viscoelastic modulus in the case of emulsions without particles. In the presence of particles, the elastic modulus of the interface is less affected by hydrophobic than hydrophilic particles.

This observations were obtained with a paraffinic crude oil and its reconstituted fractions. A more precise analysis of the aromatics and resins in each oil fractions by spectroscopy techniques will be tentatively performed in order to correlate the molecular oil structure with the emulsion behavior.

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Notes
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■ REFERENCES

(1) Speight, J. G. Petroleum asphaltenes Part1 Asphaltenes, resins, and the structure of petroleum. *OGST* **2004**, *59*, 467−477.

(2) Mullins, O. C. The asphaltenes. *Annu. Rev. Anal. Chem.* **2011**, *4*, 393−418.

(3) Rodgers, R. P.; McKenna, A. M. Petroleum analysis. *Anal. Chem.* **2011**, *83*, 4665−4687.

(4) Barré, L.; Simon, S.; Palermo, T. Solution properties of asphaltenes. *Langmuir* **2008**, *24*, 3709−3717.

(5) McLean, J. D.; Kilpatrick, P. K. Effects of asphaltene solvency on stability of water-in-crude oil emulsions. *J. Colloid Interface Sci.* **1997**, *189*, 242−253.

(6) Bouriat, P.; El Kerri, N.; Graciaa, A.; Lachaise, J. Properties of a two-dimensional asphaltene network at the water-cyclohexane interface deduced from dynamic tensiometry. *Langmuir* **2004**, *20*, 7459−7464.

(7) Dicharry, C.; Arla, D.; Sinquin, A.; Graciaa, A.; Bouriat, P. Stability of water/crude oil emulsions based on interfacial dilatational rheology. *J. Colloid Interface Sci.* **2006**, *297*, 785−791.

(8) Yarranton, H. W.; Sztukowski, D. M.; Urrutia, P. Effect of interfacial rheology on model emulsion coalescence. I. Interfacial rheology. *J. Colloid Interface Sci.* **2007**, *310*, 246−252.

(9) Freer, E. M.; Radke, C. J. Relaxation of asphaltenes at the toluene/water interface: diffusion exchange and surface rearrangement. *J. Adhes.* **2004**, *80*, 481−496.

(10) McLean, J. D.; Kilpatrick, P. K. Effects of asphaltene aggregation in model heptane-toluene mixtures on stability of water-in-oil emulsions. *J. Colloid Interface Sci.* **1997**, *196*, 23−34.

(11) Bauget, F.; Langevin, D.; Lenormand, R. Dynamic surface properties of asphaltenes and resins at the oil-air interface. *J. Colloid Interface Sci.* **2001**, *239*, 501−508.

(12) Quintero, C. G.; Noïk, C.; Dalmazzone, C.; Grossiord, J. L. Formation kinetics and viscoelastic properties of water/crude oil interfacial films. *OGST* **2009**, *64*, 604−616.

(13) Spiecker, P. M.; Gawrys, K. L.; Trail, C. B.; Kilpatrick, P. K. Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. *Colloids Surf., A* **2003**, *220*, 9−27.

(14) Ese, M. H.; Yang, X.; Sjöblom, J. Film forming properties of asphaltenes and resins. A comparative Langmuir−Blodgett study of crude oils from North Sea, European continent and Venezuela. *Colloid Polym. Sci.* **1998**, *276*, 800−809.

(15) Zhang, L. Y.; Xu, Z.; Masliyah, J. H. Langmuir and Langmuir−Blodgett films of mixed asphaltene and a demulsifier. *Langmuir* **2003**, *19*, 9730.

(16) Aske, N.; Orr, R.; Sjöblom, J. Dilatational elasticity moduli of water-crude oil interfaces using the oscillating pendant drop. *J. Dispersion Sci. Technol.* **2002**, *23*, 809−825.

(17) Tadros, T. Application of rheology for assessment and predication of the long-term physical stability of emulsions. *Adv. Colloid Interface Sci.* **2004**, *108−109*, 227−258.

(18) Torres, L. G.; Iturbe, R.; Snowden, M. J.; Chowdhry, B. Z.; Leharne, S. A. Preparation of o/w emulsions stabilized by solid particles and their characterization by oscillatory rheology. *Colloids Surf., A* **2007**, *302*, 439−448.

(19) Kang, W.; Xu, B.; Wang, Y.; Li, Y.; Shan, X.; An, F.; Liu, J. Stability mechanism of W/O crude oil emulsion stabilized by polymer and surfactant. *Colloids Surf., A* **2011**, *384*, 555−560.

(20) Binks, B. P. Particles as surfactants − similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21−41.

(21) Li, C.; Liu, Q.; Mei, Z.; Wang, J.; Xu, J.; Sun, D. Pickering emulsions stabilized by paraffin wax and laponite clay particles. *J. Colloid Interface Sci.* **2009**, *336*, 314−321.

(22) Yan, Z.; Elliot, J. A. W.; Masliyah, J. H. Roles of various bitumen components in the stability of water-in-diluted-bitumen emulsions. *J. Colloid Interface Sci.* **1999**, *220*, 329−337.

(23) Yan, N.; Gray, M. R.; Masliyah, J. H. On water-in-oil emulsions stabilized by fine solids. *Colloids Surf., A* **2001**, *193*, 97−107.

(24) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503−546.

(25) Cui, Z. G.; Yang, L. L.; Cui, Y. Z.; Binks, B. P. Effects of surfactant structure on the phase inversion of emulsions stabilized by mixtures of silica nanoparticles and cationic surfactant. *Langmuir* **2009**, *26*, 4717−4724.

(26) Frelichowska, J.; Bolzinger, M.-A.; Chevalier, Y. Pickering emulsions with bare silica. *Colloids Surf., A* **2009**, *343*, 70−74.

(27) Binks, B. P.; Lumsdon, S. O. Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* **2000**, *16*, 8622−8631.

(28) Yan, N.; Masliyah, J. H. Characterization and demulsification of solids-stabilized oil-in-water emulsions. Part 1. partitioning of clay particles and preparation of emulsions. *Colloids Surf., A* **1995**, *96*, 229−242.

(29) Binks, B. P.; Lumsdon, S. O. Pickering emulsions stabilized by monodisperse latex particles: effects of particle size. *Langmuir* **2001**, *17*, 4540−4547.

(30) Sullivan, A. P.; Kilpatrick, P. K. The effect of inorganic solid particles on water and crude oil emulsion stability. *Ind. Eng. Chem. Res.* **2002**, *41*, 3389−3404.

(31) Sztukowski, D. M.; Yarranton, H. W. Oilfield solids and water-in-oil emulsion stability. *J. Colloid Interface Sci.* **2005**, *285*, 821−833.

(32) Kralova, I.; Sjöblom, J.; Øye, G.; Simon, V.; Grimes, B. A.; Paso, V. Heavy crude oils/particle stabilized emulsions. *Adv. Colloid Interace Sci.* **2011**, *169*, 106−127.

(33) Binks, B. P.; Clint, J. H.; Whitby, C. P. Rheological behavior of water-in-oil emulsions stabilized by hydrophobic bentonite particles. *Langmuir* **2005**, *21*, 5307−5316.

(34) Drelich, A.; Gomez, F.; Clausse, D.; Pezron, I. Evolution of water-in-oil emulsions stabilized with solid particles. Influence of added emulsifier. *Colloids Surf.,A* **2010**, *365*, 171−177.

(35) Ravera, F.; Santini, E.; Loglio, G.; Ferrari, M.; Liggieri, L. Effect of nanoparticles on the interfacial properties of liquid/liquid and liquid/air surface layers. *J. Phys. Chem. B* **2006**, *110*, 19543−19551.

(36) Pichot, R.; Spyropoulos, F.; Norton, I. T. Competitive adsorption of surfactants and hydrophilic silica particles at the oil-water interface: Interfacial tension and contact angle studies. *J. Colloid Interface Sci.* **2012**, *377*, 396−405.

(37) Hannisdal, A.; Ese, M.-H.; Hemmingsen, P. V.; Sjöblom, J. Particle-stabilized emulsions: Effect of heavy crude oil components pre-adsorbed onto stabilizing solids. *Colloids Surf., A* **2006**, *276*, 45.

(38) *ASTM. Annual Book of Standards*; American Society for Testing and Materials: Philadelphia, PA, 1995; Methods D-2007 and D6560 for SAR and A analysis, respectively.

(39) *ASTM. Annual Book of Standards*; American Society for Testing and Materials: Philadelphia, PA, 1995; Method D664-11a for TAN analysis.

(40) Quintero, C. G.; Noïk, C.; Dalmazzone, C.; Grossiord, J. L. Modelling and characterisation of diluted and concentrated water-in-crude oil emulsions: comparison with classical behavior. *Rheol. Acta* **2008**, *47*, 417−424.

(41) Yan, N.; Maham, Y.; Masliyah, J. H.; Gray, M. R; Mather, A. E. Measurement of contact angles for fumed silica nanospheres using enthalpy of immersion data. *J. Colloid Interface Sci.* **2000**, *228*, 1−6.

(42) Forny, L.; Saleh, K.; Denoyel, R.; Pezron, I. Contact angle assessment of hydrophobic silica nanoparticles related to the mechanisms of dry water formation. *Langmuir* **2010**, *26*, 2333−2338.

(43) Benjamins, J.; Cagna, A.; Lucassen-Reynders, E. H. Viscoelastic properties of triacyglycerol/water interfaces covered by proteins. *Colloids Surf., A* **1996**, *114*, 245−254.

(44) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; John Wiley & Sons, Inc.: NewYork, 1997.

(45) Daniel-David, D.; Le Follotec, A.; Pezron, I.; Dalmazzone, C.; Noïk, C.; Barré, L.; Komunjer, L. Destabilization of water-in-oil emulsions by silicone copolymer demulsifiers. *OGST* **2008**, *163*, 65−173.

(46) Jeribi, M.; Almir-Assad, B.; Langevin, D.; Hénaut, I.; Argillier, J. F. Adsorption kinetics of asphaltenes at liquid interfaces. *J. Colloid Interface Sci.* **2002**, *256*, 268−272.

(47) Yang, X.; Verruto, V. J.; Kilpatrick, P. K. Dynamic asphaltene-resin exchange at the oil/water interface: time-dependent W/O emulsion stability for asphaltene/resin model oils. *Energy Fuels* **2007**, *21*, 1343−1347.

(48) Whitby, C. P.; Fornasiero, D.; Ralston, J.; Liggieri, L.; Ravera, F. Properties of fatty amine-silica nanoparticle interfacial layers at the hexane-water interface. *J. Phys. Chem. C* **2012**, *116*, 3050.

(49) Ravera, F.; Ferrari, M.; Liggieri, L.; Loglio, G.; Santini, E.; Zanobini, A. Liquid-liquid interfacial properties of mixed nanoparticles-surfactant systems. *Colloids Surf., A* **2008**, *323*, 99−108.

(50) Freer, E. M.; Wong, H.; Radke, C. J. Oscillating drop/bubble tensiometry: effect of viscous forces in the measurement of interfacial tension. *J. Colloid Interface Sci.* **2005**, *282*, 128−132.

(51) Wang, J.; Yang, F.; Liu, G.; Xu, J.; Sun, D. Pickering emulsions stabilized by a lipophilic surfactant and hydrophilic platelike particles. *Langmuir* **2009**, *26*, 5397.

(52) Midmore, B. R. Preparation of a novel silica-stabilized oil/water emulsion. *Colloids Surf., A* **1998**, *132*, 257−265.

(53) Horozov, T. S.; Binks, B. Particle-stabilized emulsions: a bilayer or a bridging monolayer? *Angew. Chem., Int. Ed.* **2006**, *45*, 773−776.