



HAL
open science

Interfacial rheology of low interfacial tension systems using a new oscillating spinning drop method

José Zamora, Ronald Marquez, Ana Forgiarini, Dominique Langevin,
Jean-Louis Salager

► **To cite this version:**

José Zamora, Ronald Marquez, Ana Forgiarini, Dominique Langevin, Jean-Louis Salager. Interfacial rheology of low interfacial tension systems using a new oscillating spinning drop method. *Journal of Colloid and Interface Science*, 2018, 519, pp.27-37. 10.1016/j.jcis.2018.02.015 . hal-04037300

HAL Id: hal-04037300

<https://hal.science/hal-04037300v1>

Submitted on 20 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Interfacial rheology of low interfacial tension systems using a new oscillating spinning drop method

José M. Zamora¹, Ronald Marquez², Ana M. Forgiarini², Dominique Langevin^{3*}, Jean-Louis Salager²

¹Centro de Innovación Tecnológica CITEC, Universidad de Los Andes, Mérida-Venezuela

²Laboratorio FIRP, Universidad de Los Andes, Mérida-Venezuela

³Laboratoire de Physique des Solides, CNRS UMR 8502, Université de Paris Saclay, France

Abstract

When surfactants adsorb at liquid surfaces, they not only decrease the surface tension, they confer rheological properties to the surfaces. There are two types of rheological parameters associated to interfacial layer compression and shear. The elastic response is described by a storage modulus and the dissipation by a loss modulus or equivalently a surface viscosity. Various types of instruments are available for the measurements of these coefficients, the most common being oscillating pendant drops instruments and rheometers equipped with bicones. These instruments are applicable to systems with large enough interfacial tensions, typically above a few mN/m.

We use a new type of instrument based on spinning drop oscillations, allowing to extend the interfacial rheology studies to low and ultralow interfacial tension systems. We present examples of measurements with systems of high and low tension, discuss the possible artifacts and demonstrate the capability of this new technique. We emphasize that the data shown for low interfacial tensions are the first reported in the literature. The instrument is potentially interesting for instance in enhanced oil recovery or demulsification studies.

Key words : Surfactants, asphaltenes, surface elasticity, surface viscosity, spinning drop

1. Introduction

Surface active agents, such as surfactants, adsorb at surfaces. In the case of fluid surfaces such as air-water or oil-water interfaces, the interfacial tension γ decreases. In addition, the adsorbed layers confer rheological properties to the interface, i.e. responses to compression and shear deformations [1]. These rheological properties affect many phenomena involving interfacial flow such as wetting, multiphase flow, emulsification and emulsion stability, foaming and foaming stability, motion of drops or bubbles, propagation of waves at surfaces. It is now recognized that it is not possible to model these different phenomena taking into account only the interfacial tension.

The measurement of the interfacial rheological properties is much more difficult than the measurement of the interfacial tension and it is only recently that suitable commercial instruments became available. A recent review can be found in [2]. As in bulk viscoelastic fluids, the rheological behavior is described by storage and loss moduli. In the case of a linear response to a sinusoidal deformation, the loss modulus is the product of the viscosity by the frequency. One of the difficulties come from the fact that the adsorbed layers are usually rather compressible (at the difference of bulk fluids which are essentially incompressible), and both compression and shear parameters should be determined. This determination requires different type of instruments, for instance oscillating drops for the compression properties and oscillating bicones for the shear properties [2]. These two methods allow investigating the variation of the parameters upon the amplitude of the deformation. This is very useful as the responses of adsorbed layers to deformations are frequently non-linear.

Surfactant adsorbed layers are fluid-like, their shear storage modulus is zero, leaving only three independent rheological parameters for their characterization: compression modulus E , compression viscosity η_c and shear viscosity η_s . Surfactants can exchange between the bulk and the interface, which results into an apparent but important frequency variation of the measured values of E and η_c . The rheological parameters can be also frequency dependent due to of relaxation processes in the interface. Oscillating drops and bicones allow measuring rheological parameters at low frequencies (typically below 10 Hz). Other techniques, such as wave propagation allow to explore rheological responses at higher frequencies [2].

The commercial instruments were developed for the determination of interfacial properties of systems with interfacial tensions above a few mN/m. Most interfaces have tensions in this range, even the oil-water interfaces in the presence of surfactant, currently found in emulsions. In some cases however, the interfacial tensions are ultralow, and these instruments cannot be used. In microemulsion systems for example, the interfacial tensions can only be measured with spinning drop tensiometers [3] or surface light scattering [4]. Spinning drop tensiometers were used as routine apparatus since the pioneering EOR studies back in the 70's in the University of Texas, where the first models were commercialized. Slattery et al proposed to measure the surface compression properties in these systems by varying sinusoidally the drop area [5]. This method has been developed in the FIRP laboratory [6] and the present paper will give examples of its potential. An instrument based on this principle has been recently commercialized by DataPhysics. [7] So far and to our knowledge, only three publications reported the use of this instrument with surfactant systems of interfacial tensions between about 2 and 10 mN/m. [8-10] Note that spinning drop instruments were used to investigate the deformation of polymerized capsules [11] and of interfaces between polymeric liquids [12]. In these cases, the interfaces have a large shear modulus and the behavior observed was complex.

It has been shown in many studies that emulsion stability correlates well with interfacial rheology, especially when the stabilizing species are irreversibly adsorbed at the oil-water interfaces, as for instance with crude oils containing asphaltene molecules [13]. It is not yet clear which are the most important rheological parameters, compression or shear, storage or loss moduli. This is likely because these parameters are all correlated with the molecular packing in the interfacial layer: the denser the packing, the higher the moduli. The rheological parameters have also been found correlated with the efficiency of demulsifiers: the lower the moduli in the presence of demulsifiers, the better their efficiency [14]. Again, it is not clear yet which parameter best describes the demulsifier action: shear viscosity [15], shear storage modulus [16], both shear modulus and shear viscosity [17] both shear and compression viscosities [18], storage compression modulus (and not loss modulus) [19] or high frequency compression modulus [20]. More investigations are therefore needed. The measurements of the interfacial rheological parameters become difficult when the interfacial tension falls below a few mN/m. The oscillating spinning drop is therefore a promising instrument to explore the rheological behavior of interfaces in this low tension range, which is often found with demulsifiers in petroleum production [21] [22] [23]

In the following, we will recall the theoretical background of interfacial rheology, then describe the custom built instrument used and end showing various examples of applications: surfaces of pure fluids or of surfactant solution, crude oil-water interfaces with and without surfactant added.

2. Definition of surface rheological parameters

Gibbs proposed to define surface properties as *excess properties* [24]. Let us consider for instance a solution of surfactant with a bulk concentration C equal to C_0 far from the surface and increasing close to the surface due to the adsorption process. The surface concentration, also called *surface excess* can be obtained as:

$$\Gamma = \int_{-\infty}^0 C(z) - C_0 dz - \int_0^{+\infty} C(z) dz$$

where the position of the surface is the plane $z=0$. This position is arbitrary, and is usually chosen so that the surface excess of the solvent is zero. The formalism of excess properties can be applied to surface rheological parameters as well [25].

The measurement of the surface shear modulus with an oscillating bicone is made by measuring the total torque opposing the rotation of the bicone, and then subtracting the contributions of the two bulk liquids. The measurement of the surface compression modulus with an oscillating drop is more direct, although based on the same formalism. After adsorption, the interfacial tension γ is lowered with respect to the tension of the bare interface γ_0 by a quantity Π called *surface pressure*. When the layer is compressed along the axis x , an interfacial tension gradient arises associated to a force $F_x = \partial\gamma/\partial x = -\partial\Pi/\partial x$, analog to the bulk force in a medium where the pressure p is not uniform. This force is sometimes called *Marangoni force*. By analogy with the three dimensional case, the compression modulus can be written as:

$$E = -A \frac{\partial\Pi}{\partial A} \quad (1)$$

Since for insoluble surface layers, Γ is inversely proportional to A :

$$E_{insol} = \Gamma \frac{\partial \Pi}{\partial \Gamma} \quad (2)$$

When dissipation is present, the force per unit area is the sum of elastic and viscous contributions. If the deformation is small (linear response) and sinusoidal, of angular frequency ω , the expressions of the force can be generalized using complex moduli: $\tilde{E} = E' + iE'' = E' + i\omega\eta_E = E \exp(i\phi)$ for compression and $\tilde{G} = G' + iG'' = G' + i\omega\eta_S = G \exp(i\phi')$ for shear. Let us note that many authors use the name *dilatational* or *dilatational* instead of *compression* rheology. One can obtain the real E' and imaginary E'' components from the phase angle ϕ : $E' = E \cos \phi$, $E'' = \omega \eta_E = E \sin \phi$. In the absence of relaxation processes affecting the compression modulus, the phase angle ϕ is zero and the adsorbed layer behaves as a pure elastic solid body, whereas if the viscous dissipative losses dominate, then the phase angle is close to 90° . Interfaces with a phase angle between 0° and 90° are viscoelastic.

When the surface active species is soluble in one of the two fluids in contact, it can be expelled from the surface upon compression. This is frequently the case with short chain surfactants, especially the nonionic surfactants that can exchange freely between the adsorbed layer and the bulk solution. In the case of air-water interfaces in quiescent conditions, the surfactant motion in the bulk is controlled by diffusion. Levich [26] calculated the effective compression modulus in the case of a sinusoidal compression of the surface with a frequency ω for a pure nonionic surfactants. Using the common formulation of Lucassen and van den Tempel [27]:

$$E' = E_{insol} \frac{1+\Omega}{1+2\Omega+2\Omega^2} \quad E_{insol} = \Gamma \frac{\partial \Pi}{\partial \Gamma} \quad \Omega = \sqrt{\frac{D}{2\omega}} \frac{\partial C}{\partial \Gamma} \quad (3)$$

where D is the surfactant diffusion coefficient in bulk; E' is equal to E_{insol} at high frequencies, and tends to zero when ω become small. The characteristic relaxation time is such as $\omega\tau_D=1$ and $\Omega=1$, i.e.:

$$\tau_D = \frac{2}{D} \left(\frac{\partial \Gamma}{\partial C} \right)^2 \quad (4)$$

This relaxation produces a dissipation, resulting in a contribution to the surface compression viscosity η_E :

$$\eta_E = \frac{E_{insol}}{\omega} \frac{\Omega}{1+2\Omega+2\Omega^2} \quad (5)$$

η_E is small at small and high frequencies and is maximum around $\omega\tau_D=1$. It should be stressed that the compression parameters given in equations 3 and 5 are not intrinsic to the system. For instance, when the thickness h of the bulk phase is very small and when the amount of surfactant in bulk is less than the amount of surfactant at the surface ($C < \Gamma/h$), the exchanges between bulk and surface are constrained, and E is closer to E_{insol} than predicted by eq. 3 [28].

In practice, the intrinsic compression modulus E_{insol} can be calculated when the variation of the interfacial tension with concentration is known. Indeed one can then calculate the surface concentration Γ using the Gibbs equation

$$\Gamma = \frac{1}{k_B T} \frac{\partial \gamma}{\partial \ln C} \quad (6)$$

for a nonionic surfactant. Note that this equation can only be used below the critical micellar concentration (*cmc*), because above this concentration, micelles form and the surface tension remains constant [29]. In general, the surface concentration reaches a limit value Γ_∞ close to the *cmc* [30]. Above the *cmc*, micelles are present, and the exchange time between micelles and surface can become long and equations 3-5 need to be modified [31]. These equations were also generalized for

binary surfactant mixtures, including soluble and insoluble surfactants [32]. In the case of ionic surfactants, equations 3-5 are not valid and more complex treatments are necessary [33].

The relation between equilibrium bulk and surface concentrations is frequently approximated by the *Langmuir equation*:

$$\frac{c}{a} = \frac{\Gamma/\Gamma_{\infty}}{1-\Gamma/\Gamma_{\infty}} \quad (7)$$

where a is the *Szyszkowski* concentration, smaller than the *cmc*. One can see from equation 7 that the derivative $d\Gamma/dC$ becomes very small when Γ approaches Γ_{∞} , meaning that the characteristic frequency Ω becomes high and the elastic modulus E small. More complex expressions incorporate interactions between molecules at the surface, such as the Frumkin equation and others.

Equations 3-7 do not apply to irreversibly adsorbed species at the interface, such as asphaltenes [34]. In this case, the elastic modulus can also depend on frequency due to relaxations inside the surface layer. Consolidated (aged) asphaltene layers are frequently glassy and the elastic modulus exhibits frequency variations similar to those seen with glasses [35].

3. Oscillatory Spinning Drop Interfacial Rheometer

3.1 Description of the instrument

The determination of interfacial tension (IFT) with a spinning drop instrument is based on the axial elongation of a drop of the less dense phase in the denser continuous phase [5]. If the drop length L is larger than four times its radius a , the IFT is determined using Vonnegut's approximation [36]:

$$\gamma = \frac{\omega_{rot}^2 a^3 \Delta\rho}{4} \quad (8)$$

where $\Delta\rho$ is the density difference between the two fluids and ω_{rot} is the angular frequency of rotation. Expressions for $L < 4a$ were derived, but are less easy to handle. Experiments are usually performed with long drops for which equation 8 applies. Typical drop volumes are around 10 μL .

The oscillating spinning drop method was analysed theoretically by Slattery et al.[5]. A custom built instrument was devised in the FIRP laboratory and is depicted in Figure 1. The instrument is a standard spinning drop tensiometer to which an additional software has been added : model RI-1000 (FIRP Laboratory-CITEC, Universidad de Los Andes, Venezuela) made in the CITEC workshop [36]. It includes a spinning capillary of internal diameter 4 mm which is coupled to a motor and to a transducer. The capillary rotates at a speed which is controlled by a PID unit. In order to vary the drop area, the rotational speed can be varied sinusoidally at frequencies between 0.0166 and 0.25 Hz. The device automatically takes pictures at desired time intervals (down to 0.05 sec). Each picture allows determining the droplet diameter, which is automatically recorded together with the rotational speed. Then, the droplet diameter and the rotational speed are used to calculate the IFT using equation 8. The interfacial area is calculated assuming that the drop is a cylinder with two hemi-spherical caps.

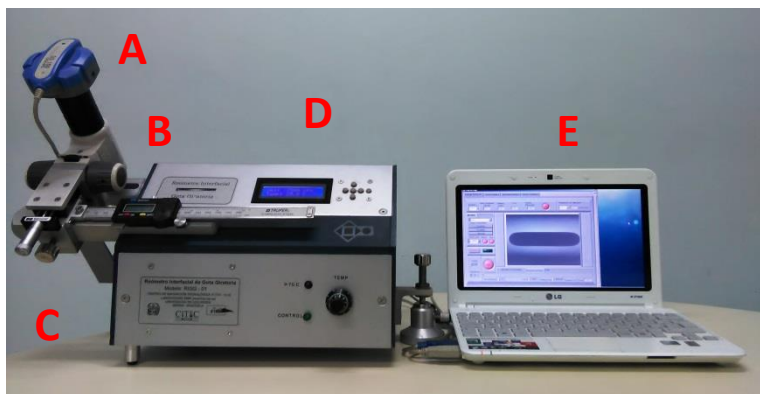


Figure 1. Recent version of a spinning drop rheometer made at CITEC-FIRP ULA. A: Digital Camera B: Microscope C: Mechanical arm and spinning chamber where the capillary is placed D: Body of the equipment and digital screen where rpm and temperature of the capillary are shown E: computer with computational software where the data is acquired and processed.

3.2 Description of the liquid samples

The instrument was tested with the following liquids:

- oil phases :
 - toluene and cyclohexane, technical grade, provided by Sigma Aldrich and Fisher Scientific respectively
 - Hamaca crude oil from the Orinoco oil belt (Venezuela). This heavy oil contains 17 % asphaltenes, its API number is 8, its acid number is 2 mg KOH/g. Asphaltenes were extracted from Hamaca crude oil by precipitation in n-heptane as presented in [37]
- water phase :
 - double distilled water (pure water)
 - double distilled water containing 5 g/L NaCl, analytical grade, from Merck, Germany (brine).
- Surfactants :
 - sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, from Sigma-Aldrich, USA.
 - ethoxylated nonylphenols, with an average number of ethylene oxide groups per molecule of 6 (NPEO6, $M_w = 440$, HLB = 10.9) and 8 (NPEO8 $M_w = 572$ Da, HLB = 12.3), nonionic surfactants, from WITCO.

In the 70's, the equilibration was carried out inside the capillary tube and was often taking a long time, sometimes with inconvenience such as the dissolution of the drop during equilibration. Another disadvantage with such a water-to-oil ratio very different from unity, is the alteration of the bulk and interfacial compositions because of partitioning effects. Here, we pre-equilibrate equal volumes of oil and water in test tubes for about 24 h before loading the capillary. With this procedure, a constant tension value is attained very quickly, generally in less than 1 h.

Various systems were studied in order to assess the validity of the technique:

- Pure liquid: Sec-butanol/air
- Soluble surfactants:

- SDBS solutions in water (1 g/L)/air
- Mixed solutions of NPEO6 and NPEO8 in water/ cyclohexane. The composition of the surfactant mixture was adjusted in order to be in the vicinity of the minimum interfacial tension (equivalent EO number 6.4). The surfactant concentration was varied between 0.015 and 2 g/L.
- Insoluble surface-active species: Hamaca crude oil (or its asphaltenes) diluted in toluene or cyclohexane. Asphaltene concentrations were varied between 0.1 and 10 g/L, in order to reduce the viscosity below about 10 mPa.s
- Mixtures of soluble and insoluble surface active species
 - SDBS solutions (1 g/L) in brine/Hamaca crude oil diluted in toluene
 - NPEO8 surfactant solutions in brine /Hamaca crude oil diluted in cyclohexane to achieve an asphaltene concentrations of 2 g/L (surfactant concentration scan from 0 to 800 mg/L). This system was used by Delgado et al. in a demulsification study [38].

The experiments were performed at a temperature of $30\text{ }^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

3.3 Description of the experimental procedure and of the data analysis

The previously equilibrated aqueous and oil phases are inserted then into the capillary, then equilibrated at $30\text{ }^{\circ}\text{C}$ and the drops formed. The magnification of the camera is adjusted from 10X to 40X according to the drop radius (for high IFT, 10X is used, while for low and ultralow IFTs, 20X to 40X are used). Then the rotation velocity is chosen according to IFT. The ranges usually used for high, low and ultralow IFTs are 7000-10000 rpm, 4000-7000 rpm and 3000 to 4000 rpm respectively. The frequency of variation of the rotation speed was generally set to 0.1 Hz. The amplitude of the oscillation was about 1000 rpm in order that the variation of interfacial area remains below 10% and to keep the rheological response linear.

A photograph of filaments of known diameter is used to calibrate the instrument. The corresponding error on the diameter is estimated to be about $\pm 1\mu\text{m}$, which leads to an error of 0.3 % for the tensions in the range of 10 mN/m (drop radius $\sim 1\text{ mm}$) and up to 2 % for tensions of the order of 0.01 mN/m. The error on rotation speed is $\pm 50\text{ rpm}$, corresponding to an error on the tension of about 2 % for a rotation velocity of 5,000 rpm. The densities are measured with an Anton Paar density meter (model DMA 4500 M) to within ± 0.0001 , and the corresponding error on $\Delta\rho$ and γ is about 0.1%. The overall error on the interfacial tension measurements is then between 2 to 5%, being the lowest for the largest tensions. Note that this estimated error is consistent with the measurement reproducibility.

The data shown in ref 8 indicate that the accuracy on the tensions measured with the Dataphysics instrument during the variation of the rotation speed is about 2% while the tensions measured are of the order of 10 mN/m. The overall accuracy of our instrument is therefore quite similar to that of the commercial one.

We show in Figure 2 experiments performed with interfaces between brine containing 800 ppm NPEO8 and Hamaca crude oil diluted in cyclohexane with an asphaltene content of 2 g/L of interfacial

tension 0.84 mN/m. Figure 2 shows the sinusoidal variation of the rotational speed versus time together with the drop aspect when the angular velocity is maximum and minimum.

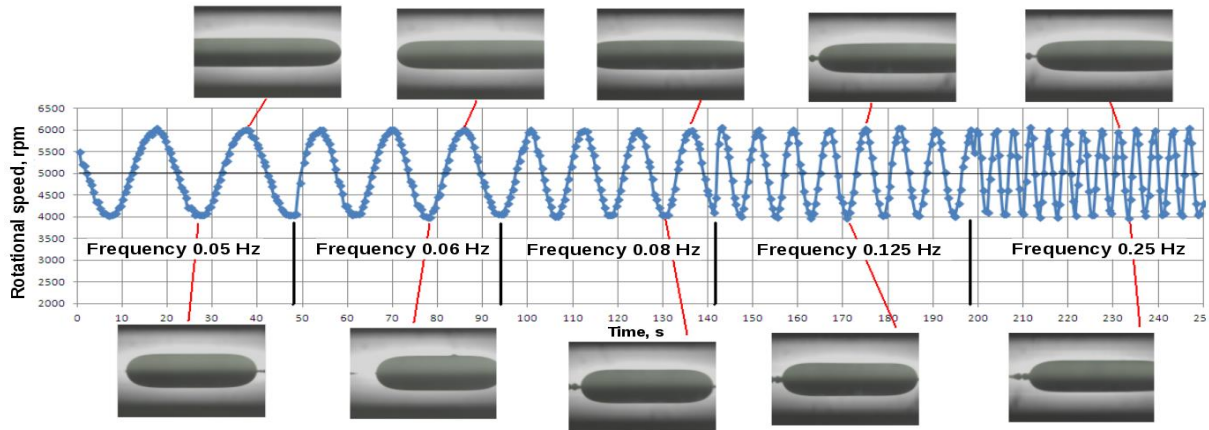


Figure 2. Sinusoidal variation of the rotational speed with time. The microphotographs shown were taken at minimum and maximum interfacial area. Each point marks the moment where the photographs are taken and the drop diameter measured. Interfaces between brine containing 0.8 g/L NPEO8 and Hamaca crude oil diluted in cyclohexane with an asphaltene content of 2 g/L.

In the following, it will be assumed that the viscoelastic response of the interface is linear. When the interfacial area is varied sinusoidally with a given angular frequency ω , the response is the sum of an elastic response, in phase with the excitation, and of a viscous response, shifted by 90° with respect to the excitation. Using complex numbers as in §2:

$$\tilde{E} = E' + iE'' = E \exp(i\phi)$$

with : $E' = E \cos \phi$ and $E'' = \omega \eta_E = E \sin \phi$; E' is sometimes called *storage modulus* and E'' *loss modulus*. The amplitude of the response is related to E , the phase shift being ϕ .

Here the excitation is the area change :

$$A = A_i + \Delta A \exp(i\omega t)$$

and the response is the change in interfacial tension

$$\gamma = \gamma_i + \Delta\gamma \exp(i\omega t + i\phi)$$

From Equation 1, we can write the interfacial compression modulus E as:

$$E = -A \frac{\partial \Pi}{\partial A} = A \frac{\partial \gamma}{\partial A} = A_i \frac{\Delta\gamma}{\Delta A} \quad (9)$$

Here we use quasi-static interfacial tension data, exactly as in the well-known pendant drop method. Bulk viscous stresses can introduce an apparent sinusoidal contribution to the interfacial tension, even for surfactant-free systems [39]. This contributions together with other possible sources of errors made using equation 9 will be discussed in § 4 together with experimental data.

In the present instrument, the parameters E , ϕ , E' , E'' and η_E are calculated by the computational software. Figure 3 shows a typical sinusoidal variation of interfacial tension and interfacial area.

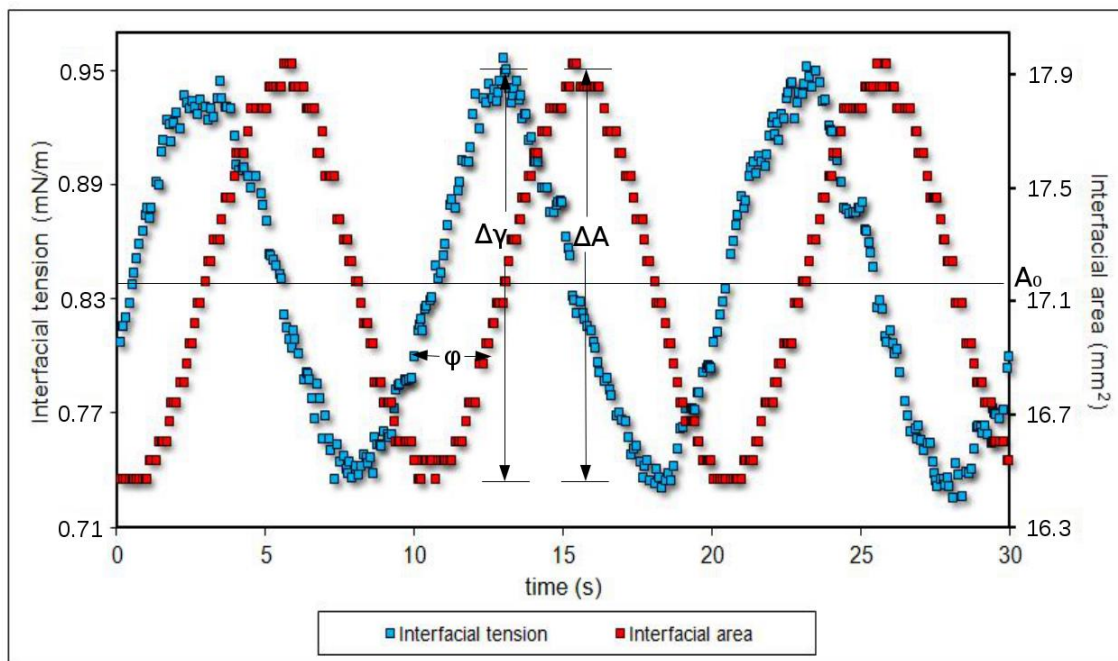


Figure 3. Oscillatory variation of the interfacial area and of the interfacial tension for an oscillatory deformation Frequency 0.1 Hz. Same system as in figure 2.

The experimental error combines the error on the surface tension and on the surface area. The overall error on the interfacial moduli is then between 4 to 10%, being the lowest for the largest tensions and larger for the lowest tensions.

4. Example of measurements

4.1 Surfactant free system

In order to check if the calibration of the instrument was correct, the behaviour of an air bubble in secondary butanol was first checked. One sees in figure 4 that the surface tension does not change when the drop area is varied, the modulus E is zero as expected when no surface layer is present. The measured surface tension was (22.0 ± 0.5) mN/m, while the literature value is 23.0 mN/m at 20°C [40]. Taking into account the fact that surface tensions decrease with temperature by about 0.1 mN/m per degree [41], the measured tension is in good agreement with the literature value

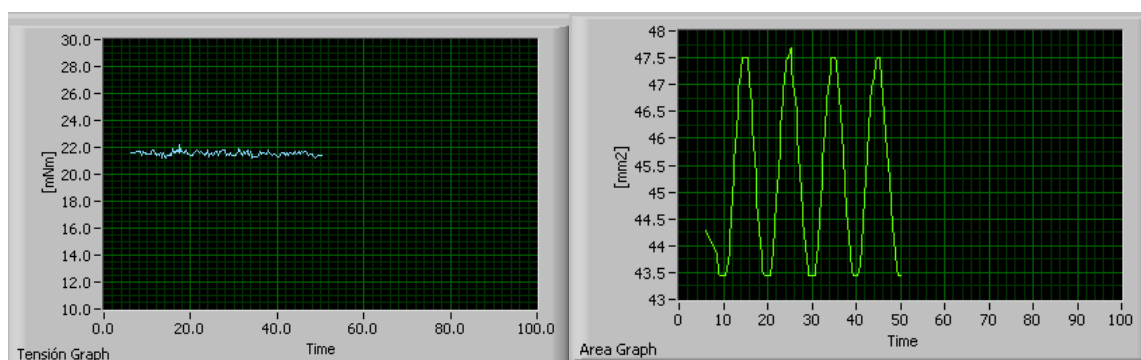


Figure 4. Surface tension (left) and surface area (right) for a drop of sec-butanol. Rotation velocity between 6000 and 7000 rpm

4.2 Soluble surfactant systems

Aqueous solutions of 1 g/L SDBS were studied. The critical micellar concentration (*cmc*) of this surfactant in water is 2 mM, or 0.7 g/L [42]. The surface tension that we measured for the solution is 27 mN/m, comparable to a reported one [42] (~32 mN/m). The difference is likely due to residual impurities. The elastic modulus E measured at a frequency of 0.1 Hz is 42.8 ± 1.8 mN/m and the phase angle $85.1 \pm 2.3^\circ$, leading to a storage modulus of 3.6 ± 2.0 mN/m.

In order to check if these parameters are similar to those measured with other methods, we performed pendant drop experiments with a KSV CAM 200 instrument and this SDBS solution. The results were $E = 4.3 \pm 0.1$ mN/m and $\phi = 36.0 \pm 2.5^\circ$, leading to $E' = 3.4 \pm 1.2$ mN/m. The value of E' is compatible with that measured with the spinning drop instrument, but the phases ϕ are very different. There is therefore a big discrepancy on the values of the loss modulus: $E'' = 2.5 \pm 1.7$ mN/m for the pendant drop and $E'' = 42.6 \pm 2.0$ mN/m for the spinning drop.

The measured E' and E'' are not intrinsic parameters, and are affected by diffusion as seen in §2. They might also be affected by convection in the spinning drop instrument, due to the high rotation velocities, possibly explaining the higher measured dissipation. We therefore made experiments changing the hydrodynamic conditions: velocity of rotation, amplitude of the deformation, bubble volume. The results are shown in table 1.

Rotation velocity rpm	E mN/m	Phase angle ϕ degrees	Bubble's volume μL
3,500-4,500	39.5 ± 0.3	89 ± 1.2	23
3,500-5,500	41.9 ± 0.3	89 ± 1.5	26.7
4,000-5,000	40.2 ± 0.9	89 ± 1.5	23
	40.1 ± 1.3	87 ± 1.6	26.7
4,250-4,750	45.3 ± 2.6	81 ± 3.1	26.7
5,000-6,000	41.6 ± 1.4	90 ± 1.1	23
5,000-7,000	42.5 ± 1.9	85 ± 2.1	26.7
5,000-8,000	43 ± 1.4	85 ± 2	26.7
5,500-6,500	41.8 ± 1.5	85 ± 1.7	26.7
5,750-6,250	45 ± 2.5	86 ± 1.8	26.7
6,000-7,000	41.7 ± 2.5	80 ± 2.5	23
7,000-8,000	44.8 ± 1.4	90 ± 1.4	23
8,000-9,000	45.8 ± 1.6	89 ± 1.4	23
9,000-9,500	44.8 ± 3.1	88 ± 3.5	2.3
9,000-10,000	38.9 ± 2.2	87.5 ± 3.5	2.3

Table 1. Modulus E and phase angle for bubbles in the SDBS solution. The errors quoted are the mean square deviation of the measurements (typically 5)

One sees in table 1, that the values of the modulus and phase angle are not significantly affected by the hydrodynamic conditions. We varied the frequency of rotation by a factor 3, the amplitude of deformation by a factor 6 and the bubble volume by a factor 10. If the adsorption-desorption process was affected by convection, the value of the modulus should depend on the velocity of rotation, but it does not. Furthermore, the storage modulus is the same than for the pendent drop measurement, which is only affected by diffusion. In fact and as shown by Slattery et al [5], the velocity of the fluid is mainly parallel to the drop (or bubble) surface, and the only convection expected is that induced from the sinusoidal variation in drop radius. However, this variation is similar to that used in pendent drop instruments, where convection was shown to be negligible.

The significant phase difference between the two drop methods led us to investigate other possible sources of artifacts.

- One possible source of error could arise from viscous dissipation in the bulk liquid. This effect has been addressed by Freer and Radke in the case of the oscillating pendent drop [39], as mentioned in §2. They report that viscous dissipation leads to an apparent additional interfacial tension variation, negative and proportional to the capillary number, i.e. to the amplitude of area variation, to its frequency and to the difference in viscosity between the drop and the exterior. This contribution is shifted by $\pi/2$ with respect to the excitation. This result holds for the spinning drop case. Table 1 shows that the phase does not change when the amplitude of area variation increases. Numerical estimations confirm that the bulk viscous friction cannot be responsible for the high value of the phase.
- Another source of error could be the friction with the wall of the capillary. This effect has been calculated by Slattery et al and could be significant if the radius of the drop is not much smaller than the radius of the capillary [5]. In order to change the drop radius, different intervals of rotational speed were studied. Measurements with a very small bubble were also performed. One sees in table 1 that neither the modulus, nor the phase change within error bars, while the radius changed by a factor 10.

Table 1 also shows that in the range of amplitudes used, the rheological response is linear for the amplitudes of area variation used. The difference in phase measurements between pendent and spinning drops will be further discussed in § 4.5

We show now measurements performed with surfactant systems of very low tension. In this case, we could not compare the data with pendent drop experiments, because the technique is no longer suitable in the range of tensions studied. Figure 5 illustrates the variation of interfacial tension and elastic modulus for the interface between cyclohexane and the mixed solution of nonionic surfactants.

One sees in figure 5 that the tension and the modulus decrease with surfactant concentration, the *cmc* being around 0.4 g/L. The elastic modulus also decreases with concentration as expected from a diffusion controlled mechanism (equations 3-5). The systems studied here contain two surfactants which are about as soluble in water and in oil. Equations 3-5 are therefore not appropriate for the calculations of the elastic modulus. However, theories for mixtures show that if the surfactants are

similar (similar surface activities and diffusion coefficients), equations 3-5 are good approximations. In the case of partitioned surfactants, theory also shows that these equations are good approximations, provided an effective diffusion coefficient is used [43]. We have therefore used equations 3-5 and 7 in order to estimate roughly the modulus E .

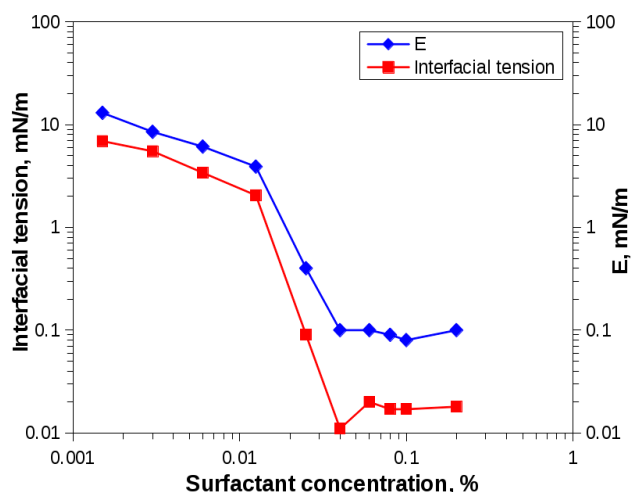


Figure 5. Interfacial tension and elastic modulus for the interface between cyclohexane and the mixed solution of nonionic surfactants (EO=6.4). Equilibration time 1h. .

We used typical values for surfactants $E_{ins} = 2 \Pi \sim 100 \text{ mN/m}$, $D = 4 \cdot 10^{-10} \text{ m}^2/\text{s}$, $\Gamma_{\infty} \sim 1 \text{ mg/m}^2$, $a \sim \text{cmc}/10 = 0.04 \text{ g/L}$ [44] and equations 3-5 and 7, one finds and $E \sim 30 \text{ mN/m}$ for a surfactant concentration of 0.04 g/L (0.004%), $E \sim 2.5 \text{ mN/m}$ for a surfactant concentration of 0.1 g/L (0.01%) and $E \sim 0.25 \text{ mN/m}$ for a surfactant concentration of 0.3 g/L (0.03%). Although very rough, these estimations leads to numbers of the same order than those measured.

4.3 Insoluble surface active species : asphaltenes in a solvent/brine interfaces

At the difference of the nonionic system presented above, the interfaces in the systems containing asphaltenes do not have low tensions and can be studied with other methods. The study of these systems was performed for the sake of comparison with literature studies.

4.3.1 Time evolution

The interfacial elastic modulus for the Hamaca crude oil dissolved in toluene containing 10 g/L asphaltenes/brine (5 g/l NaCl) is shown in Figure 6. As commonly observed, the interfacial tension decreases slowly with time, the decrease being generally attributed to the irreversibility of the adsorption and to the consolidation of the interfacial layer [13]. One sees in figure 6 that the elastic modulus increases as well, also a consequence of the consolidation of the layer. In the following, we have limited the measurements to aging times of 1 to 2 hours. The interfacial tensions do not evolve anymore, while the moduli continued to increase. Since our purpose is here to test the instrument, the precise age of the interface will not influence the discussion, provided of course that the measurements are performed rapidly enough. A typical measurement time, including about 5 trials to test the repeatability requires 10 min.

The values of the elastic modulus are comparable to those measured by other authors [45-50]. However, in these other works the phase angle was small and the loss modulus E'' small compared to

E'' . Here, the phase ϕ is higher than values currently reported in these systems and close to 90° . This means that the loss modulus E'' is larger than the storage modulus E' , while in pendent drop experiments E' is usually larger.

In order to see if the phase is also smaller in pendent drop experiments as in the case of SDBS solutions, we also performed pendent drop experiments with the crude oil system. The results were $\gamma = 14.9 \pm 0.16$ mN/m, $E = 8.4 \pm 1.1$ mN/m and $\phi = 30.6 \pm 1.8^\circ$, leading to $E' = 7.2 \pm 1.9$ mN/m. Similarly to the SDBS solution, the values of E' are compatible with those measured with the spinning drop (see figure 6) but the phases ϕ are very different, about 30° with the pendent drop, similar to those reported by many authors with similar asphaltene systems, while the phase is close to 90° with the spinning drop. There is therefore again a big discrepancy on the values of the loss modulus: $E'' = 4.3 \pm 2.1$ mN/m for the pendant drop and $E'' = 45.4 \pm 0.78$ mN/m for the spinning drop.

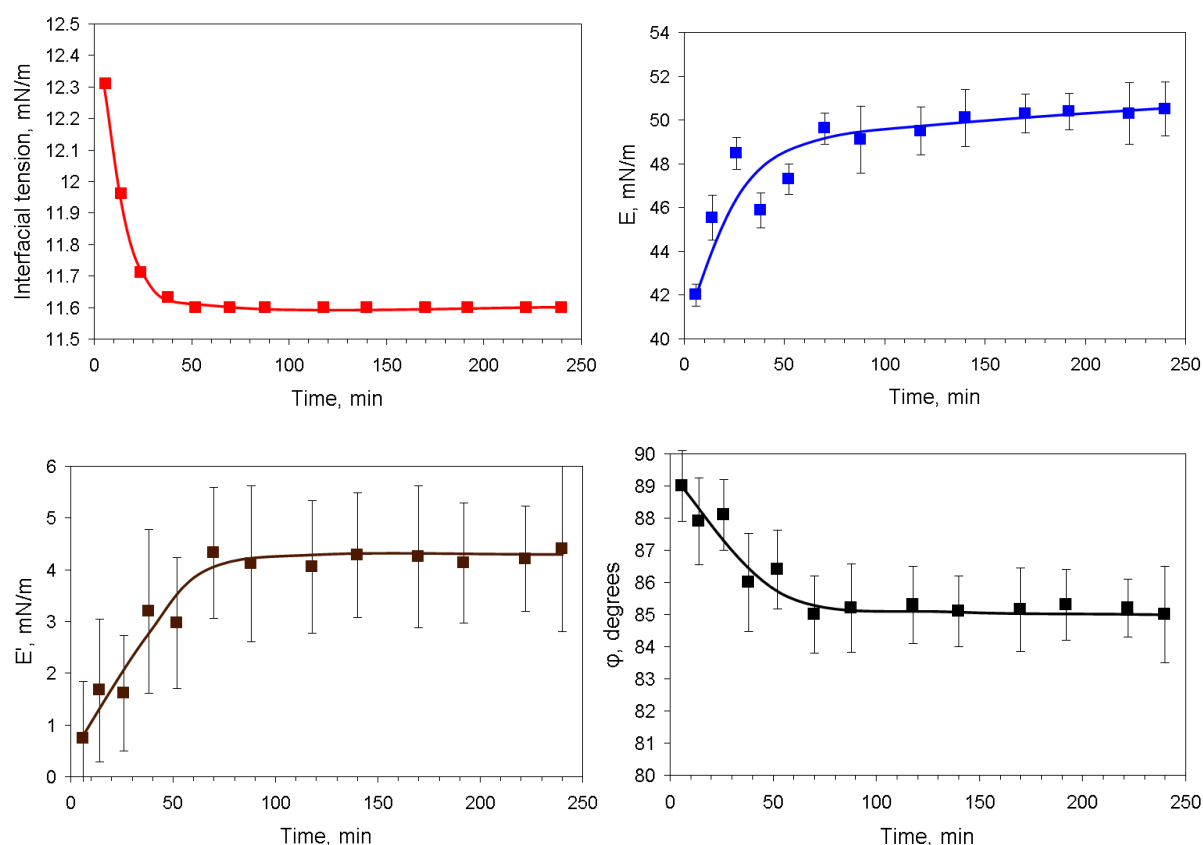


Figure 6. Interfacial tension, elastic modulus E , storage modulus E' and phase angle ϕ versus aging time for the interface between brine and Hamaca crude oil diluted in toluene (asphaltene concentration of 10 g/L). Frequency=0.1 Hz.

This difference led us to check if the measured values depended on hydrodynamic conditions (velocity of rotation, amplitude of deformation). The results are shown on table 2. Again neither the modulus, nor the phase change within error bars, ruling out the effect of viscous dissipation in the bulk liquid: the phase does not change when the velocity of rotation or the amplitude are changed. The friction with the wall of the capillary can be ruled out as well. Table 2 also shows that in the range of amplitudes used, the rheological response is linear for the amplitudes of area variation used.

Rotation velocity rpm	E mN/m	Phase angle ϕ °	Relative area variation %
7,000-8,000	39.6 ± 1.1	85.9 ± 1.5	6.0
8,000-9,000	45.7 ± 1	86.7 ± 0.7	5.2
9,000-10,000	47.5 ± 3.9	84.9 ± 2.6	4.4
7,500-9,500	44.5 ± 3.3	85.6 ± 2.3	8.8
7,000-10,000	47.5 ± 1.6	86.4 ± 2.2	16.0

Table 2. Modulus E and phase angle for interfaces between brine and Hamaca crude oil diluted in toluene (10g/L asphaltenes). The errors quoted are the mean square deviation of the measurements (typically 5)

4.3.2 Role of solvent

Figure 7 shows results for Hamaca crude oil diluted in various solvents: toluene, a good solvent of asphaltenes and cyclohexane, a solvent intermediate between toluene (good solvent) and alkanes (poor solvents).

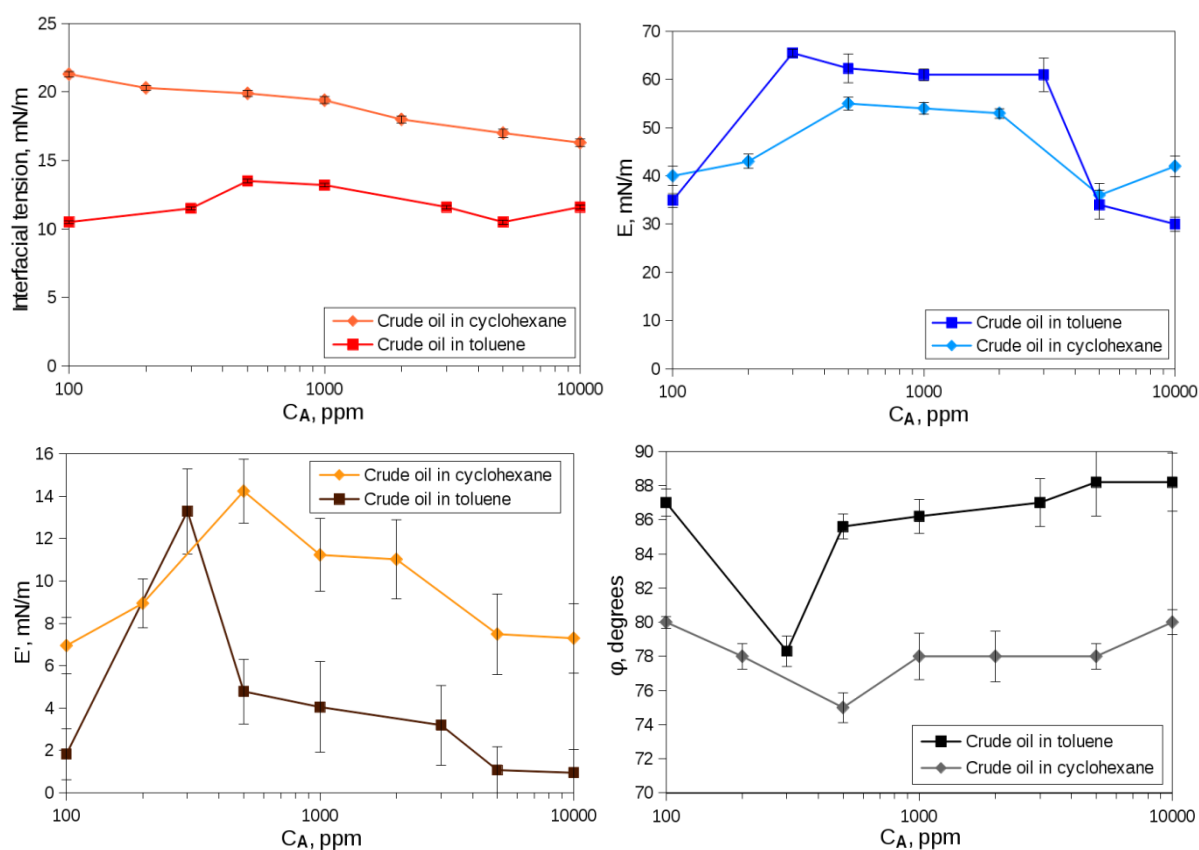


Figure 7. Interfacial tension, elastic modulus, storage elastic modulus and phase angle versus asphaltene concentration for interfaces between brine and dilutions of Hamaca crude oil in two solvents, toluene and cyclohexane. Equilibration time 1 h.

The total modulus E is larger for the toluene solutions, while the storage modulus E' is lower. The last result correlates with the stability of the emulsions made with these systems: the emulsions made with the toluene dilutions of crude oil are less stable than those made with cyclohexane dilutions [51]. As discussed in the introduction, it is indeed considered that the largest the elastic modulus, the

better the emulsion stability. We see here that the modulus to be considered appears to be the storage modulus. The total modulus is large for toluene, because the loss modulus is large.

Many authors reported the formation of *skins* at these interfaces upon compression, especially with asphaltene poor solvents [52, 53]. We sometimes noted in the instrument used here the formation of patches looking like pieces of skins, but a skin covering the whole drop was never observed. This is probably because the layers studied do not possess a large enough elastic shear storage moduli.

4.3.3 Comparison between dilutions of crude oil and asphaltene solutions

Figure 8 shows the frequency variation of the elastic modulus, storage elastic modulus and phase angle of Hamaca crude oil dissolved in toluene and Hamaca crude oil asphaltenes dissolved in toluene (same asphaltene concentration, 10 g/L) against brine (5 g/l NaCl) interfaces. It is observed that the system with asphaltene diluted in toluene possesses an interfacial elastic modulus higher than the system with crude oil diluted in toluene system, whatever the frequency. This is associated with a better emulsion stability, as found by Angle et al. with bitumen [49] This lower value of the elastic modulus for the crude oil dilutions or asphaltene solutions is related to the fact that the other components of the oil, among them the resins, contribute to improve the asphaltene solubility, hence decrease the adsorbed amounts.

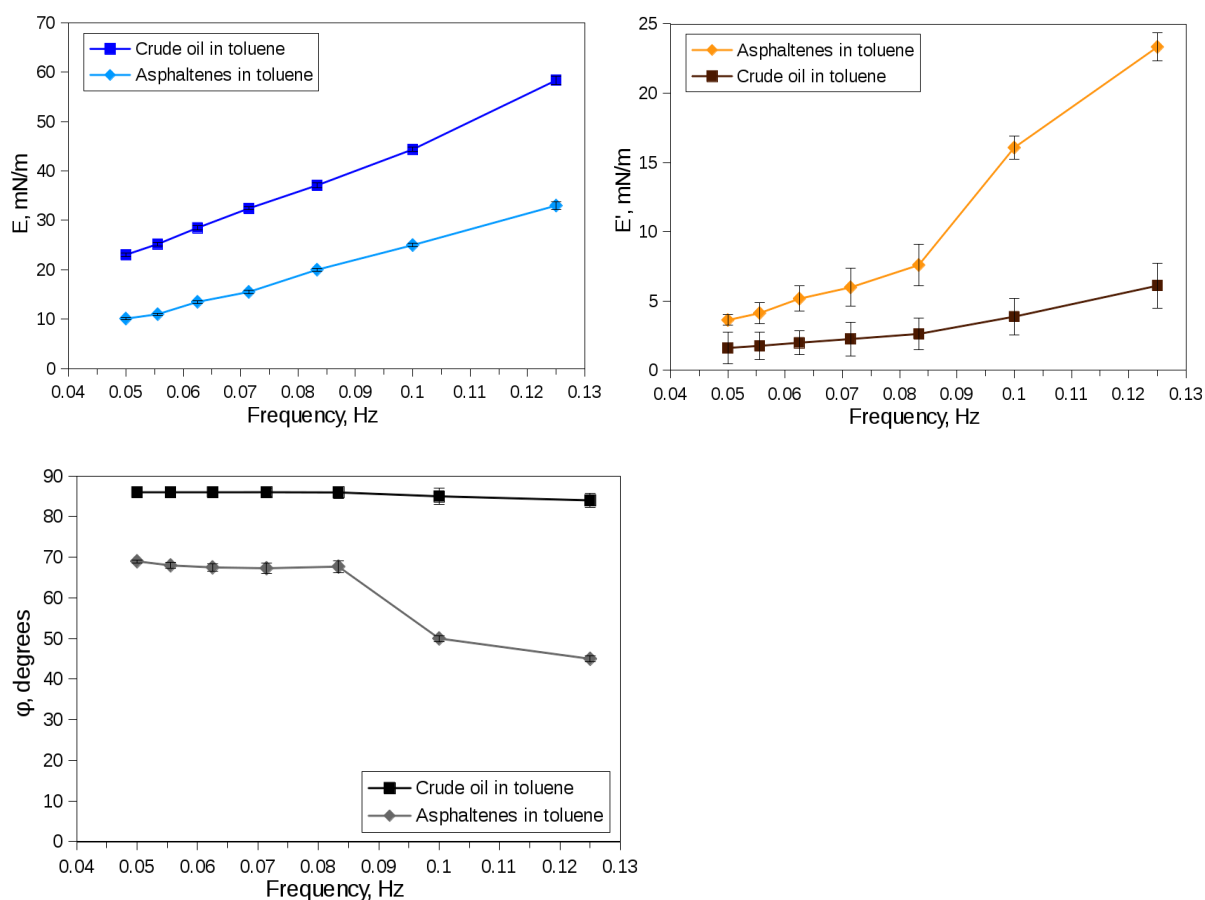


Figure 8. Frequency sweep for the Hamaca crude oil diluted in toluene and Hamaca asphaltenes diluted in toluene interfaces with brine. IFT=11.6 mN/m for the crude oil diluted in toluene and IFT=11.9 mN/m for the asphaltene diluted in toluene systems. Equilibration time 1 h.

Figure 8 also shows that the elastic modulus increases with the frequency, as observed by many authors with other instruments [16, 34, 35, 46, 48-50, 54-57].

4.4 Mixtures of soluble and insoluble surfactants : surfactant solutions in brine/diluted crude oil interfaces

In order to evaluate the potential of the technique in the range of low interfacial tensions, systems containing surfactant were investigated, in particular a surfactant with a demulsifier action[38]. Demulsifiers are surfactants that stabilize emulsions of the opposite nature, for instance here, oil in water emulsions, while asphaltenes stabilize water in oil emulsions. When well chosen demulsifiers are added to asphaltene stabilized emulsions, they destabilize them. However, as mentioned in the introduction, the precise mechanism of their action is not yet fully elucidated. Since it is likely related to interfacial rheology, measurements are desirable, especially in the low IFT range where no method was available until now.

Figure 9 shows the frequency variations of the modulus and phase for interfaces between Hamaca crude oil diluted in toluene and brine with or without 1 g/L SDBS . As before, the elastic modulus E increases with frequency; E decreases by two orders of magnitude when surfactant is added. The addition of surfactant decreases the phase angle as seen by Chavez et al for the shear rheology [58]

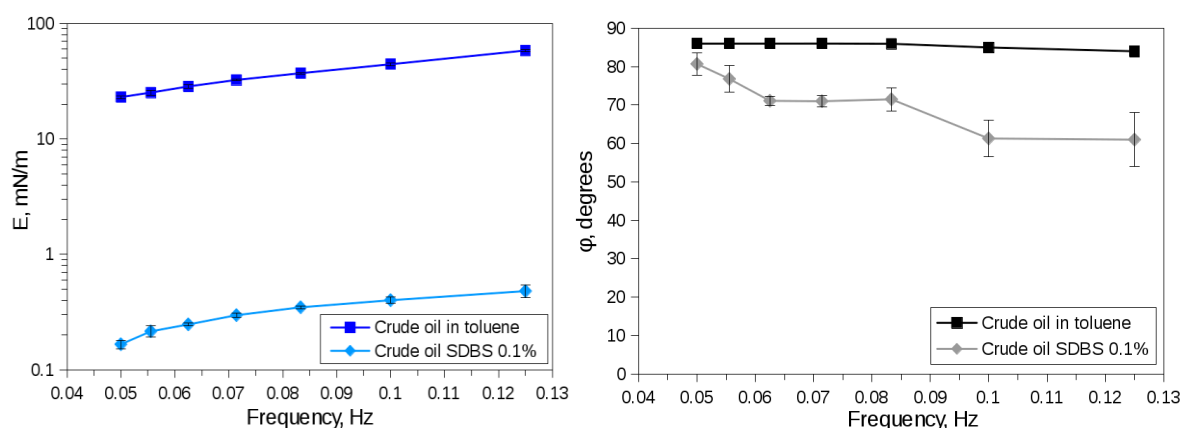


Figure 9. Frequency sweep for the Hamaca crude oil diluted in toluene (10 g/L asphaltenes)/brine and brine with SDBS (1 g/L). With the surfactant, the IFT is 0.11 mN/m. Equilibration time 1h.

Experiments have also been done with a hydrophilic non-ionic surfactant, NPEO8, used as demulsifier in a previous work [23]. The time variation of the interfacial tension between surfactant solutions in water and 2 g/L Hamaca crude oil in cyclohexane is depicted in figure 10. The interfacial tension decreases with time due to the adsorption of surfactant and asphaltenes at the interface. The decrease is more pronounced for small surfactant concentrations as expected. The tension is also smaller for larger surfactant concentrations as discussed in the introduction.

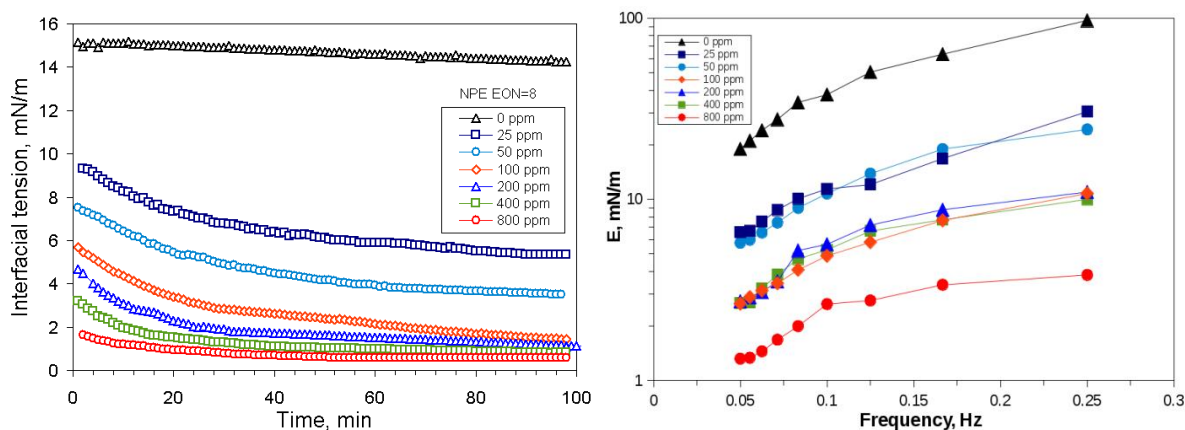


Figure 10. Left: Dynamic interfacial tension for the NPEO8/Hamaca crude oil diluted in cyclohexane (asphaltene concentration 2 g/L)/water. Right: Elastic modulus measured after 100 min.

In these systems, the interfacial tensions reach constant values after about 1 h varying between 5.89 and 0.74 mN/m when the surfactant concentration increases from 25 to 800 mg/L. The moduli decrease with surfactant concentration and increase with frequency also as usual. The phase angle remains high and varies between 82 and 86°.

These type of surfactants have a demulsifier action with crude oil emulsions [38] [51]. It is thus seen that the spinning drop instrument allows obtaining information not only on interfacial tension, but also on interfacial rheology, offering a way to understand better demulsifier action.

More complete studies, including systems with ultralow interfacial tensions will be presented in forthcoming publications.

4.5 Comparison with the oscillating pendent drop method

Asphaltenes are irreversibly adsorbed and as a consequence, the measured rheological parameters are intrinsic ones. The two interfacial viscosities are therefore expected to be comparable. In their calculations, Slattery et al included both interfacial viscosities, compression and shear (but no storage moduli) [5]. Because the spinning drop is studied in a configuration where its length is much larger than its radius, one can view the drop deformation as an elongational deformation, in which case, the modulus measured is the Young modulus E_{Young} . In two dimensions, this modulus is the sum of the compression and shear moduli: $E_{\text{Young}} = E + G$ [59]. The modulus measured with methods using spinning and pendent drops are therefore different.

The fact that the measured E' are similar here is also understandable, since for interfaces with surfactant solutions, the shear modulus G is zero. In the case of asphaltene solutions in a good solvent such as toluene, G becomes only measurable after a day or so [16]. The values of E'' are different, because they include Surface shear viscosity contributions.

The differences in E'' observed with the SDBS solutions are more surprising, because pure surfactants usually have low shear viscosities [2]. But the SDBS used contains surface active impurities that may increase the surface shear viscosities, as for instance dodecanol with sodium dodecyl sulfate.

It should finally be mentioned that because the shape of the pendent drop is not perfectly spherical, the modulus measured with this method is not exactly the compression modulus, but also contains contributions of the shear modulus [60].

5. Conclusions

Surface rheology is a complex notion but it seems to control many applications [1] [2]. It therefore deserves attention and progresses are desirable. The necessity to take into account surface elastic effects due to surface tension gradients when the interface is compressed is now recognized. Surface viscous effects also play important role in surface motion. When irreversibly adsorbed surface agents are present, the interfacial layers can also behave as solid bodies and present a resistance to shear

Various types of instruments are available for the measurements of surface rheological parameters, elastic and loss moduli, for both compression and shear [2]. The most common instruments make use of oscillating pendent drops or are rheometers equipped with bicones. These instruments are applicable to systems with large enough interfacial tension, typically above a few mN/m.

In order to go beyond this limitation, we used a new type of instrument based on oscillating spinning drops. We demonstrate the capability of the new technique presenting examples of surface rheological studies of systems with high, low and ultralow interfacial tensions. We discussed the possible artifacts arising from surfactant convection, viscous losses in the bulk fluid or when the drop is too close to the wall of the container. We have shown that the interfacial moduli can be determined with a very good accuracy (a few %), even for interfacial tensions as low as 0.01 mN/m. This is not actually the lowest limit and in a future paper we will present results for systems with tensions down to 0.001 mN/m.

The rheological parameters determined with the instrument are related to uniaxial compression, the elastic modulus being a surface Young modulus. For an interface, this modulus is the sum of the compression and the shear moduli. For soluble surfactants, the shear modulus is zero, but when irreversibly adsorbed molecules such as asphaltenes are present, the shear modulus can take appreciable values. The loss modulus is also the sum of the corresponding compression and shear loss moduli. It would be interesting to make a comparison between the moduli measured with a spinning drop and the pure shear response as measured with an interfacial shear rheometer. Such a comparison is planned in a future work.

The new instrument opens the way to rheological characterizations of interfaces with low tension, which has been so far impossible due to the limitations of the existing instruments. Interfacial rheology studies of low tension systems for enhanced oil recovery is now possible and no doubt it will important new findings for the understanding of the stability of the corresponding emulsions. It also opens the way to new studies of demulsifiers, which frequently lower oil-water interfacial tensions below 1 mN/m, and thus to a better understanding of their action. Demulsification is a very general problem, encountered only in dehydration or desalting in the petroleum production and refining but also in many other industries. Future work along these lines is currently in progress.

Acknowledgements

The authors thank Gerardo Quevedo and all the staff at the Center of Technology Innovation CITEC at Universidad de Los Andes, Venezuela who contributed to the conception and realization of the instrument. We thank Alain Cagna from Teclis for useful comments concerning possible contributions of bulk viscous losses. The Postgraduate Cooperation Program (PCP franco-venezolano) is thanked for having helped professors and students to travel between France and Venezuela.

References

- [1] D.A. Edwards, H. Brenner, D.T. Wasan, *Interfacial Transport Processes and Rheology*, Butterworth-Heinemann, 1991.
- [2] D. Langevin, *Rheology of Adsorbed Surfactant Monolayers at Fluid Surfaces*, in: S.H. Davis, P. Moin (Eds.) *Annual Review of Fluid Mechanics*, Vol 46, 2014, pp. 47-65.
- [3] J.L. Cayias, R.S. Schechter, W.H. Wade, Utilization of petroleum sulfonates for producing low interfacial-tensions between hydrocarbons and water, *Journal of Colloid and Interface Science*, 59 (1977) 31-38.
- [4] A. Pouchelon, J. Meunier, D. Langevin, D. Chatenay, A.M. Cazabat, Low interfacial-tensions in 3-phase systems obtained with oil-water surfactant mixtures, *Chemical Physics Letters*, 76 (1980) 277-281.
- [5] J.C. Slattery, J.D. Chen, C.P. Thomas, P.D. Fleming, Spinning drop interfacial viscometer, *Journal of Colloid and Interface Science*, 73 (1980) 483-499.
- [6] J.L. Salager, *Principles of the spinning drop tensiometer*. Cuaderno FIRP E705-A, Mérida, Venezuela, 2005.
- [7] <http://www.dataphysics.de/2/start/products/spinning-drop-tensiometer/software-modules/>, in.
- [8] L. Zhang, Q.T. Gong, Z.H. Zhou, W.N. Wang, S. Zhao, J.Y. Yu, Study of Interfacial Dilational Properties by the Spinning Drop Technique, *Acta Physico-Chimica Sinica*, 25 (2009) 41-46.
- [9] W. Wang, K. Li, P.Y. Wang, S. Hao, J. Gong, Effect of interfacial dilational rheology on the breakage of dispersed droplets in a dilute oil-water emulsion, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 441 (2014) 43-50.
- [10] B. Wei, R. Wu, L. Lu, X. Ning, X. Xu, C. Wood, Y. Yang, Influence of Individual Ions on Oil/Brine/Rock Interfacial Interactions and Oil-Water Flow Behaviors in Porous Media, *Energy & Fuels*, 31 (2017) 12035-12045.
- [11] H. Rehage, M. Husmann, A. Walter, From two-dimensional model networks to microcapsules, *Rheologica Acta*, 41 (2002) 292-306.
- [12] J.D. Martin, S.S. Velankar, Unusual behavior of PEG/PPG/Pluronic interfaces studied by a spinning drop tensiometer, *Journal of Colloid and Interface Science*, 322 (2008) 669-674.
- [13] D. Langevin, J.F. Argillier, Interfacial behavior of asphaltenes, *Advances in Colloid and Interface Science*, 233 (2016) 83-93.
- [14] P.K. Kilpatrick, Water-in-Crude Oil Emulsion Stabilization: Review and Unanswered Questions, *Energy & Fuels*, 26 (2012) 4017-4026.
- [15] D.T. Wasan, J.J. McNamara, S.M. Shah, K. Sampath, N. Aderangi, Role of coalescence phenomena and interfacial rheological properties in enhanced oil-recovery - overview, *Journal of Rheology*, 23 (1979) 181-207.
- [16] Y. Fan, S. Simon, J. Sjoblom, Interfacial shear rheology of asphaltenes at oil-water interface and its relation to emulsion stability: Influence of concentration, solvent aromaticity and nonionic surfactant, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 366 (2010) 120-128.

- [17] W.L. Kang, G.L. Jing, H.Y. Zhang, M.Y. Li, Z.L. Wu, Influence of demulsifier on interfacial film between oil and water, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 272 (2006) 27-31.
- [18] S. Mukherjee, A.P. Kushnick, Effect of Demulsifiers on Interfacial Properties Governing Crude Oil Demulsification, in: *Oil-Field Chemistry*, American Chemical Society, 1989, pp. 364-374.
- [19] J. Tao, P. Shi, S.W. Fang, K.Y. Li, H. Zhang, M. Duan, Effect of Rheology Properties of Oil/Water Interface on Demulsification of Crude Oil Emulsions, *Industrial & Engineering Chemistry Research*, 54 (2015) 4851-4860.
- [20] Y.H. Kim, D.T. Wasan, P.J. Breen, A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 95 (1995) 235-247.
- [21] J.-L. Salager, Fundamental basis for the action of a chemical dehydrant. Influence of the physical and chemical formulation on the stability of an emulsion, 1990.
- [22] A. Goldszal, M. Bourrel, Demulsification of crude oil emulsions: Correlation to microemulsion phase behavior, *Industrial & Engineering Chemistry Research*, 39 (2000) 2746-2751.
- [23] M. Rondon, P. Bouriat, J. Lachaise, J.L. Salager, Breaking of water-in-crude oil emulsions. 1. Physicochemical phenomenology of demulsifier action, *Energy & Fuels*, 20 (2006) 1600-1604.
- [24] J.W. Gibbs, *The Collected works*, Longmans, Green and co., 1928.
- [25] F.C. Goodrich, The theory of capillary excess viscosities, *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences*, 374 (1981) 341-370.
- [26] V.G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, 1962.
- [27] J. Lucassen, M. Van Den Tempel, Dynamic measurements of dilational properties of a liquid interface, *Chemical Engineering Science*, 27 (1972) 1283-1291.
- [28] A.A. Sonin, A. Bonfillon, D. Langevin, Role of surface elasticity in the drainage of soap films, *Physical Review Letters*, 71 (1993) 2342-2345.
- [29] F. Evans, W. Wennerström, *The Colloidal Domain*, second ed., Wiley, 1999.
- [30] J.R. Lu, M. Hromadova, R.K. Thomas, J. Penfold, Direct Determination by Neutron Reflection of the Structure of Triethylene Glycol Monododecyl Ether Layers at the Air/Water Interface, *Langmuir*, 9 (1993) 2417-2425.
- [31] J. Lucassen, Adsorption-kinetics in micellar systems, *Faraday Discussions*, 59 (1975) 76-87.
- [32] Q. Jiang, J.E. Valentini, Y.C. Chiew, Theoretical-models for dynamic dilational surface-properties of binary surfactant mixtures, *Journal of Colloid and Interface Science*, 174 (1995) 268-271.
- [33] A. Bonfillon, D. Langevin, Electrostatic model for the viscoelasticity of ionic surfactant monolayers *Langmuir*, 10 (1994) 2965-2971.
- [34] E.M. Freer, C.J. Radke, Relaxation of asphaltenes at the toluene/water interface: Diffusion exchange and surface rearrangement, *Journal of Adhesion*, 80 (2004) 481-496.
- [35] C. Dicharry, D. Arla, A. Siquin, A. Graciaa, P. Bouriat, Stability of water/crude oil emulsions based on interfacial dilatational rheology, *Journal of Colloid and Interface Science*, 297 (2006) 785-791.
- [36] A. Couper, R. Newton, C. Nunn, A simple derivation of vonnegut equation for the determination of interfacial-tension by the spinning drop technique, *Colloid and Polymer Science*, 261 (1983) 371-372.
- [37] B.M. Aguilera, J.G. Delgado, A.L. Cardenas, Water-in-Oil Emulsions Stabilized by Asphaltenes Obtained from Venezuelan Crude Oils, *Journal of Dispersion Science and Technology*, 31 (2010) 359-363.
- [38] J.G. Delgado-Linares, J.C. Pereira, M. Rondon, J. Bullon, J.L. Salager, Breaking of Water-in-Crude Oil Emulsions. 6. Estimating the Demulsifier Performance at Optimum Formulation from Both the Required Dose and the Attained Instability, *Energy & Fuels*, 30 (2016) 5483-5491.
- [39] E.M. Freer, H. Wong, C.J. Radke, Oscillating drop/bubble tensiometry: effect of viscous forces on the measurement of interfacial tension, *Journal of Colloid and Interface Science*, 282 (2005) 128-132.
- [40] <https://pubchem.ncbi.nlm.nih.gov/compound/2-Butanol#section=Heat-of-Vaporization>, in.

- [41] A.W. Adamson, A.P. Gast, *Physical Chemistry of Surfaces*, 6th Revised edition ed., John Wiley & Sons Inc, 1997.
- [42] G.B. Ray, I. Chakraborty, S. Ghosh, S.P. Moulik, A critical and comprehensive assessment of interfacial and bulk properties of aqueous binary mixtures of anionic surfactants, sodium dodecylsulfate, and sodium dodecylbenzenesulfonate, *Colloid and Polymer Science*, 285 (2007) 457-469.
- [43] V.I. Kovalchuk, personal communication, manuscript in preparation.
- [44] J. Lucassen, D. Giles, Dynamic surface properties of nonionic surfactant solutions, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 71 (1975) 217-232.
- [45] G. Alvarez, S. Poteau, J.-F. Argillier, D. Langevin, J.-L. Salager, Heavy Oil-Water Interfacial Properties and Emulsion Stability: Influence of Dilution, *Energy & Fuels*, 23 (2009) 294-299.
- [46] J.P. Rane, S. Zarkar, V. Pauchard, O.C. Mullins, D. Christie, A.B. Andrews, A.E. Pomerantz, S. Banerjee, Applicability of the Langmuir Equation of State for Asphaltene Adsorption at the Oil-Water Interface: Coal-Derived, Petroleum, and Synthetic Asphaltenes, *Energy & Fuels*, 29 (2015) 3584-3590.
- [47] F. Liu, S. Darjani, N. Akhmetkhanova, C. Maldarelli, S. Banerjee, V. Pauchard, Mixture Effect on the Dilatation Rheology of Asphaltenes-Laden Interfaces, *Langmuir*, 33 (2017) 1927-1942.
- [48] L.M. Ligiero, C. Dicharry, N. Passade-Boupat, B. Bouyssiere, P.M. Lalli, R.P. Rodgers, C. Barrere-Mangote, P. Giusti, P. Bouriat, Characterization of Crude Oil Interfacial Material Isolated by the Wet Silica Method. Part 2: Dilatational and Shear Interfacial Properties, *Energy & Fuels*, 31 (2017) 1072-1081.
- [49] C.W. Angle, Y. Hua, Dilational Interfacial Rheology for Increasingly Deasphalted Bitumens and n-C5 Asphaltenes in Toluene/NaHCO₃ Solution, *Energy & Fuels*, 26 (2012) 6228-6239.
- [50] H.W. Yarranton, D.M. Sztukowski, P. Urrutia, Effect of interfacial rheology on model emulsion coalescence - I. Interfacial rheology, *Journal of Colloid and Interface Science*, 310 (2007) 246-252.
- [51] M. Rondon, J.C. Pereira, P. Bouriat, A. Graciaa, J. Lachaise, J.L. Salager, Breaking of water-in-crude-oil emulsions. 2. Influence of asphaltene concentration and diluent nature on demulsifier action, *Energy & Fuels*, 22 (2008) 702-707.
- [52] J.E. Strassner, Effect of pH on interfacial films and stability of crude oil-water emulsions, *Journal of Petroleum Technology*, 20 (1968) 303-&.
- [53] J. Czarnecki, K. Moran, On the stabilization mechanism of water-in-oil emulsions in petroleum systems, *Energy & Fuels*, 19 (2005) 2074-2079.
- [54] P. Bouriat, N. El Kerri, A. Graciaa, J. Lachaise, Properties of a two-dimensional asphaltene network at the water - Cyclohexane interface deduced from dynamic tensiometry, *Langmuir*, 20 (2004) 7459-7464.
- [55] N. Anton, T.F. Vandamme, P. Bouriat, Dilatational rheology of a gel point network formed by nonionic soluble surfactants at the oil-water interface, *Soft Matter*, 9 (2013) 1310-1318.
- [56] T.L. Sun, L. Zhang, Y.Y. Wang, B. Peng, S. Zhao, M.Y. Li, J.Y. Yu, Dynamic dilational properties of oil-water interfacial films containing surface active fractions from crude oil, *Journal of Dispersion Science and Technology*, 24 (2003) 699-707.
- [57] C.G. Quintero, C. Noik, C. Dalmazzone, J.L. Grossiord, Formation Kinetics and Viscoelastic Properties of Water/Crude Oil Interfacial Films, *Oil & Gas Science and Technology-Revue D Ifp Energies Nouvelles*, 64 (2009) 607-616.
- [58] T.E. Chavez-Miyauchi, A. Firoozabadi, G.G. Fuller, Nonmonotonic Elasticity of the Crude Oil-Brine Interface in Relation to Improved Oil Recovery, *Langmuir*, 32 (2016) 2192-2198.
- [59] L. Landau, E. Lifshitz, *Theory of Elasticity*, Addison Wesley, 1959.
- [60] A. Yeung, L.C. Zhang, Shear effects in interfacial rheology and their implications on oscillating pendant drop experiments, *Langmuir*, 22 (2006) 693-701.