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# Interfacial characterisation of dispersed components in produced water

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## **Preface**

This work has been conducted at the Ugelstad Laboratory at the Department of Chemical Engineering, Norwegian University of Science and Technology in Trondheim, during the spring of 2012.

I would like to acknowledge my supervisors Mona Eftekhardadkhah, Bartlomiej Gawel and Professor Gisle Øye, for all their helpful advice and guidance. Master student Sulalit Banerjee is to be thanked for his contribution in the early stage of the project. Researcher Sébastien Simon is also to be acknowledged for his much precious help and for keeping me company during long week-ends in the lab, as well as the entire Ugelstad laboratory for contributing to a pleasant work environment.

Finally, I want to thank my husband Cedric for all his help, support and patience. (Jtmtpp)

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology.

Trondheim, 27.06.2012

Caterina Lesaint-Rusu

## **Abstract**

While a number of studies have investigated the processes responsible for the decay of the interfacial tension between crude oil and water with time, there is a great need for an improved understanding of the mechanisms involved. Herein, we investigate the influence of content for several different crude oils on their interfacial properties, interfacial tension and interfacial rheological parameters. The influence of the water phase composition has also been studied.

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## 1. Introduction

Produced water is water co-produced with oil and gas during petroleum production. Worldwide the average production of water is three times higher than the petroleum production, and the water content continues to increase as the oil fields become more mature. Pollutants like dispersed oil and solids must be separated from the produced water streams prior to discharge or reinjection, and efficient and reliable treatment processes are required. This means that it is necessary to understand the mechanisms that govern the separation efficiency at the molecular level, and the interfacial properties are crucial in this respect. The main objective of this master thesis work is to measure interfacial tensions and interfacial rheology parameters at the oil/water interface between different crude oils and crude oil fractions and aqueous solutions. Therefore, herein we investigate the influence of acid and base content for two different crude oils on their interfacial properties, interfacial tension and interfacial rheological parameters, as well as the influence of oil composition for a number of oil samples. The influence of the water phase composition has also been studied.

In order to optimize the treatment of water in oil emulsions, it is essential to understand how they are stabilized. The predominant mechanism whereby petroleum emulsions are stabilized is through the formation of a film with elastic and/or viscous properties<sup>1</sup>. The study of dilational viscoelasticity properties of the interfacial film provides a basis for understanding the stability of emulsion<sup>2</sup>. The interfacial properties will thus be later on correlated with the formation and separation efficiency of corresponding oil-in-water emulsions. While a number of studies have already investigated the processes responsible for the decay of the interfacial tension between crude oil and water with time, there is a great need for an improved understanding of the mechanisms involved.

## 2. Experimental section

### 2.1. Materials

Nine different crude oils were used for this study. They will be referred to herein by using capital letters: A, B, ..., I. The coding for these oils is included in Annex 2. The majority of these crude oils have been previously characterized and the characterization data can be found in Annex 1. In the case of crude oils A and B, the acid and the base components were extracted and the measurements were performed on the acid- and base-extracted fractions. Measurements for sample A were conducted in a previous study and the results were used for comparison in this thesis.

These crude oils were chosen on the basis of their different chemical and physical properties, such as the difference in the content in resins and asphaltenes (oil components well known for their important interfacial film properties), as well as notable differences in the density and viscosity values.

Four different water phases were also used in this study: pure water, synthetic brine “with all ions”, synthetic brine without carbonates and synthetic brine without divalent ions (e.g.  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ). The salt water phases composition was decided in such a way that the ionic strength remains the same for all three; this is because in this study we aimed at checking the influence of other parameters (i.e. oil and brine composition) and thus the influence of the ionic strength on the interfacial properties is disregarded. The exact compositions of the water phases are given in Table 1.

The materials (oil and water phases) were chosen this way in order to allow studying interfacial properties of oils with a wide variety of compositions and physical and chemical properties in presence of different ions in the water phase.

Table 1: Chemical composition of the water phases.

Ions	Pure water (ppm)	Synthetic brine (ppm)	Synthetic brine without divalent ions (ppm)	Synthetic brine without bicarbonates (ppm)
Cl <sup>-</sup>	0	62810	67020	62810
Na <sup>+</sup>	0	35393	43483	35393
Ca <sup>2+</sup>	0	3253	0	3253
Mg <sup>2+</sup>	0	909	0	909
HCO <sub>3</sub> <sup>-</sup>	0	218	218	0
SO <sub>4</sub> <sup>2-</sup>	0	49	45	49

During preparation of the brine waters, special care was given to the order in which the salts were dissolved. In order to prevent the carbonate precipitation, first the components containing chloride ions were dissolved, then the sulphates and finally the carbonates. After salt dissolution the brines were stirred for at least 24 hours before being used for measurements.

Interfacial film properties were investigated for acid-free and base-free fractions of oil B in presence of all four water compositions, while for the other oils (i.e. diluted C, diluted D, E, F, G, H and I) measurements were performed only in presence of synthetic brine “with all the ions”.



## 2.2. The oscillating pendant drop: Method

The interfacial tension and rheology of the oil water films were studied with a Sinterface PAT-1M apparatus. In Figure 1, a photograph of the instrument is shown. The procedure for using the instrument can be found in annex 4.

The instrument consists of a basic platform on which all parts are safely mounted: a computer controlled dosing system, an adjustable temperature-controlled measuring cell, a CCD-camera with fixed objectives, a high-performance frame grabber installed in the PC and a cold back lighting with continuously adjustable intensity.

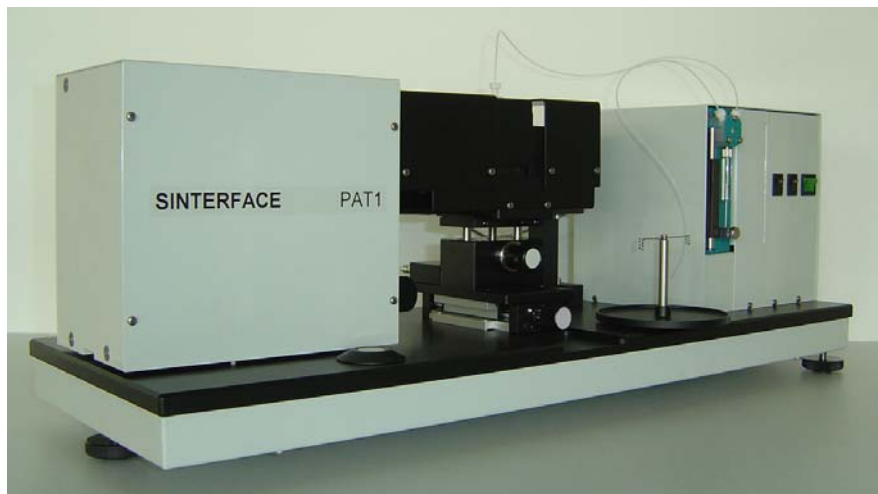


Figure 1: PAT-1 (Profile Analysis Tensiometer) from SINTERFACE

From the drop profile (given by the Gauss-Laplace equation, which relates the curvature of a liquid meniscus to the surface tension  $\gamma$ ) and the known densities of both the oil and the aqueous phases, the interfacial tension is calculated. The syringe is connected to a computer-controlled piston through which the droplet volume is changed.

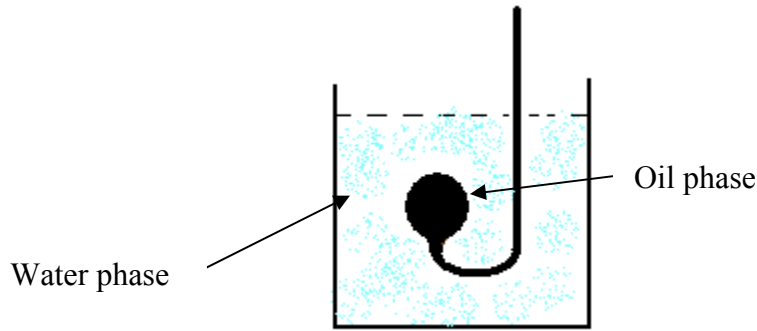


Figure 2: Schematic representation of the interfacial tension measurement.

In this study the interface oil-water was created by forming an oil droplet in the water phase in a small cuvette via a bent needle with a 0.5 mm diameter (Figure 2). In order to begin the measurements as close as possible to the interfacial tension of a new interface, a droplet was formed and released for each experiment and immediately after a new droplet was formed and the measurement was started right away. The volume of the droplet was kept constant for the dynamic interfacial measurements and was varied in a sinusoidal manner with periods ranging from 10s to 100 s for the interfacial rheology measurements. During these experiments the interfacial tension was recorded versus time. The drop volume was oscillated around  $10 \text{ mm}^3$  with amplitude of 5% (when possible, the volume was set at  $15 \text{ mm}^3$  while the amplitude was kept at 5%, to ensure that the results are more reliable; however, for some of the oil samples, the droplet could not be set to a volume of more than  $10 \text{ mm}^3$ ).

By changing the droplet volume periodically in a sinusoidal manner the interfacial response can be studied. The Gibbs interfacial dilatational modulus  $E$  can be described by the change in interfacial area and tension.

$$E = \frac{d\gamma}{d \ln A}$$

The interfacial dilatational modulus is a complex function of the angular frequency  $\omega$ , where the real part,  $E_d$ , is attributed to the interfacial elasticity and the imaginary part,  $\eta_d$ , is attributed to the interfacial viscosity.

$$E = E_d + i\omega\eta_d = E' + iE''$$

Here  $E'$  is the storage modulus and  $E''$  is the loss modulus of the interface.

All the measurements were performed at 50 °C and in order to check their reproducibility, all experiments were repeated at least three times. The reproducibility was very good for all the measurements.

Two different types of experiments were conducted: dynamic interfacial tension and interfacial rheology. The dynamic interfacial tension experiments were performed for 4000 s followed by 3000 s of rheology with varying oscillation frequencies (0.1, 0.04, 0.02 and 0.01 Hz) while the interfacial rheology experiments were performed for 4000s with a constant frequency (0.1 Hz).

It should be mentioned that two different Sinterface instruments were used for this study. Although they are quite similar, the differences between them reside in the treatment of the data, as well as in their sensibility to light and vibrations. In order to make sure that the results were reproducible, one measurement on the same system and with the same conditions was performed on both. The result consists of two very similar curves, displayed in Figure 3:

It should be mentioned that during some of the measurements on one of the Sinterface PAT1 M instruments (i.e. the “old” Sinterface”), there were some problems caused by condensation of water vapors on one of the lenses, caused by the temperature gradient between the cuvette and the lense and by room humidity. Since Sinterface employs an optical method for measuring the interfacial tension, the instrument did not detect the interface anymore shortly after the measurement was started (Figure 3’). Silica beads were used in order to prevent condensation on the lense.

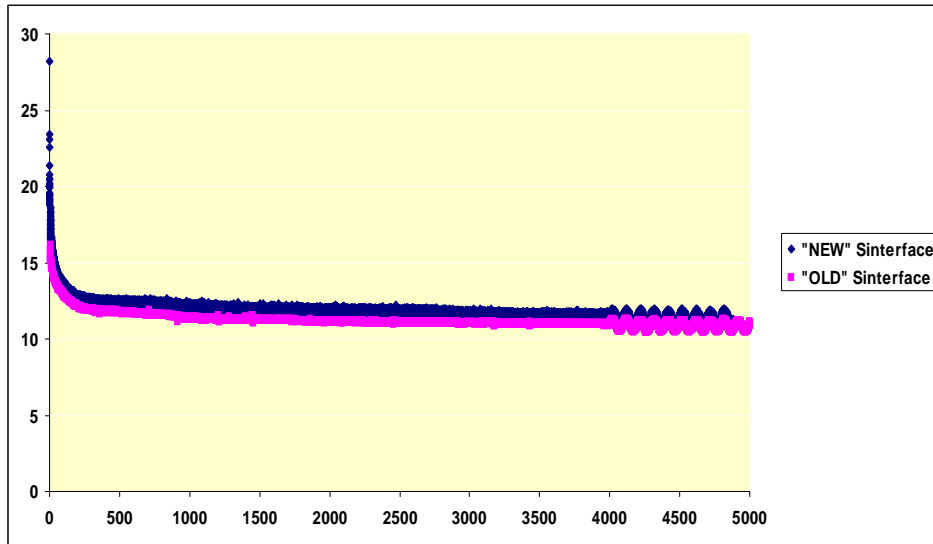


Figure 3. Check of reproducibility on the two instruments

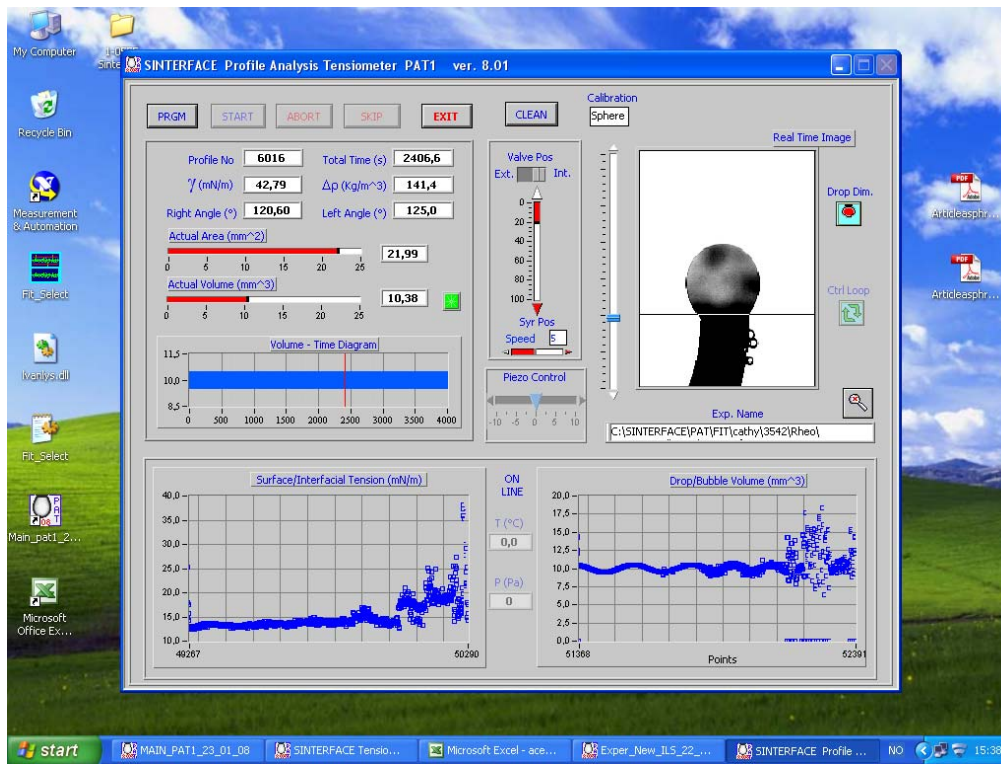


Figure 3': Result of condensation of water on an optical part of the instrument

### 2.3. Ultraviolet (UV) spectroscopy

The ultraviolet and visible spectra of organic compounds are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone pair orbital and an unfilled non-bonding and anti-bonding orbital. Above 200nm, excitation of electrons from p- and d-orbitals and  $\pi$ -orbitals, and especially,  $\pi$ -conjugated systems are readily measured and give informative spectra<sup>3</sup>.

The intensity of absorption of the sample is given by the Beer-Lambert law:

$$A = \epsilon.c.l = \log \frac{I_0}{I}$$

where A is the absorbance,  $\epsilon$  is the molar extinction absorptivity (L.mol.cm), c is the concentration of the absorbing species(mol/L), l is the length of light that passes through the sample (cm) and  $I_0/I$  is the ratio of intensity of the incident beam and intensity of transmitted light.

### 2.4. Multivariate Data Analysis

Multivariate data analysis is a tool used to find essential information in a large data set. When using multivariate data analysis on a chemical data set one refers to it as chemometrics<sup>4</sup>.

Multivariate data analysis is used when there is a need to find correlations between two or more variables or simply to determine parameters that cannot be obtained through direct measurements. This analysis technique has been often used in the field of petroleum chemistry.

Partial Least Squares Regression (PLS) analysis is used to fit a model to observed data in order to quantify the relationship between two groups of variables (x and y).

### 3. Results and Discussion

Herein, dynamic interfacial tension and interfacial dilational rheology of oil-water films were determined. The organization of the Results and Discussion section follows these two main objectives.

#### 3.1. Dynamic interfacial tension

For these experiments, the volume of the droplet is kept constant with time. This is very important because a reduction of the drop volume would lead to increased surface pressure and significant measurement errors. Also, as aforementioned, the measurement of the interfacial tension starts as soon as the interface is created; this provides with information on processes that take place at this interface before the equilibrium is established, which is why one can talk about “dynamic” interfacial tension.

For all the systems studied, plots of interfacial tension decay versus time follows a logarithmical decay function. A typical curve describing the variation of interfacial tension with time is shown in Figure 4. In the early stage of the measurement we observe a fast decay corresponding to a diffusion process<sup>5</sup> followed by a slower decay which corresponds to a reorganization of the interfacial components until equilibrium is reached. This relaxation is slow and seems to deviate from a diffusion controlled adsorption mechanism<sup>5,6</sup>. The experimental data can be fitted with a biexponential model:

$$\gamma = \gamma_0 + A \exp\left(-\frac{\tau}{t_1}\right) + B \exp\left(-\frac{\tau}{t_2}\right)$$

With  $t_1$  and  $t_2$ , the characteristic times for diffusion and reorganization, respectively.

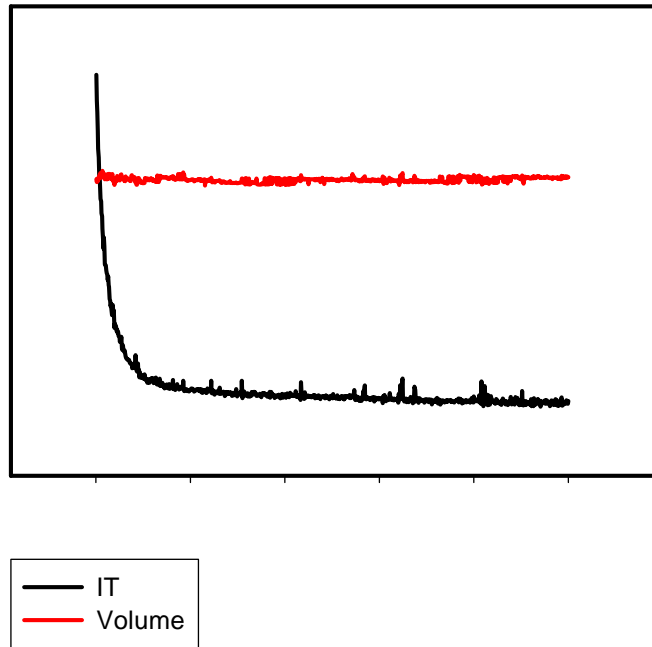


Figure 4. Variation of interfacial tension with time when the droplet volume is kept constant

Figure 5 shows the plots of the interfacial tension as a function of time for the acid extracted fraction of sample B, while in figure 6 the variation of interfacial tension with time is shown for the base extracted fraction of the same crude oil.

It can be seen here that the highest near-equilibrium value for the interfacial tension was recorded for the system involving pure water and the lowest for the one without divalent ions. The values obtained by curve-fitting with the biexponential function are given in Table 2.

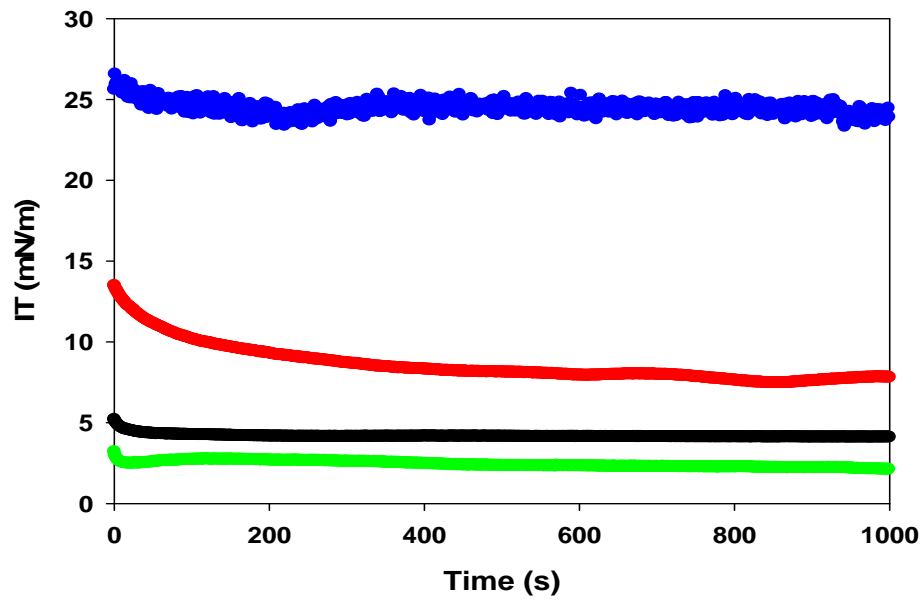


Figure 5: Dynamic interfacial tension between the acid extracted fraction of crude oil B and different water phases: pure water (blue curve), synthetic brine (black curve), brine without divalent ions (green curve) and brine without carbonates (red curve).



Table2. Values for interfacial tension,  $t_1$  and  $t_2$  for the acid extracted fraction of oil B in presence of the four water compositions.

Water phase		Near-equilibrium interfacial tension (mN/m)	$t_1$ (s)	$t_2$ (s)
Acid extracted fraction of oil B	Pure water	<b>22.18</b> (3.17)	<b>778,2</b> (1043)	<b>778,35</b> (1043)
	Synthetic brine	<b>4.15</b> (0.15)	<b>23,74</b> (12)	<b>253,7</b> (210)
	Synthetic brine without bicarbonates	<b>7.17</b> (0.016)	<b>118,2</b> (117)	<b>229</b> (38,7)
	Synthetic brine without divalent ions	<b>1.94</b> (0.28)	<b>3,62</b> (0,11)	<b>558,7</b> (784,9)

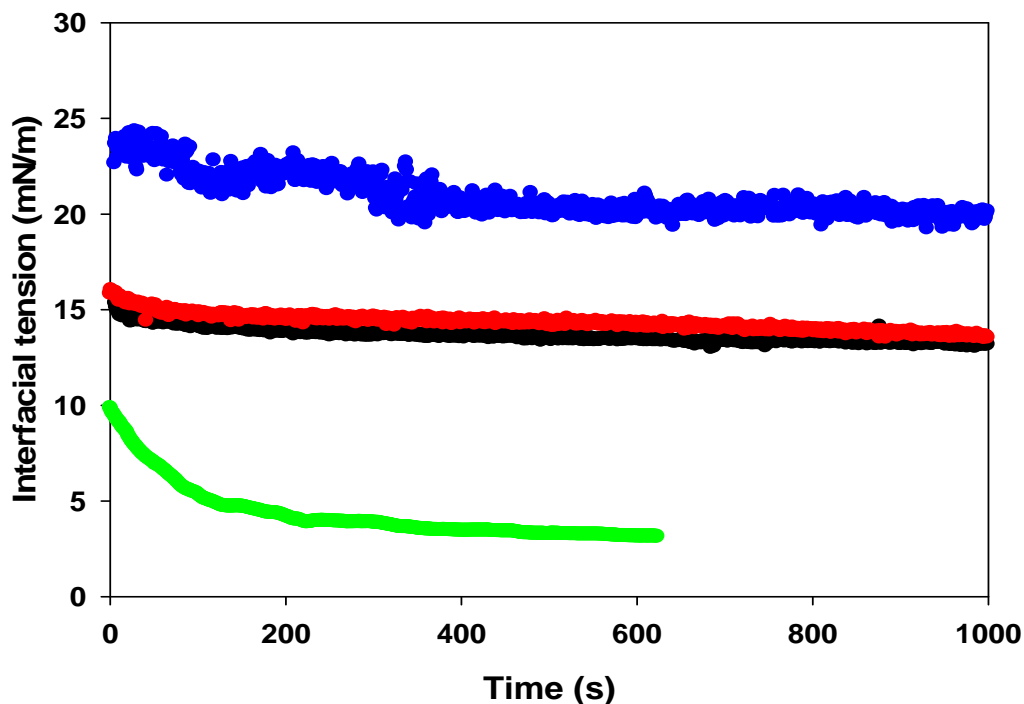


Figure 6: Dynamic interfacial tension between the base-extracted fraction of crude oil B and different water phases: pure water (blue curve), synthetic brine (black curve), brine without divalent ions (green curve) and brine without carbonates (red curve).

The corresponding values for the base-extracted fraction of sample B are given in Table 3.

For both fractions in synthetic brine without divalent ions (green curves), the interfacial tension is so low that the droplet detached itself from the needle shortly after the measurement was started. However, the measurement points that were recorded were in sufficient to determine the near-equilibrium value of the interfacial tension by fitting the curve to the bi-exponential function.

Table 3: Values for interfacial tension,  $t_1$  and  $t_2$  for the base extracted fraction of oil B in presence of the four water compositions.

Water phase	Near-equilibrium	$t_1$ (s)	$t_2$ (s)	
	interfacial tension (mN/m)			
Pure water	<b>21.29</b> (2.02)	<b>154,8</b> (179,8)	<b>323,31</b> (58,5)	
Synthetic brine	<b>12.95</b> (0.65)	<b>48,7</b> (21,7)	<b>792,7</b> (641)	
Base-extracted fraction of oil B	Synthetic brine without bicarbonates	<b>13.81</b> (0.42)	<b>32,9</b> (3,32)	<b>712,2</b> (438)
	Synthetic brine without divalent ions	<b>2.67</b> (0.72)	<b>97,12</b> (43,3)	<b>414,4</b> (405)

The fitting of the data with the biexponential function yielded good results for the near-equilibrium interfacial tension values. However, the characteristic times for diffusion and reorganization ( $t_1$  and  $t_2$ ) display quite high standard deviations.

From this data, it can be observed that for both acid- and base-free oil fractions the interfacial tension when no ions are present in the water phase is significantly higher than for the other systems. This means that the presence of salt has a major influence on the interfacial properties of the oil droplet. Furthermore, it seems that when no divalent ions are present in the aqueous bulk phase (green curves), the interfacial tension is much lower than for the other water compositions. This is possibly due to a "screening" effect that the bicarbonate ions have on the polar head groups of the surface active molecules. This effect possibly leads to a reduction of the electrostatic repulsions between these head groups which causes a more efficient packing of

surface active molecules at the oil/water interface (i.e. a more important number of surface active molecules at the interface) and thus to a lower interfacial tension.

On the other hand, when bicarbonate ions are extracted from the aqueous phase (red curve), the interfacial tension displays values similar to those obtained with the synthetic brine with all the ions and higher than the one without divalent ions. This might be explained by the fact that, since all the salt waters have the same ionic strength, the one that contains divalent ions has a much smaller number of ions in solution. This might mean that it is less favourable for the system to have ions be transported from the aqueous phase to the interface, because of a significant loss of entropy. The screening effect is thus diminished and the packing of surface active molecules at the interface not as efficient as in the case of oil/divalent ions-free water system.

The same trend was observed in a previous study for another oil sample (crude A). The results are given in annex 3. The difference between these two oils however is that, while for sample A the acids seem to be more interfacially active than the bases, for sample B the inverse result is observed. The near-equilibrium values for the measured interfacial tension are lower for the acid extracted fraction than for the base extracted one. It might seem thus, on first approach, that for sample B the bases are more interfacially active than the acids.

By looking at the characterization data for these oils, one can see that there are notable differences in the SARA fraction characterization data. Thus, while the amount of saturates is significantly higher for the crude oil A acid- and base-extracted fractions, the amounts of aromatics, resins and asphaltenes are higher for the same fractions of crude B. Also, for the base-free fraction of crude B, the TAN (total acid number) is significantly higher than for the other fractions.

It is well known that aromatics and resins are the most aromatic and most polar compounds of petroleum, while the saturates are non-polar<sup>7</sup>. Generally, asphaltenes and resins are also the compounds with the highest interfacial activity in crude oils.

From the characterization data, it can be seen that the bases in oil B are mostly found in the resin fraction. In the acid-free fraction, the resin to asphaltene ratio(R/A) is significantly higher than the one in the base-free fraction (32.48 mN/m vs respectively 13.27 mN/m). It was

found previously that compounds like resins and aromatics may solubilize asphaltene aggregates<sup>1</sup>; moreover, several authors have suggested that colloidal asphaltene aggregates may adsorb at oil/water interfaces and stabilize the interfacial film more readily than individual asphaltene molecules<sup>8-11</sup>. It is thus possible that, since in the acid-free fraction of crude oil B this R/A ratio is higher than in the base-free fraction, a higher amount of resins (and thus possibly bases – although one can see that the TBN value is much lower in the acid-free fraction and one might conclude that a high amount of bases is removed along with the acids in the acid removal process) is available to move to the interface and lower the interfacial tension in this particular fraction. The amounts of aromatics are the same in both fractions.

Also, in the base-free fraction of oil B, the TAN and TBN values indicate that the acids are almost entirely still in the fraction, while also a small amount of bases are present. Specific acid-base interactions might hinder the transport of part of the acids towards the interface.

Another observation for both fractions of oil B is that there are some “bumps” in the interfacial tension curves in presence of pure water. The cause is uncertain, but is believed that such a phenomenon might be due to uneven molecular weight distribution of the surfactants<sup>12</sup>.

A general observation for these systems is that the bases are more interfacially active in crude oil B than the acids, as can be observed from the measurements performed on the original crude B (experiments were performed prior to this master project). An obvious remark is that the compositions of the water phase (salt addition) and the ion valency, as well as the composition of the oil phase have a significant influence on the interfacial properties.

Due to lack of time, measurements were not performed on the acid- and base-extracted fractions of crude oil C.

The same type of experiment was performed on oil/water systems involving crude oils C, D, E, F, G, H and I and synthetic brine with all the ions. The results are presented herein in figure 7 and table 4. Two of these oils, namely C and D) were diluted with toluene in order to decrease the capillary number and to diminish inertial effects caused by high viscosity. This will be discussed in more detail in the section dedicated to the capillary number.

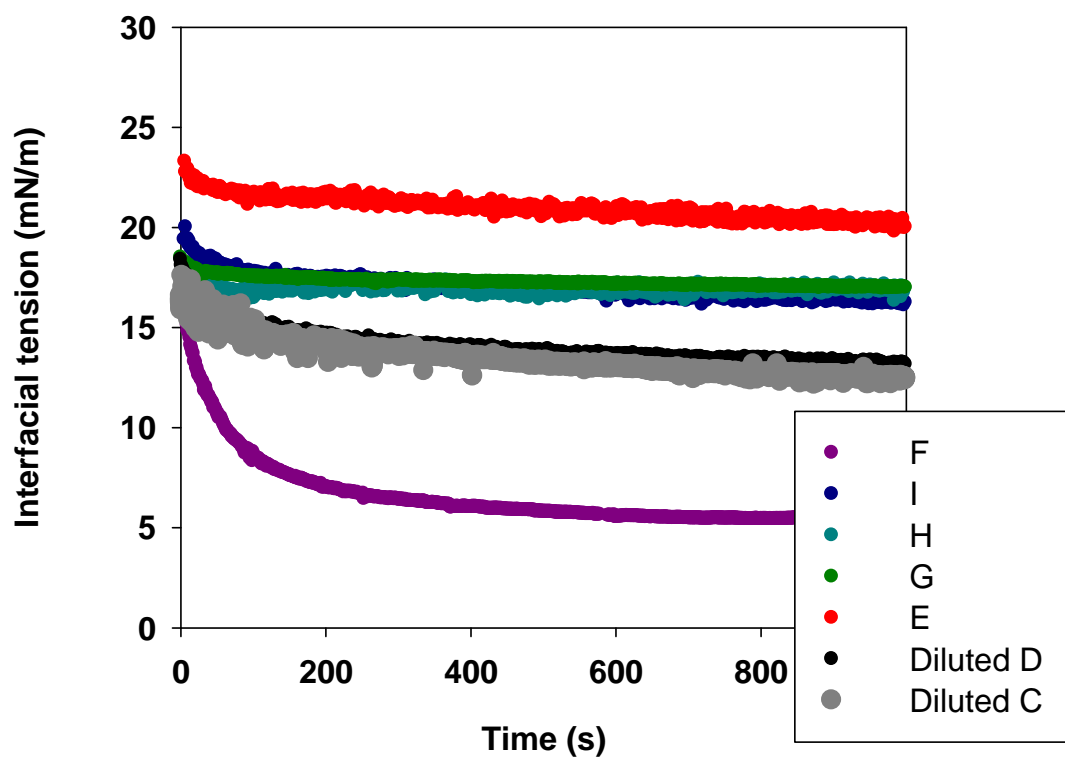


Figure 7: Dynamic interfacial tension between different oils and synthetic brine with all the ions.

It can be seen that similar values for near-equilibrium interfacial tension are obtained for the two diluted oils (C and D). The same observation can be made for oils G, H and I. In the SARA fraction characterization data for these oils (Annex 1), the polarity increases from the saturates fraction (non-polar) and the aromatics fraction (low polarity) to the resins and asphaltenes fractions (the most polar compounds in crude oils). It would appear that with an increase of content of low-polarity components in these oils, there is a tendency for the interfacial tension to be lower, possibly due to a decrease in polar interactions in bulk. This would render the interfacially active species more readily available to move to the interface.

Table 4: Values for interfacial tension,  $t_1$  and  $t_2$  for crude oils C, D, E, F, G, H and I at the interface with synthetic brine with all the ions.

Oil phase	IT [mN/m]	t <sub>1</sub> (s)	t <sub>2</sub> (s)
<b>F</b>	<b>4,82 (0,65)</b>	<b>33,3 (11,1)</b>	<b>200 (80)</b>
C	11,26 (0,23)	3,45 (4,4)	250 (187,5)
<b>I</b>	<b>16,03 (1,6)</b>	<b>28,6 (24,5)</b>	<b>714,3 (1530,6)</b>
<b>H</b>	<b>16,61 (0,39)</b>	<b>384,6 (259,9)</b>	<b>384,6 (259,9)</b>
<b>G</b>	<b>16,86 (0,07)</b>	<b>25 (13,1)</b>	<b>666,7 (622)</b>
<b>D</b>	<b>12,56 (0,47)</b>	<b>59,9 (32,3)</b>	<b>500 (400)</b>
<b>E</b>	<b>15,12 (2,15)</b>	<b>22,7 (4,4)</b>	<b>3333,3 (2222,2)</b>

After 4000 s of dynamic interfacial tension measurements, when the systems have reached a near-equilibrium state, experiments of rheology have been conducted where the droplet volume is modified by oscillations with varied frequencies (0.01, 0.02, 0.04 and 0.1 Hz). The typical shape of the obtained curved is displayed in figure 8.

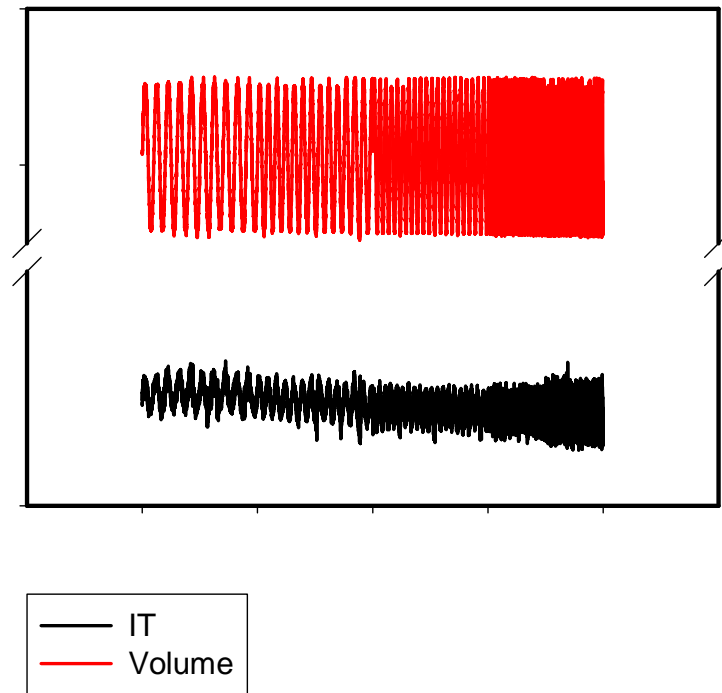


Figure 8: Droplet volume oscillations with varied frequency (0.01, 0.02, 0.04 and 0.1 Hz).

These experiments allow obtaining two parameters: Gibbs' interfacial elasticity and viscosity (i.e. storage modulus and loss modulus respectively). The storage modulus  $G'$  is a measure of the elasticity of the film. The loss modulus  $G''$  represents a combination of internal relaxation processes and relaxation due to transport of matter between the surface and the bulk<sup>12</sup>. The results obtained for Crude B are shown in figures 9 and 10 for the acid and the base extracted fractions, respectively. These figures don't contain the droplet volume oscillations for the systems with divalent-free ions water, since for these measurements the droplet detached itself from the needle before the oscillations were set to start.

For both fractions in presence of pure water, the difference between the two moduli is relatively high, which indicates that the interfacial film has a more solid-like behavior.



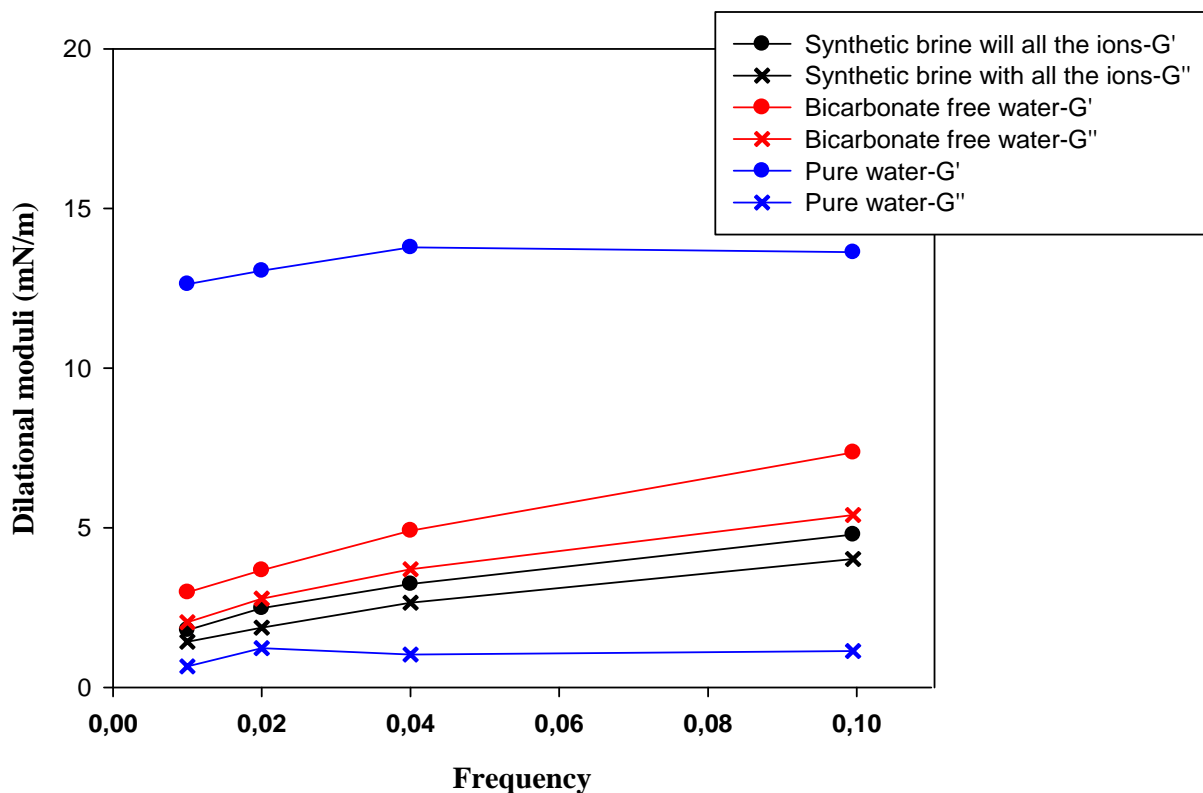


Figure 9 Dilational moduli versus frequency for the acid-extracted fraction of crude B.

It can be seen that for both acid-extracted and base-extracted fractions of crude B and pure water the elastic modulus is much larger than the viscous modulus ( $G' \gg G''$ ). Surface area and interfacial tension oscillations are almost in phase. The interfacial films for this system seem to be more elastic and more "solid-like" than for the other films

It was discussed in previous studies that if loss modulus is solely due to viscous friction, then it should increase with frequency; if the loss is caused by diffusional exchange with the bulk, the opposite frequency dependency is expected<sup>13</sup>. The reason for a near-constant value may be a combination of these effects<sup>12</sup>.

The low variation of the loss modulus with frequency indicates thus that for the systems acid- and base-extracted B/ pure water, there is some diffusional exchange between the surface and the bulk. This can be explained by the fact that, since there are no ions in the water phase, the packing of interfacially active molecules at the interface is less efficient and they might be able to

desorb more readily due to the fact that the electrostatic interactions between the head groups are more important than when ions are present in the water phase.

For the other systems in figures 9 and 10 one can see that the increase of the two moduli with frequency is quite small, although one can add that the increase for the elastic modulus is slightly stronger than for the viscous modulus.

For the system base-extracted B/ synthetic brine with all ions it seems that the difference between the two moduli is higher than for the corresponding system with acid-extracted fraction. This might indicate that acids will create a more elastic interfacial film than bases in presence of synthetic brine.

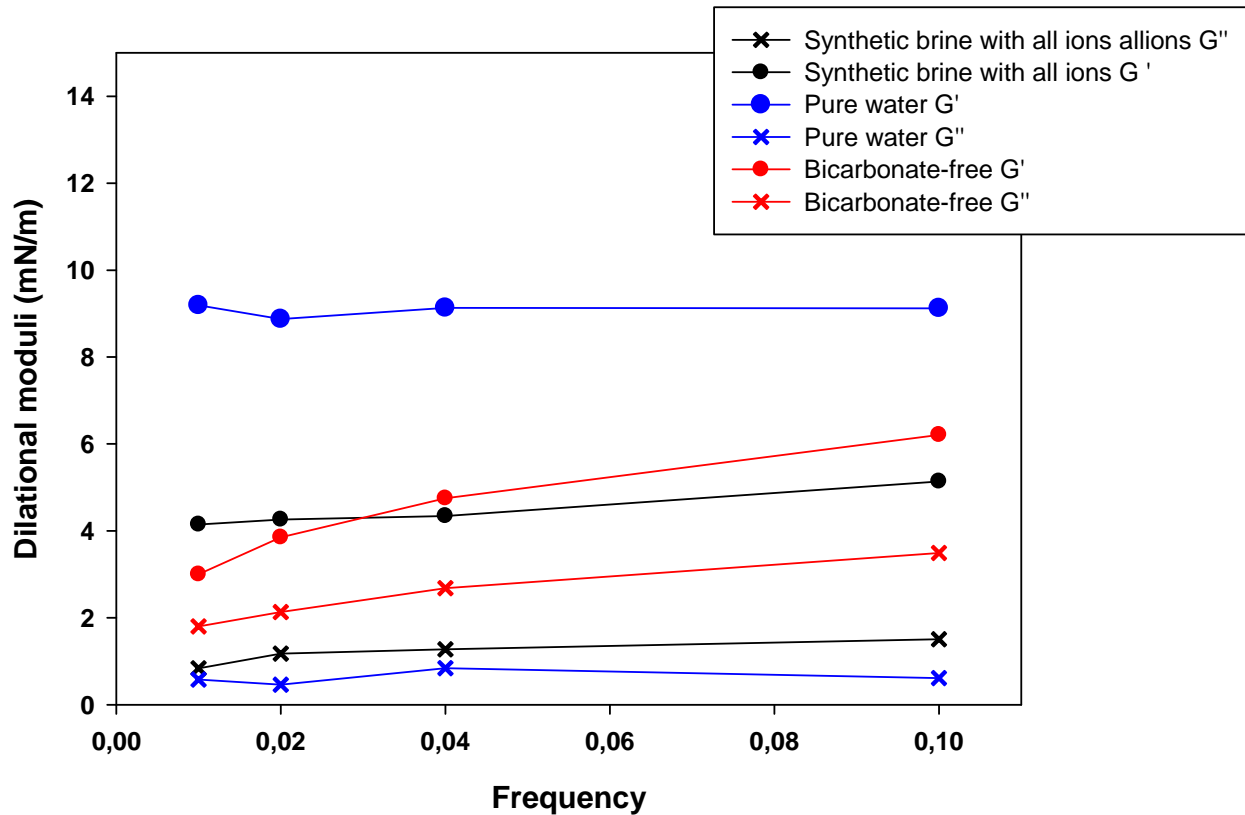


Figure 10 Dilational moduli versus frequency for the base-extracted fraction of crude B.

Figure 11 contains the data for the dilational moduli only for oils E, G, D (diluted) and H versus frequency and in presence of synthetic brine with all the ions. For oil F the droplet

detached itself from the needle shortly after the experiment began, probably due to initial high-rate diffusion of surface active molecules to the interface or to high difference in density between the two phases; the oscillations with varied frequency after 4000 s could not be performed. Oil I did not display a nice sinusoidal response of the interfacial tension when the droplet volume was oscillated; it was then not possible to calculate the viscous and elastic parts of the complex surface dilational moduli for this oil.

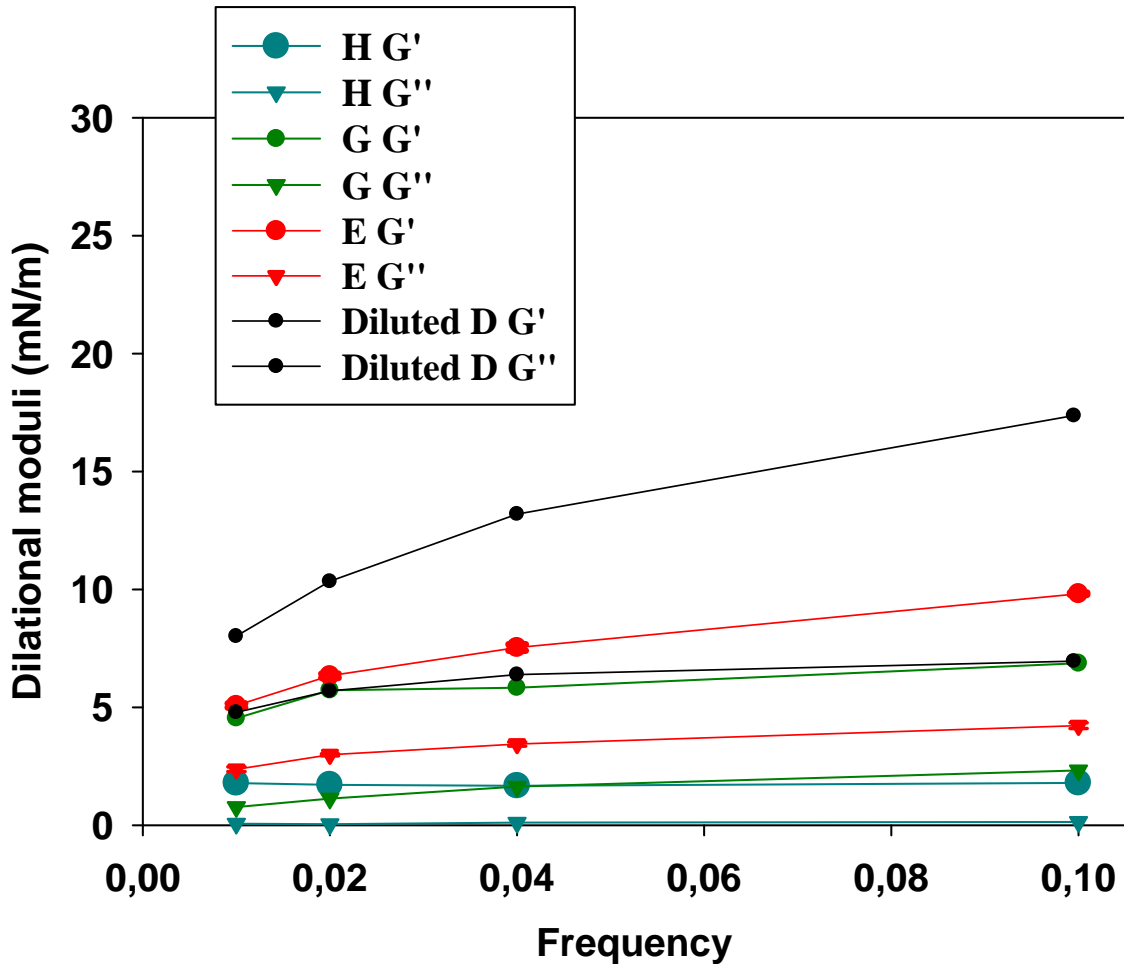


Figure 11 Dilational moduli versus frequency for oils D (diluted), E, G and H in presence of synthetic brine with all the ions.

By comparing these curves one can see that oil D (diluted) forms the more elastic interfacial film among these oils. Oil H shows the lowest dependency of the moduli with frequency and also the least elastic interfacial film. One important difference between these oils

is the asphaltene content. Oil D has a much higher viscosity than oil H, probably due to a high paraffinic content. It also contains approximately 2,5 times more asphaltenes. It is possible that, in addition to adsorption of asphaltenes to the interface, small solid particles such as waxes may contribute to the formation of an elastic layer as well.

### 3.2. Interfacial dilational rheology

Interfacial rheology measurements involve determination of interfacial rheological properties by dilatation of the droplet (modifying the interfacial area). Interfacial tension is measured as a function of change in interfacial area to give the complex modulus:

$$G^* = \frac{d(\gamma)}{d(\ln A)}$$

A typical variation of the interfacial tension with time at constant frequency is shown in figure 12:

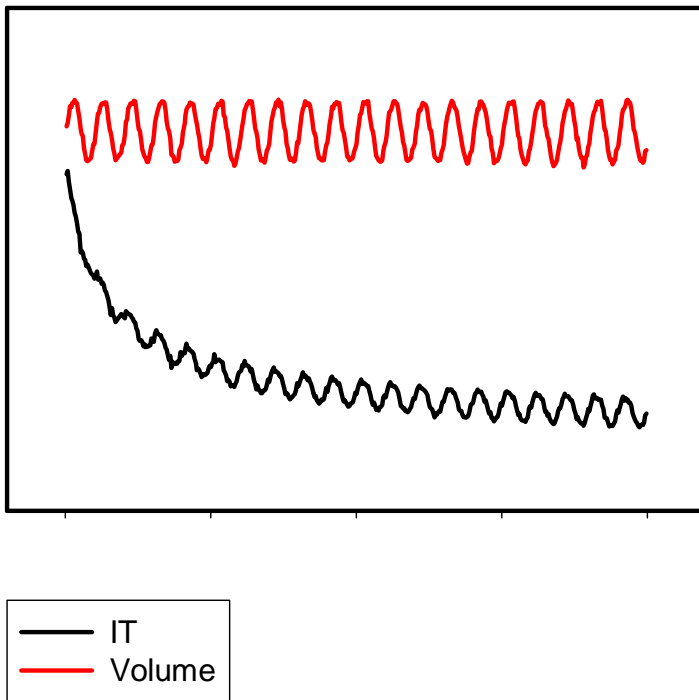


Figure 12: Droplet volume oscillations with varied frequency (0.01, 0.02, 0.04 and 0.1 Hz).

The phase angle between the deformation and the response gives the elastic and viscous moduli  $G'$  and  $G''$  (also known as storage modulus and respectively loss modulus):

$$G' = G^*(\omega) \cos(\delta)$$

$$G'' = G^*(\omega) \sin(\delta)$$

The interfacial elasticity and viscosity play an important role in droplets interactions and emulsion properties. In purely elastic materials the stress and strain occur in phase. In purely viscous materials there is a phase difference between stress and strain and the phase angle between them is  $90^\circ$ . Viscoelastic materials are between purely elastic and purely viscous materials.

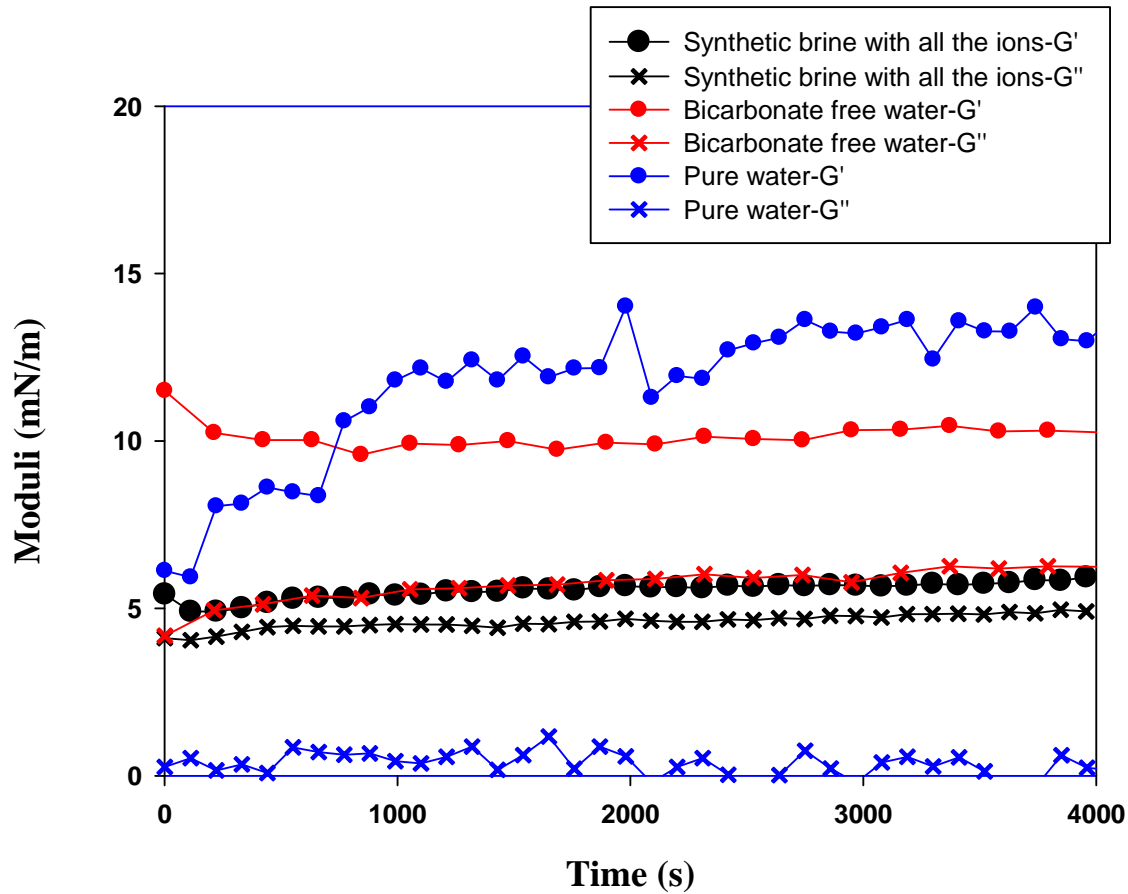


Figure 13 Dilational moduli variation with time at constant frequency for the acid-extracted fraction of crude B.

Figures 13 and 14 show the evolution of  $G'$  (elastic modulus) and  $G''$  (viscous modulus) with time for acid-extracted sample B and base-extracted sample B respectively.

From these measurements, as previously observed, the composition of the water phase has an influence on the interfacial properties of the oil droplet. The more solid-like films were formed by the systems acid-extracted B/ pure water and base-extracted B/ bicarbonate-free water. Generally the moduli are quite constant with time, except for one system (i.e. acid-extracted B in presence of pure water) for the increase of elasticity with time might indicate a molecule

reorganization at the interface. This can be explained again by the lack of ions in the water phase and thus the lower ability of molecules to pack efficiently.

For the base-extracted B in presence of pure water the measurements did not provide a nice sinusoidal variation of interfacial tension.

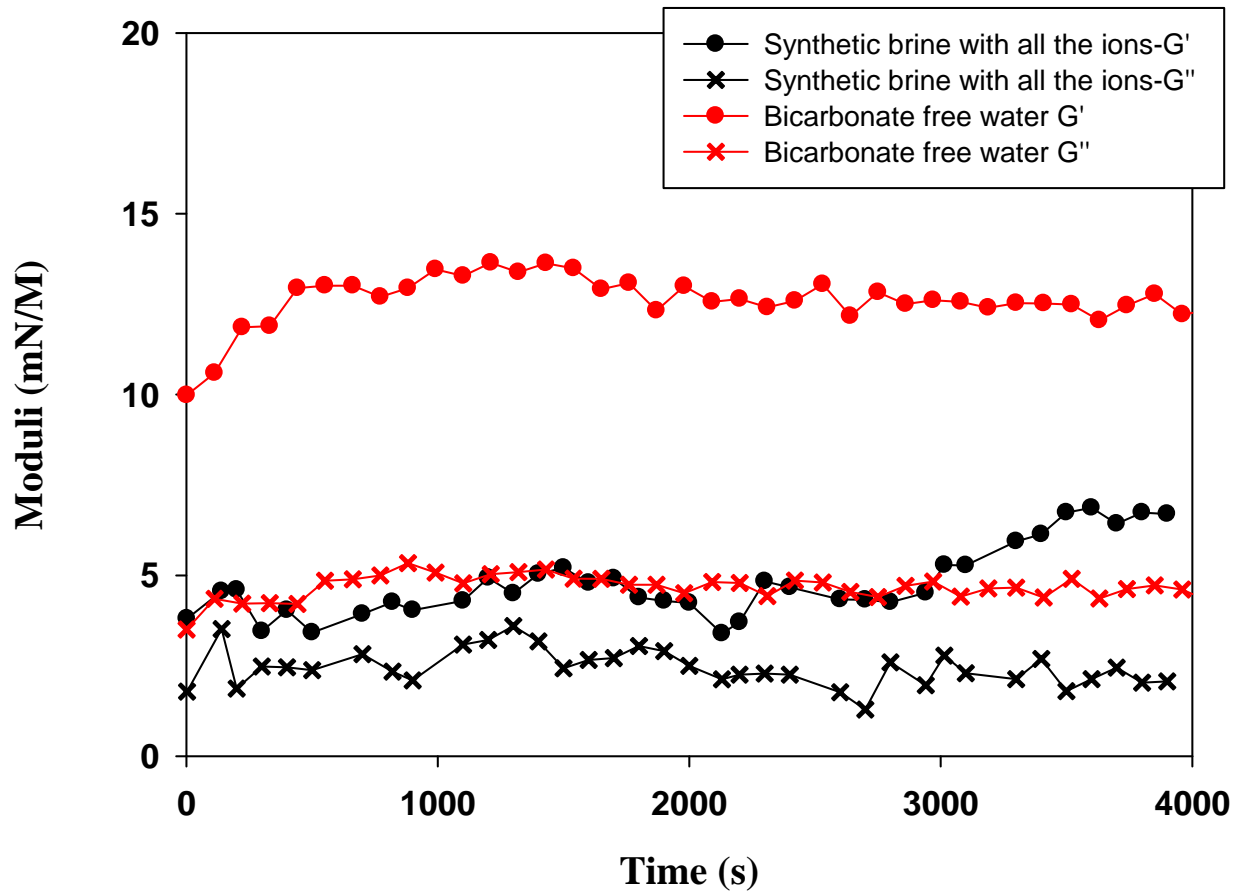


Figure 14 Dilational moduli variation with time at constant frequency for the base-extracted fraction of crude B.



In figure 15 the evolution of  $G'$  and  $G''$  is shown for crudes E, G, H and diluted D.

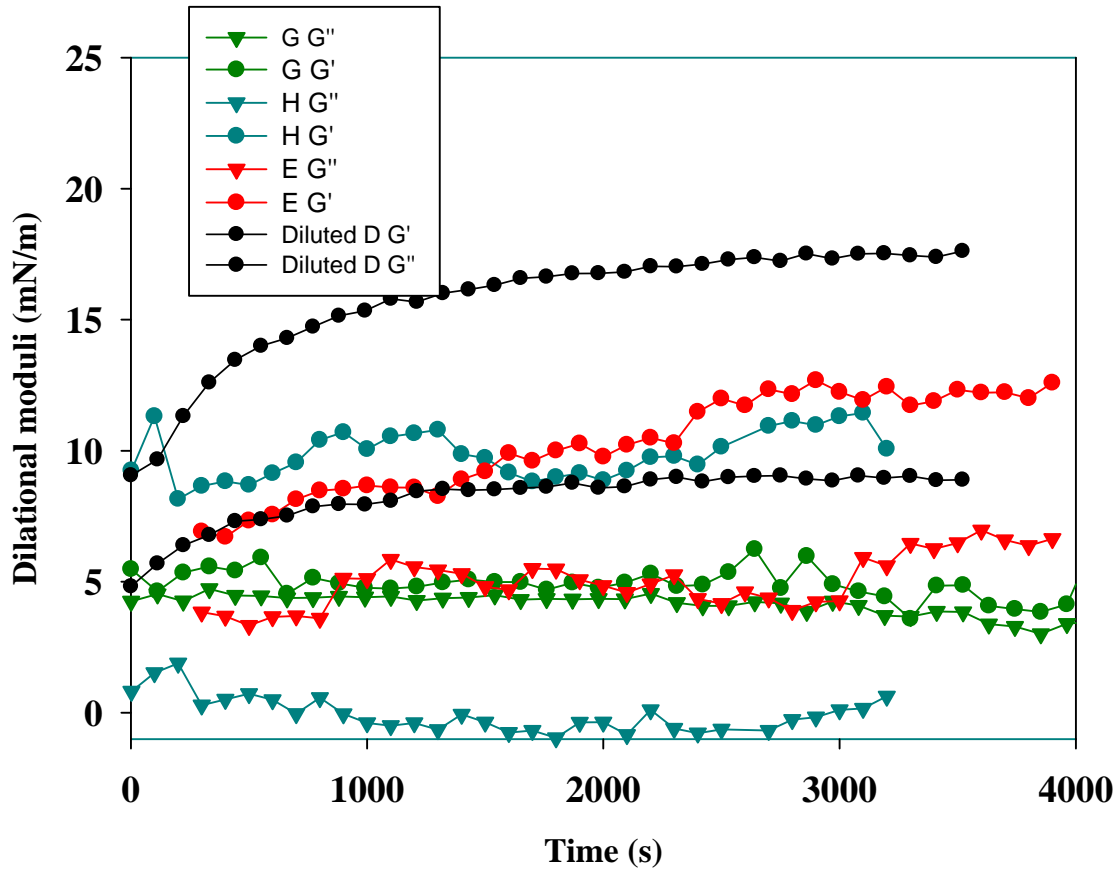


Figure 15 Dilational moduli variation with time at constant frequency for oils E, G and H.

In the case of oils D and E, the elastic modulus  $G'$  increases with time, more strongly for oil D. The interfacial film becomes more rigid with time which indicates a reorganization of molecules at the interface. For oils H and G, the interface seems to be less dynamic. The difference between them however is that while for oil H the interfacial film is much more elastic than viscous, for oil G the two moduli display very similar values.

### 3.2.1. Capillary number

With strong relevance to this study, Freer et al.<sup>14</sup> recently raised caution for reporting interfacial rheological properties using the oscillating drop technique due to the effect of viscous forces on the droplet shape. In the case of a static drop, analysis of the drop shape by Young-Laplace equation is exact as the only forces acting on the drop are gravity and interfacial tension. However, for oscillating drop experiments viscous forces also can influence the shape of the drop. Freer et al. showed that for clean fluid/fluid interfaces, the measured interfacial tension oscillates sinusoidally with the same frequency as the modulation of the drop volume. When the Capillary number  $Ca$ , defined as the ratio of viscous to capillary forces, was beyond a certain value viscous forces distorted the drop shape and lead to false interfacial tension results.

$$Ca = \frac{\Delta\mu\omega\Delta V}{\gamma_0 a^2}$$

Where  $\Delta\mu$  is the difference in viscosity between the two phases,  $\omega$  is the oscillation frequency,  $\Delta V$  is the amplitude of volume oscillation,  $\gamma_0$  is the equilibrium interfacial tension, and  $a$  is the radius of the capillary<sup>5</sup>.

To sum up one can say:

- Oscillating drop technique assumes that the only forces acting upon the droplet shape are gravity and interfacial tension
- The measured interfacial response of samples can be influenced by the viscosity of the droplet
- The contribution of viscous forces could be the explanation of an apparent viscoelastic behavior for non-surfactant systems
- The limit at which the measurements are affected is governed by the Capillary number
- In the literature, the interfacial rheology measurements are distorted at capillary number higher than approximately 0.002<sup>5,14</sup> although this criterion is apparatus dependent..

The capillary numbers calculated for all the samples were estimated to be inferior to the values given in Table 5. For sample E most of the characterization data was not available at the time

where this thesis was written and the capillary number could not be estimated. However, the viscosity of this oil did not appear to be high and the measurements were conducted as they were for the oils with low capillary number. Original crudes C and D displayed capillary number values superior to 0,002. It was thus necessary to reduce this value. To avoid instrumental problems due to the viscous nature of heavy oil, it is common practice to dilute the sample<sup>1</sup>. Oils C and D were thus diluted with toluene 70:30 vol.

Table 5: Capillary numbers estimated for the different oil samples

Oil phase	Capillary number
Acid extracted A	11.34E-7
Base extracted A	9.34E-7
Acid extracted B	1,11E-3
Base extracted B	1,43E-3
Diluted C	0,0019
F	2,9E-4
I	0,0006
H	0,00018
G	0,001
Diluted D	0,0007
E	-

### 3.2.2. Effect of dilution

In order to check the effect of dilution on the interfacial properties of oils, several measurements were done involving crude oil C with several dilution extents. The results for dynamic interfacial tension with time can be seen in Figure 16.

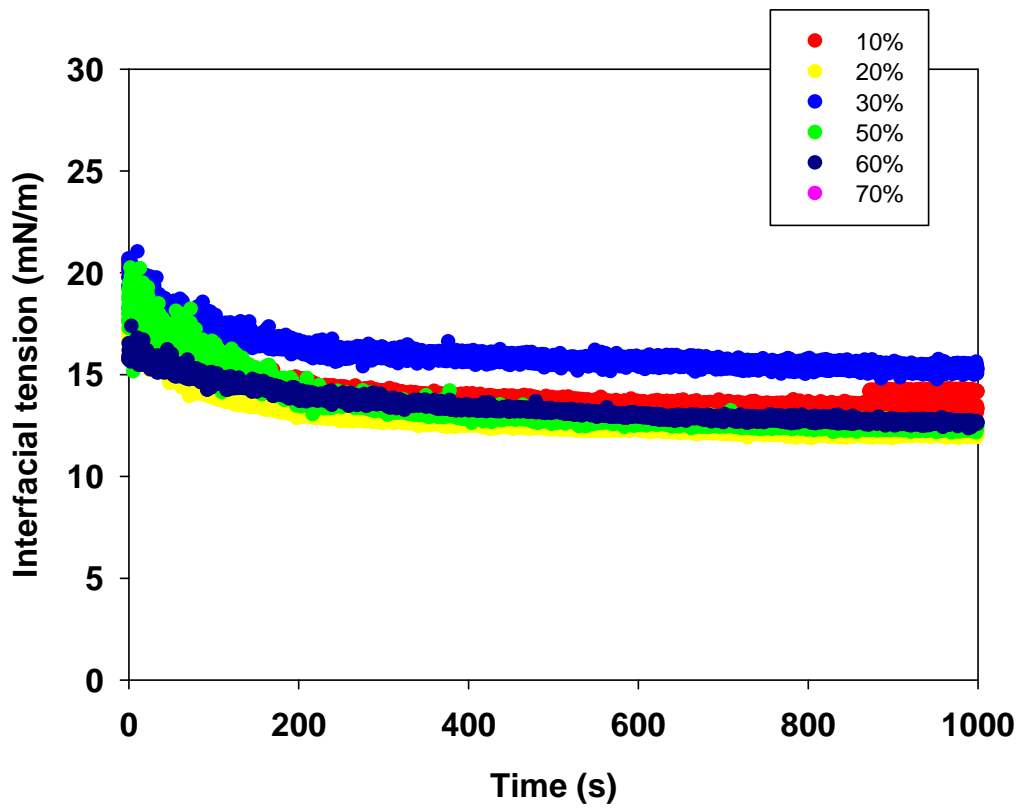


Figure 16 Variation of the interfacial tension with time for several dilutions of oil C.

It can be said that dilution of the oil did not affect the near-equilibrium interfacial tension for the seven dilutions (Table 6 and Figure 17) to a too large extent.

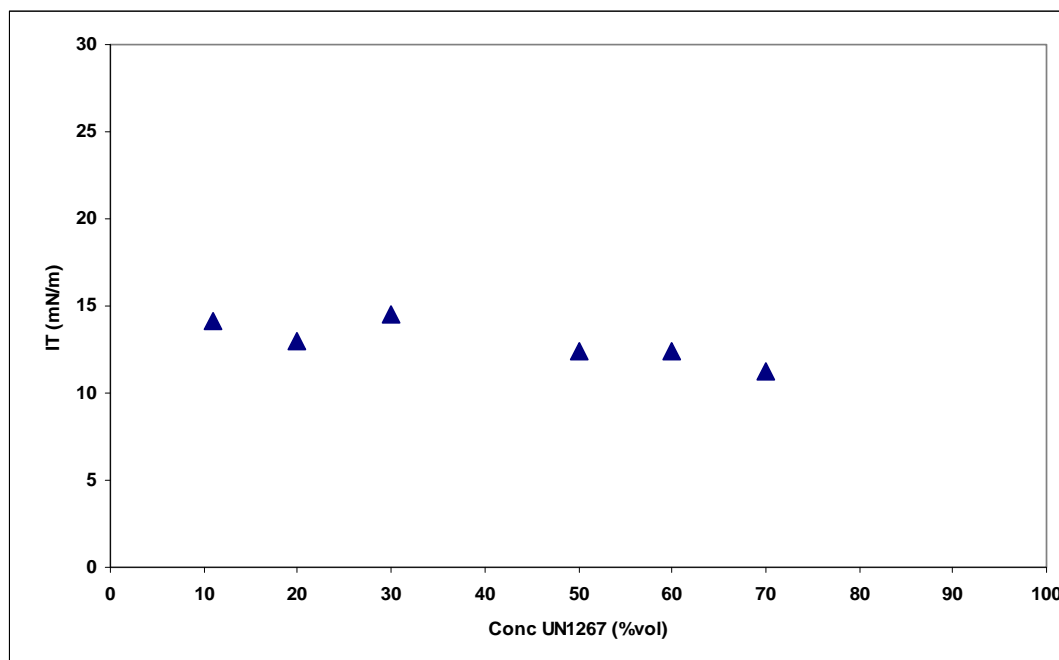


Figure 17 Near-equilibrium interfacial tension variation with dilution for oil C and synthetic brine with all the ions water phase.

In Figure 18 however, it can be noticed that dilution of the oil has a greater effect on the dilational moduli; this confirms to a certain extent the findings of Hannisdal et al.<sup>5,6</sup>

It is expected that for oils C and D the interfacial tension should be lower for the original oils than for the diluted ones, since when diluting them the concentration of the interfacially active compounds is reduced and the diffusion flux is diminished. However, toluene was used as a solvent; toluene is a good solvent for asphaltenes and resins; since these are amongst the compounds in crude oil that contribute to a high viscosity the most, the viscosity is lowered by adding toluene. This means that the transport of the interfacially active molecules to the interface is less hindered than in the more viscous original oils. It is thus difficult to evaluate to an exact extent the influence of dilution on interfacial properties at the oil-water interface.

Table 6. Near-equilibrium interfacial tension variation with dilution

Conc. UN1267 (% Vol)	$\gamma_0$ (mN/m)	StD
11	14.12	0.66
20	12.96	0.94
30	14.56	0.52
50	12.42	0.60
60	12.44	0.21
70	11.26	0.23

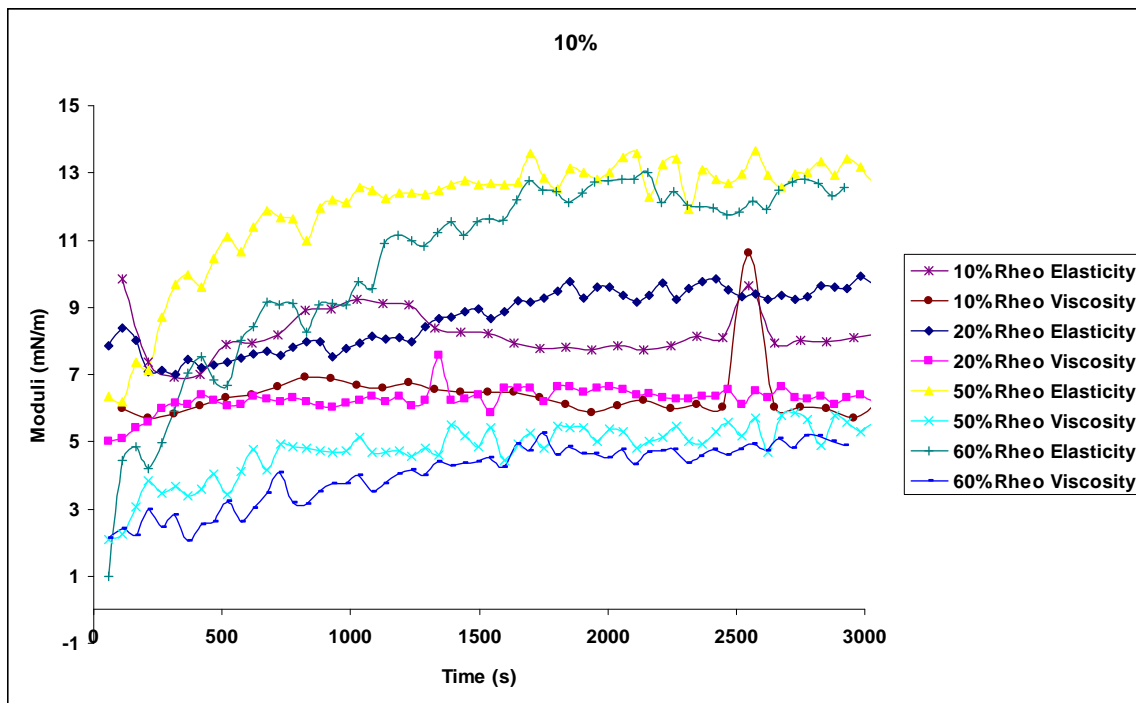


Figure 18. Dilational moduli for the different dilutions of oil C and synthetic brine with all the ions water phase.

### 3.3. Analysis of the water phase after measurements

The water phases after each measurement performed on the Sinterface PAT1m instrument were collected and their pH was measured.

The initial pH values for the four water compositions are:

- 5,5 for pure water
- 7,1 for the synthetic brine with all the ions
- 7,9 for the divalent ions-free water
- 6,05 for the bicarbonate ions-free water

It can be seen that the pH changes significantly only in the case of interfacial tension measurements with pure water (increase for the acid extracted fraction and decrease for the base extracted fraction). This might suggest that protonation of bases in the acid-free oil and respectively dissociation of acids in the base-free oil might occur when the oil and water phases are brought in contact. The evaluation of the pH is given in Table 7 for the acid- and base-extracted fractions of oil B and in table 8 for the other oils. The values written in bold characters correspond to dynamic interfacial measurements, whereas the ones written in italic characters to interfacial rheology measurements.



Table 7 pH values for water phases for acid- and base-extracted fractions of oil B and all the water compositions.

Oil Phase	Water Phase							
	Synthetic brine		Bicarbonate ions free brine		Divalent ions free brine		Pure water	
Acid extracted B	<b>7.2</b>	7.3	<b>6.1</b>	6.4	<b>7.8</b>	8.02	<b>6.4</b>	6.9
Base Extracted B	<b>7.4</b>	7.4	<b>6.5</b>	6.6	<b>8.04</b>	8.03	<b>4.7</b>	4.4

Table 8 pH values for water phases oils D to I

Oil Phase	Synthetic brine with all the ions	
D	<b>7.2</b>	7.2
E	<b>7.2</b>	7.2
F	<b>7.2</b>	7.25
G	<b>7.2</b>	7.25
H	<b>7.3</b>	7.3
I	<b>7.25</b>	7.2

Figures 19, 20 and 21 show a representative part of the spectra obtained by Ultraviolet (UV) spectroscopy analysis of the water phases after the measurements. It is clear that all the water

phases seem to contain very small amounts of components that might have crossed the interface from the oil bulk to the water phase. However, since the absorbance is directly proportional to concentration and we have no knowledge of the concentration of these components, it is safe to only resume to one observation: higher absorbance at the 200 nm wavelength for the water phases originating from pure water/acid- and base-extracted oil B interfacial measurements (blue and dark blue curves) indicate that there is a bigger change in the pure water phase than in the other water compositions, just as the pH measurements indicated. Since it could be seen that the curve of the variation of interfacial tension with time presented some “bumps”, it is possible that the interface with pure water is more dynamic on a molecular level than the other water compositions.

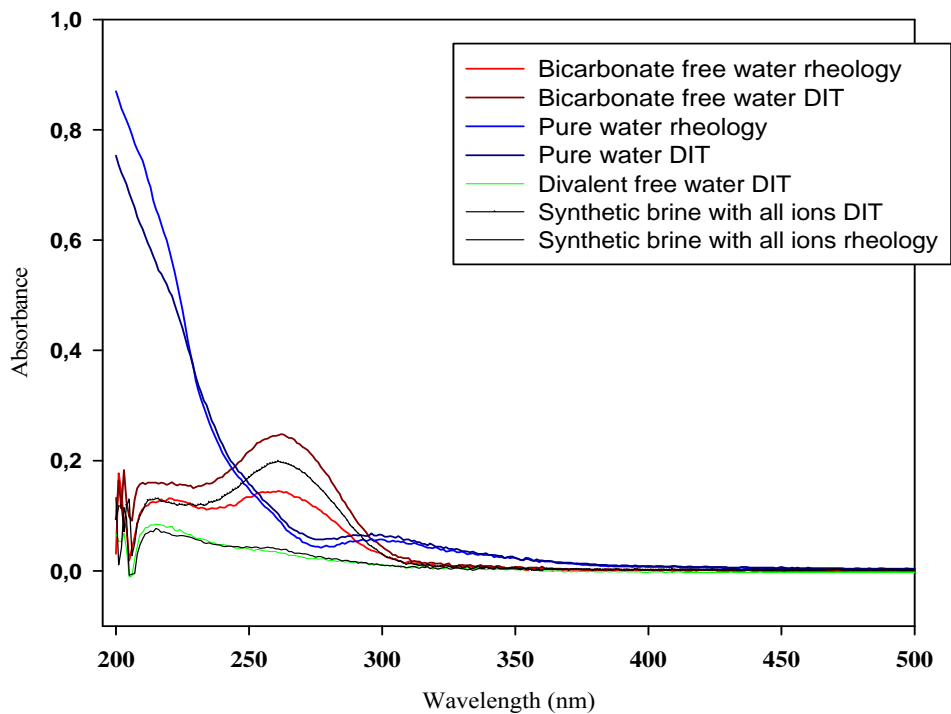


Figure 19 Ultraviolet (UV) spectra of the water phases after measurements for the acid-extracted fraction of oil B.

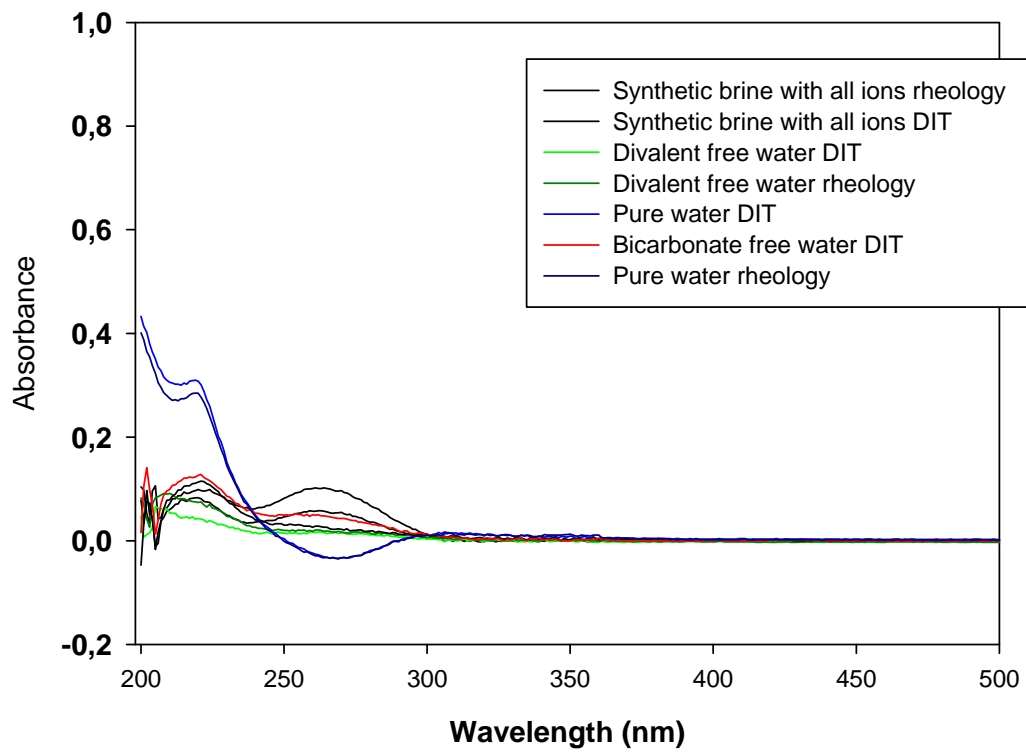


Figure 20 Ultraviolet (UV) spectra of the water phases after measurements for the base-extracted fraction of oil B.

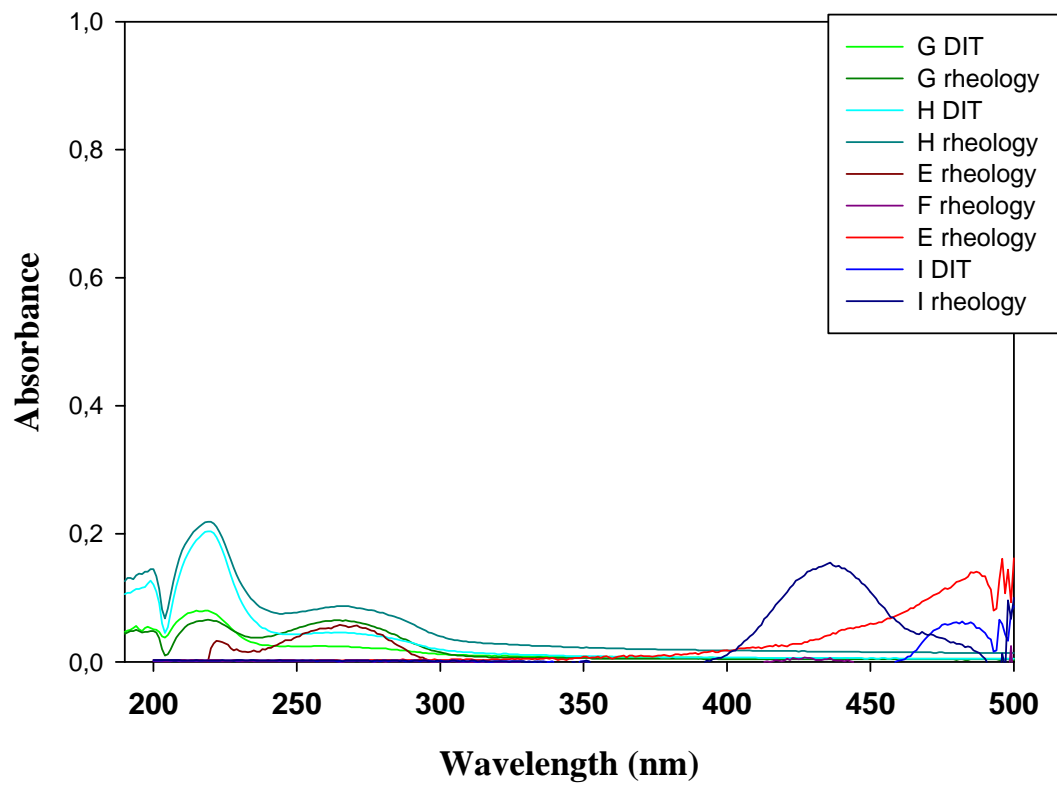


Figure 21 Ultraviolet (UV) spectra of the water phases after measurements for oils D to I.

### 3.4. Multivariate Data Analysis

Partial Least Squares analysis (PLS) was used on a set of data in an attempt to correlate the near-equilibrium interfacial tension values to characterization data of oil samples.

Table 9. Data set used for PLS analysis

	S	A	R	A	TAN	TBN	Density	IFTeq	
A-AC-EX	77,78	20,42	1,65	0,15	0,000	0,598	0,8132	12,34	Y
A-Baes-EX	78,20	20,82	0,93	0,06	0,081	0	0,7622	10,24	
B-AC-EX	47,74	41,21	10,72	0,33	0,200	0,68	0,9185	4,15	
B-Base-EX	47,72	41,17	10,35	0,77	2,171	0,258	0,9242	12,95	
C-diluted	19,93	64,7	7,64	9,75	0,400	0,94	0,9046	11,26	
D-diluted	41,02	51,63	6,23	1,75	0,240	1,043	0,9067	12,56	
F	62,00	31	5,90	0,69	0,290	1,46	0,8188	4,82	
G	53,00	14,4	30,00	2,5	2,150	2,87	0,9166	16,86	
H	60,00	30	9,00	0,66	2,650	0,79	0,8646	16,61	
I	52,00	32	13,90	2,12	1,430	3,04	0,8954	16,03	
X variables									

Partial Least Squares analysis was performed on the data set in table 9. By using two factors, the model managed to use 68% of the x-data in order to explain 51% of the y-variables.

In the score plot (Figure 22) it can be seen that there are two large groups of samples explained by factor 1: oils G, H, I and base-extracted B with relatively high TAN values in one group and the rest of the samples in the other group. Factor 2 separates oils C, D and acid-extracted B.

These oils seem to have similar behavior; however, this is difficult to interpret.

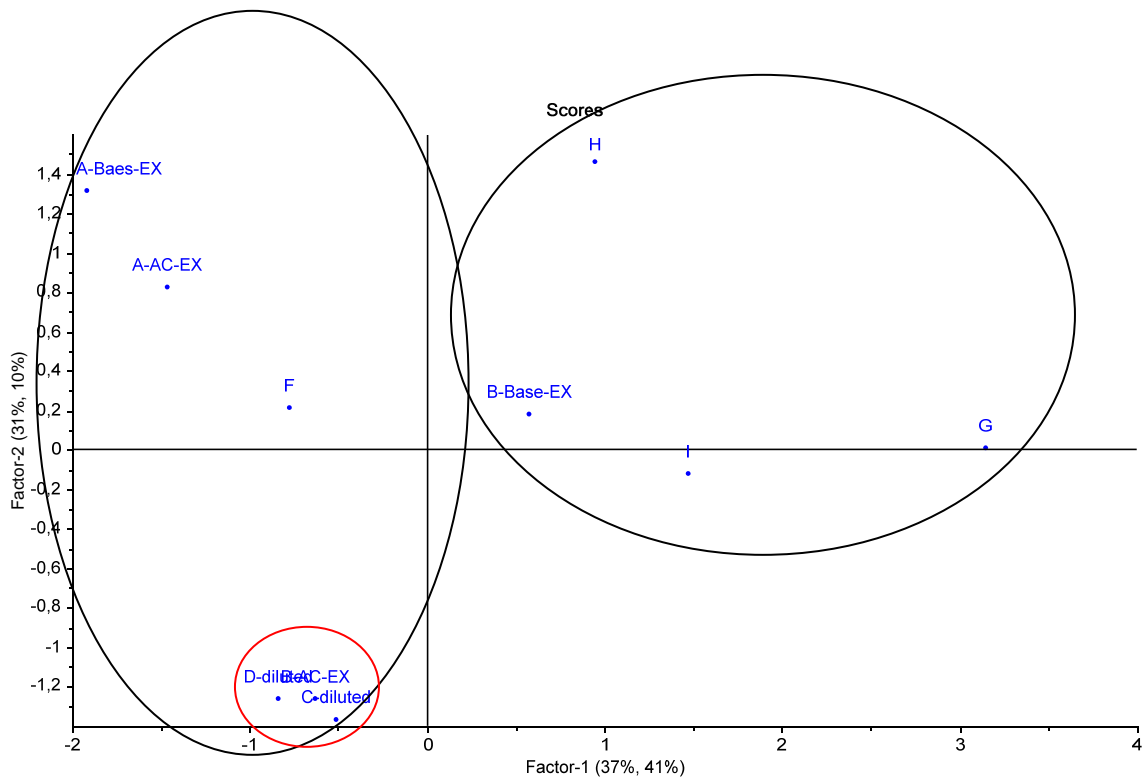


Figure 22 Scores plot for the used data set

By looking at the scores and loading plot (figures 22 and 23) it can be seen that this model suggest a correlation between near-equilibrium interfacial tension and TAN (total acid number) values for the samples with high content in acids.

This model explains only 51% of the y-variable. Oils are very complex mixtures and in order to obtain a better model one needs a larger data set (i.e. more samples or more characterization data).

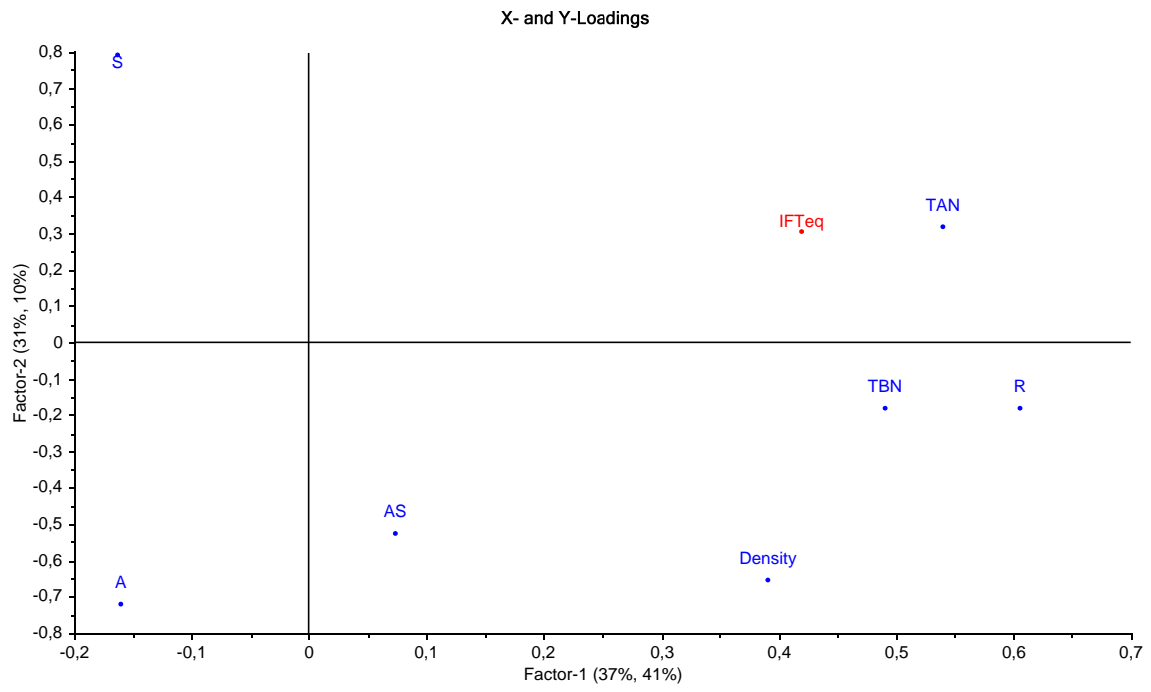


Figure 23 Loadings plot for the used data set

#### 4. Conclusions and Future work

The goal of this study was to determine the main parameters controlling the interfacial properties of crude oil-water interfaces in order to better understand the factors that influence the petroleum emulsion stability. To fulfill this goal, the interfacial properties (dynamic interfacial tension and interfacial rheology) of a matrix comprising different water phases and crude oil samples were determined.

The main observations obtained from the measurements are as follows:

- Acid and Base components in crude oils are surface active and reduce interfacial tension.
- Presence of salt has a major influence on the interfacial properties of the oil droplet. The kinetics of film formation is influenced by the presence and nature of ions in the water phase.
- Oil composition and properties have a large effect on the interfacial behavior of oil/water systems.
- All the systems have viscoelastic properties: they exhibit both viscous and elastic characteristics when undergoing deformation. All these systems have more or less more elastic than viscous behavior.
- Film elasticity for the acid free crude oil is significantly higher than for the base free one.
- The number of oils included in this study is not sufficient for developing a reliable enough model through Partial Least squares analysis.

The obtained results allow to better understand the behavior and properties of oil/water interfaces. The results will be later on correlated with emulsion stability in the context of improving the process of oil removal in produced water.



### Suggestions for future work:

- More oils should be included in this study in order to have a larger data set and to create a more reliable model for Multivariate Data Analysis.
- The acid and base extracted fractions of crude oil C should also be taken into consideration. These fractions should be studied in their diluted form in order to reduce the capillary number.
- Asphaltenes and resins can be extracted from crude oils. Total acid number (TAN) and Total Base Number (TBN) measurements could be used on solutions of asphaltenes and solutions of resins in appropriate solvents (e.g. toluene), in order to determine to what extent the acids and bases are present in the asphaltenes/resins. Also, interfacial tension measurements could be performed on solutions of asphaltenes and resins in an appropriate solvent.
- More experiments should be performed on a crude oil that is not too heavy and on which it's possible to perform dynamic interfacial tension and interfacial rheology measurements while not-diluted. Capillary number could be in this case diminished by modifying other parameters instead of the viscosity. Interfacial properties could then be included in the comparison for different oil concentrations.
- In this study the solvent for dilution was toluene, which is a good solvent for asphaltenes. Another solvent should be found in order to make sure it is an intermediary solvent for asphaltenes and that asphaltenes keep their aggregation state. Cyclohexane is a good candidate since it is an intermediary solvent for asphaltenes between toluene (good solvent) and heptane (bad solvent)<sup>15</sup>.
- The fitting of the data with the bi-exponential function yielded good results for the near-equilibrium interfacial tension values; however, the characteristic times for diffusion and reorganization ( $t_1$  and  $t_2$ ) generally display quite high standard deviations. A new function should be found to fit the data.

## References

1. Hemmingsen, P. V.; Silset, A.; Hannisdal, A.; Sjöblom, J., Emulsions of Heavy Crude Oils. I: Influence of Viscosity, Temperature, and Dilution. *Journal of Dispersion Science and Technology* **2005**, *26* (5), 615-627.
2. Wang, Y.; Zhang, L.; Sun, T.; Zhao, S.; Yu, J., A study of interfacial dilational properties of two different structure demulsifiers at oil-water interfaces. *Journal of Colloid and Interface Science* **2004**, *270* (1), 163-170.
3. Williams, D. H.; Fleming, I., *Spectroscopic Methods in Organic Chemistry*. 5th edition ed.; UK., 1995.
4. S.Wold; Esbensen, K.; Geladi, P., Principal component analysis,. *Chemometrics and Intelligent Laboratory Systems 2* **1987**, 37-52.
5. Hannisdal, A.; Orr, R.; Sjoblom, J., Viscoelastic properties of crude oil components at oil-water interfaces. 1. The effect of dilution. *Journal of Dispersion Science and Technology* **2007**, *28* (1), 81-93.
6. Hannisdal, A.; Orr, R.; Sjoblom, J., Viscoelastic properties of crude oil components at oil-water interfaces. 2: Comparison of 30 oils. *Journal of Dispersion Science and Technology* **2007**, *28* (3), 361-369.
7. J.G.Speight, *The Chemistry and technology of Petroleum*,. 3 ed ed.; 1998.
8. McLean, J. D.; Kilpatrick, P. K., Effects of asphaltene aggregation in model heptane-toluene mixtures on stability of water-in-oil emulsions. *Journal of colloid and interface science* **1997**, *196* (1), 23-34.
9. Førdedal, H.; Nodland, E.; Sjöblom, J.; Kvalheim, O. M., A Multivariate Analysis of W/O Emulsions in High External Electric Fields as Studied by Means of Dielectric Time Domain Spectroscopy. *Journal of Colloid and Interface Science* **1995**, *173* (2), 396-405.
10. Djuve, J.; Yang, X.; Fjellanger, I. J.; Sjöblom, J.; Pelizzetti, E., Chemical destabilization of crude oil based emulsions and asphaltene stabilized emulsions. *Colloid and Polymer Science* **2001**, *279* (3), 232-239.

11. Spiecker, P. M.; Gawrys, K. L.; Kilpatrick, P. K., Aggregation and solubility behavior of asphaltenes and their subfractions. *Journal of Colloid and Interface Science* **2003**, 267 (1), 178-193.
12. Myrvold, R.; Hansen, F. K., Surface Elasticity and Viscosity from Oscillating Bubbles Measured by Automatic Axisymmetric Drop Shape Analysis. *Journal of Colloid and Interface Science* **1998**, 207 (1), 97-105.
13. Lucassen-Reynders, E. H., *Anionic surfactants physical chemistry of surfactant action*. Marcel Dekker, INC: New York, N.Y., USA: Basel, Switzerland, 1981; Vol. 11, p 473.
14. Freer, E. M.; Wong, H.; Radke, C. J., Oscillating drop/bubble tensiometry: effect of viscous forces on the measurement of interfacial tension. *Journal of Colloid and Interface Science* **2005**, 282 (1), 128-132.
15. Dicharry, C.; Arla, D.; Sinquin, A.; Graciaa, A.; Bouriat, P., Stability of water/crude oil emulsions based on interfacial dilatational rheology. *Journal of Colloid and Interface Science* **2006**, 297 (2), 785-791.

Annex 1: Characterization of the crude oil samples.

These characterizations have been done at Ugelstad lab by Sulalit Bandhyophadyay during the summer 2011.

Sample A and its acid- and base-free fractions:

	Original Crude	Acid free	Base free
Saturates (%)	79.66	77.78	78.20
Aromatics (%)	18.29	20.42	20.82
Resins (%)	1.92	1.65	0.93
Asphaltenes (%)	0.12	0.15	0.06
TAN (mg/g)	0.2	/	0.081
TBN (mg/g)	0.597	0.598	/
Density (g/cm <sup>3</sup> , at 50 °C)	0.7830	0.8132	0.7622
Viscosity (mPa.s, at 50 °C)	1.493	1.568	1.590
Water content (ppm)	593	3	41
Wax Content (mg/g)	20	27	28

Sample B and its acid- and base-free fractions:

	Original Crude	Acid free	Base free
Saturates (%)	44.35	47.74	47.92
Aromatics (%)	38.76	41.21	41.09
SARA Resins (%)	16.39	10.72	10.22
Asphaltenes (%)	0.49	0.33	0.77
TAN (mg/g)	2.28	/	2.17
TBN (mg/g)	4.48	0.68	/
Density (gr/cm <sup>3</sup> , at 50 °C)	0.8955	0.9185	0.9242
Viscosity (mPa.s, at 50 °C)	17.87	15.96	13.28
Water content (ppm)	740	111	76
Wax Content (mg/g)	44	58	34

Samples C to I:

	C	D	E	F	G	H	I
Saturates (%)	25,61	58.6		62.19	53.5	60	52.03
Aromatics (%)	49.55	30.9		31.22	29.9	30	31.99
SARA Resins (%)	10.91	8.9		5.89	14.4	9	13.86
Asphaltenes (%)	13.93	2.5		0.69	2.5	0.7	2.12
TAN (mg/g)	0.57	0.34	0.27	0.29	2.15	2.65	1.43
TBN (mg/g)	1.342	1.49	-	1.465	2.87	0.79	3.044
Density (gr/cm <sup>3</sup> , at 50 °C)	0.918	0.93	0.8122	0.8188	0.9166	0.8646	0.8954
Viscosity (mPa.s, at 50 °C)	70.436	-	-	4.654	-	-	32.78
Water content (ppm)	2.5	457	47.1	719.2	8.47	-	16.4
Wax Content (mg/g)	127.425	-	-	7.52	-	-	8.39

Annex 2: coding of the crude oils:

<b><i>Crude oil</i></b>	2934	3542	UN1267	Dompap	Epcon	3482	Grane	Heidrun	3564
<b><i>Code</i></b>	A	B	C	D	E	F	G	H	I

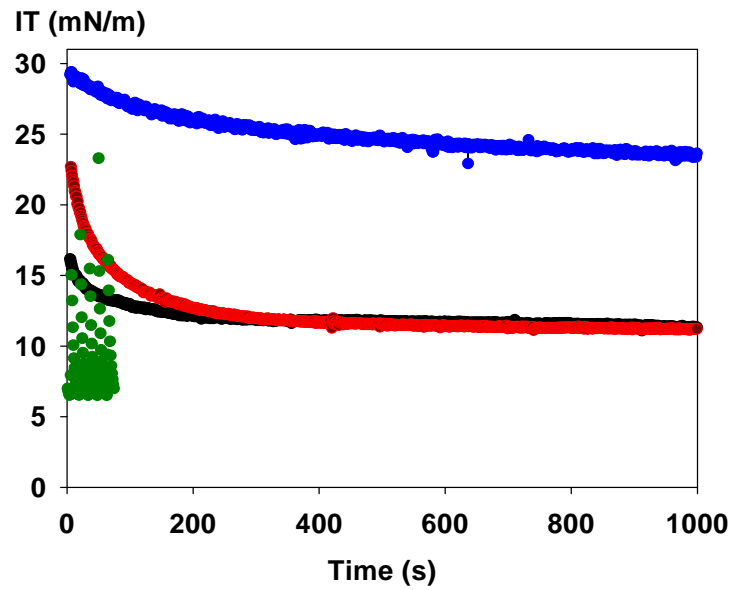
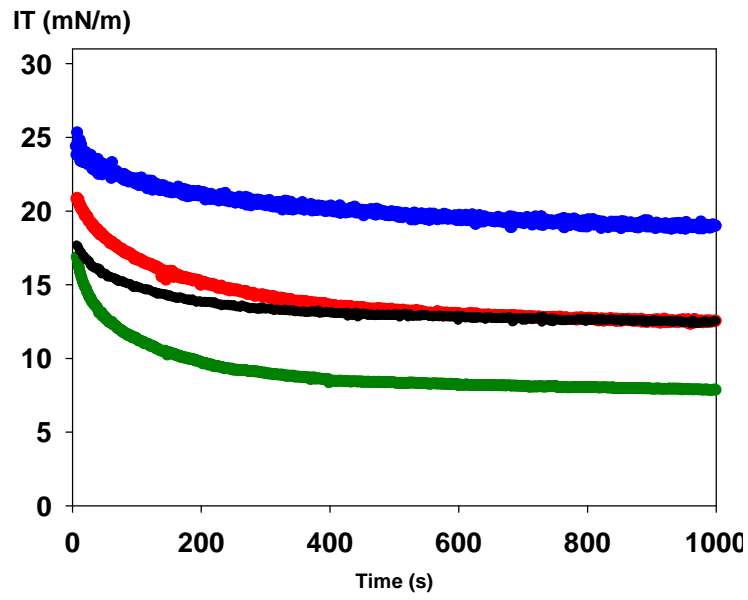
Annex 3:

Table: Interfacial tension and characteristic times for diffusion and reorganization for both oil A fractions and all the water systems.


	Water phase	Equilibrium interfacial tension (mN/m)	StD	t <sub>1</sub> (s)	StD	t <sub>2</sub> (s)	StD
Acid extracted	Pure water	18,63	0,01	41,44	7,18	400,64	22,66
	Synthetic brine	12,34	0,78	19,97	7,02	151,48	12,55
	Synthetic brine without bicarbonates	12,38	0,55	35,17	4,83	254,49	9,77
	Synthetic brine without divalent ions	8,07	0,07	44,27	17,42	261,24	76,56
Base extracted	Pure water	20,75	2,19	74,95	20,28	801,28	45,33
	Synthetic brine	10,24	1,79	58,45	4,10	2500	1178,5
	Synthetic brine without bicarbonates	11,11	0,21	33,85	0,57	169,49	17,67
	Synthetic brine without divalent ions	-	-	-	-	-	-

Interfacial tension measurements for crude A:





Dynamic interfacial tension between acid free (top) or base free (bottom) crude A with pure water (blue curve) synthetic brine (black curve), brine without divalent ions (green curve) and brine without carbonates (red curve).

 Faculty of Natural Sciences and Technology	<h1>PROCEDURE</h1>	Last revision :
	Title: Sinterface PAT-1M	Page 56 of 64
Department: Chemical Engineering	Procedure number: 1	
Revision number:	Developed by: Andreas L. Nenningsland	
	Approved by: Camilla I. Dagsgård	
	Maintained by: Andreas L. Nenningsland	

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REV No. – DATE	ORIGINATOR	CHECKER	APPROVER
<b>This document is subjected to AUDIT.</b>			

**ORIGINATOR:**

**CHECKER:**

**APPROVER:**

<b>REVISION HISTORY</b>	
<b>DATE</b>	<b>AMENDMENT DESCRIPTION</b>

## **1. PURPOSE**

Dynamic interfacial tension and interfacial rheology measurements

## **2. SCOPE**

## **3. RESPONSIBILITIES**

## **4. DEFINITIONS AND ABBREVIATIONS**

Profile Analysis Tensiometer

## **5. EQUIPMENT**

## **CHEMICALS**

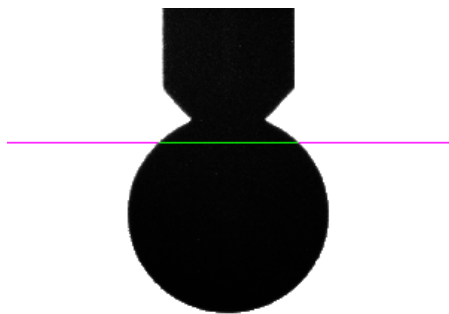
## 6. METHOD

### Initiate instrument and software:

- Main switch: on
- Left syringe switch: on
- Computer: on
- Launch the PAT-1M software from the desktop.

### Calibration:

- Chose the “Buoyant bubble” for this experiment in the lower left corner of the window
- Use a solid sphere (D = 3.0 mm or one of the others) and the magnetic needle
- Improve the focus (picture on the left in the software window) by moving the camera
- Move the line to a position similar to the picture below:



- Click on the “Calibration” icon. In the following window, chose “reference sphere” and input the radius (NOT the diameter)

- Click “OK” and hope for the best
- If an error message appears, the sphere is probably not well focused
- If the calibration is successful, write down the new values for  $C_z$ ,  $C_x$ , etc. in the journal
- Remove the solid sphere and magnetic needle, and replace with one suitable for the following experiments

#### Cleaning and droplet focusing:

- Click “Clean pump” to pass through solvents needed to clean and prepare the tubes/needle.
- Use the “Auto-prepare” function to make a droplet at set volume/area. Close the window and click the “Focus” icon. Move the horizontal bar to the droplet surface and change the camera settings (“Device” → “Camera settings”) to get a steep transition from white to black.
- Unclick “Focus”

#### Temperature control:

#### Launching experiments and analyzing results:



- Click “New experiments”
- Input sample and experimental parameters (density, concentration, droplet volume, etc.)
- Click on “Oscillation” or “Relaxation” if necessary and input the program.
- For re-use of a previously made program, open the experiment where it was used and the program information should be loaded automatically
- “OK”
- Launch with “Start”. Experiment can be stopped at any time with “Stop”.

-The results can be exported by clicking “copy elements to clipboard/excel” and the data obtained from oscillations (elasticity, viscosity...) is found by selecting “Fourier transform”.

## **7. SAFETY EQUIPMENT**

Gloves, Glasses, Portable fume hood

## **8. REFERENCES**

NTNU	Hazardous activity identification process	Risikovurdering	Nummer	Dato	
		HMS-avd.	HMSRV2801		
HMS		Godkjent av	Side	Erstatter	

Unit:

Date: 20.01.2012

Line manager:

Participants in the identification process (including their function):

Andreas L. Nenningsland, Cathy Lesaint, Camilla I. Dagsgård

Short description of the main activity/main process: Measurement of interfacial tension and interfacial rheology

ID no.	Activity/process	Responsible person	Laws, regulations etc.	Existing documentation	Existing safety measures	Comment
1	Cleaning the apparatus and the small parts (cuvette, syringe, tubings)	Andreas/Sebastien	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	Solvents like toluene, xylene, chloroform and acetone are used
2	Measuring the interfacial tension and interfacial rheology	Andreas/Sebastien	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	Solvents like toluene, xylene, chloroform and acetone are used
3	Chronic exposure to toluene	Andreas/Sebastien	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
4	Chronic exposure to THF (tetrahydrofuran)	Andreas/Sebastien	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-



5	Chronic exposure to chloroform	Andreas/Sebastian	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
6	Chronic exposure to xylene	Andreas/Sebastian	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
7	Chronic exposure to crude oil	Andreas/Sebastian	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
8	Handling chemicals in general	Andreas/Sebastian	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
9	Using a water bath for higher temperatures in the cuvette	Andreas/Sebastian		Apparatus card with instructions Operating procedure		The maximum temperature of use is 50 deg Celsius

Operating Instructions

Instrument/Apparatus: Sinterface PAT 1m		Placement: PFI, room 3342	
Serial Number: 00100168			
Original Manual:			
Log book with signature for training & maintenance:			
K:\ikp\Ugelstadlab\Teknopool - Laboratory\Equipment + data storage\Data -calibration-maintenance\InstrumentLists			
Risk Evaluation			
Date: 20.01.2012			
Archived: K:\ikp\Ugelstadlab\Teknopool - Laboratory\HMS\Risk assessment\Procedures & Method\SinterfacePAT1m			
Compulsory Protection Equipment:		Hazards:	
Safety Goggles	<input checked="" type="checkbox"/>	Fire	<input type="checkbox"/>
Gloves	<input checked="" type="checkbox"/>	Chemicals/Gasses	<input checked="" type="checkbox"/>
Hearing Protection	<input type="checkbox"/>	Electricity/Power	<input type="checkbox"/>
Protective Clothing	<input checked="" type="checkbox"/>	Temperature/Pressure	<input checked="" type="checkbox"/>
Breathing Protection	<input type="checkbox"/>	Cutting/Crushing	<input type="checkbox"/>
Shielding	<input type="checkbox"/>	Rotating Equipment	<input type="checkbox"/>
Other	<input type="checkbox"/>	Hazardous Waste	<input checked="" type="checkbox"/>
None	<input type="checkbox"/>	Out of normal working hours	<input checked="" type="checkbox"/>
		Others	<input type="checkbox"/>
		None	<input type="checkbox"/>
Operating Instructions (Attached Separate Instructions)			
Emergency Procedure (Emergency Stop Procedure, Image of Switches/Stop Procedure): None			
Maintenance Routines Frequency: Service Agreements: Maintenance Contact: Maintenance Described In Separate Attachment			
Person Responsible:		Deputy:	
Name:	Andreas L. Nenningsland	Name:	Sebastien Simon
Telephone	94159	Telephone	91657
Mobile:		Mobile:	
Signature:		Signature:	
Controlled & Updated:			
Date:	20.01.2012	Date:	
Date:		Date:	