Characterisation of Gas-Liquid Interfaces related to Offshore Produced Water Treatment.

The Influence of Crude Oil Composition and
different Brines with various pH.

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Abstract

Produced water is an environmental toxic and complex mixture, which is co-produced during gas and oil production. The aim of this study is to investigate the surface tension of the produced water with a bubble pressure tensiometer, BP100. The influence of the pH of the brine and the brine composition were studied together with the effect of the crude oil composition. The results were supposed to be related to flotation, which is a common separation technique regarding produced water treatment. To achieve a high separation efficiency the spreading coefficient must be positive and this is obtainable if the surface tension between the produced water and the gas bubbles is high. UV/VIS spectrometer was utilized to investigate other chemical properties of the produced water. Three oils (H, E and C) and four brines with various pH were investigated by BP100 and UV/VIS. An extraction of the organic compounds in two produced water samples and further investigation with IR was done. The purpose was to see if the extraction solvent and IR was an appropriate method for characterization of produced water.

On the basis of the results of this research, it can be concluded that the pH of the brine have a larger influence on the surface tension of the produced water than the composition of the brine. For crude oil H, which contain very high TAN, the greatest changes in surface tension was observed at high pH. For crude oil E, which has a very low amount of resins and asphaltenes, there were no significant changes, both in terms of pH and brine composition. Crude oil C contains a great amount of resins and asphaltenes. The influence on the surface tension were large for all pH values, and there were also observed salting-out effect. The crude oil composition regarding surface pressure did not give major trends. The UV measurements indicated that organic molecules were present in all the samples. Four peaks were observed for the samples made of brine with pH 2, contrary to only two peaks for the other samples. The maximums given for the samples of pH 2 might correspond to pyridines, quinolines and acridines (basic compounds) based on their UV spectra. Infrared spectroscopy was conducted for two samples. Absorption peaks were found, and they were related to different organic functional groups that are common for produced water. The extraction solvent used (70:30 cyclohexane/butyl acetate) worked probably and according to the results of the IR it can be concluded that the procedure is applicable for this type of studies.

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

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Signature	Place	Date

Contents

1 Introduction

When producing oil and gas there will always be some water co-produced. This water comes from the reservoir during the production. It is a complex mixture and depends on the geological and geographical location of the reservoir. Variation of the composition of the produced water will vary significant during the lifetime of the field. During 2010 it was produced 140 million m^3 produced water and 144 million m^3 oil at the Norwegian Continental Shelf. The produced water corresponds to approximately 50% of total fluids produced. Some wells can actually have water to oil ratios (water cuts) above 90%. As the field mature and more EOR techniques are implemented the produced water continue to increase [1].

During the production of oil and gas the produced water is either discharged to the sea, or reinjected into the reservoir to maintain the pressure. As the amount of this water will increase in the future the impacts on the environment will be larger. It is thus of importance to improve the separation techniques of the produced water to be able to make it more clean and less harmful for the nature [2].

The purpose of this thesis is to investigate the changes in the interfacial tension between produced water and gas bubbles at short time scale by using a bubble pressure tensiometer, BP100. The influence of the pH of the brine and the brine composition will be studied together with the effect of the crude oil composition. The results are supposed to be related to flotation, which is a common separation technique regarding produced water treatment. This process is most efficient when the spreading coefficient is large, and this is achieved when the surface tension of the produced water is high. By increasing the efficiency of the flotation process the quality of the co-produced water will be improved, which will reduce the impacts on the environment. UV/VIS spectrometer and IR spectrometer will also be utilized to investigate other chemical properties of the produced water. The project is a part of a research program sponsored by ConocoPhillips, ENI Norge, Schlumberger Division MI EPCON, Statoil and Total.

2 Background

2.1 Crude Oil

Today is the crude oil the primary energy source in the world and the demand and consumption of this source will not decrease in the next two decades. As a result of the developing economics in Asia, an increasing demand for crude oil during the recent years (1990-2006) has found place. The quality of the crude oil on the other hand has decreased, and heavy crude oils (high density and viscosity) are often present. Due to the complex composition of these oils more advanced recovery and refining technologies are required [2].

Crude oil is a complex mixture of gaseous, liquid, and solid hydrocarbons with various degree of polarity and functionality. The composition depends upon the field the oil is taken from, and it is not possible to characterize the individual molecular types due to the complexity of the oil. A hydrocarbon group type analysis is often employed. The SARA-separation is one example, and is based on the various solubility and polarity of the different compounds in the crude oil. The crude oil is separated into four groups; saturates, aromatics, resins and asphaltenes (SARA), see Figure 1.
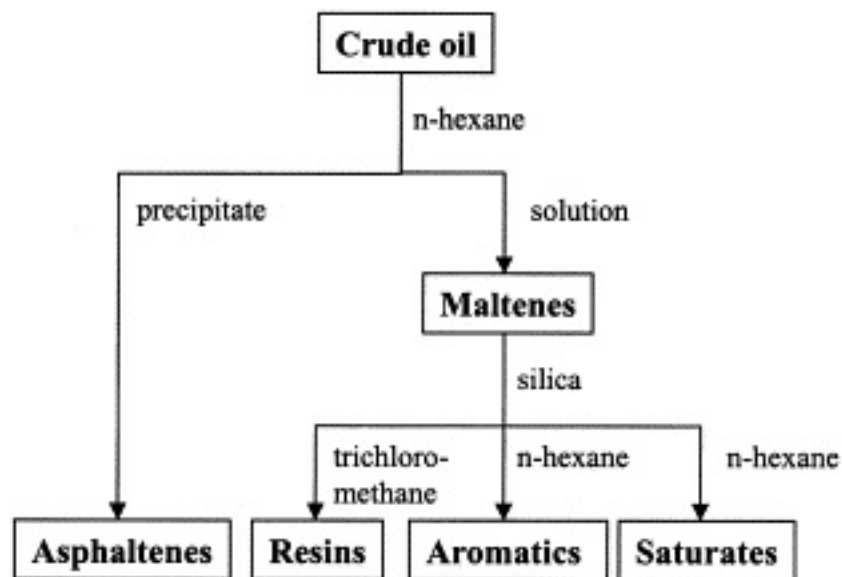

Figure 1 – SARA-separation of crude oil[2]

Saturates and aromatics are non-polar compounds in the crude oil. There are no double bonds present among the saturates and they include the alkanes and

cycloalkanes. Compounds that contain one or more benzene rings are classified as aromatics. Resins are polar molecules that often contain heteroatoms such as nitrogen, oxygen or sulfur. They are soluble in light alkanes (e.g pentane and heptane), but insoluble in liquid propane. Naphthenic acid is a common resin compound. Asphaltenes are polar molecules, like resins, but have higher molecular weight. They are insoluble and precipitate in light alkenes such as pentane, hexane or heptane. The precipitate is soluble in aromatic solvent like toluene and benzene. In general hydrocarbon content may be as high as 97% for lighter paraffinic crude oil or as low as 50% in heavy crude oils and bitumen[2].

The variation of the composition of different elements in the crude oils is given under.

Table 1 – The general compositions of different elements in crude oil[2]

Component	Wt%	Component	Wt%
Carbon	83,0 - 87	Oxygen	0,05 - 1,5
Hydrogen	10,0 - 14	Sulfur	0,05 - 6
Nitrogen	0,1 - 2,0	Metals (Ni and V)	< 0,1

2.2   Produced Water

Produced water is water from subsurface formations and is brought up to the surface during gas and oil production. It is a mixture of dissolved and dispersed components from the rock, oil and gas in the reservoir, see Table 2. The physical and chemical properties of the produced water depend upon geological formations and geographical location of the reservoir, and it will vary significant during the lifetime of the field [2].

Table 2 – The general compositions of different elements in produced water

Dispersed componetns	Dissolved components
- Oil (o/w emulsions)	- Organics (including hydrocarbons)
- Heavy metals	- Gases (CO_2, H_2S, natural gas)
- Solids (formation solids, corrosion/scale products,wax, asphaltenes)	- Inorganic salts
- Microbiological components(microorganisms)	

Produced water is the largest waste stream generated by the oil and gas industry and today it account for almost 60% of the produced volume [2]. As the field mature the water cut increases as illustrated in Figure 2. This waste stream can violate established environmental regulations due to its complex composition of hazardous dissolved and dispersed components.
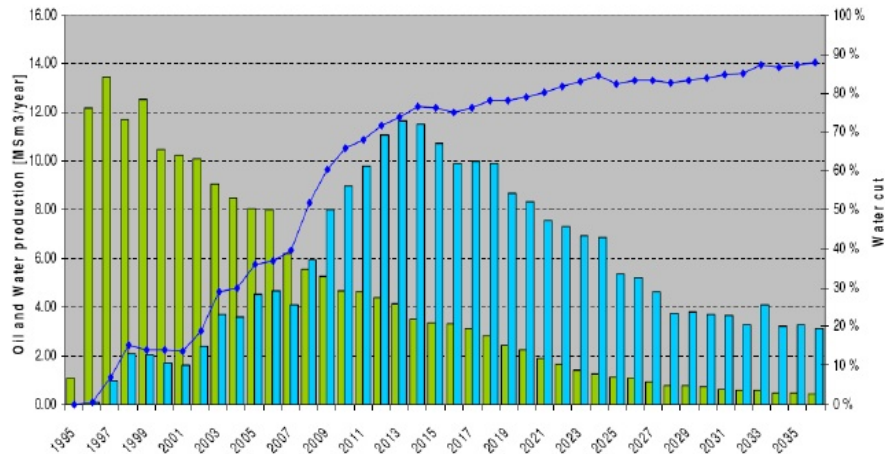
Figure 2 – Forcast of oil and water production at Heidrun field based on historical data (green bars - produced oil, turquoise bars - produced water, blue line - water cut) [2]

There are two ways of handling the produced water, either discharging it in the sea or reinject it into the reservoir to maintain the pressure. The former option is more often encountered. In 2007 the amount of water injected was 27 million m^3 and the amount discharged to sea was 162 million m^3 [2]. It is thus of high importance that the water stream is as clean as possible. By 1 January 2007 the OSPAR (Oslo-Paris Convention) Commission decided a new limit (30 ppm per month) for dispersed oil in produced water discharged into the sea [3]. Regarding the quality of the oil that has decreased, the quality of the produced water tend also to decrease simultaneously, and to be able to get beyond this new limit the produced water treatment systems need to be improved. At the same time fresh water is becoming a scarce source and the demand is increasing with the population growth. This can together with the environmental issues be important driving forces regarding the improvement of the treatments facilities. Figure 3 illustrates how the separations process is proceeded in general, and what kind of separation techniques that are often used during the process.
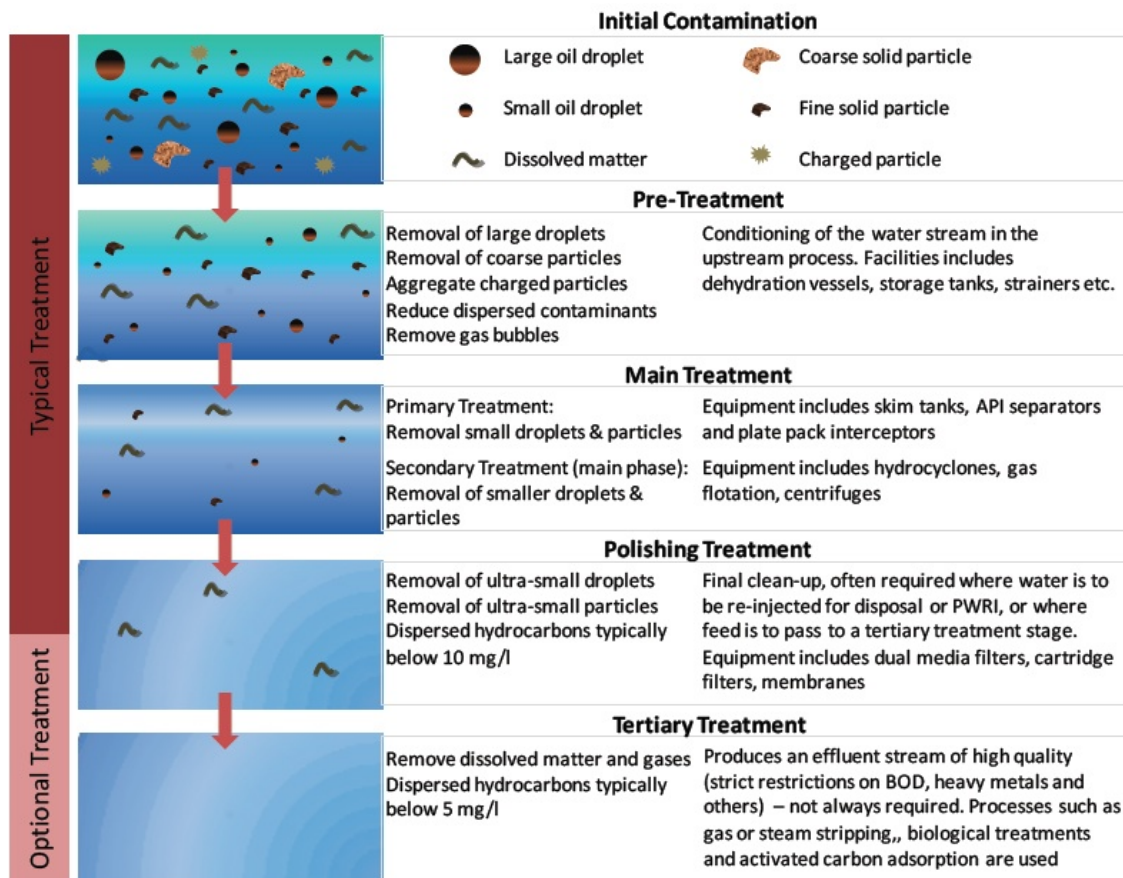
Figure 3 – A typical produced water treatment system. Modified from Shell 2009.

2.3   Gas Flotation - A Common Separation Technique

Gas flotation is a separation technique that is based on accelerated gravitational properties. There are two major methods of flotation: induced(dispersed) gas flotation (IGF) and dissolved gas flotation (DGF). In both cases are fine gas bubbles injected into a water phase containing immiscible liquid droplets (oil) or greasy solid particles, and the major difference is the average size of the gas bubble, the mixing and the hydraulic loading rating. The gas bubbles are attached to the immiscible droplets, and the density difference between the oil and the water increases, which make the oil rise faster to the surface. At the surface is the oil captured by the resulting foam which is then skimmed off.

The most important factor regarding flotation is the velocity, which is dependent upon the bubble/droplet diameter and density differences. This is illustrated by Stokes equation, which states this theory (1).

$$V = \frac{d^2 g(\rho_w - \rho_o)}{18\mu_w} \tag{1}$$

Where V is the rising or falling velocity, d is the droplet diameter, g is the gravitational acceleration, $(\rho_w\text{-}\rho_o)$ is the density difference between the continuos phase and the droplet phase (oil or gas), μ_w is the dynamic viscosity of the continuos phase. The smaller the droplets the slower is the velocity. When oil droplets are attached to gas bubbles a reduction of the oil density will occur, and hence will the density difference of oil and water increase. The oil field waste water is most often stabilized oil-in-water emulsion with droplets of diameter of 3 - 20μm. The residence time in a flotation separation unit should not be above 30 minute, and to be able to achieve this time, either the droplet size must increase (should be between 20 - 150μm) or the fluid density differences should be larger. The efficiency can be improved by coalescence of the oil droplets (breaking the emulsions), which will lead to larger droplets. To obtain coalescence the interfacial tension must be high between the two immiscible phases and this can be done by adding demulsifiers (surfactants). To get the oil droplet to spread at the gas bubble it is essential that the interfacial tension between the water and the gas phase is large, thereby will the oil spreading coefficient on a water-gas interface be positive, according to Equation (2) [4].

$$S_0 = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \tag{2}$$

Where γ_{wg} is the water-gas surface tension, γ_{ow} is the oil-water interfacial tension and γ_{og} is the oil-gas surface tension. Figure 4 illustrates how an oil droplet will tend to spread on an air bubble if the spreading coefficient is positive [4].
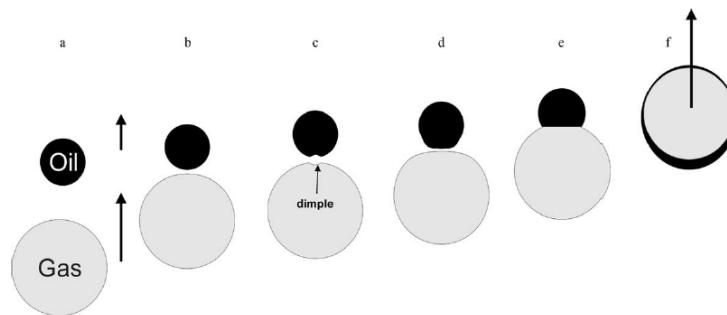
Figure 4 – The process of how the oil droplets are attached to the injected air bubbles [4].

2.4   Dynamic Surface Tension

definition for this phenomena. Either it is possible to define it as a force that is
required to avoid a reduction in the surface area, or it can be correlated to the free
energy of the surface (energy has to be applied to increase the surface area).
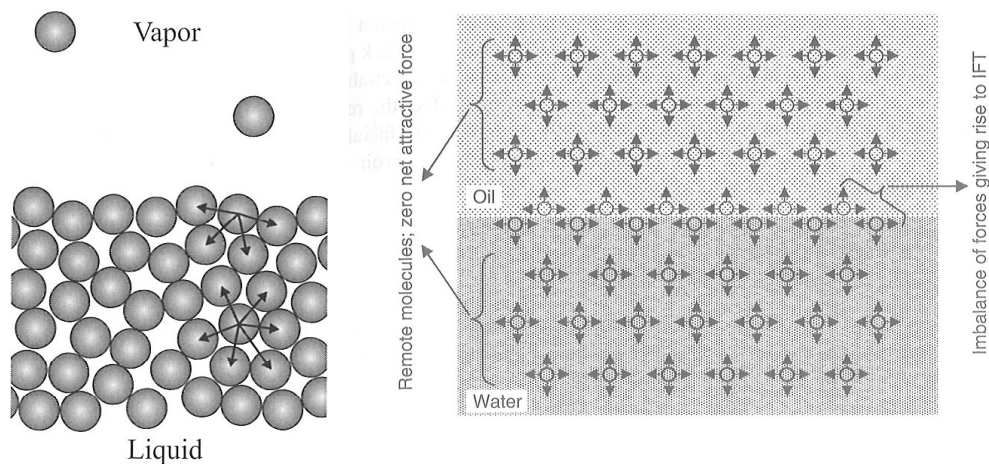
Figure 5 – The intermolecular forces in the bulk phase and at the interface/surface [5].

Dynamic surface tensions is the change in surface tension before equilibrium con-
ditions are achieved. When a new liquid/air or liquid/liquid interface are formed,
the surface composition is the same as the bulk composition. Thus is the surface
tension close to the surface tension of the pure solvent or the average surface ten-
sion of the neat components. The most surface active compounds compete for the
surface, and those that are most interfacial active adsorb to it. At equilibrium the
surface tension is constant and has obtained the lowest value for the specific solu-
tion [6]. This process is time dependent. There are various mechanisms that cause
this dynamic behavior, which include migration of the surface active components
to the interface, reorientation at the interface, interfacial reactions, and exchange
of components between the bulk phases. The time dependence of this change in
surface tension normally follows the curve given in Figure 6 [7].
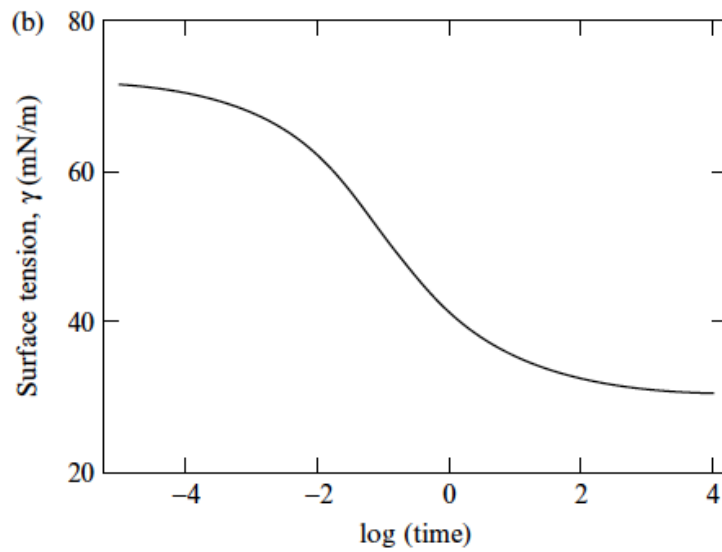
Figure 6 – The dynamic surface tensions. The surface tension is first the same as the surface tensions of the pure solvent, but with time it decreases due to diffusion of surfactants form the bulk phase to the surface/interface. [8].

In Figure 7 the same principle is illustrated, where surface active molecules are added to pure water. After stirring the mixture the surface tension is the same as for pure water, but as the surface active compounds merge to the surface the surface tension decreases and finally reach equilibrium. The figure also shows how the surface active molecules orient themselves at the surface. The hydrophobic tail is directed towards the air, due to the non-polar chain. The head group of the surfactants can either be polar, ionic or non-ionic, which makes it hydrophilic and thus are the head group directed towards the aqueous solution.
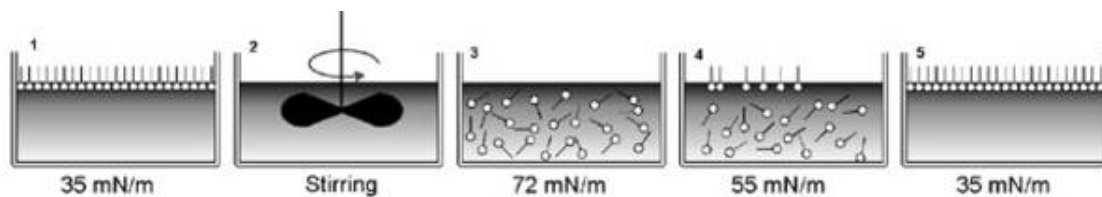
Figure 7 – The changes in dynamic surface tensions and orientation of the surface active molecules at the surface [8].

2.4.1   Surface Pressure

The surface tension decreases when surface active molecules adsorb to a surface, and thus is the required energy to increase the surface reduced [9]. The interactions

between the surface active molecules and the repulsive forces they exert on each other get stronger with the number of adsorbed molecules at the surface. This causes an decrease in surface tensioin. The surface pressure is thus the difference of the surface tension of the sub phase in absence of a monolayer and the surface tension with the monolayer present at the interface, γ_0 and γ respectively. The surface pressure, Π, is given in Equation (3) [10], and reflect the effect the surface active molecules have on the solvent.

$$\Pi = \gamma_0 - \gamma \tag{3}$$

2.5 Circumstances That Affect the Surface Tension of The Produced Water

To understand the origin of the surface properties of the co-produced water during oil and gas production two processes must be taken into consideration. These processes include the interactions at the oil/brine interface during mixing and the interactions at the surface of the produced water after preparation, and are given in Figure 8.
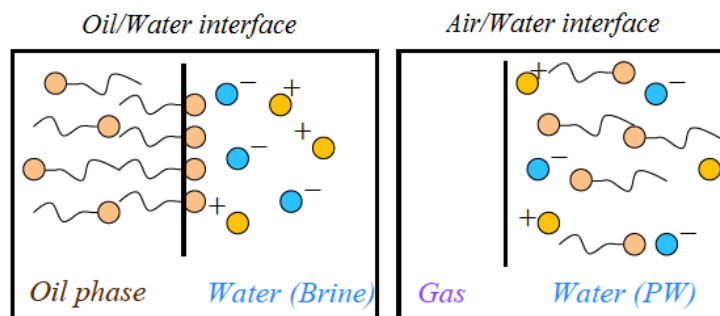
Figure 8 – Two processes that must be taken into consideration regarding the surface tension of the produced water [11].

The interactions between the crude oil and the brine and the surface properties of the produced water depend upon the type of crude oil and the type of brine that are incorporated in the process.

2.5.1 The Oil/Brine Interface

Crude oils contain different surface active compounds, which contribute different to the interactions at the interface between oil and brine. These compounds are

most often acids and bases (both dissociative and non-dissociative), and correlate to the most polar fractions in the crude oil, which are asphaltenes and resins. There are developed techniques that are able to quantify the total acid number (TAN) and the total base number (TBN), which are directly related to the resin and asphaltene amount in the crude oil. These numbers will thus reflect the acidic and basic properties of the oil.

The acidic and basic functional groups consist of heteroatoms such as oxygen, nitrogen and sulfur. A large and common acidic group encountered in the crude oils is the naphthenic acids, a complex mixture of aromatic and saturated rings, connected by aliphatic chains [12]. These acids are polydisperse in size and structure, and the smallest are easily dissolved in the aqueous phase at pHs around 5 (due to the pK$_a$), while the larger molecules are preferably oil-soluble [13]. They comprise the carboxyl acids and is incorporated in the resin fraction. The major fraction of the basic compounds in the crude oil are the nitrogen compounds. Heterocyclic compounds like pyridines, quinolines, some substituted pyrrols and alkylated benzoquinolines are the main classes within this basic group [14] [15] [16]. Both the basic and acidic compounds will influence the interfacial tension between the oil and the brine under the right pH conditions. Amine-containing bases have also been identified, but this fraction in the crude oil is rather small [17].

When a crude oil and an aqueous solution get in contact, the pH of the aqueous solution will determine what kind of acidic and basic components that will accumulate at the crude oil/brine interface, and what kind of molecules that will be exchanged between the bulk phases. The water-solubility and surface active properties are related to the pK$_a$ and pK$_b$ to the acid and the base respectively. The produced water tend to have an pH between 6 and 7.7, and this range is affected by the type of crude oil and the pH of the brine. When the pH of the brine exceeds the pK$_a$ for an acid, the acid will tend to dissociate and changes into a negative charged molecule. Consequently it becomes more water soluble and surface active and will either diffuse into the the water phase or stick better to the interfacial surface. When the pH gets below pK$_b$ (pK$_b$=14-pK$_a$) the interfacial active and water-soluble properties will increase for the basic components due to the protonation that will take place, and a positive charge is created on the molecules. The dissociation process the acids in the crude oil can undergo under the right pH conditions is illustrated in Figure 9.
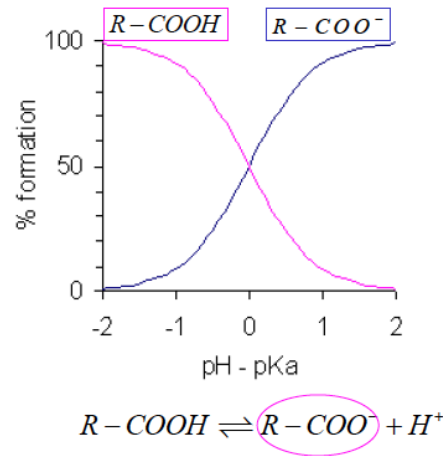
Figure 9 – The behavior of acids when the pH is over and below pK_a. When the pH exceeds the pK_a the acids tend to dissociate and achieve a charge, which make them more surface active and more water-soluble [11].

A previous study done by Gisle Øye et.al. claim the trend described over. The results given in the study show that the acidic components have not major effects on the interfacial tension at pH values around 2. It was rather the basic compounds that got an increase in interfacial activity, which is caused by the protonation of the basis at low pH values. When the pH increased to natural pH, the protonation of the basis tend to decrease, and the acids mostly govern the interfacial behavior [7].

The type of ions in the brine is also an important aspect regarding the interfacial activity, especially when it comes to the acids in the crude oil (the naphthenic acids). The main process that occur at the oil/brine interface is ion-ion interaction between dissociated acids and free cations (e.g. Mg^{2+}, Ca^{2+}, Ba^{2+} and Na^+). This process occurs because of the electrostatic attraction exerted by the cations upon the carboxyl groups on the acid. For this to take place the pH must be in the range between the pK_a and the hydroxide precipitation of the metal cations, which can occur when the pH get very high. The cations will bound sequentially to two acid monomers and an interfacial metal-acid-water-complex will be formed, as illustrated by Equation (4) and (5) [18]. The metal-mono-complex is more interfacial active than a dissociative acid monomer.

$$M^{2+} + [RCOO^-] \rightleftharpoons [M - RCOO]^+ \tag{4}$$

$$[RCOO^-] + [M - RCOO]^+ \rightarrow M - (RCOO)_2 \tag{5}$$

A metal-monoacid-complex is formed in the first step (Equation (4)). It has a positive charge and is thus more interfacial active than the metal-naphthenate-

complex that is formed in the second step. The metal-monoacid-complex will either be oil or water soluble, which will depend upon the polarity and size of the molecule. Low molecular weight molecules tend to be more water-soluble. The interfacial tension between the oil and the brine will, because of the first reaction step, decrease and then tend to arise after some time due to the formation of the less interfacial active metal-naphthenate-complex. These complexes have no net charge and will most likely migrate into one of the bulk phases, and hence reduce the density of dissociated acids at the oil/brine interface. The polarity of the complex will influence if the diffusion will take place in the brine or in the oil phase. It is also observed that the interfacial activity of the complex increases by the degree of hydration of the cation. More hydrated water surrounding the cation seem to form acid-metal-water-complexes. The degree of hydration depend upon the size of the cation and the charge density. Magnesium has a smaller radius than calcium and thus is Mg^{2+} more hydrated than Ca^{2+}, whereas magnesium binds six water molecules and calcium is only bound to two in aqueous solution. This makes magnesium more water soluble. Attractive forces between the hydrated magnesium ion and acid makes a metal-acid-water-complex with high water solubility, and thereby with higher affinity towards the oil/brine interface and thus increased interfacial acitivity. The complex will stick better to the interface and lower the interfacial tension. However, there has been done investigations about the mechanical properties of various myristic acid-cation monolayers, conducted by a Langmuir instrument, and it was not found any solid films at the surface between water and air when using magnesium in the water solution. The less water-soluble calcium product gave rigid films in the entire pH range above pK_a. Since the calcium-based-complex is less water soluble it prefer to stick to the interface even more than the magnesium-based-complex that is more water soluble, which might diffuse into the water phase. An other common ion in brine solutions is barium, which seem to mostly form a barium-diacid-complex, a natural naphthenate complex, which will tend to diffuse into the bulk phases due to the low interfacial properties. The interfacial tension will consequently decrease if only barium is present in the aqueous phase. The same yield for sodium, which is a monovalent ion, and will together with naphthenate acid create a zero charged complex [18].

In a previous study trends were present regarding the behavior of Ca^{2+} and Na^+ at the oil/brine interface. They found out that sodium ions in the brine promotes the dissociation of the acid in the crude oil, which makes them more water soluble. This might be related to the electrostatic attractive forces between the cations and the dissociative acids. The presence of the divalent calcium ions in the brine caused strong complexations with the dissociative acids that most likely resulted in interfacial films. The transport of the acid components into the water phase

will thus be prevented or the solubilization of acidic groups will be reduced [7].

The Salting-out Effect
The presence of salt in the aqueous phase can either decrease or increase the solubility of organic molecules in the water, which is knows as salting out and salting in, respectively [19]. Ions with a small radius are called kosmotropes. They have high surface charge density and exhibit stronger interactions with water than water itself [20]. Ca^{2+} and Mg^{2+} are strong kosmotropes, whereas Na^+ is a weak kosmotrope. Larger ions with smaller surface charge density is known as chaotropes. Due to their small charge density the attraction forces between the chaotropes and the water molecules will be less than the interaction between each water molecule. An very oversimplified and incomplete explanation for the salting out/in phenomena is based on the hydration forces. Ions form hydration complexes with water molecules, and thereby leaving less "free" water available for dissolved organic compounds. This means that the organic compounds that is not very soluble in water from before get even less water soluble, and is being salted-out (solubility decreases). The opposite situation is when an organic compound is getting more water soluble by adding salt, which is known as salting-in [21]. The more an ion is hydrated the less will the organic compound be soluble in the aqueous solution, and since kosmotropes tend to be more hydrated they will contribute most to the salting out effect. This is why organic compounds are in general more soluble in pure water than in brine. It is further shown by Xie et.al. that the salting-out effect increases with increasing molar volume of the organic solute, which is due to their sensitivity to the increase of cohesive forces. For most purposes NaCl, seawater and synthetic seawater solutions have equal salting-out properties at the same molar concentration. There were not found any correlations between the different electrolytes that were studied during the experiments conducted by Xie et.al. [22] [23] [24].

Overall it can consequently be expected to find organic compounds, such as acids and bases, in the produced water depending on the type of crude oil, how water soluble the organic contents in the crude tend to be regarding the pH and the ions present in the brine. The salting out effect will be an important parameter as well. The water soluble organic compounds will further affect the surface tension of the produced water.

2.5.2 The Air/Produced Water Interface

The organic compounds that have achieved more water soluble properties (e.g. metal-acid-water-complexes, protonated bases, and dissociated acids) and thus dif-

fused into the aqueous phase will show a tendency to decrease the surface tension of the produced water. These compounds prefer the surface of the water phase instead of the bulk due to their low solubility in water and their surface active properties. The lowering in surface tension will depend upon the amount of the organic compounds and their interactions with ions in the produced water. Divalent ions present in the aqueous phase will have stronger shielding properties than monovalent cations regarding the repulsive forces between the head groups on the surface active compounds from the crude oil. This will contribute to more efficient packing of the surface active molecules on the surface due to the reduced head group area [25]. Since kosmotropes (small ions with large surface charge density) is strongly hydrated they prefer to be in the bulk solution, whereas chaotropes and weak kosmotropes will tend to diffuse to the surface and effect the packing of the surface active molecules on the surface.

3   Experimental Techniques and Materials

3.1   Materials and sample preparation

Produced water is prepared by mixing oil and brine. Table 3 shows the required material and equipment for the preparation.

Table 3 – The materials, equipment and cleaning agents required for preparation of produced water samples

Materials	Equipment	Cleaning Agents
Crude oil [40 g] Synthetic brine [40 g]	- Schott bottles (250 ml, 50 ml) - Shaker - Centrifugal tubes - Separatory funnels - Pipettes	- Toluene - Milli-Q water - Acetone

Three different synthetic brines were made with similar ionic strength (I=2.0182). The brine compositions and the calculation of the ionic strength are given in Appendix A and B respectively. One of them contains a number of different salt, but the two others are a pure NaCl brine and a pure CaCl$_2$ brine. The brines were prepared in Schott bottles (1000 ml). The chlorides were first dissolved, then the sulphates and at the end the bicarbonate. Milli-Q water was used as solvent. In order to prevent precipitation the brines were stirred continuously by a magnetic stirrer when they were not in use. In addition to these brines the oils were also mixed with Milli-Q water to get an idea of the effect of pure water versus the ions in the brines. The oils investigated and their properties are given in Table 4 and Table 5.

Table 4 – The properties of the crude oils used during the experiments. The SARA composition for the different oils are given in the table.

Crude oil	Saturates [wt%]	Aromatics [wt%]	Resins [wt%]	Asphaltenes [wt%]
C	25.61	49.55	10.91	13.93
H	60	30	9	0.7
E	67.26	27.67	4.29	0.78

Table 5 – The properties of the crude oils used during the experiments. The density, viscosity and the acid and base numbers for the different oils are given in the table.

Crude oil	Density[g/cm^3]	Viscosity [cP]	TAN [mg/g]	TBN [mg/g]
C	0.938	487	0.57	1.342
H	0.88	11	2.65	0.79
E	0.83	11	0.27	1.1

For each brine the pH was supposed to be adjusted with NaOH and HCl to pH 2, 4, 6, 8, 10 and 12 before mixing with oil. To prevent impurities all of the equipment was carefully cleaned with Milli-Q water before use. Equivalent amounts [40 g] of oil and brine were poured into a Schott bottle [250 ml] and shacked on a shaker for 24 hours(speed set to 250 mot/min). The sample was poured into centrifugal tubes and centrifuged for 15 minutes at 8000 rpm or more if necessary. The final water phase was then completely separated from the oil phase by using a separatory funnel. Three parallels were made for each sample of pH C. For crude oil H and E there were only made two parallels for each sample due to a smaller accessible amount of the crude oil. See Appendix C for more detailed procedure about the preparation of the produced water.

The prepared produced water samples are listed in Table 6 with the corresponding pH of the brine and the oil that is used. More detailed information is given in Appendix D. The nomenclature of the sample names can be explained as follows; first letter is related to the crude oil, the second letter is the type of brine, and the number is the pH of the brine before preparation.

The pH of the produced water was measured right after preparation and the same day the bubble pressure tensiometer measurements were conducted. This observation was done to see how the pH of the samples might change with time after preparation. All of the samples were analyzed with the bubble pressure tensiometer (BP100) and UV visible. Two samples made from crude oil C were also investigated by Infrared spectroscopy (IR).

Table 6 – The prepared produce water samples and their names. The pH given is the pH of the brines the samples are made of. Three parallels are prepared for each sample of crude oil C, and there are two parallels for crude oil H and E.

		Type of brine			
Crude oil	pH	MQ water	Synthetic	NaCl	CaCl$_2$
C	2	C_W_2	C_S_2	C_N_2	C_C_2
	4	C_W_4	C_S_4	C_N_4	C_C_4
	6*	C_W_6	C_S_6	C_N_6	C_C_6
	10	C_W_10	C_S_10	C_N_2	C_C_10
	12	C_W_12	C_S_12	C_N_12	C_C_12
H	2	H_W_2	H_S_2	H_N_2	H_C_2
	6*	H_W_6	H_S_6	H_N_6	H_C_H
	10	H_W_10	H_S_10	H_N_10	H_C_10
E	2	E_W_2	E_S_2	E_N_2	E_C_2
	6*	E_W_6	E_S_6	E_N_6	E_C_H
	10	E_W_10	E_S_10	E_N_10	E_C_10

* The natural pH of the prepared brine

3.2 Methods

3.2.1 Bubble Pressure Tensiometer

The dynamic surface tension of produced water was to be investigated. To measure the dynamic surface tension, a bubble pressure tensiometer from Krüss (BP100) was utilized. The principle of the measurement is shown in Figure 10. Gas bubbles enters the water phase through the capillary at an exactly defined bubble generation rate. The radius of the capillary is known. To increase the bubble size the pressure in bubble must work against the surface tension of the liquid. When the radius of the bubble is the same as the radius of the capillary, the pressure reach a maximum value. This maximum pressure is detected by the instrument and the surface tension is calculated from this value by Equation (6), where P_0 is the initial hydrostatic pressure, P_{max} is the maximum pressure and r_{cap} is the radius of the capillary [26].

$$\gamma = \frac{(P_{max} - P_0) \times r_{cap}}{2} \tag{6}$$

The time from the bubble starts forming to the time that the maximum pressure is reached and detected is the age of the surface. By utilizing BP100 the surface tension appears as a function of the surface age, which is important for assessing the dynamics of surfactants.

The following illustration shows the pressure curve during bubble formation plotted as a function of time.
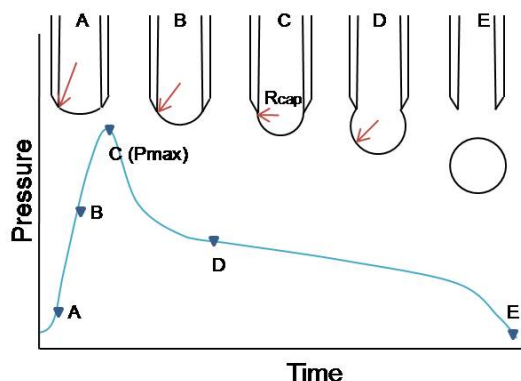
Figure 10 – Illustration of how the pressure changes during bubble formation as a function of time [26]

A: The bubble is formed. Initially the pressure is below the maximum pressure and thus is the radius of curvature of the air bubble larger than the radius of the capillary.

B: The pressure build up and the radius of the bubble is reduced.

C: The pressure curve passes through a maximum, and the air bubble radius is the same as that of the capillary, which mean that the air bubble forms an exact hemisphere.

D: The "dead time" of the measurement starts after the maximum pressure. The pressure decreases again and the radius of the air bubble becomes larger.

E: The bubble finally escapes from the capillary and rises. The cycle begins again with the formation of the next bubble [26].

Procedure
Prepared produced water samples are analyzed with BP100. The equipment and the cleaning agents required for the procedure are given in Table 7. The density of the samples is required to be able to run the BP100, and thus were the densities of the samples measured with a density meter.

Table 7 – The equipment required for BP100 and the cleaning agents

Equipment	Cleaning Agents
- Capillary	- Hot running water
- Sample vessel	- Milli-Q water
- Sand paper(emery paper with 1200 grain)	- Isopropanol

Before each measurement it is necessary to test the capillary to see if the capillary still have the proper hydrophobic coating. This is performed by using Milli-Q water as sample liquid. The surface tension is supposed to be constant at 72mN/m. The sample vessel and the capillary were cleaned with hot running water, Milli-Q water and if necessary isopropanol before each measurement. Place the capillary in the capillary holder. Pour the sample(>30ml) in the sample vessel and place it in the instrument, and raise the sample platform just beneath the capillary. If the capillary give misleading results, sanding of the capillary and a new measurement of the capillary diameter are required. When the capillary show 72mN/m for the Milli-Q water, the instrument is ready to analyze the prepared produced water samples [8]. Same procedure as for the testing of the capillary is followed for the prepared samples.

3.2.2 UV/VIS Spectroscopy

The instrument used in ultraviolet-visible spectroscopy is called UV/VIS spectrophotometer. The instrument is regularly used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Produced water contains different organic compounds depending on the reservoir conditions. Organic compounds, especially those who contain several double bonds, adsorb light in the UV or visible area of the electromagnetic spectrum [27]. The principle of the measurement is to send light through the sample, and if the light has an energy that corresponds to a possible energy transition within the molecule, some of the energy will be absorbed of the molecule. The electron will then be promoted to a higher energy orbital, and an adsorption peak will be observed [28]. Considering the fact that the produced water is a complex mixture of compounds it can be hard to verify the contents in the solution by the UV spectra of the samples.

Procedure

UV/VIS was applied to investigate if there were any differences in the components in the different produced water samples. The concentrations of the different compounds were not of interest, but the shape of the curves and the qualitative differences that could be found were studied. The equipment and the cleaning agents required for the experiment are given in Table 8.

Table 8 – The equipment required for UV/VIS and the cleaning agents

Equipment	Cleaning Agents
- Reusable cuvettes	- Ethanol
	- Acetone

Before each measurements it was important to clean the cuvettes with ethanol and acetone. The samples were diluted 3 times. The dilution solvents were the brines of different pH the produced water was made of. Two cuvettes were inserted in the instrument, one as a reference containing the pure solvent, and one for the diluted sample. The intensities of the transmitted light beams were then compared over the whole set wavelength range(from 200 nm to 800 nm) [27].

3.2.3 Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used in this study to try to identify different chemical groups in the produced water and see if this was a potential method for characterization of produced water. The instrument used for the analyzes was Tensor 37, originates from the mid IR region with wavenumber from 4000 - 200 cm^{-1}. The instrument is an internal reflection spectroscopy meter, due the ATR (attenuated total reflectance) crystal used. This enables the samples to be examined directly in the solid or liquid state without further preparation. Infrared spectroscopy is a very common and widely used spectroscopic technique, which has been utilized mainly by inorganic and organic chemists. The method is useful regarding determining and identifying structures of compounds. The properties of a chemical compound is dependent upon the functional groups present, and these groups can be identified with infrared spectroscopy. In comparison with ultraviolet and visible regions IR gives sharper adsorption peaks and thus is more sensitive to determination of functional groups within a sample. Different functional groups adsorbs different frequency of IR radiation, which mean that each molecule has a distinctive spectrum [29].

Produced water contains small amount of organic compounds, and to analyze this organic material with a Fourier transform infrared spectroscopy the organic material was required to be concentrated and thus extracted out of the produced water samples. An earlier evaluation of extraction methods regarding the organic compounds in produce water is done by Adam T. Lewis et al. and it was shown that a mixture of 70:30 cyclohexane/butyl acetate is a better solvent for the quantitative extraction [30]. Thus was this conducted for two of the prepared produced water samples.

Procedure

The purpose of this experiment was to investigate if IR is a potential method to characterize produced water samples, and thus were only two samples (C_C_ORG and C_S_8) prepared for this measurement and analyzed.

The 70:30 cyclohexane/butyl acetate mixture was first prepared. From a produced water sample was 80 mL measured in a graduated cylinder, acidified with 2 mL of concentrated HCl, poured into a Schott bottle (250 mL) and gently shaken. The 70:30 cyclohexane/butyl acetate was added to the Schott bottle at 10% of the recorded volume of the produced water (8 mL). The Schott bottle was shaken for 1 minute, and the layers were allowed to separate. A separatory funnel was used to achieve completely separation. Nitrogen gas together with heat was used to remove the extraction solvents. The organic sample evaporated down to 1/3 of original volume and was then analyzed with Tensor 37. Before each measurement it was important to run a background scanning when the crystal was clean. Three drops of the sample were put on the crystal in the IR instrument to make sure it was enough material on the crystal under the measurements. In between each drop the last drop should have evaporated before putting on a new. The solvent is then removed completely. The peaks that appear in the radiation range can then be compared with a data bank of spectra for IR, and the chemical groups can be identified.

4 Results and Discussion

4.1 The reproducibility of the instruments

The reproducibility of BP100 is given in Figure 11, and shows that the bubble pressure tensiometer gives reproducible and thereby reliable results. The sample used for the illustration is C_W_2 (crude oil C mixed with pure water of pH 2) and its three parallels. For the results the average of the parallels have been calculated and used for the illustrations and further interpretations given in Chapter 4.2 and 4.3.
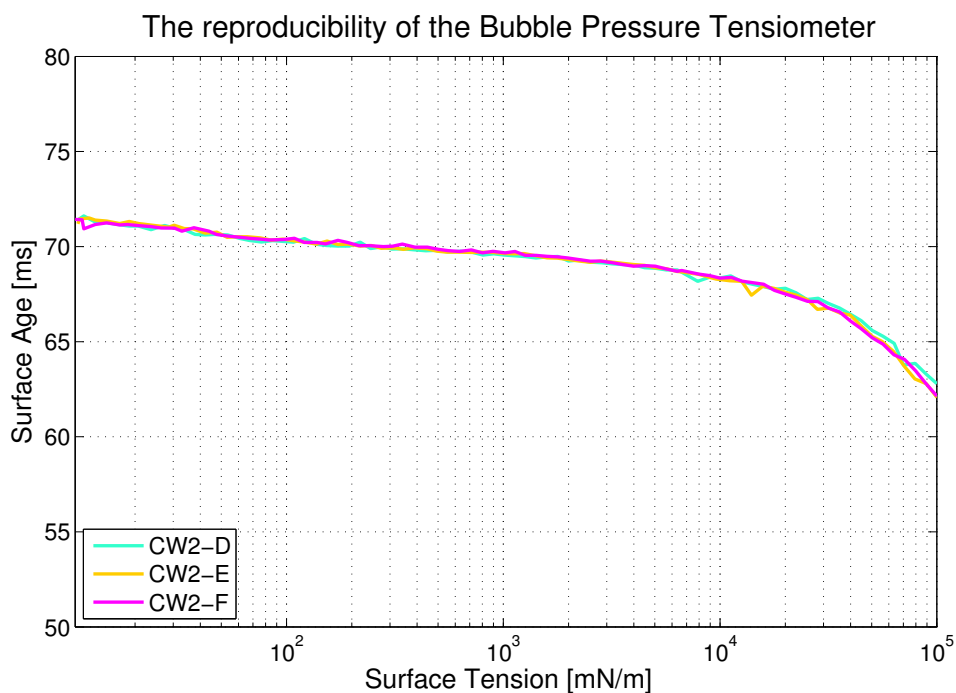
Figure 11 – The reproducibility of the measurements of sample C_W_2 with the bubble pressure tensiometer. Surface tension is plotted as a function of surface age.

The reproducibility for the UV/VIS instrument is illustrated in Figure 12, and demonstrates good reproducible results. Three parallels of sample C_W_2 is represented, and for the interpretation of the results and the figures in Chapter 4.2 and 4.3 are the average values used.
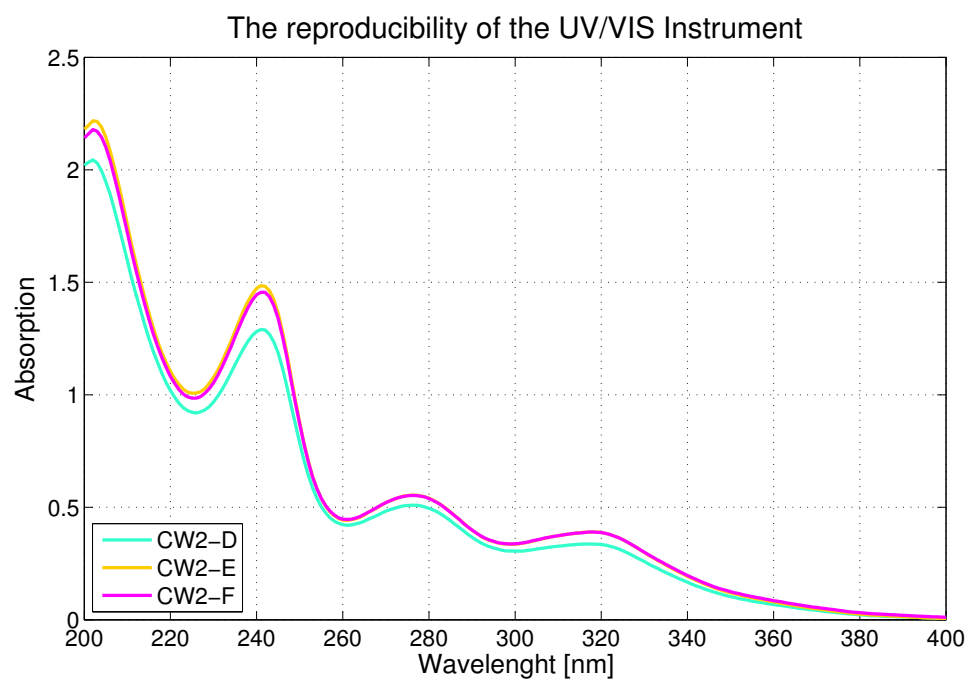
Figure 12 – The reproducibility of the measurements of sample C_W_2 with the UV/VIS instrument. The absorption is plotted as a function of wavelenght.

4.2 The Effect of the pH of the Brine on The Surface Tension of Produced Water

The results of how the pH of the brines influence the surface tension of produced water are given in the following subsections in this chapter. The curves in the figures represent the average of the three or two parallels measured for each sample. The surface tension is mainly measured of samples of brine with pH 2, natural and 10. For crude oil C more pH values were investigated, but since the differences between pH 4, 6 and 8 were minor only pH 2, natural and 10 were used for further investigation among the two other oils; crude oil E and H. The adjustment of pH of the water phases does not influence the surface tension, and consequently is the changes in surface tension caused by the crude oil components [31]. The pH of the produced water samples was measured right after preparation and the day they were analyzed with BP100. The pH did not change significant with time, see Appendix D. For the samples in the pH range of 4 to 10 the pH merged to around 6 and 7 after preparation. The samples of pH 2 and 12 were more stable, and did not change much after preparation.

During the experiments some difficulties were encountered. Synthetic brine with pH above 8.5 gave precipitation, and thus is the highest pH set to 8 for the samples made of synthetic brine. This brine contains more metal cations, and thereby will hydroxide precipitation with metal cations occur. The precipitate is most likely $Mg(OH)_2$ due to the lower solubility at pH 9 compared to the two other cations Na^+ and Ca^{2+}. It was not possible to make samples of MQ-milli water with pH of 8, which was due to that the pH would not stabilize at this value. It decreased regardless of how much acid that was added. After crude oil C had been mixed with pure water and shacked for 24 hours, it was really hard to separate the phases and thus was it required to centrifuge several times until they were clear. The samples of pH 2, 10 and 12 remained yellow/orange in color. In these samples there might have been some residual oil in the water phase after the separation. When mixing the crude oils with the NaCl brine of pH 12 a very stable emulsion was formed for all three oils. It was not possible to separate out the water phase in these samples, and thus is the highest values of pH for each brine 10 (except the samples of crude oil C). Figure 13 illus-

Figure 13 – Very strong emulsions were formed when mixing the crude oils with NaCl brine of pH 12. This is an sample made from crude oil H.

trates how these emulsions looked like after the centrifugation. The samples were really sticky and had a very high viscosity. Strong interfacial films on the interface of dissociative naphthenic acid and metal cations might have been formed, which caused these stable emulsions.

4.2.1   Crude oil H

The results from the Bubble Pressure Tensiometer

Figure 14 – The surface tension of the samples made of crude oil H and Milli-Q water. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
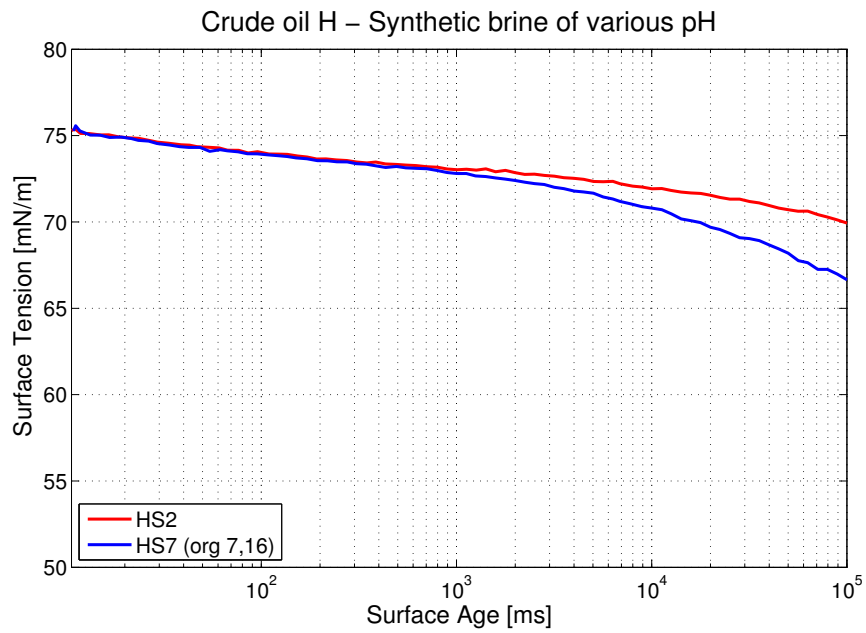
Figure 15 – The surface tension of the samples made of crude oil H and synthetic brine (brine with all ions). The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.

Figure 16 – The surface tension of the samples made of crude oil H and calcium chloride brine. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
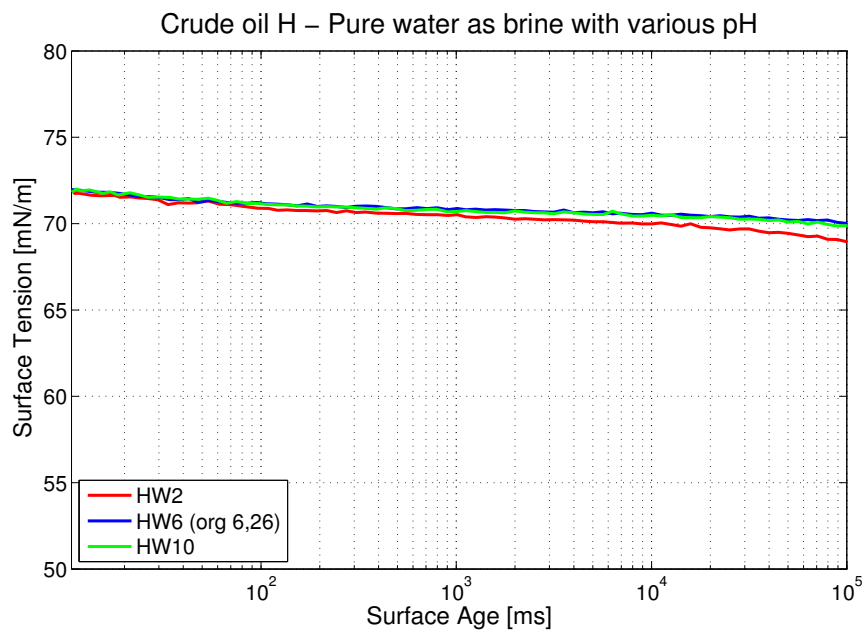
Figure 17 – The surface tension of the samples made of crude oil H and sodium chloride brine. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.

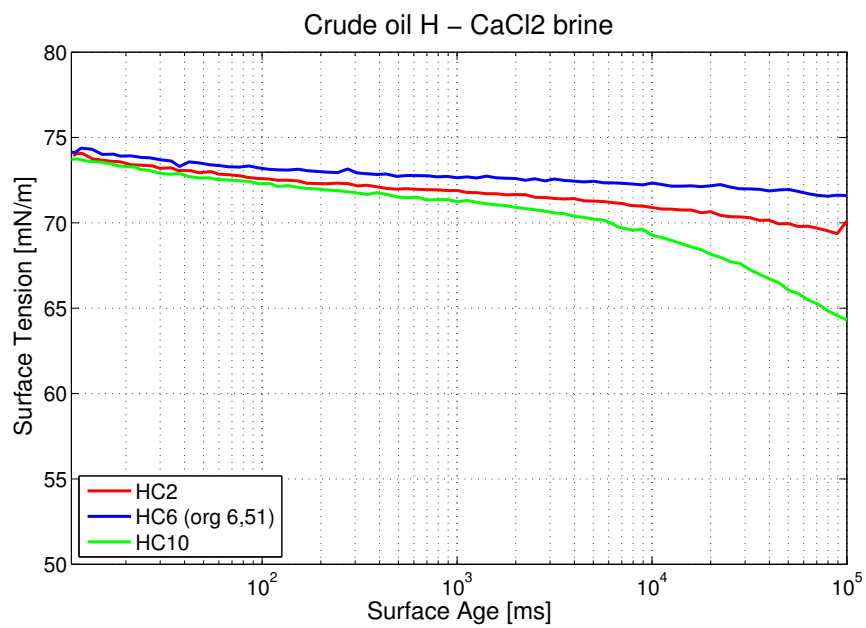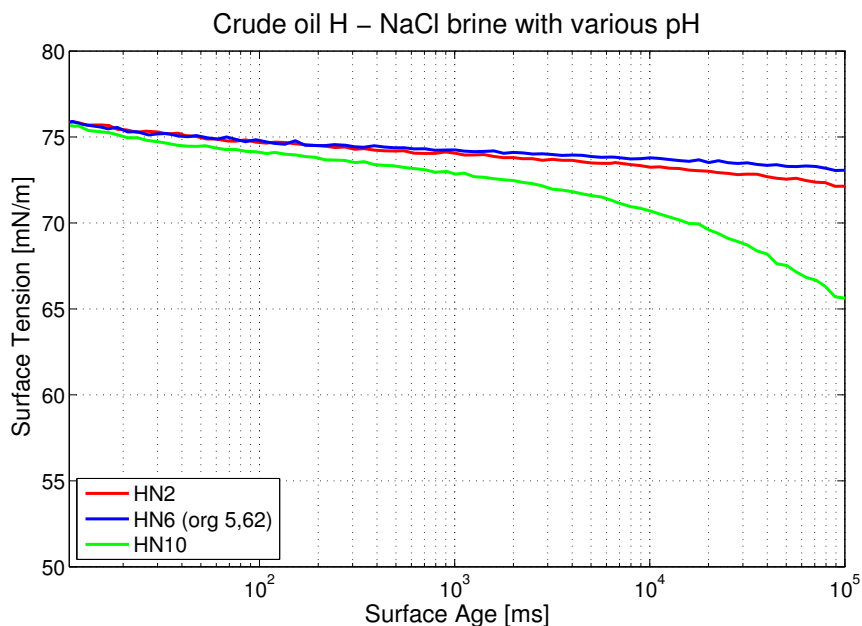Figure 14, 15, 16 and 17 give the results of the surface tension of the different samples made of crude oil H considering the change in pH. It takes time before the surface tension decreases, which is caused by the diffusion of the surface active compounds from the bulk phase to the surface. This was expected according to the theory in Chapter 1.4.

An other trend observed for crude oil H is that the effect on surface tension increases with the salinity of the water phase. The samples made of pure water do not show significant differences. Regarding the synthetic-, $CaCl_2$- and NaCl brine, the samples of highest pH have the most rapid decrease in surface tension and achieve the lowest value of surface tension within the time interval the measurements were conducted within. This was expected since the TAN for this crude oil is very high. The decrease in surface tension at high pH indicates that acid dissociation most likely have found place, and since the synthetic brine and the $CaCl_2$ brine contain Ca^{2+} ions acid-metal-water-complexes might have been formed. Due to the lowering in surface tension it implies that these complexes tend to be water soluble. The decrease in surface tension for pH 10 considering the sodium chloride brine can be caused by dissociative acids in the crude oil that have diffused into the water phase and thus affected the surface tension of the produced water. The samples that are based on pure water as brine show very small changes in surface

tension and there are minor deviations between the different samples of various pH. Considering the theory in Chapter 1.5.1 salting in was expected, which mean that organic compounds would be more water soluble in the absence of ions. This was not observed here. However there might be components from the oil phase present in the produced water that are not as surface active and thus not diffusing to the surface. Such components can be non polar organic compounds like BTEX (benzene, toluene, ethylbenzene, and xylenes). These compounds are soluble in pure water, but have minor solubility properties in high salinity solutions. The UV spectra for these samples in Figure 18 support that some compounds have been extracted from the oil phase to the pure water phase regarding the absorption intensity.

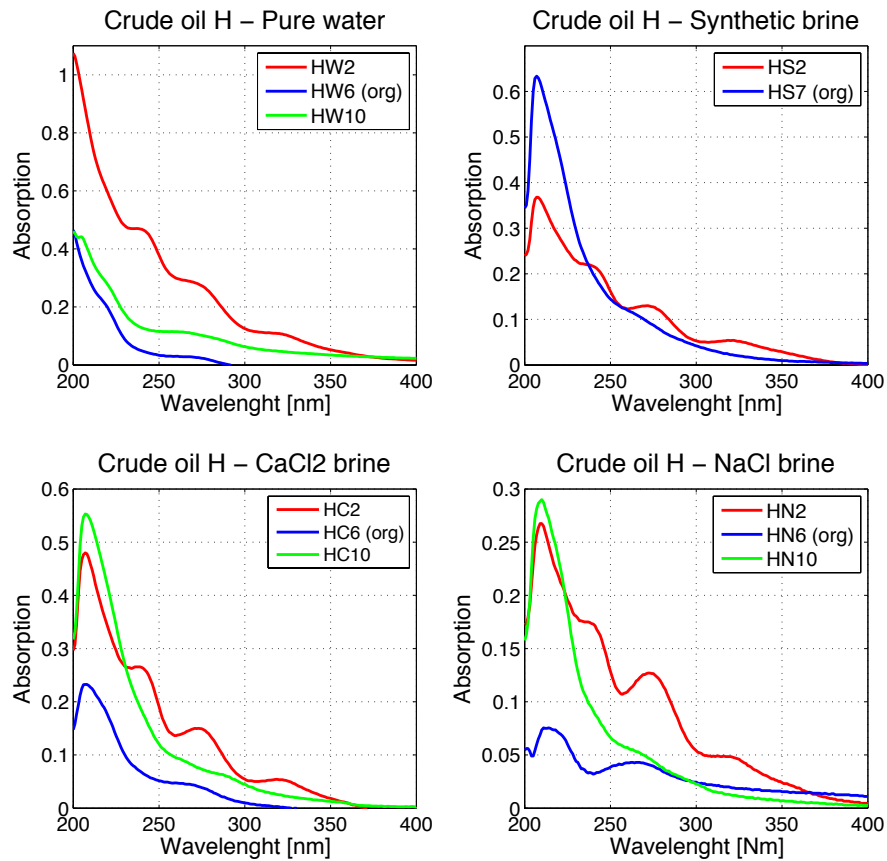**The results from UV-Visible for all four brines**

Figure 18 – The figure illustrates how the absorption varies for produced water made of crude oil H of various brines and pH. The absorption is plotted as a function of wavelength.

The UV results for crude oil H give highest intensity for the samples that have a large decrease in surface tension (samples of pH 10 for synthetic-, $CaCl_2$- and NaCl brine). For pure water the UV measurements indicate that there are organic compounds present in the samples, even though the surface tension had only a minor decrease. As mentioned above, there might be non polar organic compounds present in the pure water samples that do not tend to be surface active, but still have an impact on the absorption intensity.

The most characteristic peaks is observed for samples of pH 2. The values of the peaks of each curve is given in Figure 38 in Appendix E, and according to the table it is given that the samples of pH 2 for all brines have the same peaks, and the remaining samples have the same maximums. The samples of pH 2 have four maximums in the wavelength range of 200 to 800 nm. These maximums are located at approximately 208, 239, 273 and 320. For the other samples the peaks are located roughly around 206 and 263, see Appendix E for exact values for each brine. The difference between the samples of pH 2 and the other samples have to be associated with that other components have diffused over to the aqueous phase when the pH has reached this low value. Due to the complexity of the produced water, is is not easy to relate specific compounds or a mixture of compounds to these maximums. However, due to the low pH it can be stated that the components are most likely of basic character, since basis tend to protonate at low pH and become a charged and thus more water soluble molecule.

In the report "Investigation of HCl, $HFeCl_4$, water and crude oil components in acid-crude oil systems", they mixed a 15% HCl solution with oil and distilled water with oil. After separation the solutions were analyzed with UV/VIS spectrometer. Approximately the same result are found in that report as discovered here. The acidic solution gave four peaks in the range of 225 - 375 nm contrary to the distilled water phase where little absorption was detected at wavelengths longer than 325 nm. This indicated a predominance of components based on one or two aromatic rings in the distilled water, and nitrogen-containing compounds in the acidic phase [17]. From this study and according to the theory in Chapter 1.5.1, the compounds that might have diffused into the produced water when the brine were adjusted to pH 2, can be basic compounds such as pyridines, quinolines and acridines. From the literature it is given that these compounds have several peaks in the UV spectrum, and some of them correspond to the peaks in the samples of pH 2. The molecular structure and the absorption maximums for these compounds are given in Appendix F.

4.2.2 Crude oil E

The results from the Bubble Pressure Tensiometer

Figure 19 – The surface tension of the samples made of crude oil E and Milli-Q water. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.

Figure 20 – The surface tension of the samples made of crude oil E and synthetic brine brine with all ions. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
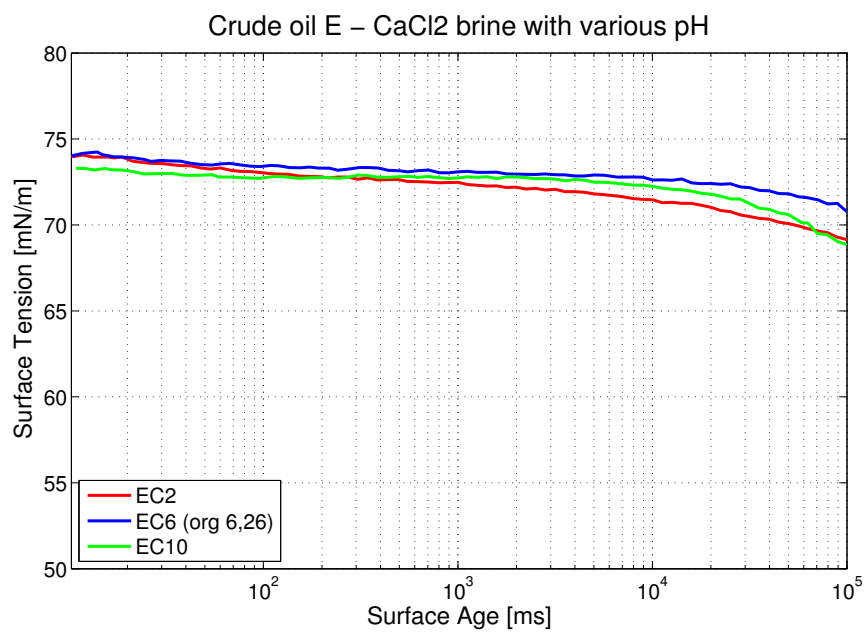
Figure 21 – The surface tension of the samples made of crude oil E and calcium chloride brine. The figure illustrate the differences for the various pH values. Surface tension is plotted as a function of surface age.
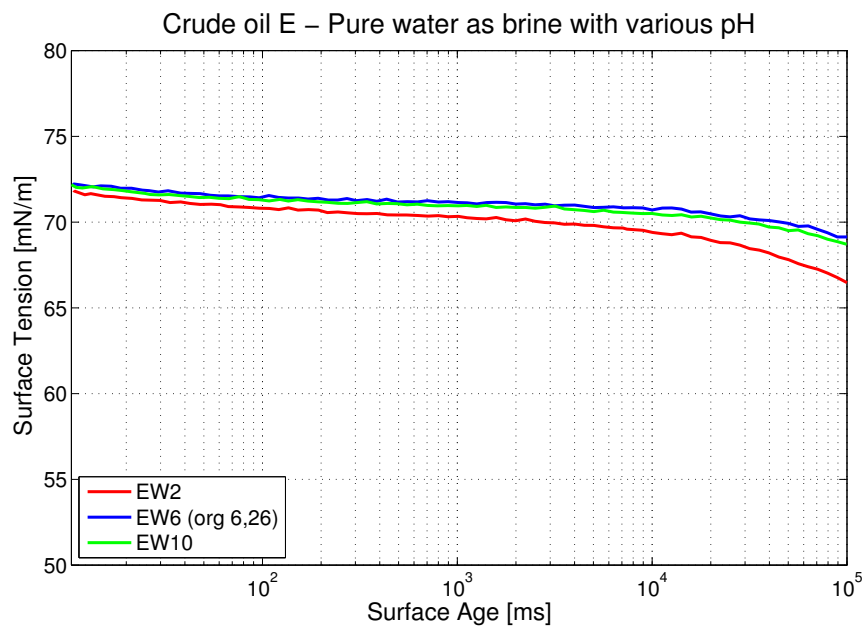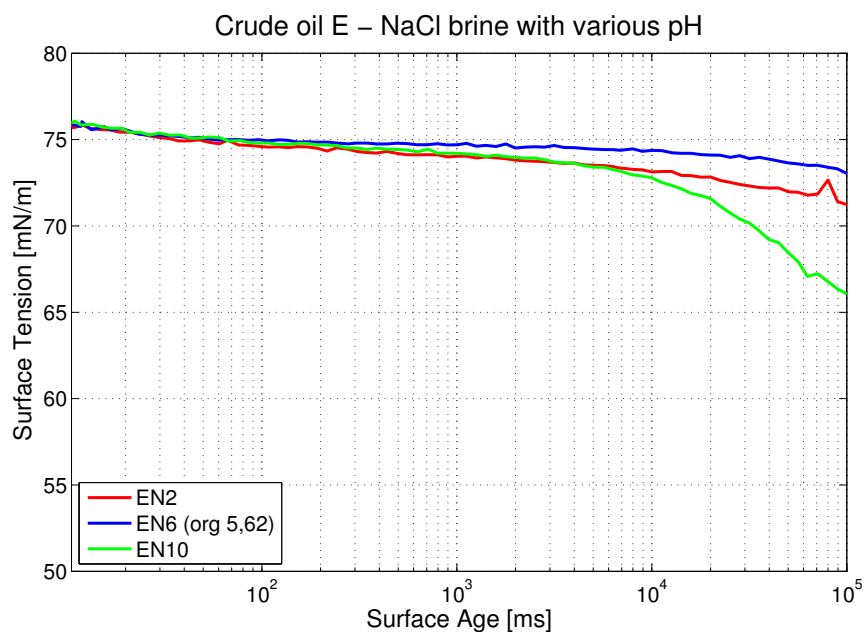
Figure 22 – The surface tension of the samples made of crude oil E and sodium chloride. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
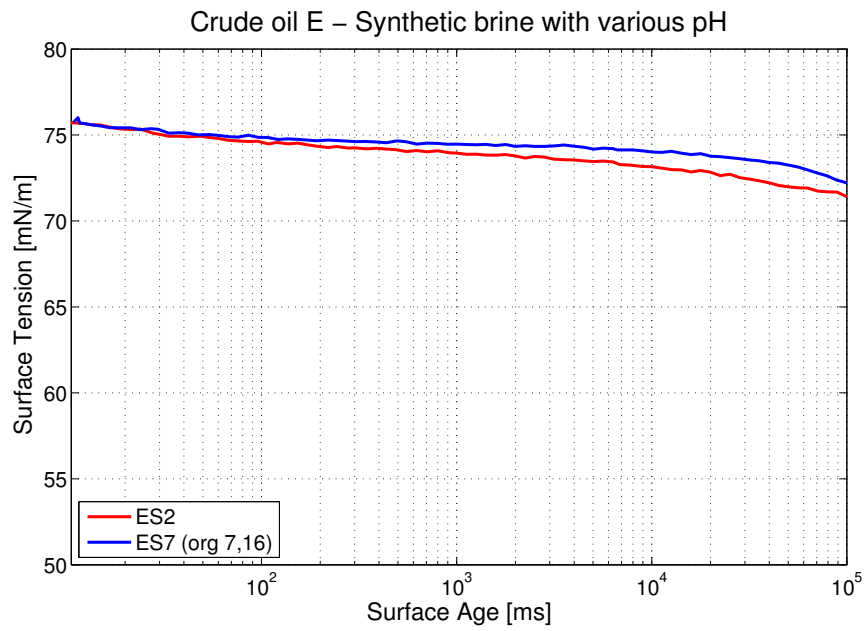
The surface tension of the samples made of crude oil E related to the various pH of the brine are given in the Figures 19 - 21. There are no significant differences between the samples of various pH made of pure water, synthetic- and $CaCl_2$ brine considering crude oil E. In the synthetic- and $CaCl_2$ brine calcium ions are present and complex formation might have happened. Due to the minor decrease in surface tension for these samples, the complexes are most likely more oil soluble than water soluble, and thereby diffused into the oil phase or sticked better to the oil/brine interphase. For the samples of pH 10 made of NaCl brine there is a marked reduction in surface tension. In thess samples there are no calcium ions present, and it can be predicted that surface active and water soluble dissociated acids is present in the samples, and caused the decrease in surface tension. Furthermore will the sodium ions generate a tighter packing of the surface active molecules at the air/water interface according to the theory given in Chapter 1.5.2, which also will contribute to a reduction of the surface tension. In general the amounts of resins and asphaltenes are very low in this crude oil, which are the most polar compounds, and that can explain why the results show only minor differences between the samples of various pH. Either less compounds have diffused over to the water phase or less compounds have diffused to the surface of the produced water and contributed to a decrease in surface tension.

The results from UV-Visible for all four brines

Figure 23 – The figure illustrates how the absorption varies for produced water made of crude oil E of various brines and pH. The absorption is plotted as a function of wavelength.

The absorption intensities for the samples made of crude oil E are given in Figure 23. Even though the surface tension of the different samples of crude oil E show minor differences, the UV measurements show that different organic molecules have been extracted to the water phase. The UV absorption does not necessary reflect the amount of organics in the sample, but rather the different organic groups present in the different molecules. As mentioned for the UV measurements regarding the pure water samples of crude oil H, the same might have found place here (BTEX present in the samples) since the absorption intensities for these samples are considerably higher than for the other brines and the surface tension measurements did not give any significant results. The samples of pH 2 have again the most characteristic peaks, and the other samples have the same peaks. The explanation regarding this for crude oil H, can be applied for this oil as well, see

Chapter 4.2.1. Even though the peaks are at the same wavelength, the shape of the curves differ according to the intensity and the width. This means that the peaks observed for the different oils must not necessarily correspond to the same compound, but can contain the same type of functional groups.

4.2.3   Crude oil C

The results from the Bubble Pressure Tensiometer
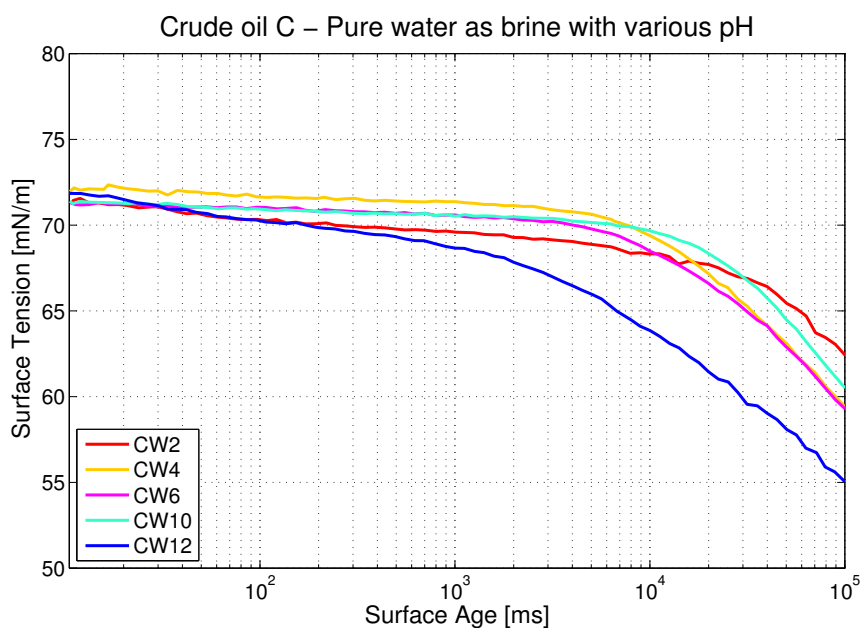
Figure 24 – The surface tension of the samples made of crude oil C and Milli-Q water. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
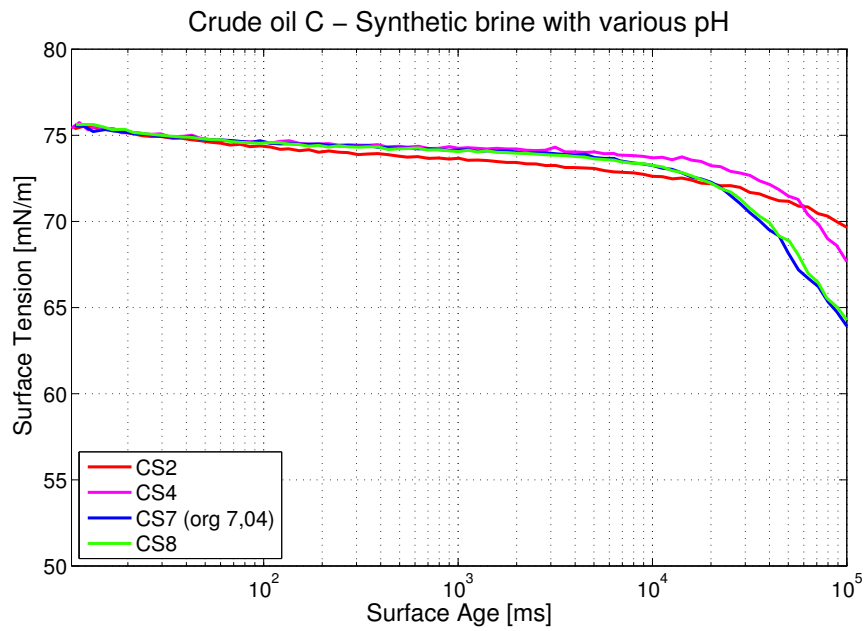
Figure 25 – The surface tension of the samples made of crude oil C and synthetic brine (brine with all ions). The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
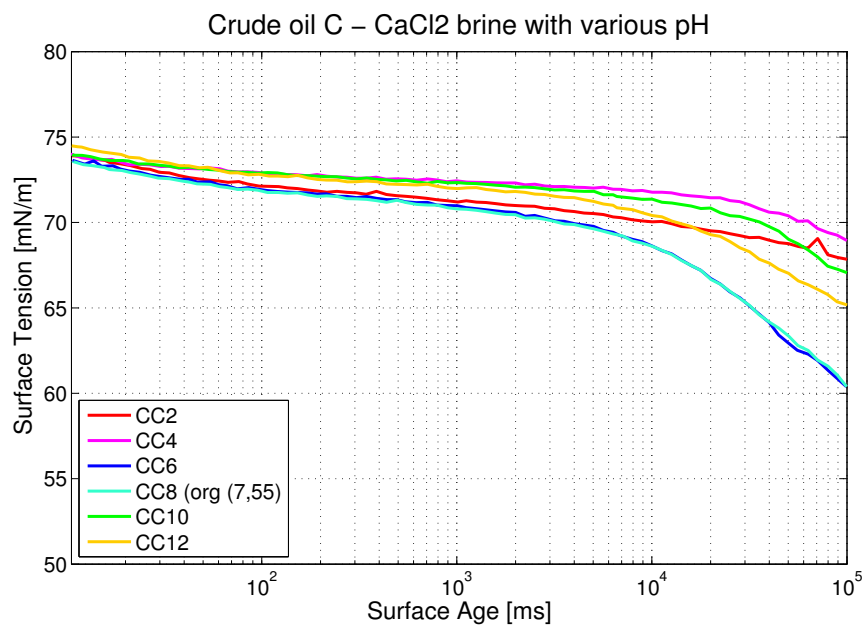
Figure 26 – The surface tension of the samples made of crude oil C and calcium chloride brine. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.
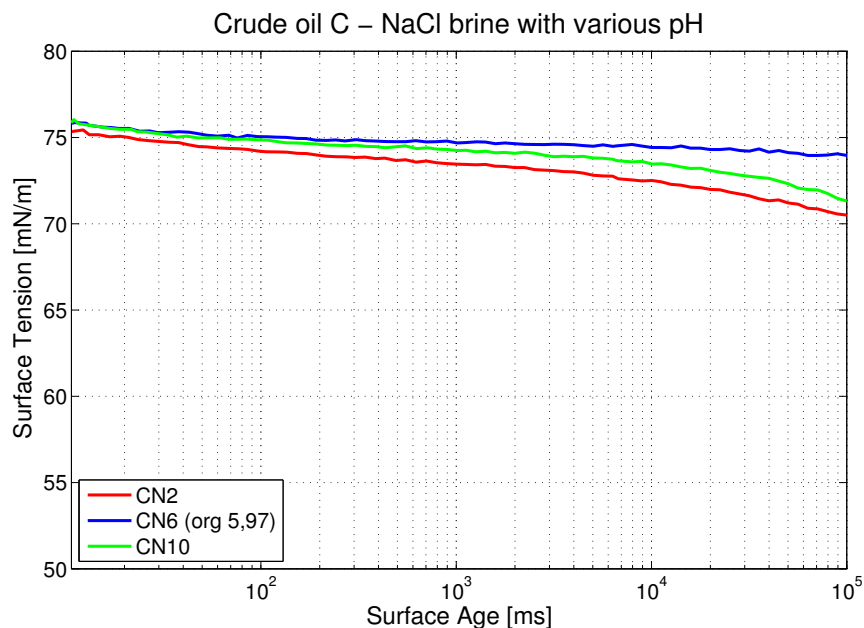
Figure 27 – The surface tension of the samples made of crude oil C and sodium chloride brine. The figure illustrates the differences for the various pH values. Surface tension is plotted as a function of surface age.

The surface tensions results of the samples made of crude oil C are given in Figure 24, 25, 26 and 27. For pure water as brine the sample of pH 12 has a faster decease in surface tension than the other samples, and ends up with the lowest value. This is not the case for the other brines. The synthetic brine and the $CaCl_2$ brine show that the samples of pH 6, 7 and 8 give the lowest surface tension. This can indicate that acids have dissociated, which make them more water soluble and they could perhaps have diffused over to the water phase. The surface tension will then decrease due to their surface active properties. However, then it would be expected a decrease in surface tension at higher pH values as well, which is not the case. Interaction between acids and calcium ions at the high pH might have been present, and the complexes can have diffused over to the oil phase, and thus is the surface tension not reduced as much. For the NaCl brine the change in surface tension for all the pH values is minor. Generally it is noticeable that the surface tension decreases most for the samples made of pure water, which implies that the organic compounds in crude oil C is more soluble in pure water than the high salinity brines. This can be related to salting-out effect, and states the theory in Chapter 1.5.1. Crude oil C contains also the highest amount of resins and asphaltenes and the TAN and TBN are relatively large, which can explain the overall large influence on the surface tension for all the samples made of this

crude. Due the large deviations across the results it is hard to find specific trends for this crude oil.

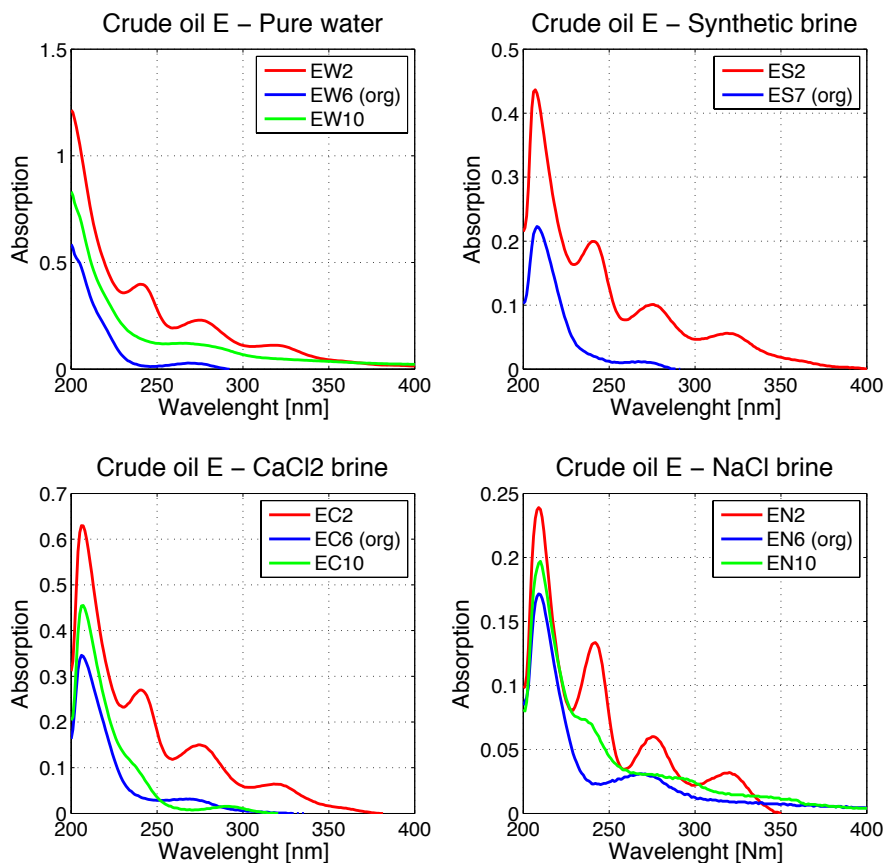## The results from UV-Visible for all four brines
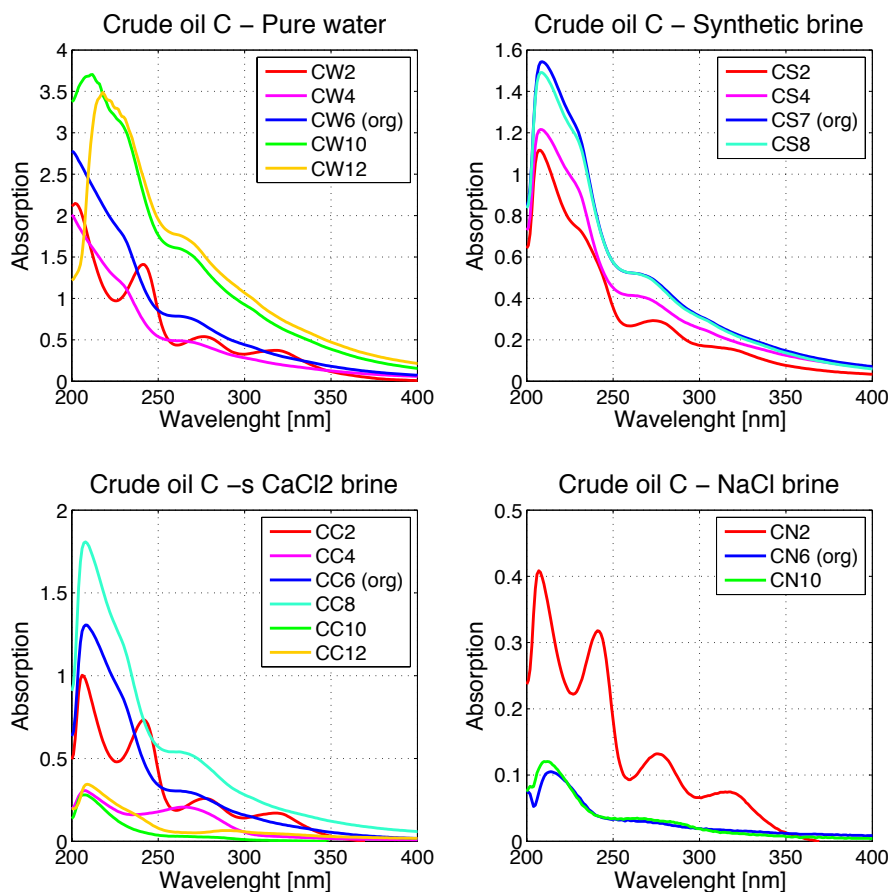
Figure 28 – The figure illustrates how the absorption varies for produced water made of crude oil C of various brines and pH. The absorption is plotted as a function of wavelength.

Figure 28 represents the results from the UV/VIS measurements of crude oil C. These results correspond to the bubble pressure tensiometer measurements considering the fact that pure water had the largest influence on the surface tension. The absorption intensities shown on Figure 28 for these samples are much higher than for the other brines. According to the figure it is also of interesest to notice that the intensities in general is higher for those samples that have the lowest surface tension given by BP100. The samples of pH 2 have again the most characteristic peaks, and the other samples have the same peaks. The explanation regarding this

for crude oil H, can be applied for this oil as well, see Chapter 4.2.1. Even though the peaks are at the same wavelength, the shape of the curves differ according to the intensity and the width. This means that the peaks observed for the different oils must not necessarily correspond to the same compounds, but can contain the same type of functional groups..

4.3 The Effect of the Brine Composition on The Surface Tension of Produced Water

4.3.1 The Surface Tension of Pure Brine Solutions

The surface tension of each pure brine is given in Figure 29. The Milli-Q water has the lowest surface tension (72 mN/m). A well-known phenomena is by adding electrolytes to a water phase the surface tension tend to increase as illustrated in the figure. According to Wagner and later extended by Onsager and Samaras, the electrolytes are in fact repelled from the air-water interface (negative absorption) due the electrostatic image repulsive interactions that occur between the electrolyte ions and the air. An other theory that needs to be taken into consideration is the ion-free layer at the air-water interface, which occur due to the hydration of the ions and also contribute to an increase in surface tension. This concept is stated by Flores-Mena [32]. In accordance to this and the theory given in Chapter 2.5.1 the calcium brine should have lower surface tension than the synthetic and sodium chloride brine, as shown in Figure 29. This is due to the more hydrated calcium ion that will tend to be more in the bulk phase, and thus will the surface of the calcium chloride brine be more similar the surface of pure water.
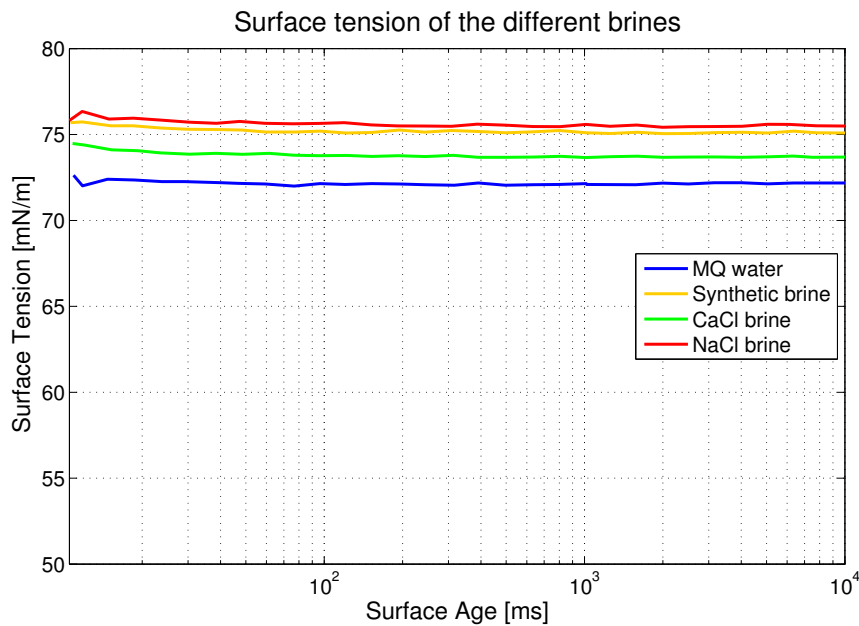
Figure 29 – The surface tension of the different pure brines. Surface tension increases with addition of electrolytes. Surface tension is plotted as a function of surface age.

4.3.2   Crude oil H
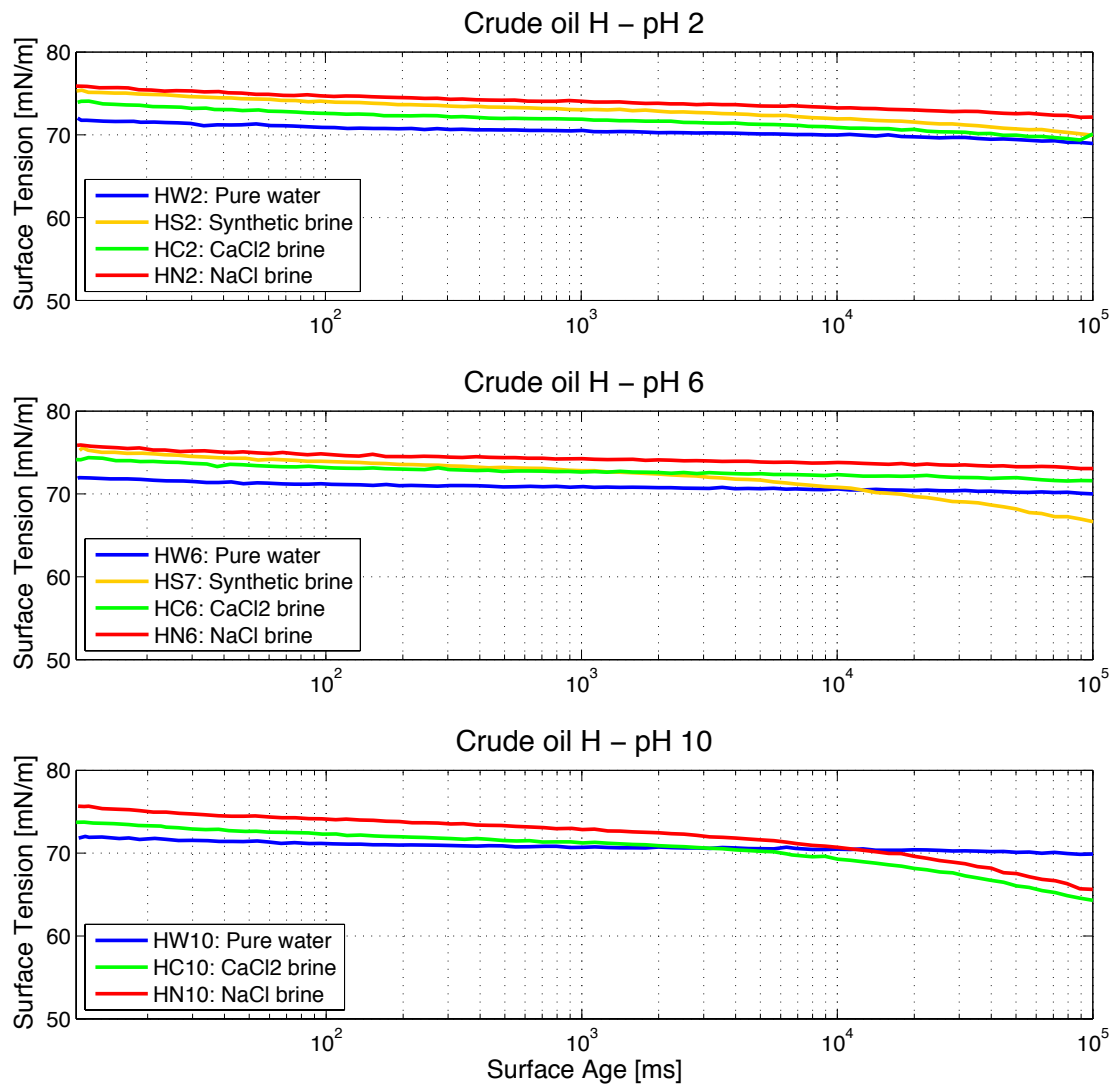
Figure 30 – The influence the brine composition of the brines has on the surface tension of the produced water samples made of crude oil H. The figure shows the results for four different water phases; pure water, synthetic brine, $CaCl_2$ brine and NaCl brine at pH 2, 6 and 10. Surface tension is plotted as a function of surface age.

Each sample of crude oil H is represented in Figure 30. The different brines show minor differences for the samples of pH 2 and 6, and the reduction in surface tension for each brine tend to decrease with the same rate. This means that the differences is caused by the original differences for each pure brine regarding the

surface tension, see Figure 29. For the samples of pH 10 the calcium chloride and sodium chloride show a marked reduction in surface tension, whereas the pure water have the same effect as for the two other pH values.

Overall the brines do not have a large influences on the surface tension. However, it can be stated that the brines of high salinity affect most at high pH. This might be due to complex formation and charged molecules, which often occur at higher pH because of the dissociation of the organic acids in the crude oil.

4.3.3 Crude oil E
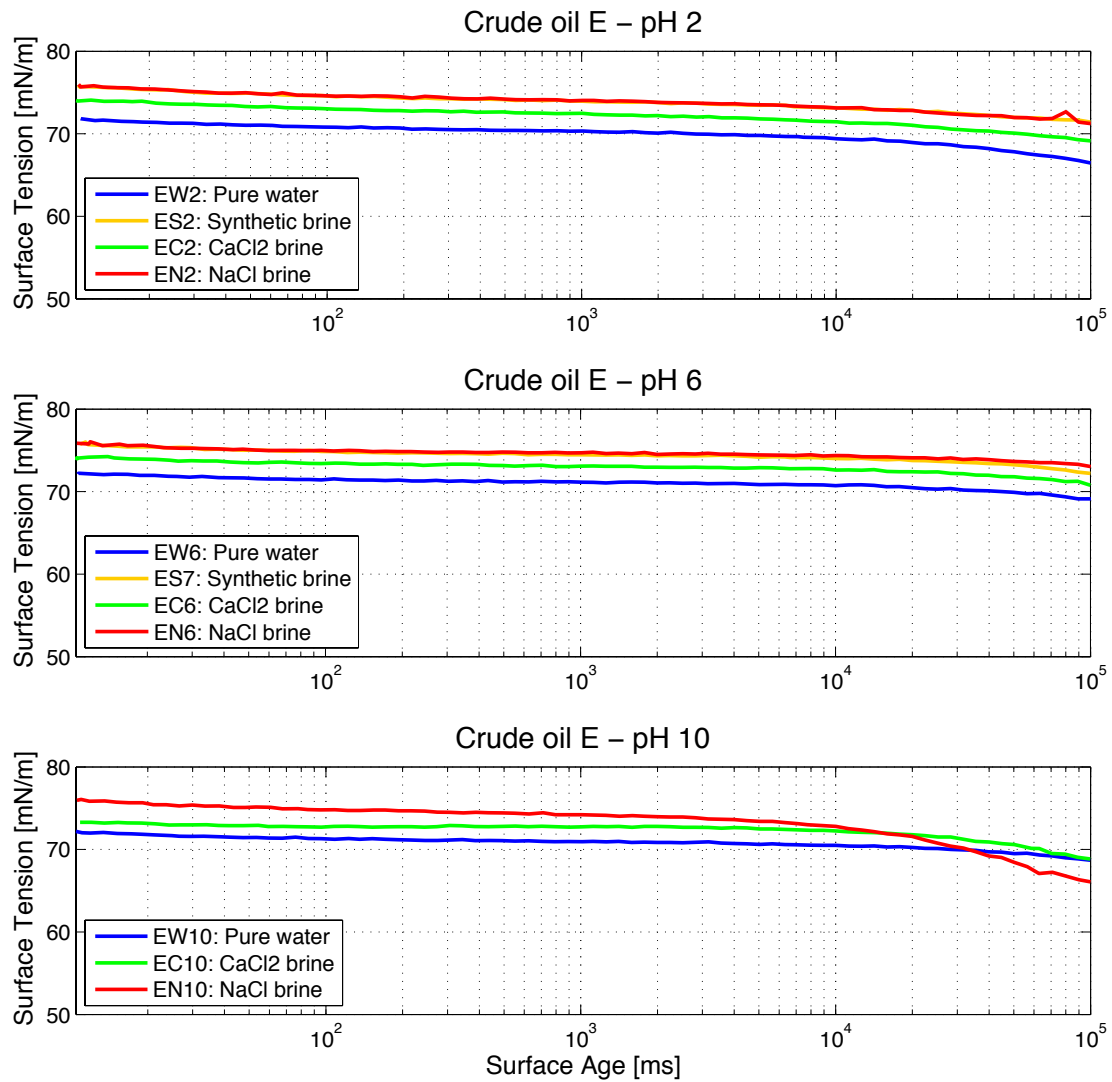
Figure 31 – The influence the brine composition of the brines has on the surface tension of the produced water samples made of crude oil E. The figure shows the results for four different water phases; pure water, synthetic brine, $CaCl_2$ brine and NaCl brine at pH 2, 6 and 10. Surface tension is plotted as a function of surface age.

The effect of the brines considering crude oil E is given in Figure 31. The differences observed for the samples of pH 2 and 6 is very similar. The brines decreases in surface tension with the same gradient, which implies that they have the same effect. When the pH is increased to pH 10 the sodium chloride brine and the $CaCl_2$ brine have a larger reduction in surface tension. In general the differences

between the brines are so small, and thus can it be said that the brines do not have a major influence on the surface tension considering crude oil E.

4.3.4 Crude oil C
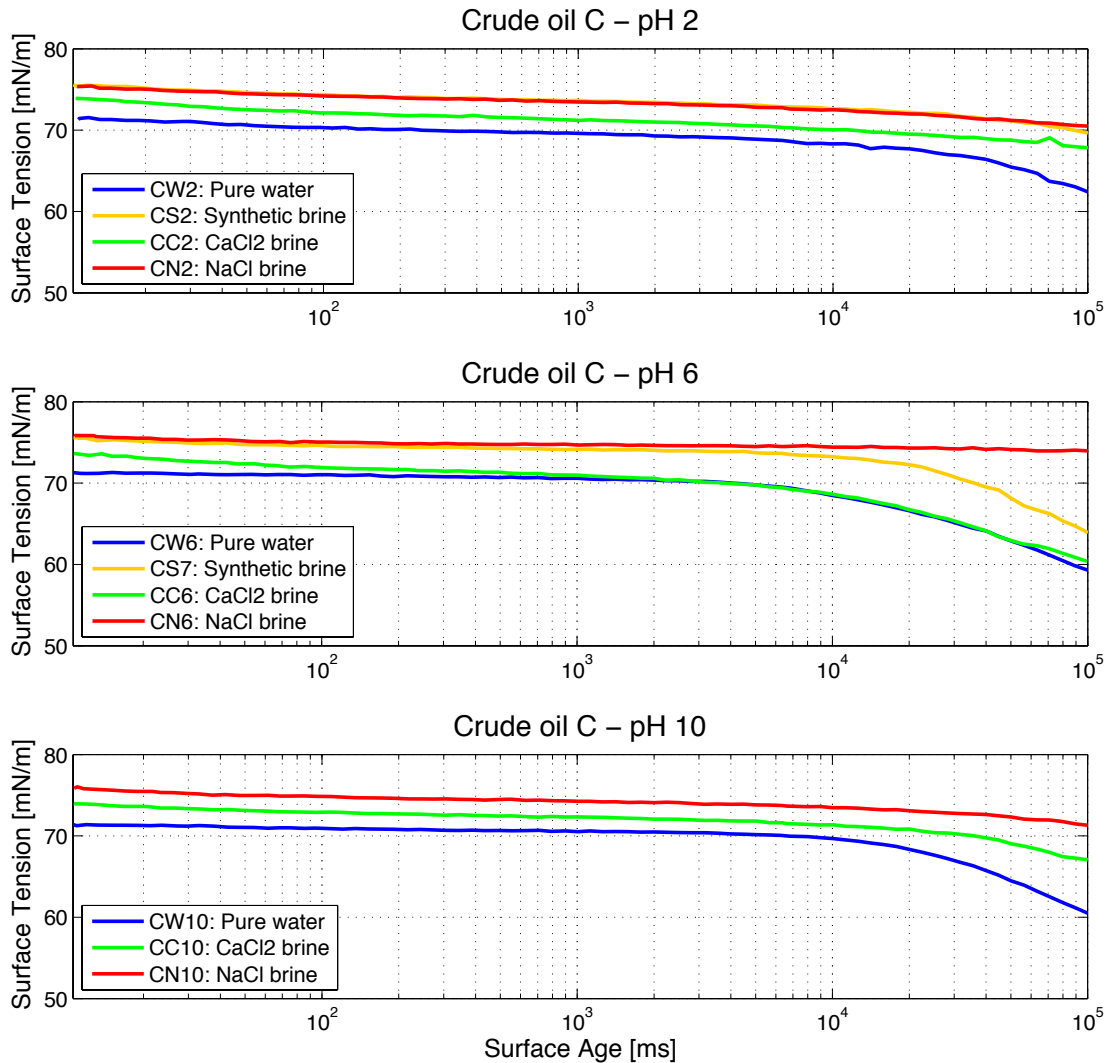
Figure 32 – he influence the brine composition of the brines has on the surface tension of the produced water samples made of crude oil C. The figure shows the results for four different water phases; pure water, synthetic brine, CaCl$_2$ brine and NaCl brine at pH 2, 6 and 10. Surface tension is plotted as a function of surface age.

Figure 32 represent how the surface tension changes from brine to brine for crude oil C. The difference in surface tension between the calcium chloride and sodium

chloride brine considering pH 2 is due to original difference between these brines given in Figure 29. Regarding the samples of pH 6 and 10 of the CaCl$_2$ brine and the synthetic brine, the surface tension tend to the decrease more, which might be due to formation of caclium-acid-water-complexes at higher pH values that probably tend to be more water soluble. The calcium ions will also contribute to tighter packing of the surface active components at the air/water interface, which also tend to decrease the surface tension. The general large influence of the pure water can be related to salting-out.

4.4 Surface Pressure

The surface pressures for the different samples is determined from Equation (3) in Chapter 1.4.1. The average value of the three last values of the surface tension for each samples has been calculated and represent γ, and the first value of the surface tension measurements represent the pure brine phase and correspond to γ_0. The results are represented in Figure 33, and summarize all the results regarding the effects of the composition of the brines and the various pH values. The higher surface pressure the greater the impact on the surface tension of the produced water samples.

Considering crude oil H, the surface pressure increases with high pH for the synthetic, the CaCl$_2$ and the NaCl brine. This has most likely to do with the high TAN of crude oil H. Naphthenic acids have dissociated due to the high pH and thereby achieved more surface active properties. Metal-acid-water-complexes have probably been formed, which have diffused into the water phase. This has affected the surface tension and caused a larger surface pressure.

Overall the effect is small for crude oil E regarding the different brines and the various pH values. In general it can be stated that the samples of low pH have some higher influence regarding the surface pressure for crude oil E. Crude oil E contain very small amount of asphaltenes and resins, and this might be the reason for why the effect on surface tension is overall so small.

For crude oil C the pure water have the largest effect on the surface tension of the produced water, which might be related to salting-out. The synthetic brine and the calcium chloride brine show higher surface pressure values around pH 6. Since there are calcium ions present in both of these brines, calcium-acid-metal-complexes might have been formed and could have diffused into the water as well. In general it is hard to state any specific trends for crude oil C, but consistently there are large influences on the surface tension, which can be related to the great amount of resins and asphaltenes in this oil.
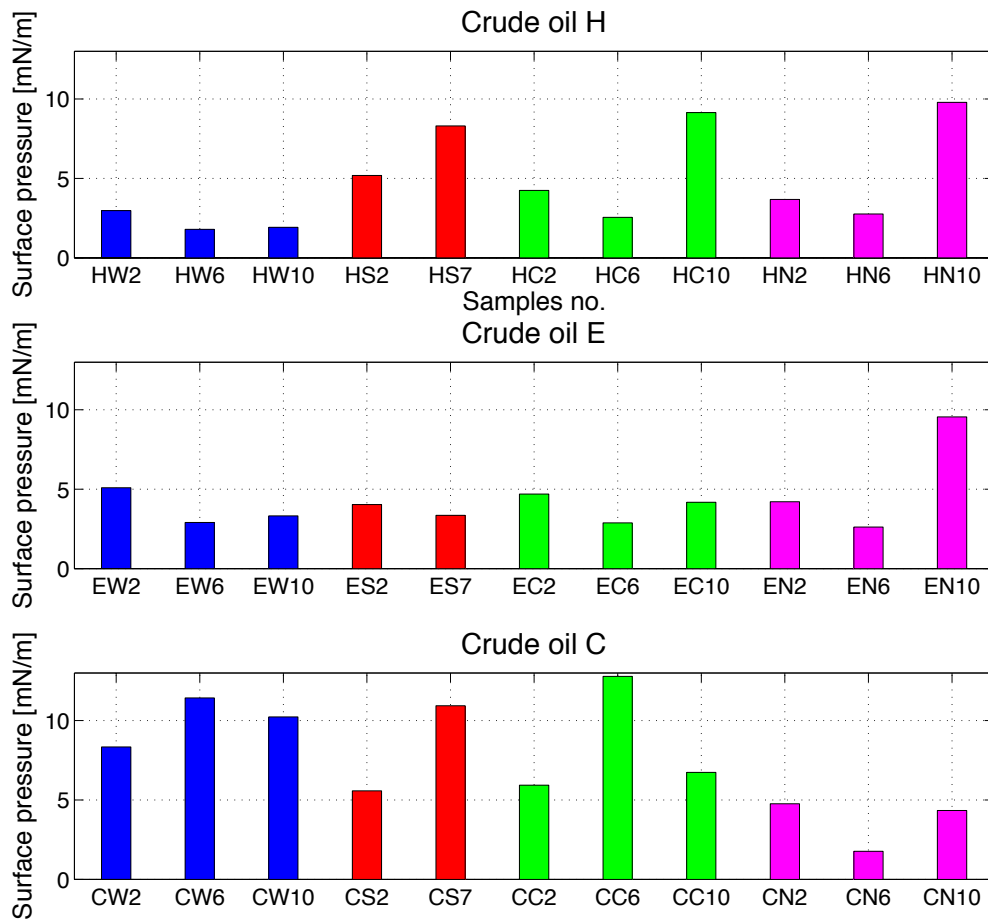
Figure 33 – The surface pressure for all the different samples. The figure shows the results of the three crude oils and the four different water phases used during the experiment. Each bar represent a sample, and the y-axis represent the surface pressure.

4.5 The Effect of The Oil Composition on The Surface Tension of The Produced Water
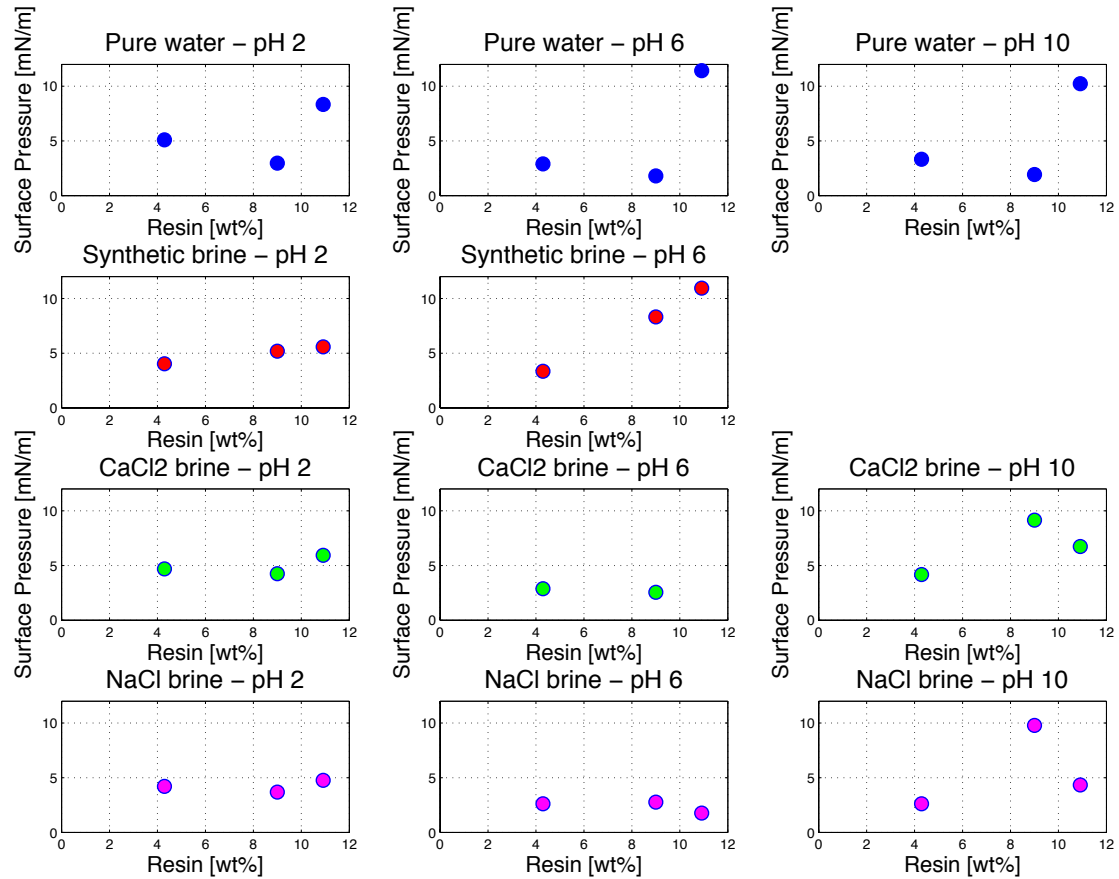
Figure 34 – The influence of the resin fraction in the crude oils. Surface pressure is plotted as a function of weight fraction.

To investigate how large influence the composition of the crude oil might have on the properties of the produced water, the surface pressure for all the samples were plotted towards the weight percentage of asphaltenes and resins. Figure 34 give an overview over how the resin fraction effect the surface pressure. Considering the synthetic brine it can be seen that the surface pressure increases with increased resin fraction, and for the pure water the surface pressure only gets large when the resin amount is very high. Apart from this, there are in general hard to find any other trends. For the NaCl and the CaCl$_2$ brine the amount of this group does not seem to play a major role.

The overview of how the asphaltenes influence the surface pressure is given in

Figure 40 in Appendix G. The only specific trend found for this fraction was that the surface pressure tend to be highest for the pure water samples when the amount of asphaltenes is considerably large.

4.6   The Infrared Spectroscopy Analysis

Two samples, C_C_6 and C_S_8, were analyzed with infrared spectrometer, and Figure 35 illustrates the absorption spectra found for the two samples. The two samples are both made of crude oil C, but of different brines (synthetic and $CaCl_2$ brine). The most interesting peaks are in the wavenumber range of 700 to 2000 cm^{-1}, and thus is the plot given in this area. These peaks corresponds to different compounds.
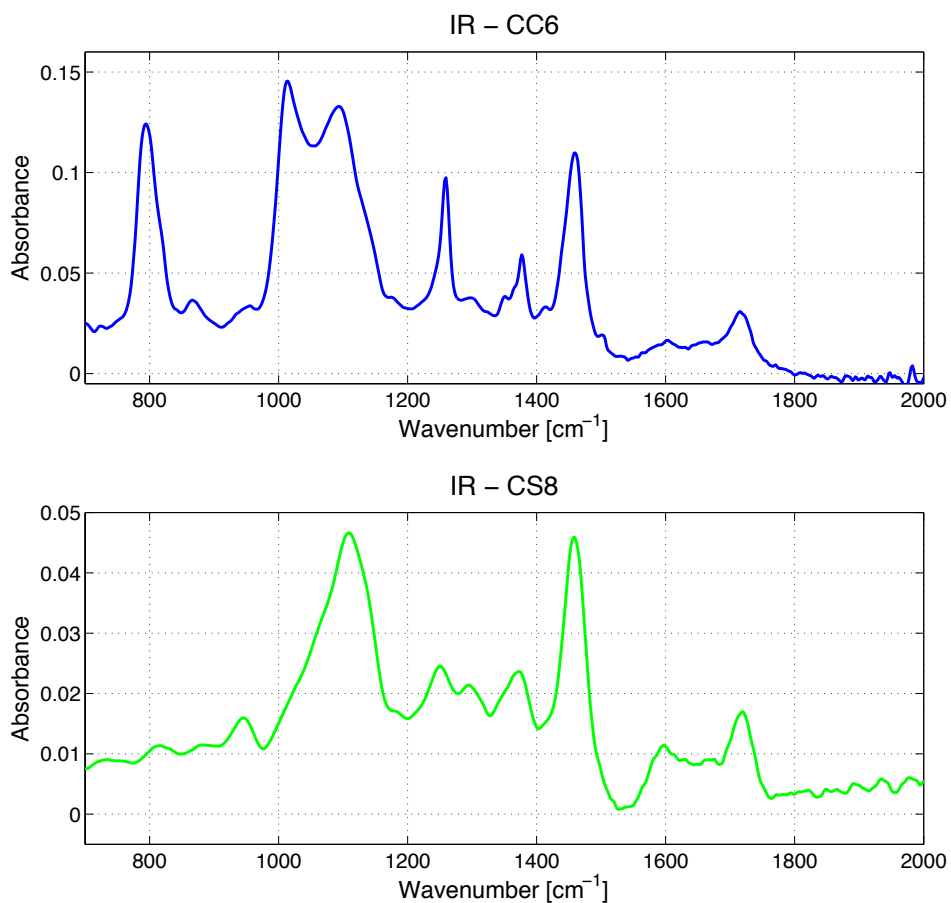
Figure 35 – The absorption spectra of the IR experiments. The samples analyzed are of crude oil C and two different brines (synthetic- and $CaCl_2$ brine). The absorption intensities are plotted as a function of wavenumber.

The absorption intensities for the two samples are very different. The highest intensity for the C_S_8 is around 0.15, but for C_C_6 it is only around 0.05. Some peaks are common for both samples, but there are some deviations represented as well. This implies that the brines do have some influence on what kind of components and the amount that are diffusing over to the water phase. However, regarding the intensity of C_S_8 there might be some components that have been vaporized from the sample during preparation of the extracted organic components. This mean that the intensity might not be directly related to the amount of organic compounds in the produced water samples.

The absorption peaks and the common functional groups for the peaks are given in Table 9. The peaks above 3000 cm^{-1} are not of large interest. They represent alkanes that are present in all the produced water samples. The functional groups found in the wavenumber range of 700-2000 cm^{-1} are common for the compounds often present in the produced water. Organics that are very soluble in water, due to their polarity, are low molecular weight (C2 - C5) carboxylic acids, alcohols and ketons. Due to their high solubility in water it can be hard to extract them into an organic phase and analyze them with IR, but since absorption peaks are observed for these functional groups at 1250 and 1718 cm^{-1}, it can be stated that such compounds are present in the produced water samples. Partially soluble compounds that also can be encountered in the produced water are hydrocarbons of higher molecular weight as aliphatic and aromatic carboxyl acids, phenols, aliphatic and aromatic hydrocarbons, and PAH (polycyclic aromatic hydrocarbons). These compounds are soluble in water at low concentrations, and the results given by the IR confess that these components can be present, see Table 9 [33]. There are also found some functional groups of nitrogen that might correspond to nitrogen-containing bases. The carboxylic acids groups found correspond to the naphthenate acids, which is included in the resin fraction.

In Appendix H the IR spectra of the pure crude oil C, the resin fraction and the asphaltene fraction are given. The three curves for these fraction are very similar. Especially one peak is of interest, which is observed around 1030 cm^{-1} for all three spectra. According to the literature the peak might indicate that sulfoxide is present in the resin and asphaltene fraction of crude oil C. This peak is largest for the resin fraction,. Since this peak can be seen in the absorption spectra for C_C_6 and C_S_8 as well, it can imply that there is a larger amount of resins than asphaltenes of this sulfoxide compounds present in the produced water samples.

In general is the absorption intensities very low, which indicates that the concentration of the compounds are low, and thus harder to detect. Overall can it be stated that this method is a potential method that can be used to characterize dif-

ferent chemical compounds in the produced water. The outcome of the IR analysis depends upon the extraction method utilized, and considering the results achieved during this experiments it is illustrated that 70:30 cyclohexane/butyl acetate is a good extraction solvent.

Table 9 – The table represent the absorption peaks of the two samples that were analyzed by IR. The peaks above 2000 cm^{-1} are not of large intereset. Literature values are used to identify the different peaks [34].

Absorption peaks [cm^{-1}]		From literature	
C_C_6	C_S_8	Frequency range [cm^{-1}]	Functional groups
2921	2923	3000-2850	Alkanes
2858	2860		
2359	2340	2300	C≡N strech (CO$_2$)
1716	1718	1760-1665	Carbonyls (general)
		1760-1690	Carboxylic acids
		1730-1715	Unsaturated esters, ketnos
1457	1458	1550-1475	Nitro compounds
		1500-1400	Aromatics
		1470-1450	Alkanes
1374	1378	1374	Alkanes
1257	1250	1335-1250	Aromatic amines
		1320-1000	Alchols, carboxylic acid, esters, ethers
		1300-1150	Alkyl halides
		1200	Phenols
		1250-1020	Aliphatic amines
1092	1109	1250-1020	Aliphatic amines, sulfoxide
1017	-	1000-650	Alkenes
794	-	900-675	Aromatics

5   Conclusion

In these experiments three oils and four brines of various pH and composition have been used. Due to the different composition and properties of the oils, the samples based of the different oils show very different behavior. Regarding the influence of the composition of the crude oil (resins and asphaltenes) and the surface pressure, there were found a trend for the synthetic brine, where the surface pressure increased as the resin- and asphaltene fraction increased. For the pure water the surface pressure increased when the amount of resins and asphaltenes became very large. Overall it is observed that the pH have a larger influence on the surface tension of the different samples than the composition of the brines.

The samples of crude oil H have a larger reduction in surface tension when the pH reach pH 10. For this oil the TAN is very high, and thereby is it assumed that the acids have dissociated and become more surface active. Regarding the NACl brine and high pH the dissociated acids tend to diffuse into the aqueous phase and affecting the surface tension. For the synthetic and calcium brine where Ca^{2+} ions are present, calcium-acids-metal-complexes might have been formed that tend to be more water soluble and diffused into the water phase. Overall it is observed that brines with high salinity affect more at high pH, which might have to do with complex formation.

Minor differences are observed for the samples of crude oil E, both in terms of the effect of pH and brine. This can be due to the low amounts of resins of asphaltenes in the crude oil.

For the samples of crude oil C there are hard to state any specific trends because of the very different results for all the brines and pHs. However, it is observed that the pure water samples have the largest influence, and this can be related to salting in. Despite the effect of the pure water, the brines seem to give approximately the same effect on surface tension. This crude oil contains the greatest amount of resins and asphaltenes, which can explain the overall large influence on the surface tension.

Considering the UV measurements the results found were the same for all the oils. That implies that the same kind of components might have been extracted to the aqueous phases. All of the samples of pH 2 gave four peaks in the wavenumber range 200 to 800 nm. These maximums are located at approximately 208, 239, 273 and 320. Due to the complexity of the produced water, is it hard to relate specific compounds or a mixture of compounds to these maximums. However, because of the low pH it can be stated that the components than can be correlated to these peaks most likely are of basic character, since basis tend to protonate at low pH.

These basic components can be pyridines, quinolines and acridines (basic-nitrogen-containing-compounds). The absorption peaks for the other samples are located around 206 and 263. Even though these peaks are common for the remaining samples, there is not necessarily the same compounds in the samples. There are many organic compounds that have the same maximum.

Infrared spectroscopy was conducted and two samples were analyzed. Absorption peaks were found, and they were related to different organic functional groups that were common for produced water. A 70:30 cyclohexane/butyl acetate solution was used as an extraction solvent to extract the organic compounds in the produced water samples. The aim of this experiment was to find out if the extraction method worked probably and if IR is an potential method to characterize chemical compounds in the produced water. According to the results the methods seem appropriate for this type of investigation regarding produced water characterization.

6 Further Work

The prepared produced water samples can be investigated more thoroughly. The IR experiments can be done for all the samples or TOC can be performed. This will give more information about the organic properties of the produced water.

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Appendices

A The Compositions of the Brines

Table 10 – The table gives the composition of the three different brines used during the experiments. The ionic strength is the same for them all.

Type of brine	Compound	Weight [g]
Original brine	NaCl	89,67
	$CaCl_2 \times 2H_2O$	11,958
	$MgCl_2 \times 6H_2O$	7,605
	$NaHCO_3$	0,3004
	Na_2SO_4	0,0665
	H_2O	890,4
CaCl brine	$CaCl_2 \times 2H_2O$	86,780
NaCl brine	NaCl	117,944

B Determination of Ionic Strength of the Original Brine and the Mass of CaCl$_2$ and NaCl

The CaCl$_2$ brine and the NaCl brine were supposed to have the same ionic strength as the original synthetic brine. The ionic strength of the original brine was determined, and from that was the mass required of CaCl$_2$ and NaCl calculated. It is assumed that the total brine solution is 1 liter.

Ionic strength is given by Equation (7).

$$I = \frac{1}{2} \sum c_i z_i^2 \tag{7}$$

The concentration of each ion is given as c_i [mol/l], the z_i is the charge number of the ion and the sum is taken over all ions in the solution. The number of moles for each salt in the mixed brine were found, and by that and the molar relations could the concentration of the ions, c_i, be found. The number of moles of each ion will correspond to the concentration c_i since the solution is assumed to be 1 liter.

Table 11 – The molecular weight, the number of moles of each species in the original brine and the determined concentration.

Compound	Weight [g]	M [g/mol]	n [mol]	c_i [mol/l]
NaCl	89,67	58,44	1,5344	1,5344
CaCl$_2$×2H$_2$O	11,958	128,996	0,0927	0,0927
MgCl$_2$×6H$_2$O	7,605	113,226	0,0672	0,0672
NaHCO$_3$	0,3004	106,998	0,0028	0,0028
Na$_2$SO$_4$	0,0665	142,05	0,0005	0,0005
H$_2$O	890,4	16,016	49,4227	49,4227

Table 12 – The concentration of each ion in the solution and the number of charge of the compounds

Ions in solution	c_i [mol/l]	z_i
Na^+	1,5344	+1
Cl^-	1,5344	-1
Ca^{2+}	0,0927	+2
Cl^-	0,1854	-1
Mg^{2+}	0,0672	+2
Cl^-	0,1343	-1
Na^+	0,0028	+1
HCO_3^{1-}	0,0028	-1
Na^+	0,0009	+1
SO_4^{2-}	0,0005	-2

The ionic strength of the original brine was determined to be 2,018. The ionic strength of the two other brines were supposed to be the same. By using this value and Equation (7), the mass determined of NaCl required to 1 liter solution was 117,944 grams and for $CaCl_2 \times 2H_2O$ it was 86,7802 grams.

C Preparation of the Produced Water Samples

The detailed procedure for preparation of the produced water samples is given under. Make three parallels for each sample at once. The procedure is for one parallel.

1. Heat up the oil to 60°C and shake it very well before mixing with brine

2. All the equipment that is supposed to be used during preparation should be cleaned with Milli-Q water and dried with compressed air.

3. Mix oil and brine (35 g of each) in a Schott bottle (250 ml).

4. Put the Schott bottle at the shaker for 24 hours at speed 250. Place a note at the shaker to make sure anyone does not change the speed.

5. Use pipettes to put the sample in centrifugal tubes (try to avoid as much oil possible), and place it in a centrifuge for 15 minutes (8000 rpm). Change the pipette tip for each parallel.

6. Set a cleaned Schott bottle (50 ml) under a separatory funnel and separate the final water phase from the oil.

7. Measure the density of one of the parallels as this value is required to run the bubble pressure tensiometer.

D An Overview of the Prepared Produced Water Samples

Samples prepared of Crude oil H

Orignal synthetic brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
H_S_ORG_A	40,013	40	24	Org(7,16)	1,0737	7,10	7,37
H_S_ORG_B	40,044	40	24	"	"	"	"
H_S_2_A	40,022	40	24	2,00	1,0732	2,24	2,21
H_S_2_B	40,027	40	24	"	"	"	"

NaCl brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
H_N_ORG_A	40,005	40	24	Org(5,62)	1,0766	5,98	6,45
H_N_ORG_B	40,042	40	24	"	"	"	"
H_N_2_A	40,039	40	24	2,00	1,0766	2,16	2,18
H_N_2_B	40,056	40	24	"	"	"	"
H_N_10_A	40,015	40	24	9,97	1,0761	7,64	7,31
H_N_10_B	40,020	40	24	"	"	"	"

CaCl2 brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
H_C_ORG_A	40,043	40	24	Org(6,51)	1,0498	5,48	6,13
H_C_ORG_B	40,027	40	24	"	"	"	"
H_C_2_A	40,023	40	24	2,00	1,0498	2,00	2,1
H_C_2_B	40,020	40	24	"	"	"	"
H_C_10_A	40,024	40	24	10,00	1,0493	6,32	6,54
H_C_10_B	40,032	40	24	"	"	"	"

Pure water (MQ)

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
H_W_ORG_A	40,052	40	24	Org(6,26)	0,9978	5,25	6,00
H_W_ORG_B	40,000	40	24	"	"	"	"
H_W_2_A	40,045	40	24	2,00	0,9974	2,11	2,08
H_W_2_B	40,009	40	24	"	"	"	"
H_W_10_A	40,015	40	24	10,07	0,9971	5,78	5,43
H_W_10_B	40,049	40	24	"	"	"	"

Figure 36 – The produced water samples that have been prepared of crude oil H. The weighted out crude oil and brine, the density, the pH of the brine and the produced water are listed in the table. PW is an abbreviation for produced water.

Samples prepared of Crude oil E

Orignal synthetic brine

Sample	Crude oil H [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
E_S_ORG_A	40,007	40	24	Org (6,63)	1,0737	7,44	7,63
E_S_ORG_B	40,017	40	24	"	"	"	"
E_S_2_A	40,036	40	24	2,00	1,0729	2,05	2,06
E_S_2_B	40,011	40	24	"	"	"	"

NaCl brine

Sample	Crude oil H [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
E_N_ORG_A	40,022	40	24	Org(5,73)	1,0759	7,30	7,21
E_N_ORG_B	40,017	40	24	"	"	"	"
E_N_2_A	40,035	40	24	2,00	1,0759	2,09	2,2
E_N_2_B	40,031	40	24	"	"	"	"
E_N_10_A	40,024	40	24	10,01	1,0762	8,10	8,18
E_N_10_B	40,039	40	24	"	"	"	"

CaCl2 brine

Sample	Crude oil H [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
E_C_ORG_A	40,016	40	24	Org(6,26)	1,0496	5,95	5,95
E_C_ORG_B	40,019	40	24	"	"	"	"
E_C_2_A	40,022	40	24	2,00	1,0495	1,97	1,97
E_C_2_B	40,006	40	24	"	"	"	"
E_C_10_A	39,996	40	24	10,08	1,0495	7,20	7,2
E_C_10_B	40,036	40		"	"	"	"

Pure water (MQ)

Sample	Crude oil H [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
E_W_ORG_A	40,031	40	24	Org(6,03)	0,9972	5,11	5,11
E_W_ORG_B	40,051	40	24	"	"	"	"
E_W_2_A	40,052	40	24	2,01	0,9972	2,14	2,14
E_W_2_B	40,018	40	24	"	"	"	"
E_W_10_A	40,015	40	24	10,06	0,9970	7,46	7,46
E_W_10_B	40,024	40	24	"	"	"	"

Figure 37 – The produced water samples that have been prepared of crude oil E. The weighted out crude oil and brine, the density, the pH of the brine and the produced water are listed in the table. PW is an abbreviation for produced water.

Samples prepared of crude oil C

Orignal synthetic brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
C_S_ORG_A	40,029	40	24	Org (7,04)	1,0690	7,16	7,17
C_S_ORG_B	40,029	40	24	"	"	"	"
C_S_ORG_C	40,024	40	24	"	"	"	"
C_S_2_A	40,003	40	24	2,03	1,0676	2,84	2,76
C_S_2_B	40,050	40	24	"	"	"	"
C_S_2_C	40,048	40	24	"	"	"	"
C_S_4_A	39,999	40	24	3,94	1,0676	6,54	6,49
C_S_4_B	40,031	40	24	"	"	"	"
C_S_4_C	40,009	40	24	"	"	"	"
C_S_8_A	40,001	40	24	7,99	1,0666	7,00	7,06
C_S_8_B	40,000*	40	24	"	"	"	"
C_S_8_C	40,016	40	24	"	"	"	"

NaCl brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
C_N_ORG_A	39,997	40	24	Org(5,97)	1,0761	7,20	7,35
C_N_ORG_B	40,044	40	24	"	"	"	"
C_N_ORG_C	40,023	40	24	"	"	"	"
C_N_2_A	40,028	40	24	2,00	1,0757	2,80	2,72
C_N_2_B	40,040	40	24	"	"	"	"
C_N_2_C	40,065	40	24	"	"	"	"
C_N_10_A	40,027	40	24	10,13	1,0762	7,56	7,41
C_N_10_B	40,020	40	24	"	"	"	"

CaCl$_2$ brine

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
C_C_ORG_A	39,976	40	24	Org (7,55)	1,0465	5,82	5,73
C_C_ORG_B	40,025	40	24	"	"	"	"
C_C_ORG_C	40,051	40	24	"	"	"	"
C_C_2_A	40,083	40	24	2,01	1,0481	2,37	2,27
C_C_2_B	40,049	40	24	"	"	"	"
C_C_2_C	40,040	40	24	"	"	"	"
C_C_4_A	40,013	40	24	3,98	1,0488	4,94	4,94
C_C_4_B	40,044	40	24	"	"	"	"
C_C_4_C	40,070	40	24	"	"	"	"
C_C_6_A	39,994	40	24	5,99	1,0463	5,72	5,63
C_C_6_B	40,032	40	24	"	"	"	"
C_C_6_C	40,027*	40	24	"	"	"	"
C_C_10_A	40,002	40	24	10,01	1,0485	6,69	6,92
C_C_10_B	40,012	40	24	"	"	"	"
C_C_10_C	40,051	40	24	"	"	"	"
C_C_12_A	40,082	40	24	11,46	1,0446	11,00	11,21
C_C_12_B	39,975	40	24	"	"	"	"
C_C_12_C	40,030	40	24	"	"	"	"

Pure water (MQ)

Sample	Crude oil C [g]	Brine [ml]	Shaking [h]	pH of brine	Density	pH of PW	pH when running BP
C_W_ORG_A	40,080	40	24	Org (5,99)	0,9978	7,15	7,36
C_W_ORG_B	40,085	40	24	"	"	"	"
C_W_ORG_C	40,117	40	24	"	"	"	"
C_W_2_D	40,014	40	24	2,00	0,9973	2,10	2,10
C_W_2_E	40,038	40	24	2,01	0,9973	"	"
C_W_2_F	40,048	40	24	"	"	"	"
C_W_10_A	40,046	40	24	10,00	0,9975	7,36	7,56
C_W_10_B	40,021	40	24	"	"	"	"
C_W_10_C	40,070	40	24	"	"	"	"
C_W_12_A	40,007	40	24	12,02	0,9987	11,8	11,75
C_W_12_B	40,043	40	24	"	"	"	"
C_W_12_C	40,020	40	24	"	"	"	"

Figure 38 – The produced water samples that have been prepared of crude oil C. The weighted out crude oil and brine, the density, the pH of the brine and the produced water are listed in the table. PW is an abbreviation for produced water.

E The Absorption Peaks Observed with UV/VIS for Each Sample

Water phase	Crude oil H [nm]			Crude oil E [nm]			Crude oil C [nm]		
	pH 2	pH 6	pH 10	pH 2	pH 6	pH 10	pH 2	pH 6	pH 10
Pure water	320, 273, 240, 201	263, 202	265, 205	320, 271, 234, 205	264, 201	265, 210	320, 276, 241, 200	271, 200	265, 200
Synthetic	320, 272, 238, 208	259, 207	(shaded)	320, 277, 232, 205	266, 209	(shaded)	320, 272, 238, 208	268, 209	(shaded)
CaCl$_2$	320, 273, 239, 207	268, 206	207	320, 277, 242, 207	266, 208	261, 206	320, 273, 239, 207	267, 206	291, 206
NaCl	320, 273, 239, 210	265, 214	209	318, 276, 241, 208	269, 217	264, 212	320, 273, 239, 210	269, 210	292, 237, 210

Figure 39 – The Absorption peaks for each sample given by UV/VIS spectrometer. The units are in nm.
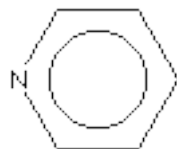
F   UV Spectra Obtained from Literature

The UV spectrum for the different compounds are obtained from NIST(National Institute of Standards and Technology) [35].
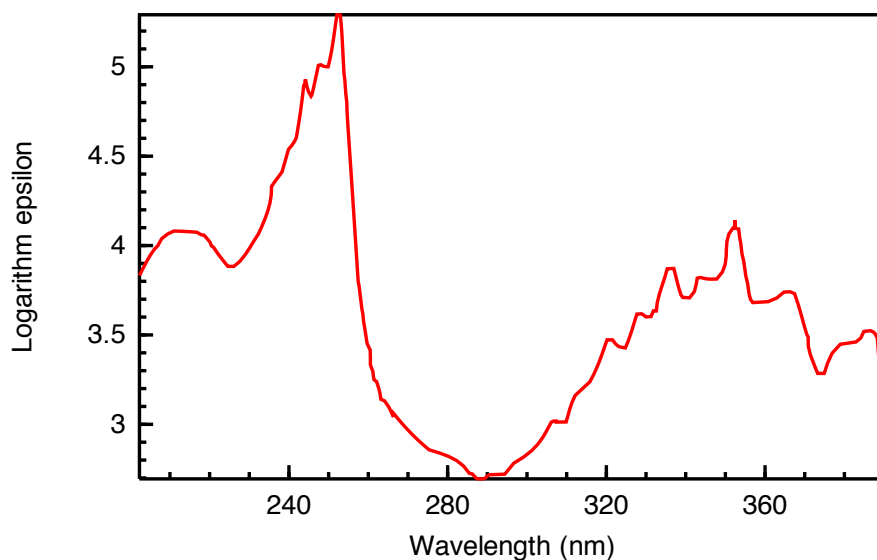
F.1   Pyridine

Peak 1: 215 nm
Peak 2: 245 nm
Peak 6: 320 nm

Pyridine
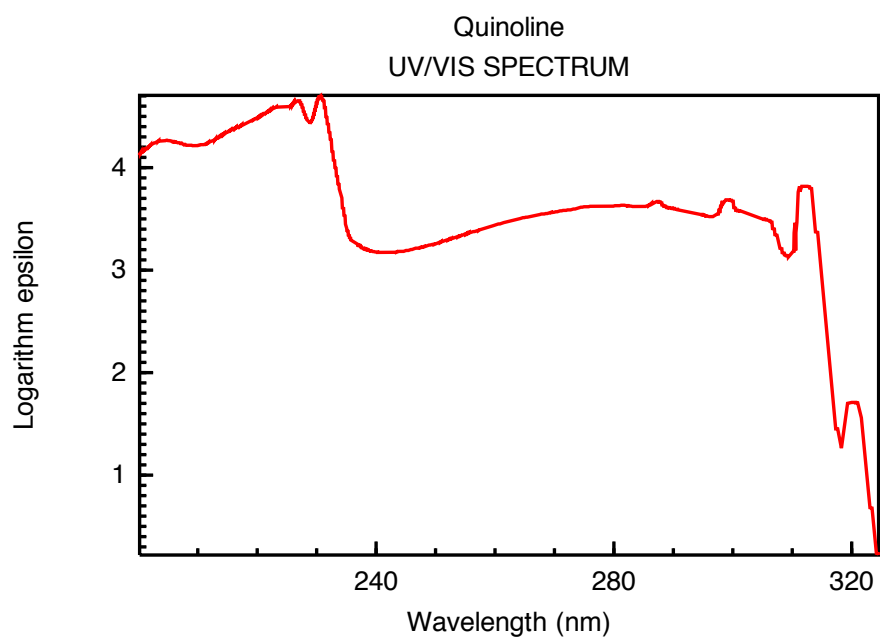UV/VIS SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

F.2   Quinoline

Peak 1: 205 nm
Peak 3: 230 nm
Peak 4: 281 nm
Peak 7: 320 nm

Quinoline
UV/VIS SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)
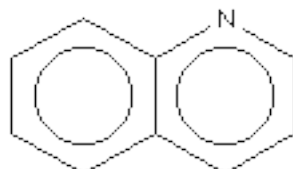
F.3 Acridine

Peak 1: 210 nm
Peak 2: 243 nm
Peak 4: 322 nm

Acridine
UV/VIS SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)
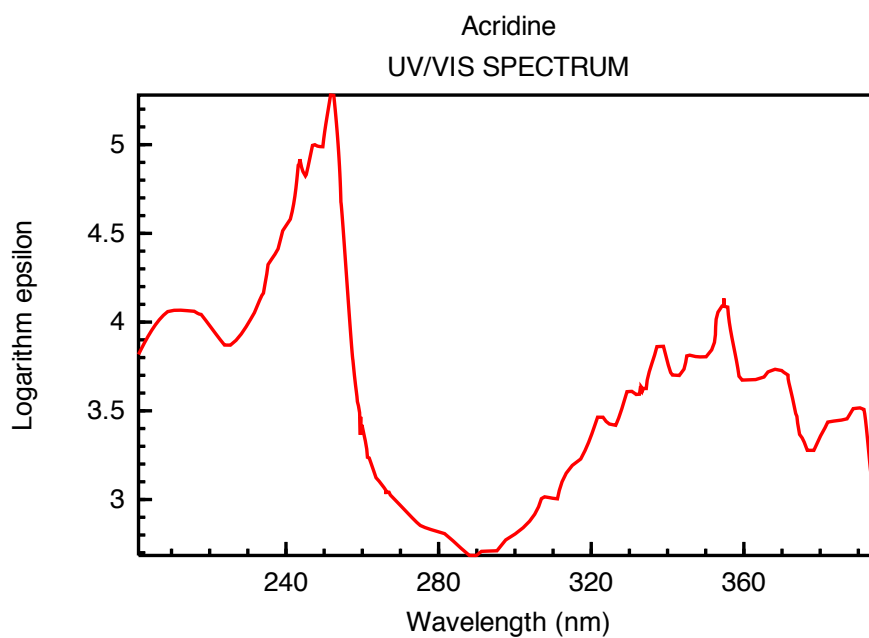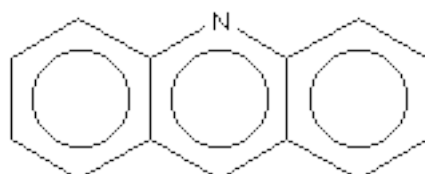
G The Influence of Asphaltenes on The Surface Pressure

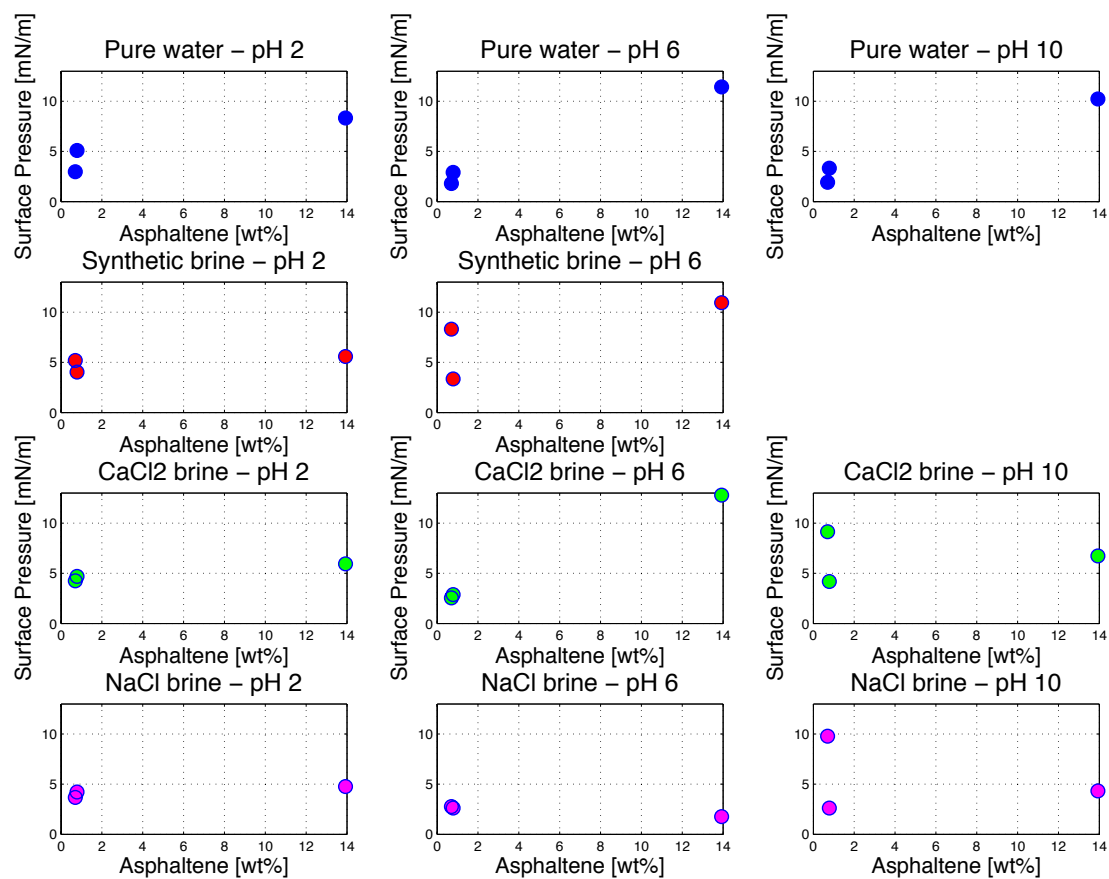
Figure 40 – The influence of the asphaltene fraction in the crude oils. Surface pressure is plotted as a function of weight fraction.

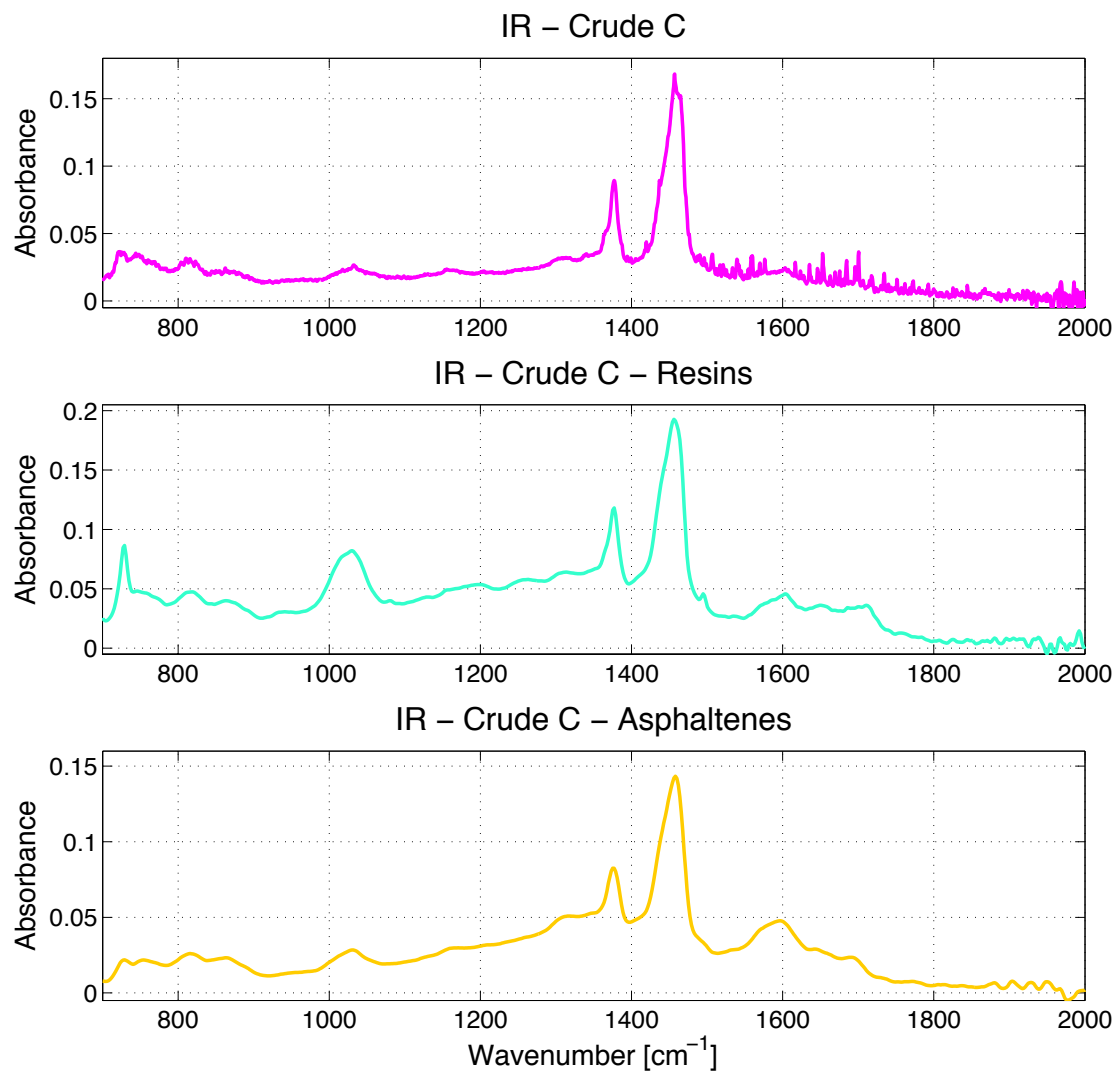# H The Absorbance Spectra for Crude Oil C

Figure 41 – The infrared absorption spectra for crude oil C. The spectra for the original crude oil C, the resin and the asphaltene fraction are given. Absorbance is plotted as a function of wavelength [36].

I Risk Assessment

		NTNU			utarbeidet av	Nummer	Dato
					HMS-avd.	HMSRV2603	4.3.2010
		HMS/KS			godkjent av	side	Erstatter
					Rektor	1 av 3	9.2.2010

	Risikovurdering

Enhet: IKP - Ugelstad laboratory
Linjeleder: Gisle Øye
Deltakere ved risikovurderingen (m/funksjon): Kaja Neeb Kløcker (Student), Gisle Øye (Veileder)
R

Dato:13-10-2012

ID nr	Aktivitet fra kartleggings-skjemaet	Mulig uønsket hendelse/belastning	Vurdering av sannsyn-lighet (1-5)	Vurdering av konsekvens:				Risiko-verdi	Kommentarer/status Forslag til tiltak
				Menneske (A-E)	Ytre miljø (A-E)	Øk/ materiell (A-E)	Om-dømme (A-E)		
1/3	Prøvepreparering	Inhalering, olje på hud, søl ved flytting av prøver fra et sted til et annet.	2	D				D2	Vær nøye med å bruke avtrekksskap når man preparer prøver, bruk og bytt hansker o
2	Målinger og analyser med Bubble Pressure Tensiometer	Søl ved flytting av prøver til glasset som hører til instrumentet	1	C				C1	Bytte hansker etter maks 10 m Bytte hansker rett etter et eventuelt søl.
	"	Inhalering ved flytting av prøver til glasset som hører til instrumentet.	2	C				C2	Ha en avtrekkshette over instrumentet.
	Vasking av utstyr med toluene, aceton, isopropanol	Søling av toluene/aceton på hud mens utstyr blir vasket. Inhalering av toluene/aceton når glasset skal tørkes med komprimert luft ved avtrekkskapet.	2	D				D1	Ha alle løsemidler (prøver elle vaskemidler) i avtrekksskap me man arbeider. Brukte/forurensede hansker burde byttes regelmessig og legges i avtrekkskapet for fordampning.

Sannsynlighet	Konsekvens	Risikoverdi (beregnes hver for seg):
1. Svært liten	A. Svært liten	Menneske = Sannsynlighet x Konsekvens
2. Liten	B. Liten	Menneske
3. Middels	C. Moderat	Ytre miljø = Sannsynlighet x
4. Stor	D. Alvorlig	
5. Svært stor	E. Svært alvorlig	

NTNU		utarbeidet av	Nummer	Dato
	Risikovurdering	HMS-avd.	HMSRV2603	4.3.2010
		godkjent av	side	Erstatter
HMS/KS		Rektor	2 av 3	9.2.2010

Konsekvens Ytre miljø

Økonomi/materiell = Sannsynlighet x Konsekvens Øk/matriell

Omdømme = Sannsynlighet x Konsekvens Omdømme

NTNU		utarbeidet av	Nummer	Dato
	Risikovurdering	HMS-avd.	HMSRV2603	4.3.2010
		godkjent av	side	Erstatter
HMS/KS		Rektor	3 av 3	9.2.2010

Sannsynlighet vurderes etter følgende kriterier:

Svært liten 1	Liten 2	Middels 3	Stor 4	Svært stor 5
1 gang pr 50 år eller sjeldnere	1 gang pr 10 år eller sjeldnere	1 gang pr år eller sjeldnere	1 gang pr måned eller oftere	Skjer ukentlig

Konsekvens vurderes etter følgende kriterier:

Gradering	Menneske	Ytre miljø Vann, jord og luft	Øk/materiell	Omdømme
E Svært Alvorlig	Død	Svært langvarig og ikke reversibel skade	Drifts- eller aktivitetsstans >1 år.	Troverdighet og respekt betydelig og varig svekket
D Alvorlig	Alvorlig personskade. Mulig uførhet.	Langvarig skade. Lang restitusjonstid	Driftsstans > ½ år Aktivitetsstans i opp til 1 år	Troverdighet og respekt betydelig svekket
C Moderat	Alvorlig personskade.	Mindre skade og lang restitusjonstid	Drifts- eller aktivitetsstans < 1 mnd	Troverdighet og respekt svekket
B Liten	Skade som krever medisinsk behandling	Mindre skade og kort restitusjonstid	Drifts- eller aktivitetsstans < 1 uke	Negativ påvirkning på troverdighet og respekt
A Svært liten	Skade som krever førstehjelp	Ubetydelig skade og kort restitusjonstid	Drifts- eller aktivitetsstans < 1 dag	Liten påvirkning på troverdighet og respekt

Risikoverdi = Sannsynlighet x Konsekvens
Beregn risikoverdi for Menneske. Enheten vurderer selv om de i tillegg vil beregne risikoverdi for Ytre miljø, Økonomi/materiell og Omdømme. I så fall beregnes disse hver for seg.

Til kolonnen "Kommentarer/status, forslag til forebyggende og korrigerende tiltak":
Tiltak kan påvirke både sannsynlighet og konsekvens. Prioriter tiltak som kan forhindre at hendelsen inntreffer, dvs. sannsynlighetsreduserende tiltak foran skjerpet beredskap, dvs. konsekvensreduserende tiltak.

NTNU

HMS

Kartlegging av risikofylt aktivitet

Utarbeidet av	Nummer	Dato
HMS-avd.	HMSRV2601	22.03.2011
Godkjent av	Side	Erstatter
Rektor	1 av 1	01.12.2006

Enhet: IKP - Ugelstad laboratory
Deltakere ved kartleggingen (m/ funksjon): Kaja Neeb Kløcker (Student), Gisle Øye (Veileder)
Kort beskrivelse av hovedaktivitet/hovedprosess: Masteroppgave student. Tittel på oppgaven: Dynamisk overflatespenning **Dato: 13.10.2012**

ID nr.	Aktivitet/prosess	Ansvarlig	Eksisterende dokumentasjon	Eksisterende sikringstiltak	Lov, forskrift o.l.	Kommentar
1	Prøvepreparering	Kaja N. Kløcker	Generelle lab rutiner	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	
2	Analyser og målinger med Bubble Pressure Tensiometer	Kaja N. Kløcker	Generelle lab rutiner Apparaturkort Instrumentprosedyre/manual	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	
3	Vasking av utstyr med toluen, aceton og isopropanol	Kaja N. Kløcker	Generelle lab rutiner Kjemikalie dataark	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	