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Characterisation of gas-liquid interfaces related to offshore produced water treatment.

The effect of pH, brine and crude oil composition.

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Preface

This thesis was written as a final part of the master degree at the department of Chemical Engineering, NTNU. The experimental work of the study has elapsed from the end of January to the beginning of May and has been carried out at the laboratory in the PFI building and in K5 at NTNU. The thesis was part of a research program sponsored by ConocoPhillips, ENI Norge, Schlumberger Division MI Epcon, Statoil and Total.

I would like to thank my supervisor Gisle Øye for giving me the opportunity to work with this project and for guidance regarding the experimental work and the results at the weekly meetings during the laboratory work period.

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Declaration of Compliance

I hereby 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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Helle Hofstad Trapnes Date

Abstract

Produced water is water co-produced with oil and gas during petroleum production. It is a very complex mixture and contains different compounds that can have negative impact on the environments. It is therefore important that the hazardous constituents are removed from the produced water in order to comply with the environmental regulations that the governments require. As the fields mature the amount of produced water will increase and it is thus crucial to handle this by-product efficiently. The produced water is either re-injected into the reservoir or discharged to the sea. There exist several techniques for separating the oil and the water and one common method is gas flotation, where dispersed oil and particles adhere to rising gas bubbles. The efficiency of this method is largely dependent on the spreading coefficient which needs to be positive to achieve effective gas flotation. The aim of this study was therefore to investigate the surface tension between produced water and gas bubbles at short time scales. The produced water was prepared with various crude oils, various brine compositions and various pH values and the effect of these parameters on the surface tension were studied. The produced water samples were prepared by mixing crude oil and brine and then separating the two phases. Three different crude oils and three different brines in addition to pure water with various pH values were used. The surface tension of the samples was measured by a bubble pressure tensiometer (BP 100) and it was found that the changes in surface tension were largely dependent on the crude oil composition. The produced water samples made with crude oil I had most influence on surface tension at high pH values whereas the change in brine composition did not seem to influence the surface tension significantly. The samples made with crude oil B had similar effect on the surface tension regardless of the pH and composition of the brine. This indicates that other surface active compounds than acids and bases contribute to the change in surface tension. The samples made with crude oil F did not show any obvious trend regarding the surface tension for the various pH values and brine composition and the reason for this is not clear. In addition to surface tension measurements the samples were analyzed with the UV-visible spectroscopy method to get an indication of the concentration and type of compounds that was present in the produced water samples. Two samples were also measured with the IR spectroscopy method to get more information about the contents of the samples. There should be done more IR analysis and also other analysis like TOC to get more information about the contents of the produced water samples in the future.

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1. Introduction

1.1 Crude oil

The products of the petroleum refining are everywhere in our daily life. Examples are fuel, gas, plastics, paints, synthetic fibres in clothing and synthetic soap. The crude oil is a non-renewable resource and therefore the development of new technologies needed, to make use of other energy sources when the oil runs out, is constantly advancing. [1]

The crude oil is a very complex mixture and can vary a lot from one well to another. The location and age of the oil field as well as the depth of the well are factors that play an important role on the chemical and physical composition of the crude oil. The crude oil mainly consists of hydrocarbon and small amounts of organic compounds which contains sulphur, oxygen, and nitrogen and also metallic constituents as vanadium, nickel, iron and copper. [2] The elemental composition of crude oil is given in table 1 and it covers a rather narrow range for the main constituents.

Table 1: Elemental composition of crude oil [3]

Element	**Content in crude oil [wt %]**
C	80 – 87
H	10 – 14
N	0.2 – 3
O	0.05 – 1.5
S	0.05 – 6

Crude oil can be fractionated by the SARA fractionation technique which divides the oil in four general fractions: saturates, aromatics, resins and asphaltenes, see figure 1. [4]They differ in their polarity, aromaticity and solubility in an aliphatic hydrocarbon medium. [1]

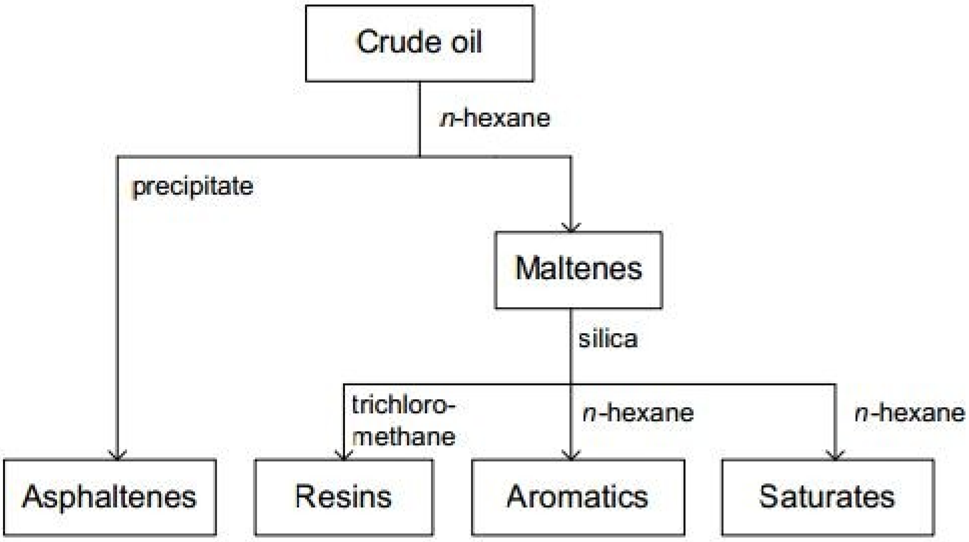

Figure 1: SARA fraction scheme. [2]

Saturates are the lightest compounds in crude oil. They are non-polar saturated hydrocarbons without double or triple bonds, like alkanes and cycloalkanes.[3]

The aromatics are compounds that have one or more benzene rings. Most of the aromatic compounds have alkyl chains and cycloalkane rings along with additional aromatic rings.

Resins consist of polar molecules which predominantly contain heteroatoms (N, O and S). This may lead to a larger density of functional groups in the resin structure and makes them capable of having strong intermolecular interactions with other polar molecules like asphaltenes. The resins are structural similar to the asphaltenes, but have lower molecular weights and higher H/C ratio than the asphaltenes. [3, 4]

Asphaltenes are polar molecules as the resins, but have the highest amount of heteroatoms. They also have the highest amount of organ metallic constituents. The asphaltene molecules consist of polycyclic aromatic clusters with varying side chains as well as heteroatoms and metals. They have been studied extensively because of the problems they cause in petroleum production due to precipitation.[2, 4]

1.2 Produced water

In oil and gas production, large volumes of liquid waste are generated.[5] Produced water is the largest waste stream in offshore oil and gas production and it constitutes about 60 percent of the produced volume.[2] In subsurface formations there are naturally occurring rocks that are saturated with fluids such as oil, gas and saline water. The water is located in vast layers below the hydrocarbons, because the density of water is higher than the density of hydrocarbons, in the reservoir rocks. The sources of this water is flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone or flow from injected fluids an additives resulting from production activities. At last there is the natural water layer in the reservoir called formation water which becomes produced water when the saline water mixed with hydrocarbons is brought to the surface.[5] As the oil and gas fields mature, the produced water volume increases and it is therefore very important that this by-product of petroleum production is managed efficiently.[2, 6]

The properties of produced water are dependent on the geographic location of the field, the geological host formation, the type of hydrocarbon produced as well as the reservoir lifetime.[2] Produced water composition may be continuously transformed when production is initiated due to injection of seawater, reinjection of produced water, reservoir stimulation, bacterial activity, introduction to chemicals and more. Produced water consists mainly of a mixture of formation water and injected water, but also dissolved organics, gases (particularly hydrogen sulphide and carbon dioxide), traces of heavy metals, dissolved minerals, suspended oil, solids like sand and silt and production chemicals. The oil in produced water is present as oil droplets and as dissolved components which are for example carboxylic acids and aromatics. The dissolved organics, which in produced water are mainly benzene, toluene, ethyl benzene, xylene (BTEX), polyaromatic hydrocarbons (PAH) and alkylphenols, can be both toxic and bio-accumulative. They are naturally found in formation water and are together with heavy metals considered the most harmful contaminants in produced water. [6]The dynamic surface tension, which is described below, can be affected by the BTEX, phenols and organic acids.[4]

During the petroleum production there are several considerations which must be taken into account regarding produced water treatment technologies. That includes space and weight limitations on the platforms, capacity, performance, and reliability of maintenance. It is important that the water production system is designed to receive continuously increasing quantities of water as oil production continues. [6]

The produced water can be treated in two ways:

1) Re-inject the produced water to the reservoir
2) Purify the produced water and discharge it to the sea

The re-injection is done to maintain the formation pressure and displacing the crude oil in the reservoir and for disposal of the water after oil/gas/water separation. It is the most environmentally friendly way to deal with the produced water, but it is expensive and not applicable in every field. The most common way to treat the produced water is to discharge it to the sea, but is also the way that effects the environment the most. It is therefore very important to focus on minimizing the water pollution before releasing the water to the environment.[2] The technologies for separating oil and water in petroleum industry are mainly divided into two main types; gravity and non-gravity based separation technologies. For non-gravity separation technologies the most common methods are Hydro cyclone technology, Filtration (Walnut Shell Filters, Sand Filters and Multi-Media Filters), Coalescing Media and Adsorption and Non-Recoverable Media. Gravity separation technologies are based on the fact that the specific gravity of oil is less than that of water so that the oil, which will rise to the surface of the water, can be skimmed off. The technologies can broadly be divided into two main categories; those that operate with assistance of gas flotation process and those that operate without. The flotation processes that are without gas assistance includes gravity separation tanks and corrugated plate interceptors.

The necessity for handling large volumes of produced water is increasing as the oil and gas fields mature. The ever tightening regulations and the need of increased production given the current high price of oil, is resulting in a significant need for more efficient treatment of produced water. Many of the existing separation technologies are widely accepted conventional methods that have been used with great success and many of the newer designs have relied on modifications to improve efficiencies, or different combinations of the same equipment. [7]

1.3 Gas flotation

The industry currently prefers the gravity settler and cyclone approach to non-dissolved oil removal. However, these methods are ineffective when the density difference between the oil and the water becomes smaller and there is less buoyancy between the two phases. The heavy crude oils (oils which have a density close to that of water) are extremely difficult to treat. That is not only because of their high viscosities and densities and foaming characteristics, but also because of their tendency to form stable emulsions with water due to waxes, asphaltites particles and other impurities present. The only effective method for cleaning non-dissolved oil in oily wastewater when the oil is heavy is by gas flotation. [8]

1.4 Aim of the study

The main points from this introduction are hence that the produced water, which is co-produced with oil and gas during petroleum production, contains pollutants like dispersed oil and solids, as well as dissolved organic and gas and it is important that these constituents are separated from the produced water streams in order to comply with the environmental regulations if the water is to be discharged to sea, or to achieve sufficient quality for reinjection of the water into the reservoir. As mentioned, a common method for removing dispersed oil and solids from the produced water is gas flotation, where oil and particles attaches to gas bubbles which rise to the surface and are then being removed. The efficiency of this method is largely determined by the surface properties of water-gas and oil-gas interfaces.

The aim of this thesis was therefore to study the changes in surface tension between produced water and gas bubbles at short time scales. The produced water used in the study was artificial and prepared with different crude oils, various brine compositions and various pH values and the effect of these parameters on the surface tension was investigated. The measurements of the surface tension were carried out using a maximum bubble pressure tensiometer. In addition, the produced water was analyzed on the UV-spectroscopy and a procedure for analyzing the produced water with IR-spectroscopy was tested.

2. Theory

2.1 The technique of gravitational separation

Gas flotation is a gravitational separation technique where gas bubbles are injected into a water phase containing immiscible oil droplets or oily solid particles so that the gas bubbles can attach themselves to the droplets and rise to the surface. This may be due to that the density difference between oil and water is increased which makes the oil lighter. When the oil droplets come to the surface they are trapped in the resulting foam and removed from the flotation chamber when the foam is skimmed off.

The velocity of the droplet to rise to the surface is a major factor in gas flotation. The Stokes equation is being used to define the rise velocity of oil droplets based on their size and density,

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

where V is the droplet settling (rising or falling) velocity, d is the droplet diameter, g is the gravitational acceleration, $\rho_w - \rho_o$ is the difference in density between continuous and droplet phase (oil or gas) and μ_w is the dynamic viscosity of continuous phase. Since the rise velocity is dependent on the bubble/droplet size the oil droplet size is very important, and the smaller the droplets the slower the rise velocity. When the oil droplets attach to the gas bubbles the oil density is reduced which makes the density difference between the oil agglomerates and water, and also the agglomerate diameter, increase which results in a faster rise rate. In a diameter range of 10 – 200 µm for solid spheres and similar sized gas bubbles, when surface active species are present in the water, the Stokes equation is valid. [8]

2.2 Attachment of gas bubbles to oil droplets

For flotation to occur the gas bubbles and oil droplets have to contact and then attach to each other. If placed in water they will rise because they are both less dense than water (except from some very heavy oils). It is important to have a long enough residence time in the separation unit to give the oil droplet and gas bubbles time to attach. To achieve this one has to increase the droplet size or the difference in fluid densities. It is also advantageous to decrease the viscosity of the continuous phase. In order to have an effective flotation process surfactants are usually added in the process. The surfactants will modify the charges between the oil droplets and the oil/gas interfaces and thus coalescence between oil droplets and gas bubbles will in turn be achieved. Surfactants are therefore important and if not a suitable concentration of surfactants are being used then spreading will not occur and the gas bubbles will rebound from the oil drops.

When oil droplets and gas bubbles are approaching each other, a thin layer or film of water is created between the droplet and the bubble, see figure 2. This film has to drain before it can rupture and the droplets can coalesce. Surfactants have a significant role here. As the liquid drains a dimple is created, which induces a pressure distribution in the film. The dimpling makes the surface expand which causes a fall in the concentration of surfactants along the oil/water and gas/water surfaces at the centre. This results in a concentration gradient between the centre region of the film and its interfaces which creates fluid movement. This fluid movement is caused by the Gibbs-Marangoni effect. When the liquid film drops to a critical thickness of approximately 0, 10 µm, the laminar layer becomes unstable and ruptures very quickly. Upon rupture, coalescence between the gas bubble-oil drops occurs. [8, 9]

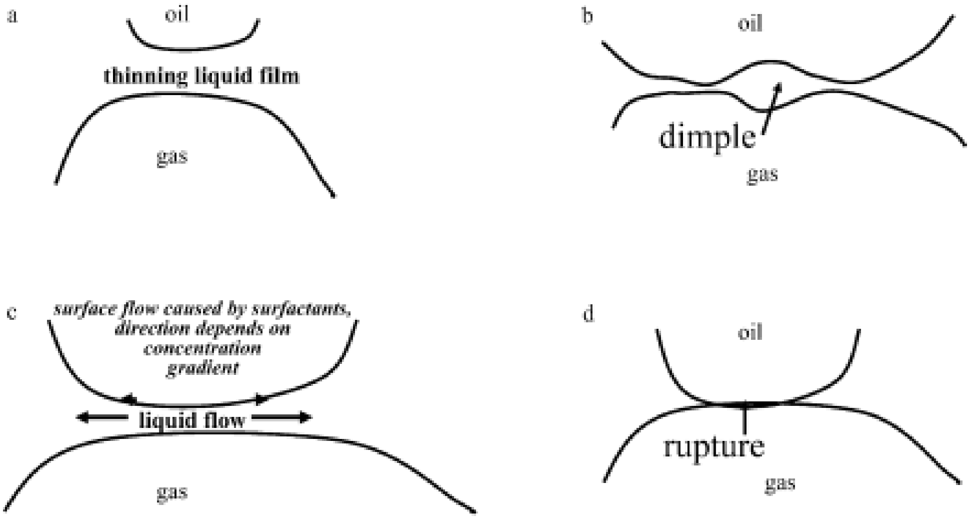

Figure 2: The attachment process between oil drop and gas bubble. (a) Water film thinning; (b) the interfacial tension gradients makes the thin film dimple; (c) the dimple disappears as the film drains and thus thins further; (d) at a critical thickness the film ruptures. [8]

The oil-gas agglomerate is not robust enough to withstand the upward rise, thus spreading of the oil over the bubble has to occur. For the gas-oil-water system, the oil spreading coefficient on a water-gas interface can be defined as:

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

where S_0 is the spreading coefficient, 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. If the spreading coefficient is positive it means that one of the tensions is larger than the sum of the two others and leads to a spreading continuous film in the water-gas interface. If it is negative the fluid will form a definite contact angle with the other two phases and the adherence of the oil to the gas bubble is weak so the agglomerate is likely to break-up as it rises. The spreading coefficient has to be positive for the gas flotation process to be effective. Spreading ensures the attachment of the oil to the bubble is maintained while it rises to the surface. If the oil droplets are less than 10 μm a very thin unstable film will form around the bubble, and it is therefore not very successful floating oil droplets at this size.[8, 9]

2.3 Surface tension

Surface tension is defined as the amount of energy or work needed to increase the surface by a unit area. The surface tension is a result of the intermolecular forces between molecules at the surface in a fluid. In the bulk phase of a liquid the intermolecular forces are canceled because the molecules are surrounded by other similar molecules. At the interface however, the forces are not equal in all directions due to the differences between the molecules in the liquid and gas phase. This imbalance results in a net force directed into the bulk of the liquid. This is illustrated in figure 3. The typical unit of surface tension is mN/m or mJ/m^2 and it depends on the surface composition or surface excess concentration of the components existing at the interface. [10]

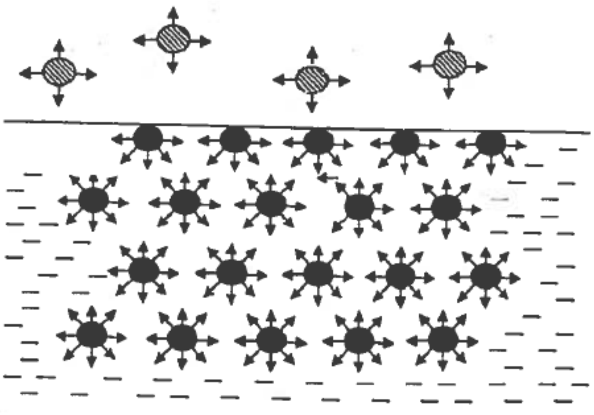

Figure 3: Intermolecular attractive forces in liquid (below) and gas (above) [11]

The dynamic surface tension is the change in surface tension before equilibrium conditions are reached. The surface composition is the same as the bulk composition at the instant when a new liquid/air surface is formed. This means that the surface tension is close to the average of the surface tensions of the neat components. Equilibrium is reached when the surface is completely occupied by surfactant molecules, and if the concentration is further increased so-called micelles will form. At equilibrium, the component with the lower surface tension will be preferentially adsorbed at the surface. This leads to an excess of the component with the lower surface tension in the surface composition and hence the surface tension of the solution will be lowered. This process is time-dependent and depends upon the diffusion of the components. The path of the time dependence of the change in surface tension for surfactants in aqueous solution is shown in figure 4. [12, 13]

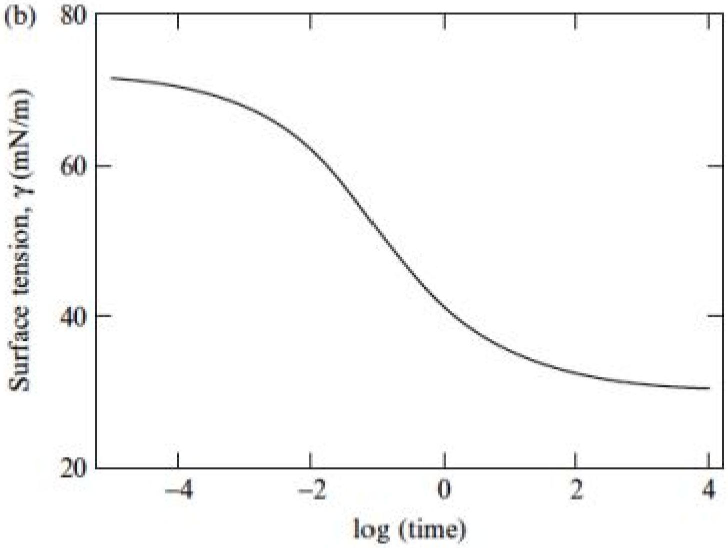

Figure 4: Illustration of the time-dependent change in the dynamic surface tension. [14]

Figure 5 illustrates how the surfactant molecules accumulate at the surface and thus causes a reduction in the surface tension. The surfactants consist of a hydrophilic (water-attracting) “head” and a hydrophobic (water-repelling) “tail where the head groups are directed towards the aqueous solution and the tails are turning towards the air. [15]

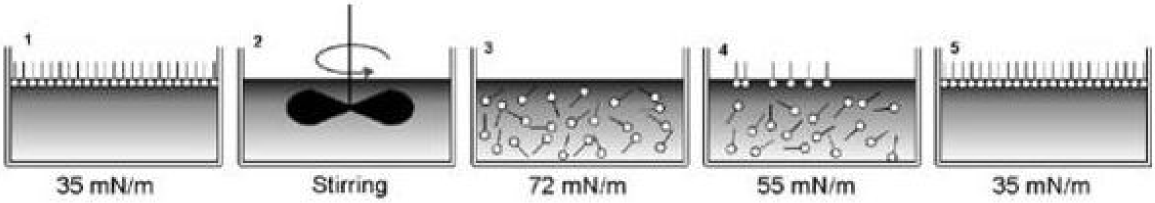

Figure 5: “Orientation of surfactants molecules”. [15]

2. 4 Circumstances that affect the surface tension of the produced water

The circumstances that affect the surface tesion of the produced water in this study are the pH of the brine and the composition of the brine. The pH affects what kind of organic compounds that will dissolve in the water phase which in turn influences the surface tension, and various brine composition contains different type of ions which influences the surface tension.

There are two main processes that should be considered relative to investigation of produced water; the oil/water interface and the air/water interface. During the preparation of the produced water sample when mixing crude oil and brine it is the interactions at the oil/water interface that is applicable. During the surface tension measurements of the produced water sample it is the interactions at the air/water interface that is investigated. Figure 6 illustrates what happens at both the different interfaces. [16]

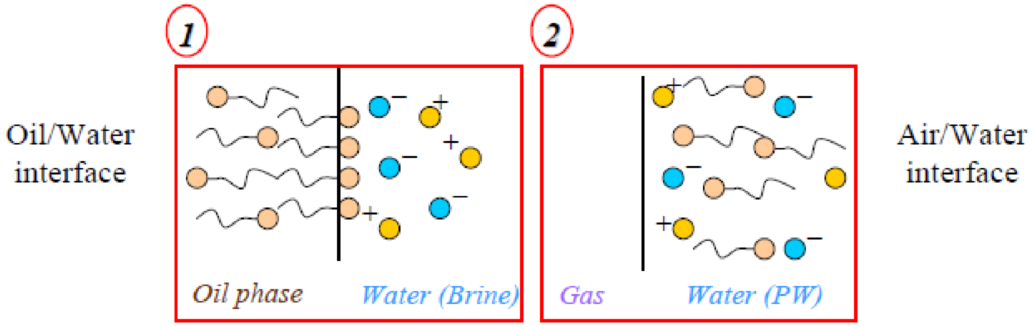

Figure 6: The figure shows what happens at the oil/water interface and the air/water interface. [16]

2.4.1 Oil/water interface

The crude oil contains both non-polar and polar fractions. The polar fractions, asphaltenes and resins, contain both acidic and basic compounds. These compounds are interfacial active and will affect the interfacial tension. The total amount of acids and bases of a crude oil is given by the total acid number (TAN) and the total base number (TBN) respectively. These values are important relative to oil characterization.[17] [3]

When the oil phase and the aqueous phase are in contact, both pH and composition of the brine will have influence on which components accumulate at the interface. The pH affects the water-solubility of the acids and bases, i.e. various components will either diffuse from the oil phase to the water phase or reside at the interface. This will influence the surface tension of the produced water since it depends on the surface active components present in the water phase.[17, 18] When the pH increases above the pKa value of the acids, the acids will dissociate and become negatively charged and thus increase the water- solubility and interfacial activity. The water-solubility of the bases will increase when the pH decreases.[19] Previous study of interfacial tension between crude oil and aqueous solution support this. It was found that the interfacial tension is governed by the basic components at low pH values. At higher pH values it is mainly the acidic components that determine the interfacial tension.[17] Changes in the interfacial tension with pH also provide evidence that both acid and bases are active at the oil/water interface.[20] This can be related to the produced water and components that influence the surface tension. If the surface tension of the produced water decreases at low pH values this indicates that basic components are present in the aqueous phase, whereas decrease in surface tension at natural pH values, which is normally between 6 and 8, and above indicates that acidic components are present in the aqueous phase. [18, 21]

The acids and bases are present in both the resin and asphaltene fractions. But the acids and bases that are water-soluble are most likely from the resin fraction since it contains smaller molecules than the asphaltene fraction. The asphaltene fraction, which contains large molecules, is hydrophobic and will be less water-soluble. A large group of acids in crude oil are the naphtenic acids. They are incorporated in the resin fraction and are carboxylic acids which cause immense problems in crude oil production. [22] The larger naphtenic acid molecules are oil-soluble, while the smallest napthenic acid molecules are soluble in water, even at pH values near the pK_a. This means that the acids may either diffuse into the water phase or they may accumulate at the water-oil interface and interact across the interface. [23]

The major fraction of the basic components in crude oil is nitrogen compounds like pyridine, quinolines and some substituted pyrroles. Nitrogen is associated to problems like poisoning of cracking catalysts and gum formation in fuel oil. [24] It has also been found Amine-containing bases, but only as small a fraction of the crude oil. At certain pH values these basic compounds will have impact on the surface tension of produced water. [25]

The nature of compounds that diffuses to the water phase is not only determined by the pH of the aqueous phase, but also by the composition of the aqueous phase. Various salts like NaCl, $CaCl_2$, and MgCl2 present in the aqueous phase will have impact on the water solubility of the various hydrocarbons. When hydrocarbons like acids diffuse to the water phase they will dissociate, at pH values above the pKa value of the acids, and give rise to negatively charge sites at the interface that needs to be compensated by a diffuse layer of counterions. In the case of pure water, the only counterions present is H^+, but when adding salt they provide additional counterions in much higher concentration than H^+ ions and these will dominate the diffuse layer surrounding the interface. This will result in enhanced dissociation of acidic compounds and reduction in interfacial tension.[17] Interactions between organic acids and metallic cations, when operating at pH values between the pK_a and the hydroxide precipitation of the metallic cation, are mainly ion-ion interactions between dissociated acids and free cations. Interaction between dissociated acids and metallic cations may either establish an electric double layer at the interface or a chemical reaction between the compounds. Which process that occurs depends on the concentration of the compounds, the pH of the aqueous phase and the valency and the degree of hydration of the metallic cations. [20, 23]

When salts are added to the water phase there will be interfacial reactions between metal cations and dissociated acids which form complexes with various abilities. The complexations between Na^+ ions and dissociated acids are weak. Consequently, the presence of Na^+ will promote dissociation of acidic groups at the interface and thus increase their water solubility. With high concentrations of Na^+ more interfacially active components can accumulate at the interface and thus lower the interfacial tension. This is due to the fact that Na^+ ions reduces the repulsion forces between the neighboring negative charges and thus provides more space for the interfacial active components at the interface. The Ca^{2+} ions, however, tend to form strong complexes with the dissociated acids and formation of interfacial films which will hinder or reduce solubilization of acidic components into the aqueous phase. These complexes can be either water-soluble or oil-soluble. The extent of film formation is largely dependent on the amount of Ca^{2+} present. [17] The reaction between divalent cations like Ca^{2+} and dissociated acid monomers to form complexes comprises two reaction steps which involves sequential binding of two acid monomers to one cation.

$$M^{2+} + 2(RCOO^-) \overset{k_1}{\leftrightarrow} \underset{k_{-1}}{\longleftrightarrow} [M - RCOO]^+$$

$$+RCOO^- \underset{k_2}{\rightarrow} M - (RCOO)_2$$

The decrease in interfacial tension is assumed to arise from the first reaction step, where formation of a positive metal – monoacid complex occurs. This complex is more interfacially active than a single dissociated acid monomer. [23]

2.4.2 Salting – out effect

The presence of salt can either increase or decrease the solubility of organic molecules in water. Structure making salts like NaCl, KCl, Na_2SO_4 etc, decrease the solubility of non – polar organic compounds. This phenomenon is called salting-out. The opposite effect is known as salting-in, which increases the solubility of non-polar organic molecules by large polarizable inorganic salts like lithium perchlorate and most organic salts like butyl ammonium bromide. [26]

The salting-out effect results from various interactions like the hydration of the ions, and the interactions of the hydrated ions and the non-electrolyte. The explanation of salting-out effect from consideration of hydration forces is simplistic but incomplete since it does not take into account the effect of ions and water structure. Nonetheless, it gives somehow an understanding of the effect of salts in a solution. When ions are in contact with water, water molecules will orient themselves around the ions, thus forming water-ion complexes. This shields the ions from interacting with the solute. Cations are especially prone to form these complexes, consequently leaving less “free” water available to dissolve the liquid. [27, 28]

In order to understand the various ions properties in water it is necessary to know how the ions interact with water. Water is a highly structured liquid due to an extensive network of hydrogen bonds. Adding ions to the water will affect this structure by enhancing or reducing the extent of hydrogen bonding. The ions interaction with water can therefore be classified into “water structure makers” or “water structure breakers”. The small ions will break hydrogen bonds due to their high charge density which causes strong electrostatic ordering of nearby waters. However, the larger ions have low charge density which causes the surrounding water molecules to be largely hydrogen bonded. Water structure makers and water structure breakers are also commonly referred to as kosmotropes and chaotropes respectively.[29-31] The chlorine ion is a weak chaotrop, sodium is a weak kosmotrop, whereas calcium and magnesium are strong kosmotropes. This means that Ca^{2+} will decrease the solubility of the non-polar organic compounds in a larger extent than Na^{+}. [20]

2.4.3 Air/water interface

The produced water sample contains acids, bases and other organic molecules from the crude oil and salts from the brine. In the water the salts and acids dissociate and the bases protonate, thus, various ions will be present at the air/water interface of produced water.

If the water phase contains only salts, and not any organic molecules, the surface tension of water will be increased compared to the surface tension of pure water. When the salts are added to the water phase they dissolve and divide into separate ions which will raise the surface tension. The extent of the increase in surface tension is dependent on the salt. Comparing Ca^{2+} ions with Na^{+} ions the surface tension will be higher when having Na^{+} ions in the water phase than Ca^{2+} ions. This is because Ca^{2+} ions are more hydrated, i.e. they are surrounded by more water molecules, than Na^{+} which means that the Ca^{2+} ions will rather be in the bulk phase than at the surface. [32]

When both salts and organic molecules are present in the water phase the salts can have various properties which affect the surface tension. It has been found that salts with salting-out behavior in aqueous solution promote surface adsorption of organic molecules, resulting in lower surface tension. Salting out drives more organic molecules to become more densely packed at the interface and the intermolecular interaction between surface organic molecules may become stronger in the presence of salt. The effect of salt depends on the nature and the concentration of both the salt and the organic molecule. The presence of salt in the water phase increases the surface tension of water, but organic adsorbates reduce the surface tension of water. This means that in a solution containing both inorganic and organic solutes the surface tension depends on the composition of the mixture. [26]

When salts and bases are present in water they increase the surface tension of the water. A previous study showed that in salt solutions and bases the positively charged ions, such as alkali cations, are repelled from the surface, while the anions, such as halides or hydroxide, will have varying propensity for the surface. However, in the presence of acids the surface tension will be reduced. In an aqueous phase with high pH the acids are dissociated and will accumulate at the surface. If ions are present they will reduce the repulsion forces that exist between the negatively charged acids allowing the acids to pack more closely together and thus more acids can accumulate at the surface and reduce the surface tension. [33] [18]Another study supports that presence of salts and acids in a water solution have opposite effect on the surface tension than presence of salts and bases. The dissociation of acidic groups at the interface is promoted by presence of Na^+ ions. High concentration of Na^+ ions will lower the repulsion forces between the neighboring negative charges, allowing more interfacially active components to adsorb at the surface. This will result in decrease in surface tension. [17]

3. Experimental techniques

3.1 Maximum bubble pressure method

The dynamic surface tension can be measured by many different techniques that cover the time interval from milliseconds to hours.[34] Some of the methods are Wilhelmy plate method, pendant drop method, spinning bubble or drop method, oscillating jet method, maximum bubble pressure method and Du Noüy ring method.[34, 35] In this study the maximum bubble pressure method has been used to measure the dynamic surface tension.

The maximum bubble pressure method is a classical method in interfacial science and is of great interest in recent times. [34] The method was introduced already 150 years ago and has been in continually development since then. It is a very easy method and the only technique that can measure dynamic surface tension in the short time range down to milliseconds and below.[36] It seems to be the only reliable technique that gives access to very short adsorption times.[37]

A schematic representation of the bubble pressure tensiometry is showed in figure 7. The pump compresses air in order to produce a continuous gas flow which is being measured by the gas flow sensor. The gas flow is damped to a smooth and constant flow by the gas flow capillary and the gas volume. The pressure sensor measures the pressure of the gas volume which is proportional to the maximum capillary pressure and thus proportional to the surface tension.[4]

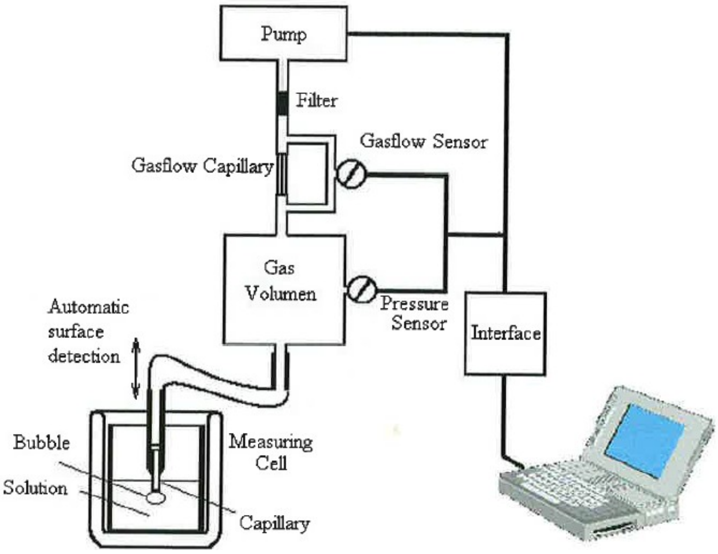

Figure 7: Schematic representation of the working principles of a bubble pressure tensiometer. [4]

Gas bubbles are produced in the liquid from a software-controlled flow of air emerging from a capillary whose radius is known. During this process a high-precision pressure sensor determines the maximum pressure whose value is recorded by the instrument. The surface age is the time from the start of bubble formation to maximum pressure. The instrument measures the surface tension as a function of surface age by varying the speed of bubble formation. Figure 8 shows the step of bubble formation and each step is described below.[38]

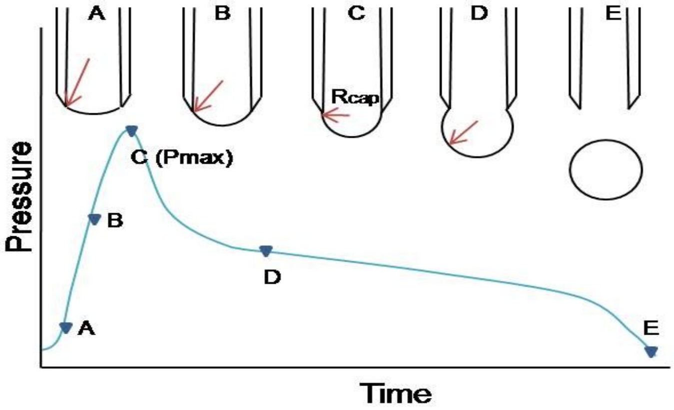

Figure 8: Schematic presentation of change of pressure during bubble formation plotted as a function of time. [4]

A, B: The first thing that happens is that the bubble is formed at the capillary tip. In the beginning the pressure is below the maximum pressure and the radius of curvature of the air bubble is larger than the radius of the capillary.

C: When the pressure curve passes through a maximum the air bubble radius is the same as that of the capillary. The air bubble is at this point forming an exact hemisphere. The surface tension can be determined using the Laplace equation:

$$\sigma = \frac{(Pmax - P0) \times r}{2}$$

Where σ is the surface tension, P_{max} is the maximum pressure, P_0 is the hydro-static pressure in the capillary and r is the inner radius of the capillary.

D: After the maximum is reached the “dead time” of the measurement starts where the pressure decreases again and the radius of the air bubble becomes larger.

E: Finally the bubble escapes from the capillary and rises. Then the formation of the next bubble begins and the cycle repeats itself.[38]

3.2 UV-spectroscopy method

In ultraviolet-visible spectroscopy the intensity of light passing through a sample is measured, and compares it to the intensity of light before it passes through the sample. The instrument used is called a UV-visible spectrophotometer. UV spectroscopic data gives quantitative information of solutions of transition metal ions and highly conjugated compounds. [39]

It involves the spectroscopy of photons in the UV-visible region which means it uses light in the visible and adjacent – near ultraviolet (UV) and near infrared (NIR) – ranges. In the visible ranges the absorption directly affects the color of the chemicals and in this region the molecules undergo electronic transitions. [40] Organic compounds, especially those with a high degree of conjugation, absorb light in the UV or visible regions of the electromagnetic spectrum and the solvents are often water for water-soluble compounds, and ethanol for organic-soluble compounds.

The Beer-Lamberts law is the principle behind absorbance spectroscopy.

$$A = \varepsilon c L$$

Where A is absorbance, ε is molar absorptivity of the compound or molecule in solution, c is the concentration of the solution and L is the path length of the cuvette. [39]

3.3 IR – spectroscopy method

Infrared (IR) spectroscopy is a spectroscopic technique that measures the absorption of different IR frequencies by a sample positioned in the path of an IR beam. The IR spectroscopic analysis is used to determine the chemical functional groups in a sample. Different functional groups absorb specific frequencies of IR radiation that are characteristic for their structure. The IR spectra are obtained by detecting changes in transmittance (or absorption) intensity as a function of frequency. An IR spectrum can be obtained from samples in many different forms, such as liquid, solid and gas. However, many materials are opaque which makes it necessary to dissolve or dilute the samples in order to obtain spectra.

The IR spectrum of every molecule is unique which means that one can identify an organic compound by finding a reference IR spectrum that matches that of the unknown compound. There exist a large number of reference spectra for vapor and condensed phases.

The absorbance at any frequency for a single compound in a homogenous medium is expressed as

$$A = abc$$

where A is the measured sample absorbance at the given frequency, a is the molecular absorptivity at the frequency, b is the path length of source beam in the sample and c is the concentration of the sample. This equation is known as Beer's law and states that the intensities of absorption bands are linearly proportional to the concentration of each component in the homogenous solution. [41]

4. Materials and procedures

4.1 Materials

The produced water samples were prepared by mixing crude oil and brine. Table 2 shows the materials and equipment used for the preparation.

Table 2: The required materials, equipment and cleaning agents for produced water sample preparation

Materials	Equipment	Cleaning agents
- Crude oil B [40 g] - Crude oil F [40 g] - Crude oil I [40 g] - Synthetic brine [40 g] - NaCl brine [40 g] - $CaCl_2$ brine [40 g] - Milli – Q water [40 g]	- Schott bottles (250 ml, 50 ml) - Saker - Centrifugal tubes - Separatory funnels - Pipettes	- Toluene - Milli – Q water - Acetone

4.1.1 Crude oils

Three different crude oils were used for produced water preparation. In table 3 the physicochemical properties of the crude oils are presented.

Table 3: The physicochemical properties of the crude oils.

Crude oil	**Density [g/cm^3]**	**Viscosity [cP]**	**Saturates [%]**	**Aromatics [%]**	**Resins [%]**	**Asphaltenes [%]**	**TAN [mg/g]**	**TBN [mg/g]**
B	0.92	78.44	44.35	38.76	16.39	0.49	2.28	4.48
F	0.84	16.00	62.20	31.00	5.90	0.70	0.29	1.47
I	0.91	159.13	52.03	31.99	13.86	2.12	1.43	3.04

4.1.2 Brine solutions

Three different brines in addition to pure water (Milli-Q water) were used for the produced water sample preparation, all with similar ionic strength (I = 2,0182). The brine composition and the calculation of the ionic strength are given in Appendix A and B respectively. The brines were prepared in Schott bottles (1000 ml). Synthetic brine contained various salts dissolved in Milli – Q water. The salts were dissolved in a specific order where the chlorides were dissolved first, then the sulphates and at the end the bicarbonate. NaCl brine and $CaCl_2$ brine consisted of only NaCl and Milli – Q water and $CaCl_2$ and Milli – Q water respectively. All the brines were stirred continuously in order to prevent precipitation.

4.2 Procedures

4.2.1 Produced water preparation

The pH of the brines was adjusted with NaOH and HCl to achieve the various pH values. Equivalent amounts of oil and brine were mixed together and the bottles were put in the shaker at a speed of 250 mot/min for 24 hours. Then the samples were poured in centrifugal tubes and centrifuged at 8000 rpm for 15 min. Most of the oil was removed with pipettes before gravity separators were used to get the final water phase completely separated from the oil. The pH of the samples was measured right after the preparation. All equipment was cleaned carefully and dried with air before use. For more detailed description about the produced water sample preparation see Appendix C.

The prepared produced water samples with their corresponding pH and brine are presented in the tables 7-9 in Appendix D. It was made 16 different produced water samples with three parallels each for crude oil B, 13 different produced water samples with three parallels each were made for crude oil F, and also 13 different produced water samples were made for crude oil I, but with two parallels each. All samples were analyzed with the bubble pressure tensiometer (BP 100) and UV-visible spectrophotometer. Two of the samples were also measured with the IR spectrophotometer.

4.2.2 Density measurements

It was necessary to measure the density of the produced water samples before the surface tension analysis since the density value has to be registered on the bubble pressure tensiometer in order to measure the surface tension.

For measuring the produced water samples a DMA-5000 density meter was used, see figure 9. The sample was injected with a syringe in the white tube to the left (next to the number 1), trying to not inject air bubbles along with the sample. Then the density measurements could start and the result was printed automatically. The sample was removed and the tube was cleaned automatically with toluene and petroleum ether.

Figure 9: Anton Paar DMA-5000 density meter. [42]

4.2.3 Dynamic surface tension measurement

The measurements of the dynamic surface tension were performed by KRÜSS Bubble pressure tensiometer BP100, see figure 10.

Figure 10: Krüss BP100 bubble pressure tensiometer. [43]

Before starting the measurement the capillary and the vessel were cleaned very well. First, the capillary and the vessel were rinsed with hot water, then with Milli-Q water and at the end dried with air. If contamination occurred, which could not be removed by water and Milli-Q water, isopropanol had to be used before rinsing with Milli-Q water and dried with air.

If the capillary was not hydrophobic, a coating to the inner wall of the capillary needed to be applied to prevent unclean bubble formation and measuring errors. This was done by moistening a piece of sand paper with a small amount of water and then passing the capillary tip perpendicular through the water drop on the sand paper applying a slight pressure. Then the capillary was rinsed well and dried with air. The inner capillary diameter had to be measured after each sanding because the sanding could change the capillary diameter.

The surface tension of water was always measured first making sure that the system was completely clean. After the capillary diameter and the water surface tension were measured and the results were good, the produced water samples could be measured.

The cleaned capillary was attached at the tensiometer and the cleaned vessel was filled with sample and placed in the sample holder. The holder was then moved upwards until the surface of the produced water almost touched the capillary. The needed parameters such as density, immersion depth, time range and stirring speed was filled in and the measurements of the sample could start. The experiments were done with: an immersion depth of the capillary of 10 mm, a bubble age ranging from 10ms – 100s and without stirring.

4.2.4 UV-spectroscopy measurement

The instrument had to be turned on 30 min before the measurement could start. The cuvettes were rinsed with Milli-Q water and acetone and dried with air. First both cuvettes were filled with solvent, which was brine, and measured to make sure that disturbances, absorbance in cuvettes and air in the instrument was removed. The cuvettes were cleaned again and the inner cuvette was filled with the reference and the outer cuvette was filled with the sample. Then the measurement was started. The samples for all the crude oils were diluted three times with the corresponding brine and pH before measuring.

4.2.5 Extraction procedure and IR-spectroscopy measurement

The procedure of extraction to prepare the samples for the IR analysis was basically done as described in the study of Adam T. Lewis et al. [44] Two samples were chosen for preparation and analysis on the IR spectroscopy, crude oil B and synthetic brine with pH 4 and crude oil B and pure water with pH 4. The procedure is described for one sample. The three parallels from the sample were mixed together to achieve 80 ml of produced water in total. Then HCl (2 ml) was added and at last the solvent, which was 70:30 cyclo hexane/butyl acetate, (8 ml) was added. The mixture was shaken for about 1 min and then poured into a separation funnel. In order to allow the layers to separate completely the final steps of the preparation were done the day after. An illustration of the two layers is presented in figure 11. When the layers were completely separated, the top layer, i.e. the organic phase, was separated from the aqueous phase and dried with N_2 gas to remove extraction solvents. After the drying the sample was ready to be analyzed on the IR spectroscopy.

Figure 12: Fourier-Transform (Mid) Infrared Spectrophotometer. [45]

Figure 11: Illustration of the organic phase and the aqueous phase.

The instrument used was a fourier-transform (Mid) infrared spechtrophotometer called Tensor 27 which was equipped with a Bruker Golden Gate diamond ATR (Attenuated Total Reflection) cell, see figure 11. The cell was first cleaned with ethanol and wiped with paper before one drop of the sample was added to the cell. After the drop had dried another drop was added. When the second drop had dried a third drop was added etc. Six drops were added in total before the sample was measured.

5. Results and discussion

5.1 Challenges during the lab work period

Not many issues encountered during the period with lab work, but still there were some difficulties that are worth mentioning. At the beginning the intention was to make produced water samples with three different crude oils, three different brines and pure water (Milli – Q water), and six different pH values. Therefore, the produced water samples made with crude oil B and $CaCl_2$ brine, which was the starting crude oil and brine, has pH values of 2, 4, original, 10 and 12. The original pH was the natural pH of the brines and can be found in the tables 7-9 in Appendix D. It was also intended to make samples with pH 8, but due to problems with adjusting the pH of the brine this was not possible. However, after having made samples with three different brines the number of pH values was reduced to three. It appeared from the first results that the influence of the pH on the produced water was quite similar in the pH range of 4 to 8. Consequently, it was decided that the extreme pH values like 2 and 10 or 12 were the most interesting ones in addition to the original pH. In the beginning produced water samples with pH 12 was made, but it appeared that precipitation occurred above pH 10 for all brines except for $CaCl_2$ brine. For synthetic brine the precipitation occurred already above pH 8. This may be due to the fact that synthetic brine contains more metal cations which may result in hydroxide precipitation with metal cations and most probably $Mg(OH)_2$ is the precipitate since Ca^{2+} and Na^+ dissolves at higher pH values than 8. Figure 12 shows how the samples looked like after centrifuging. For the produced water samples made with crude oil F and I, it was necessary to centrifuge more than just once, and for some samples the centrifuging needed to be done several times which ended up being very time consuming. But this was necessary to get as much produced water out of the sample as possible.

Figure 13: Illustration of precipitation of a produced water sample after centrifugation.

5.2 The surface tension of the brines and pure water

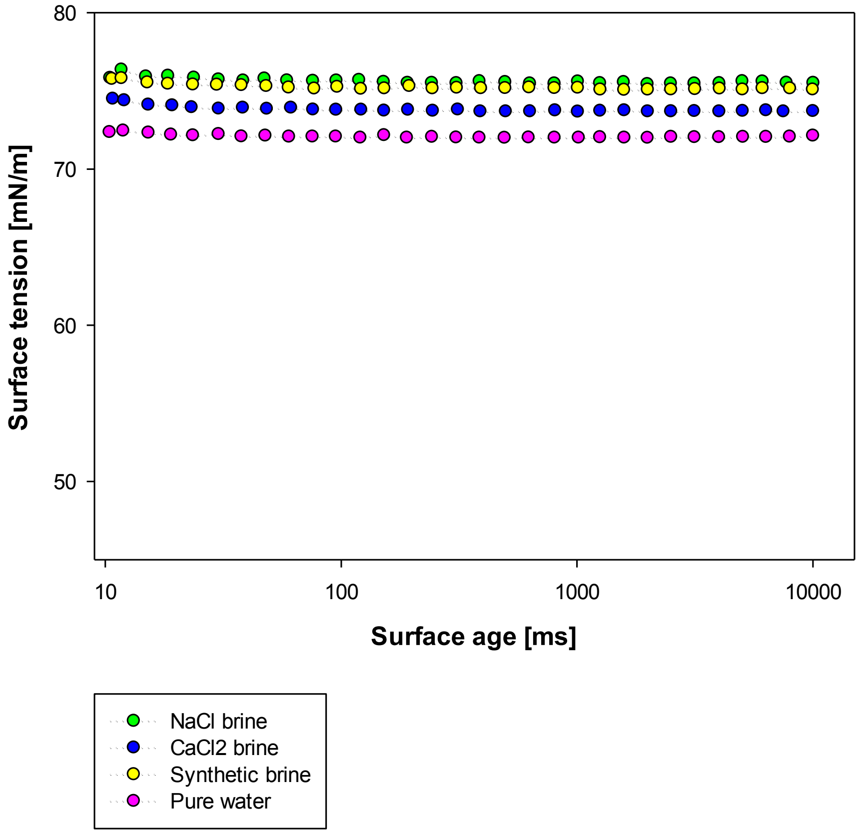

Figure 14: The surface tension of the various brines with their natural pH.

Figure 13 presents the surface tension of the various brines with their natural pH values. The surface tension of synthetic brine with the pH 2, 4, original and 8 has been measured in an earlier study [46] , and it was founded that the pH itself did not affect surface tension. That is the reason why it is not necessary to measure the brines with all the various pH values. According to this figure it is clear that presence of salt in the water results in higher surface tension than that of pure water. The reason why NaCl brine and synthetic brine have higher surface tension than $CaCl_2$ brine may be due to the fact that the Ca^{2+} ions are more hydrated than the Na^+ ions. This means that the Ca^{2+} ions will rather be in the bulk phase than at the surface and thus the surface tension of Ca^{2+} will be more equal to the surface tension of water. This is in accordance with section 2.4.3. However, there is no decrease in surface tension during the measurement which indicates that it is the compounds from the crude oil that contributes to the changes in surface tension.

5.3 Crude oil I

5.3.1 The effect of pH

The results of the dynamic surface tension measurements of produced water samples with crude oil I are presented in figure 14-17. They show how the pH of the brines influences the surface tension of produced water. Each curve represents the average value of the three parallels for each sample. The reproducibility of the bubble pressure tensiometer (BP 100) with the produced water sample made with crude oil B and synthetic brine with pH original is given in Appendix E which shows that the results from BP 100 are reliable (standard deviation is 4,178).

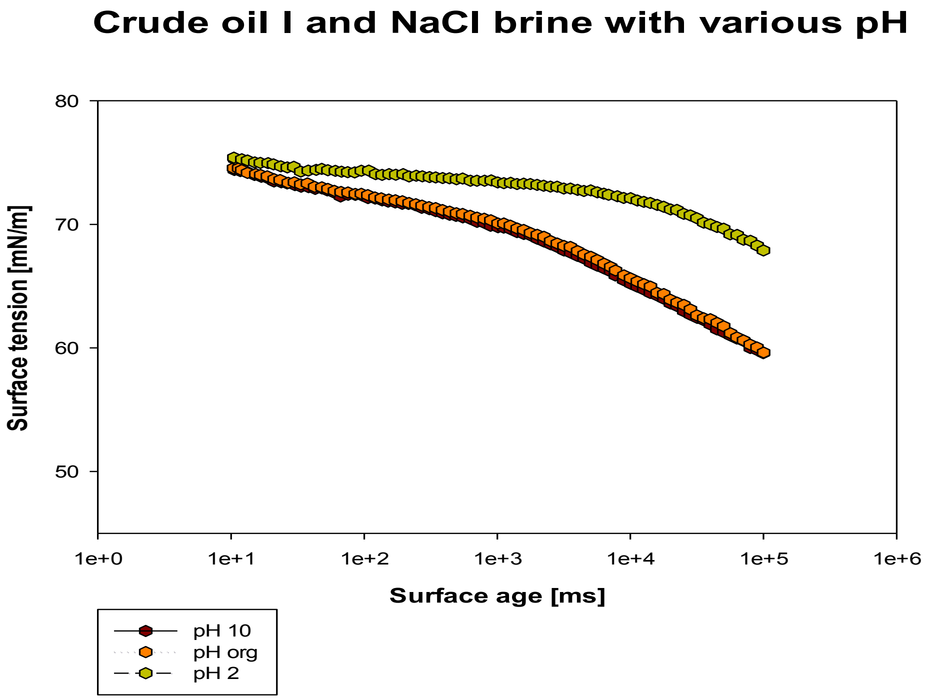

Figure 15: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I and NaCl brine with various pH.

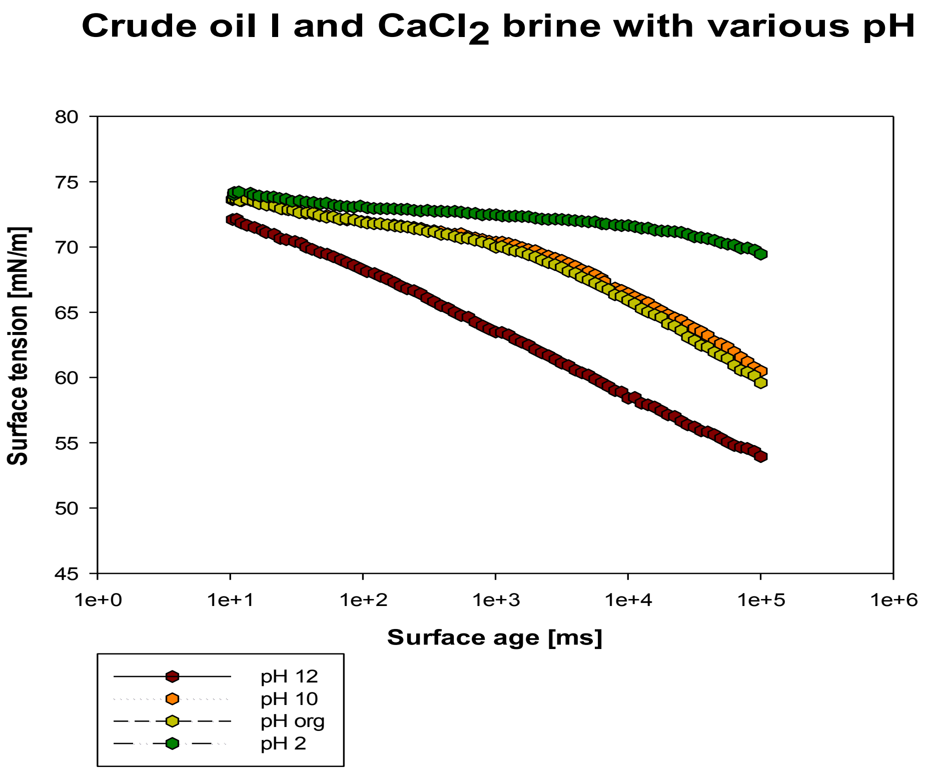

Figure 16: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I and $CaCl_2$ brine with various pH.

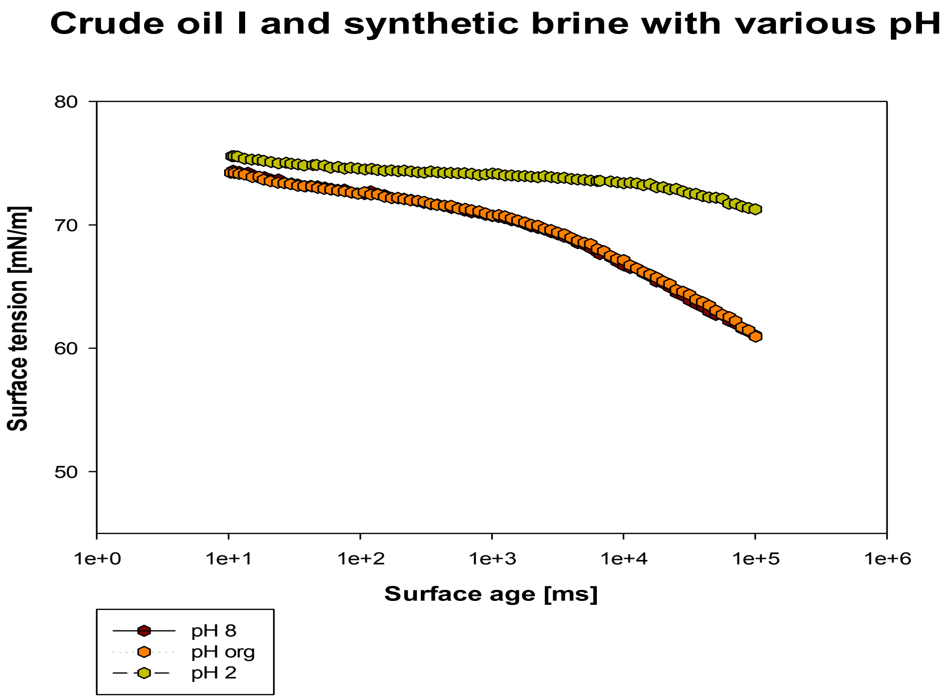

Figure 17: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I and synthetic brine with various pH.

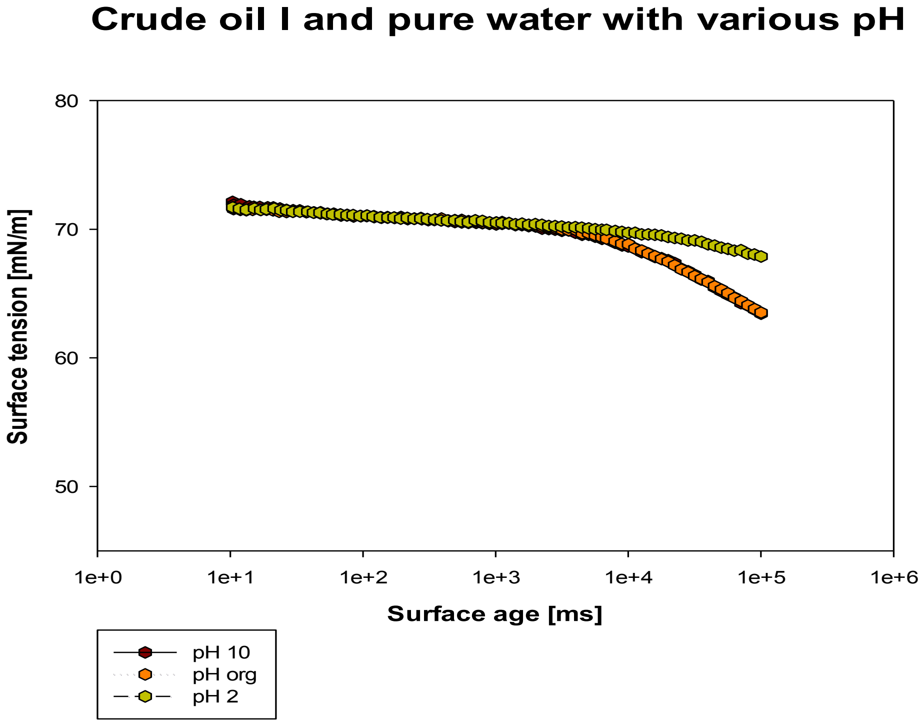

Figure 18: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I and pure water with various pH.

The results in surface tension for crude oil I show very evident trends. The decrease in surface tension is very little at low pH, but as the pH increases the decrease in surface tension is more significant. This applies to all three brines and pure water. From the figures it clearly takes time before the decrease in surface tension is considerable. This is because the surface active compounds need time to diffuse from the bulk phase to the surface and according to section 2.3 this was expected. When the surface active compounds have adsorbed at the surface they cause a decrease in surface tension.

The samples with pH 2 have high surface tension and it decreases very little during the measurement. The reason for this might be that the components that have diffused from the oil phase to the water phase under low pH conditions are less surface active or that the concentration of surface active compounds are lower. According to section 2.4.1 basic compounds are most likely to be present in solutions with low pH values. It may be that the bases in crude oil I are less surface active than the acids.

At the original pH and pH 10 the decrease in surface tension is similar and it is larger than for pH 2. This might be explained by the fact that under high pH conditions dissociated acidic compounds will most likely be in the water phase and in the presence of ions they will reduce the surface tension, see section 2.4.3. Since the surface tension is similar for pH original and pH 10 it seems like the concentration of surface active compounds or type of surface active compounds in the water phase are similar at this pH range. The sample with $CaCl_2$ brine with pH 12 shows an even larger decrease in surface tension compared to pH 10. This may indicate that the components present in the water phase at pH 12 are even more surface active than the components at pH 10 or that the concentration of surface active components are higher at pH 12.

5.3.2 The effect of brine composition

Figure 18-20 show how the composition of the brine influences the surface tension of produced water at pH 2, pH original and pH 10 respectively. Each curve represents the average value of the three parallels for each sample.

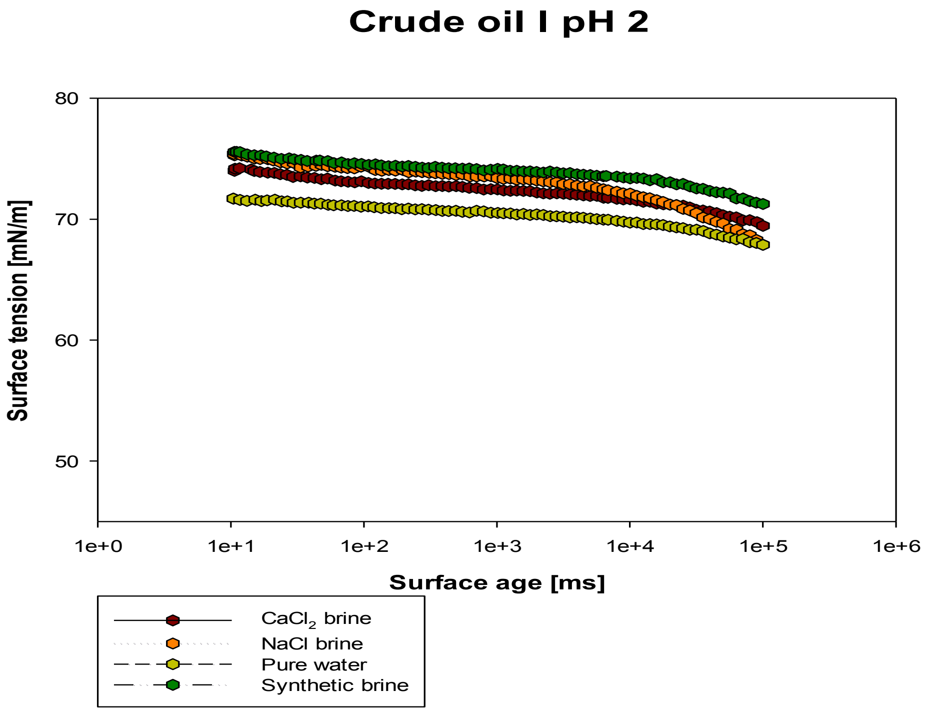

Figure 19: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I, pH 2 and various brine composition.

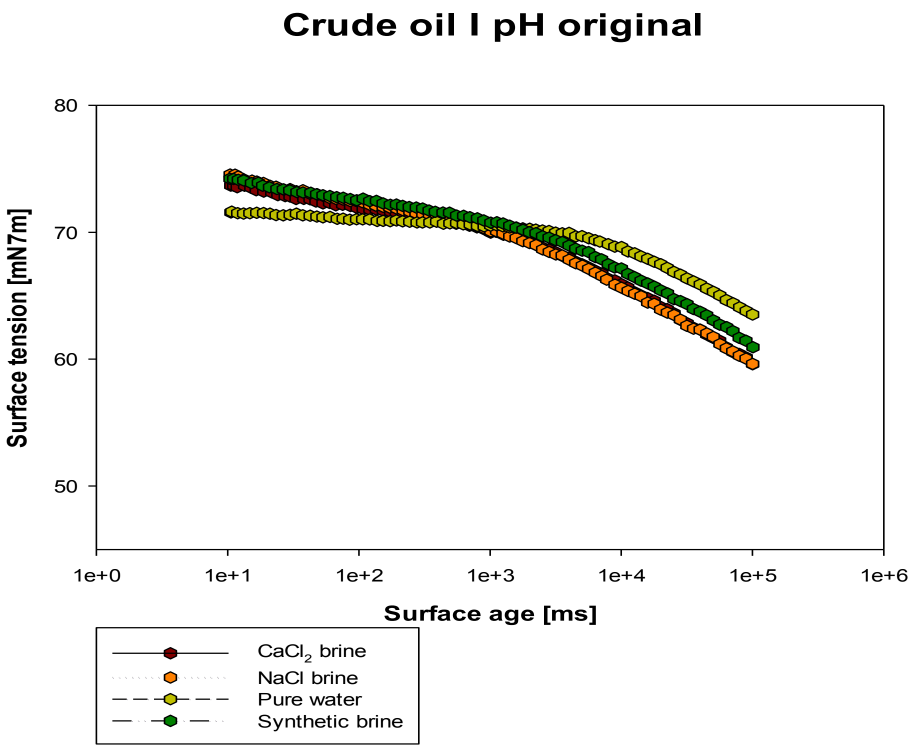

Figure 20: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I, pH original and various brine composition.

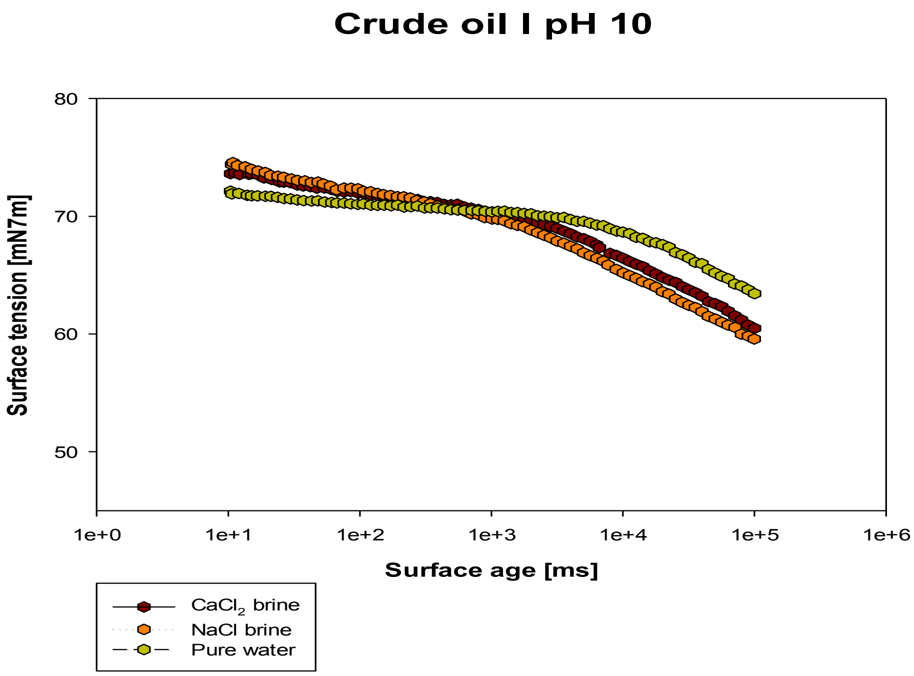

Figure 21: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil I, pH 10 and various brine composition.

The difference in brine composition does not seem to have that much influence on the surface tension. According to the figures the various brines have quite similar surface tension for the various pH values. For pH 2, pure water has the lowest surface tension, which might be due to the fact that when salts and bases are present in water they will increase the surface tension. This is in accordance to section 2.4.3. The three brines have similar surface tension at pH 2.

Figure 19 and figure 20 show the surface tension of the different brines at pH original and pH 10. The curves have similar behavior and they have more decrease in surface tension than at pH 2. NaCl brine and $CaCl_2$ brine starts at same surface tension value and they have the same decrease in surface tension. Pure water starts at a lower surface tension value but does not have as much decrease as the other brines. Acids are most likely to be present in the water phase at high pH values and this might explain why the decrease in surface tension is higher for the brines containing salts compared to pure water. The presence of salt promotes dissociation of acids which in turn reduces the surface tension. This is explained in section 2.4.3. However, the difference of pure water and the brines are not big and therefore it seems like the brines and pure water have the same influence on surface tension at pH original and pH 10.

5.3.3 Results of the UV - visible

The results of the UV-visible measurements of produced water samples with crude oil I are presented in figure 21-24. Each curve represents the average value of the three parallels for each sample. The reproducibility of the UV-visible spectrophotometer with the produced water sample made with crude oil B and synthetic brine with pH original is given in Appendix F which shows that the results from UV-visible are reliable.

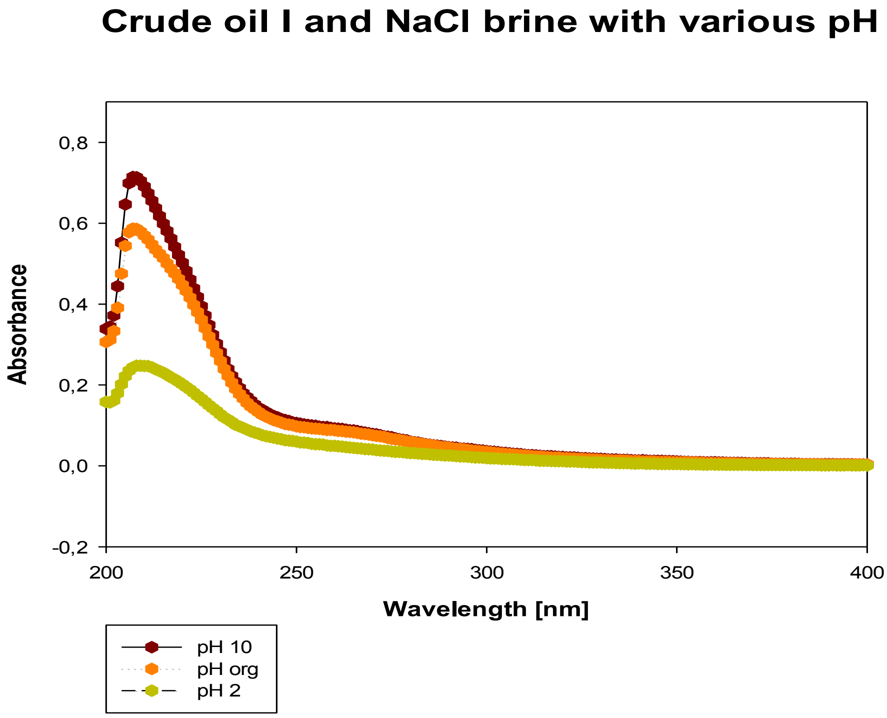

Figure 22: UV spectra of produced water with crude oil I and NaCl brine with various pH.

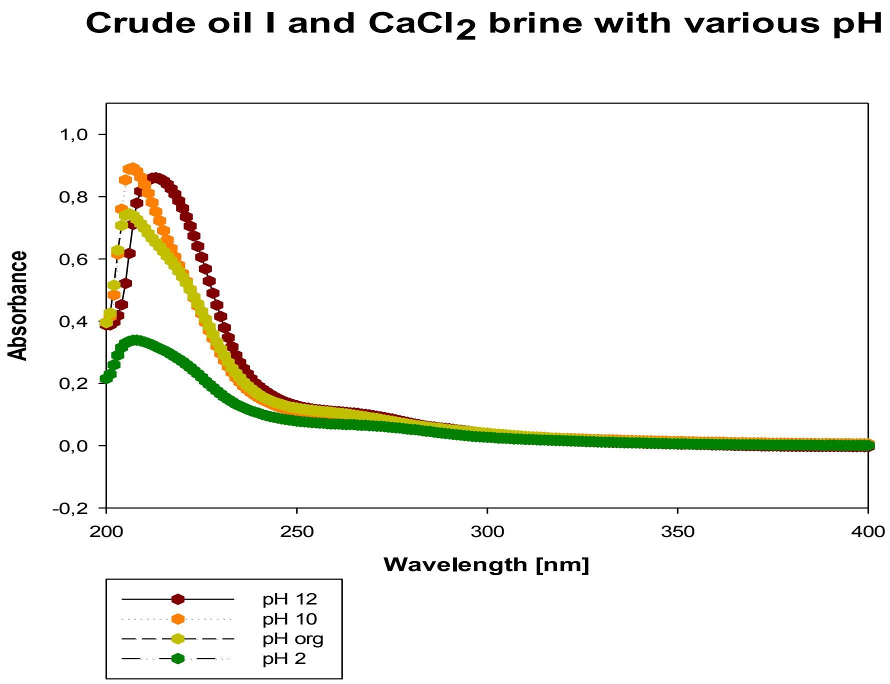

Figure 23: UV spectra of produced water with crude oil I and $CaCl_2$ brine with various pH.

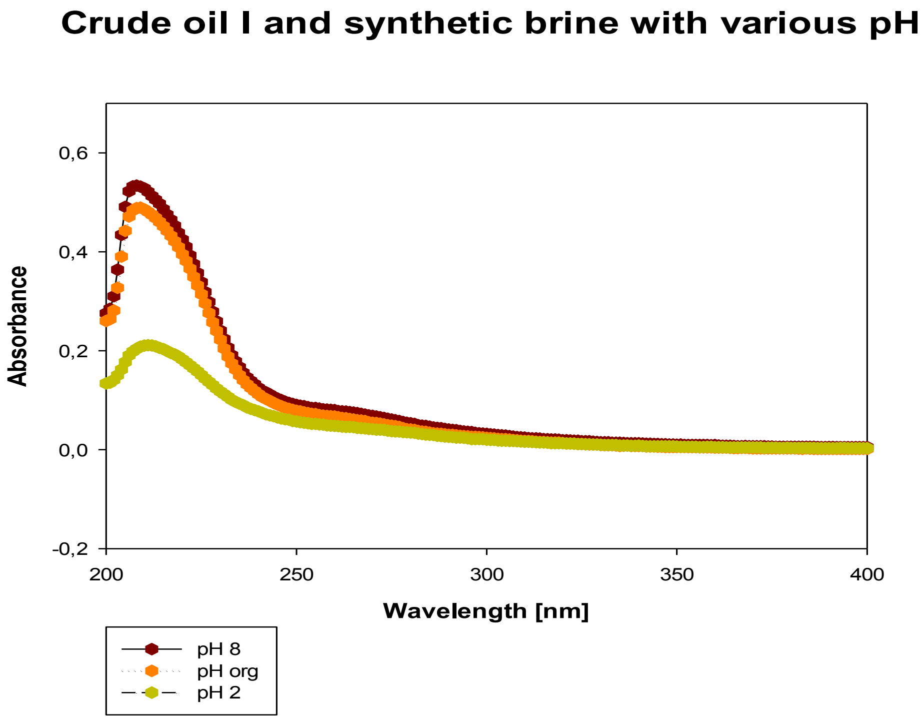

Figure 24: UV spectra of produced water with crude oil I and synthetic brine with various pH.

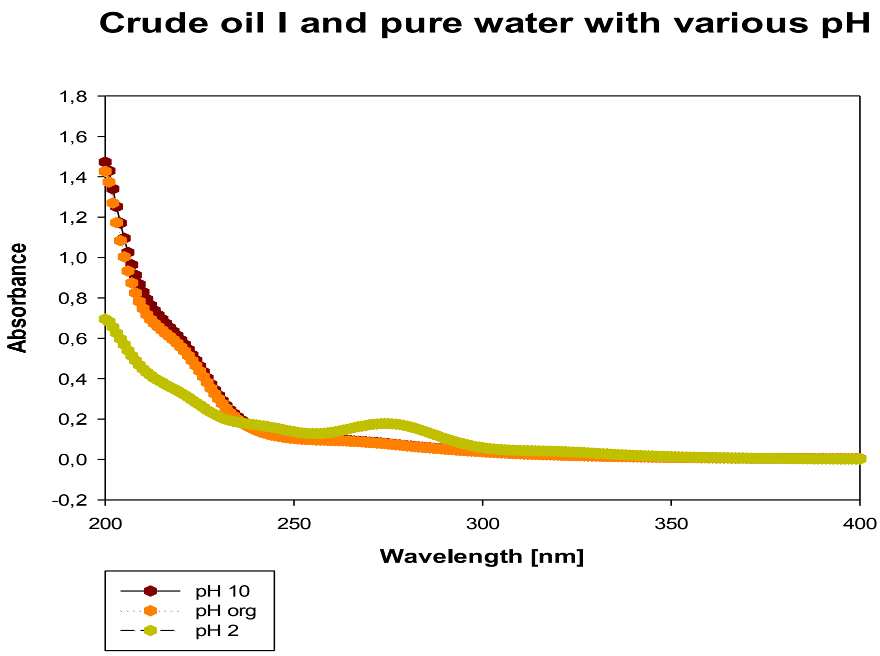

Figure 25: UV spectra of produced water with crude oil I and pure water with various pH.

The figures show that all the samples have almost the same type of curve with one peak at around 210 nm. This indicates that the produced water samples made with crude oil I contain the same kind of compounds. The UV results might suggest that same type of compounds is in the water phase at both low and high pHs, although the theory says that bases are most likely present at low pH values and acids at high pH values. The sample with pure water and pH 2 has a peak around 275 nm which is not seen in the other curves. This might say that this sample has an additional compound present in the water phase, but it might not necessarily have to be surface active. The peaks show quite low absorption and the peak representing pH 2 is the lowest. This might indicate that the compounds absorbing at this wavelength are present in low concentrations in the water phase at pH 2 which can help explain the small decrease in surface tension.

5.4 Crude oil B

5.4.1 The effect of pH

The results of the dynamic surface tension measurements of produced water samples with crude oil B are presented in figure 25-28. The figures show how the pH of the brines affects the surface tension of produced water.

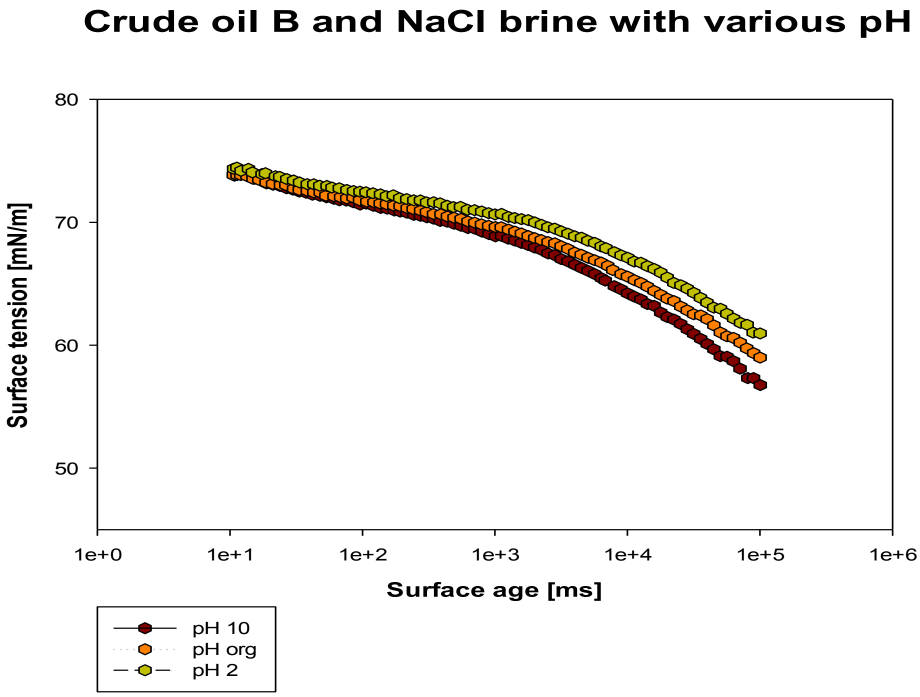

Figure 26: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B and NaCl brine with various pH.

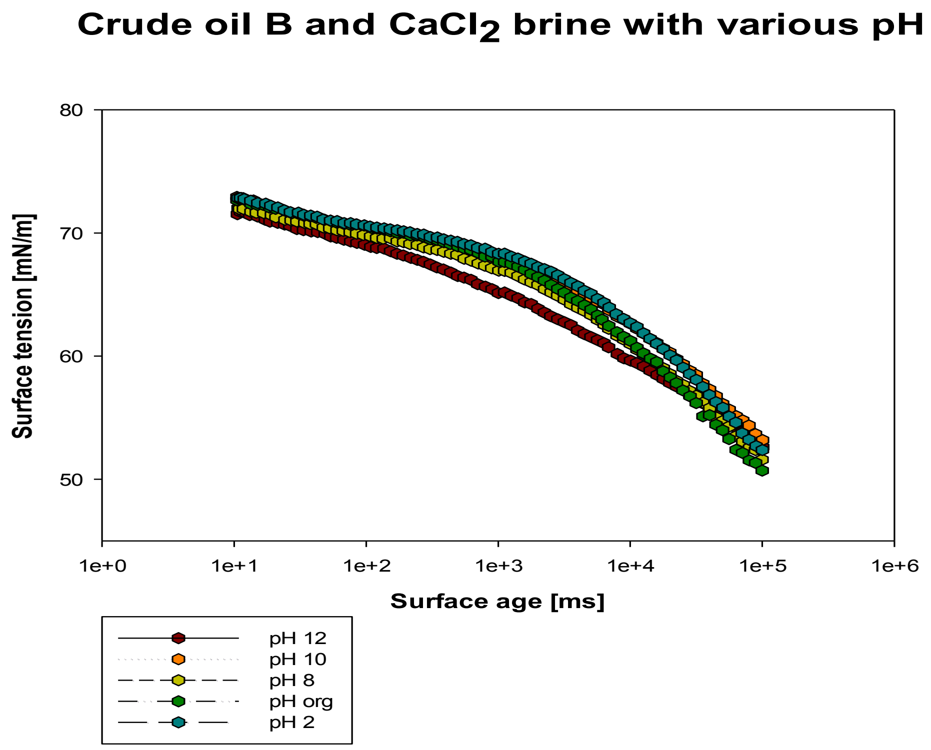

Figure 27: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B and $CaCl_2$ brine with various pH.

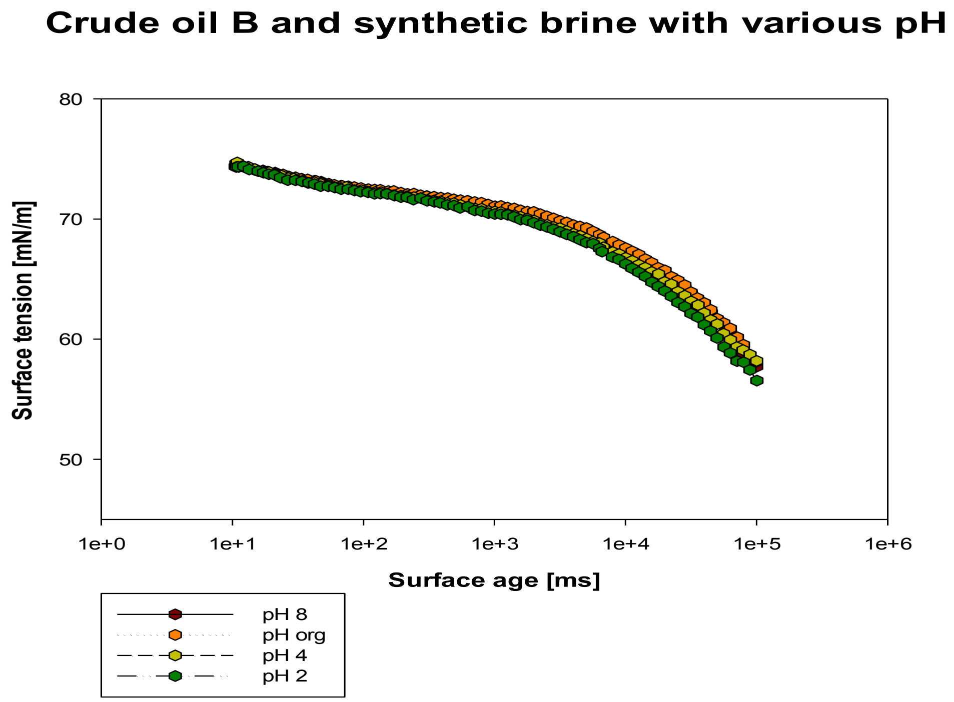

Figure 28: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B and synthetic brine with various pH.

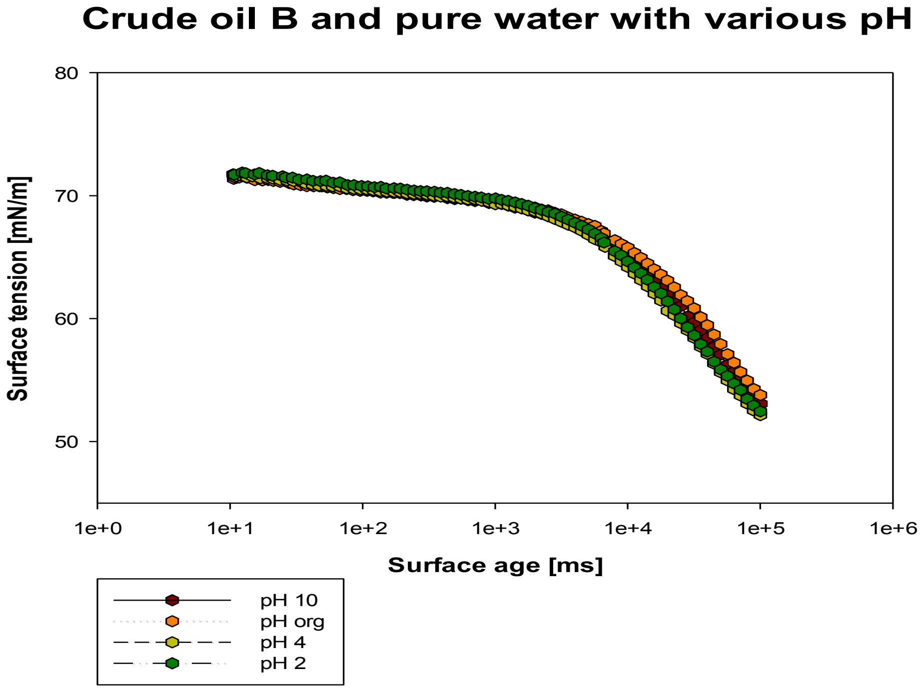

Figure 29: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B and pure water with various pH.

For crude oil B there is almost no difference in surface tension for the samples with the various pH values. Figure 24 which represents the NaCl brine shows the greatest difference where pH 10 has most decrease in surface tension and pH 2 has least decrease, which can be due to the acids present in the water phase at higher pH values, see section 2.4.3. However, here as well the differences are so small that they are negligible. This means that in the case of crude oil B the various pH values have the same influence on the surface tension. It might be that the acids and bases in this crude oil are not that water soluble and it might be other surface active compounds, like phenols, that have diffused to the water phase and influenced the surface tension. It seems like the compounds that are present in the water phase for the three brines and pure water are equally surface active for all the various pH values. It can be that they contain same type of compounds or same concentration of surface active compounds.

5.4.2 The effect of brine composition

Figure 29-31 show how the composition of the brine influences the surface tension of produced water at pH 2, pH original and pH 10 respectively.

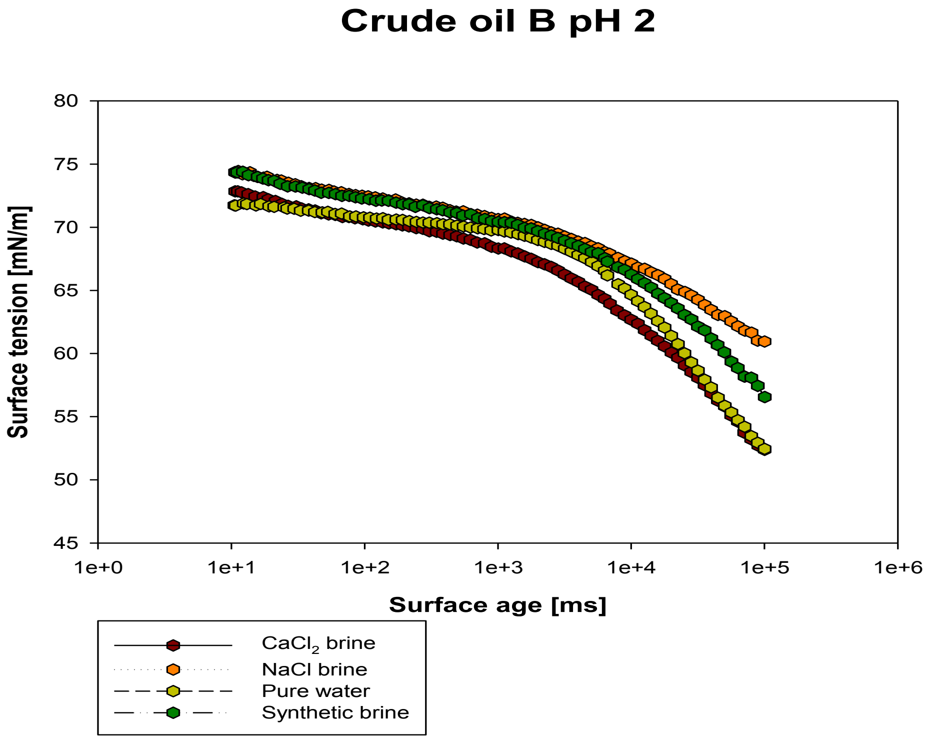

Figure 30: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B, pH 2 and various brine composition.

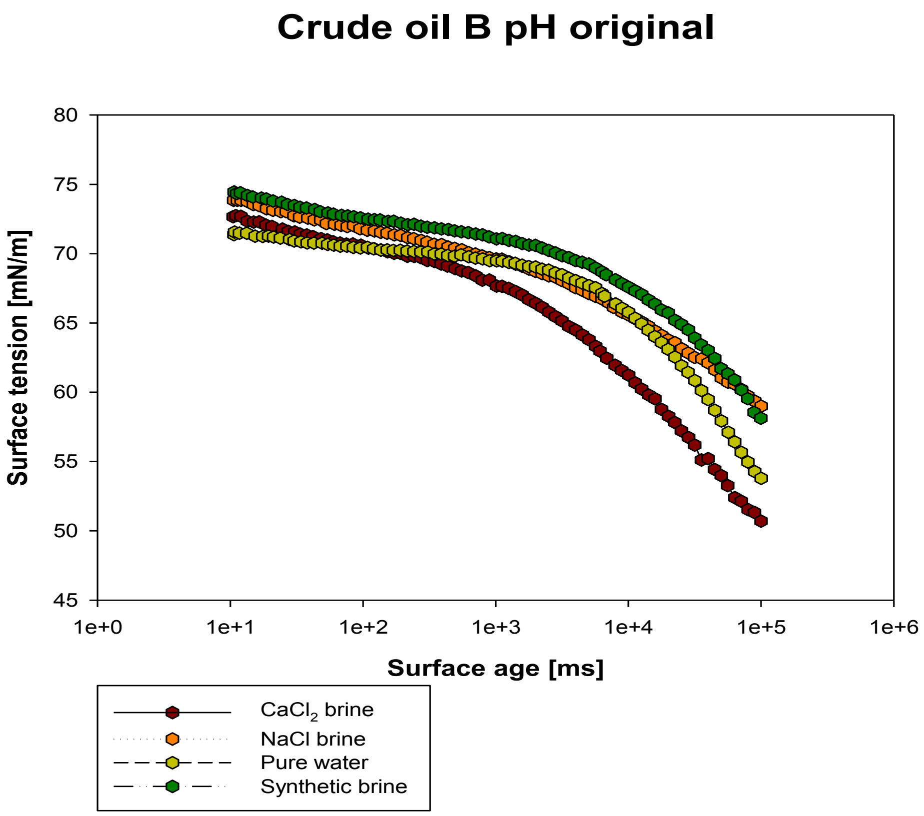

Figure 31: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B, pH original and various brine composition.

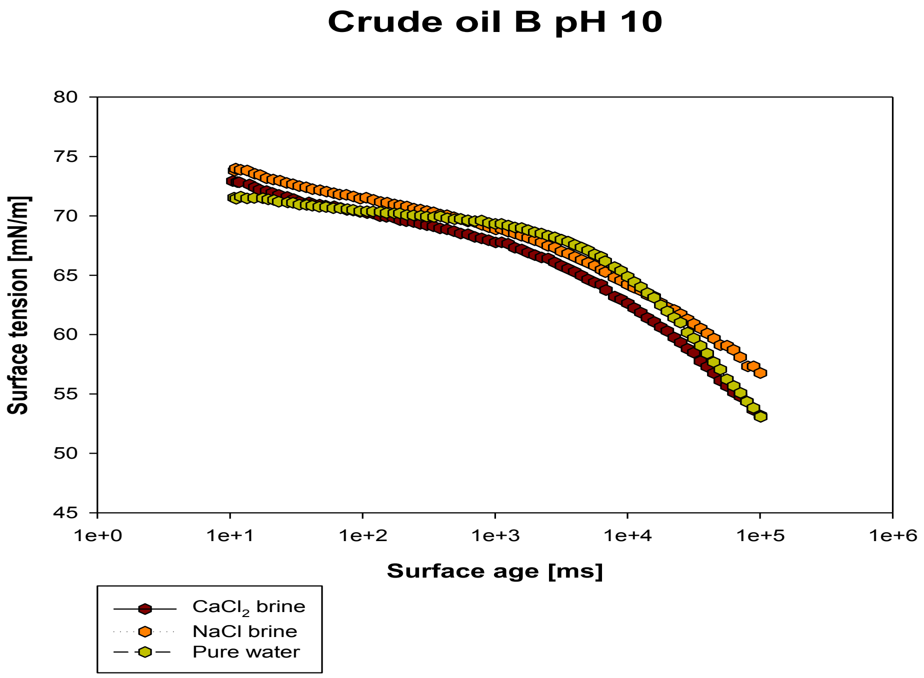

Figure 32: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil B, pH 10 and various brine composition.

From the figures it is clear that the differences in brine seem to have most influence at the lowest pH values like pH 2 and pH original. However, the difference is not very big. Figure 31 shows that at pH 10 the various brines give quite similar surface tension.

By comparing pure water, NaCl brine and synthetic brine it appears that water have more decrease in surface tension than both the two brines which might be a result of salting-out effect. NaCl is a structure making salt which can decrease the solubility of non-polar organic compounds. This means that lower amount of surface active components will diffuse to the water phase when NaCl is present and thus the surface tension will not decrease as much as for pure water, see section 2.4.2 and 2.4.3.

It might also be noteworthy that the $CaCl_2$ brine has the lowest surface tension for all pH values, although it is not that much lower compared to the other brines. This is most prominent in the case of pH original and might be due to two conditions. The Ca^{2+} ions can promote adsorption of organic molecules at the surface which will reduce the surface tension or they can form complexes with the acids which are surface active and more water soluble than oil soluble, see section 2.4.1 and 2.4.3. However, this does not apply for the results of pH 10 and therefore the explanation given above for pH original cannot be stated for sure.

5.4.3 Results of the UV – visible

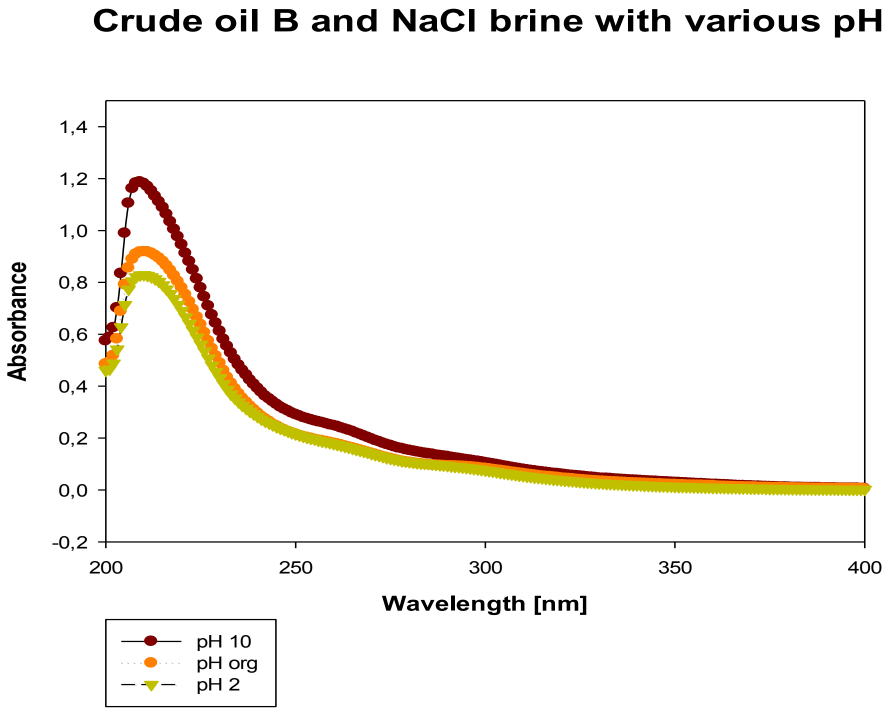

Figure 33: UV measurements of produced water samples prepared with crude oil B and NaCl brine with various pH.

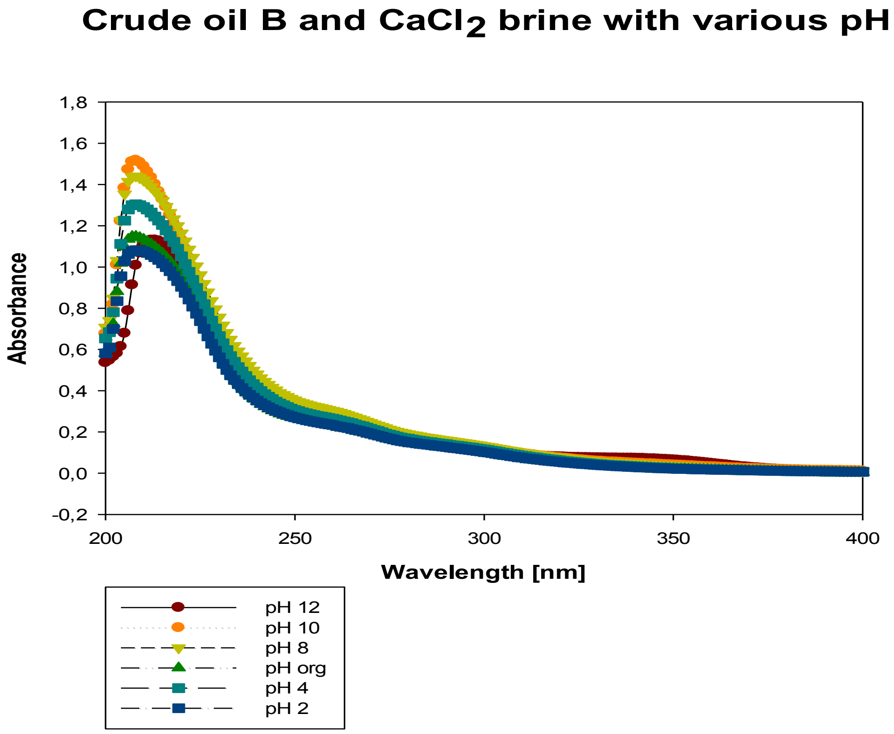

Figure 34: UV measurements of produced water samples prepared with crude oil B and $CaCl_2$ brine with various pH.

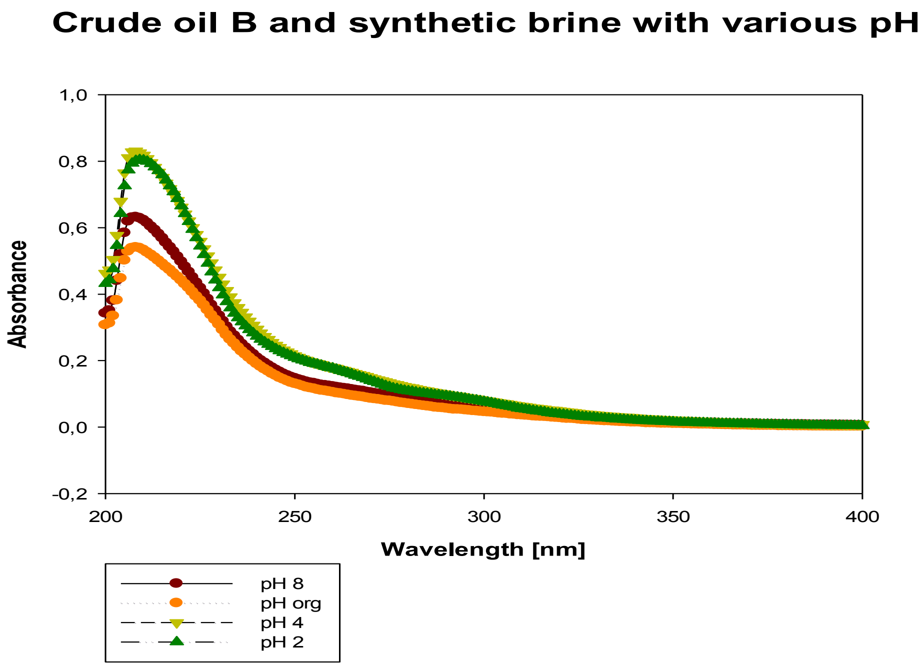

Figure 35: UV measurements of produced water samples prepared with crude oil B and synthetic brine with various pH.

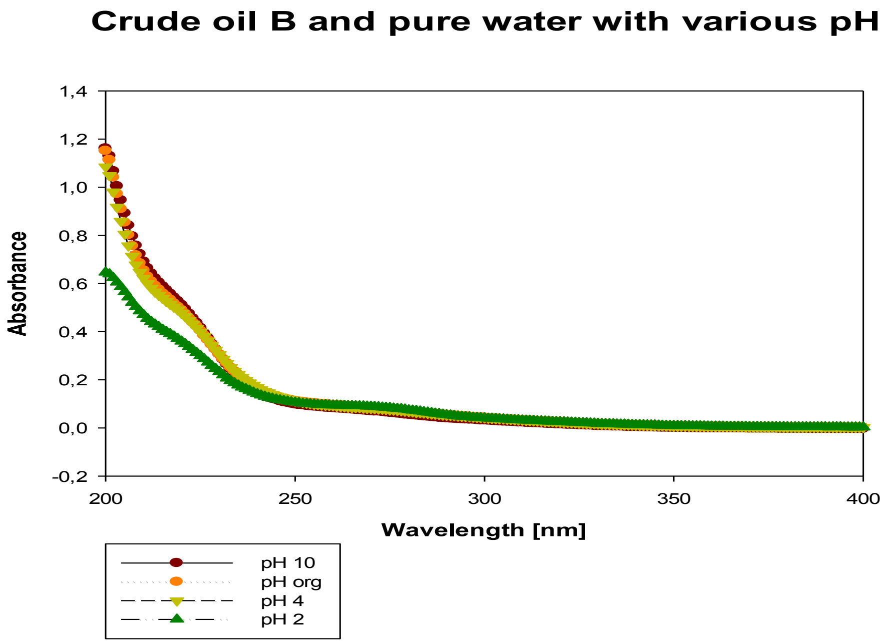

Figure 36: UV measurements of produced water samples prepared with crude oil B and pure water with various pH.

The results of the UV – visible measurements for crude oil B are presented in figure 32-35. Like crude oil I the samples of crude oil B show the same type of curve with one peak at around 210 nm, which implies that the produced water samples of crude oil B contains the same kind of compounds. There is a little difference in absorption for the various pH values, and pH 2 has the lowest absorption. This might be due to that the concentration of compounds that absorb at this wavelength is low. However, the difference is not very big. This applies for all three brines and pure water. According to figure 33, which shows that $CaCl_2$ brine have slightly higher absorption compared to the other brines, relates to the surface tension results where $CaCl_2$ brine had the lowest surface tension. In general, all figures show low absorption and same type of curve which is in accordance to the bubble pressure results which showed quite similar surface tension for the various pHs and brines.

5.5 Crude oil F

5.5.1 The effect of pH

The results of the dynamic surface tension measurements of produced water samples with crude oil F are presented in figure 36-39. The figures show how the pH of the brines affects the surface tension of produced water.

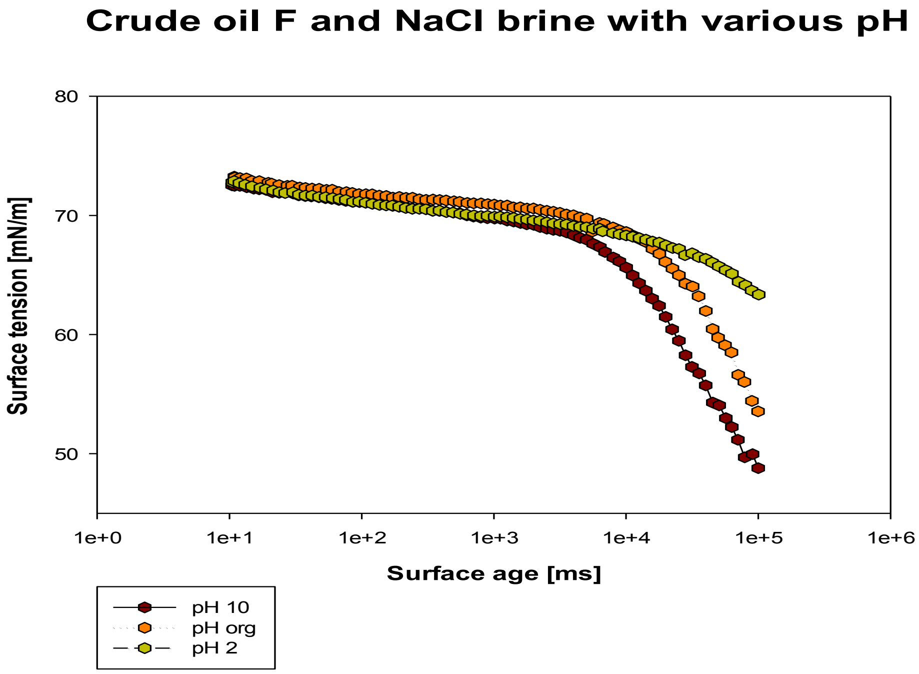

Figure 37: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F and NaCl brine with various pH.

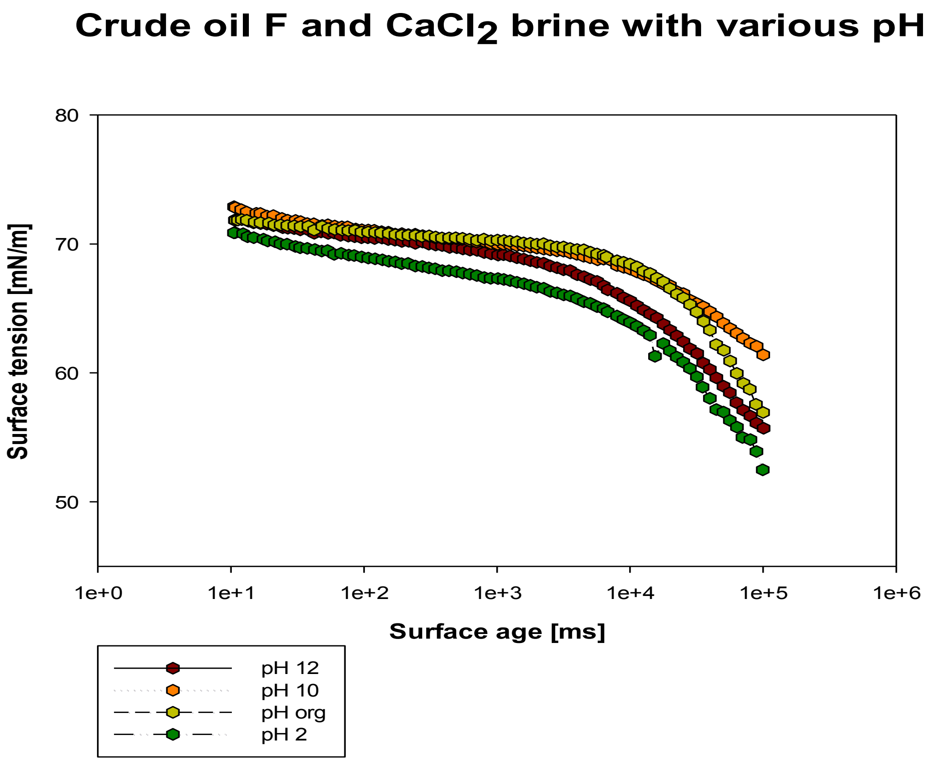

Figure 38: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F and $CaCl_2$ brine with various pH.

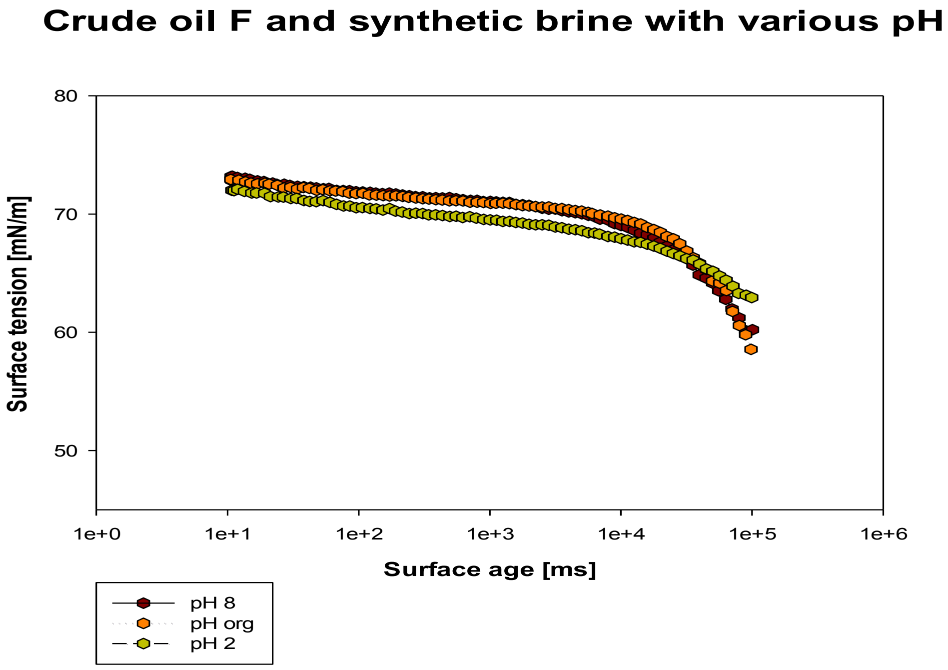

Figure 39: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F and synthetic brine with various pH.

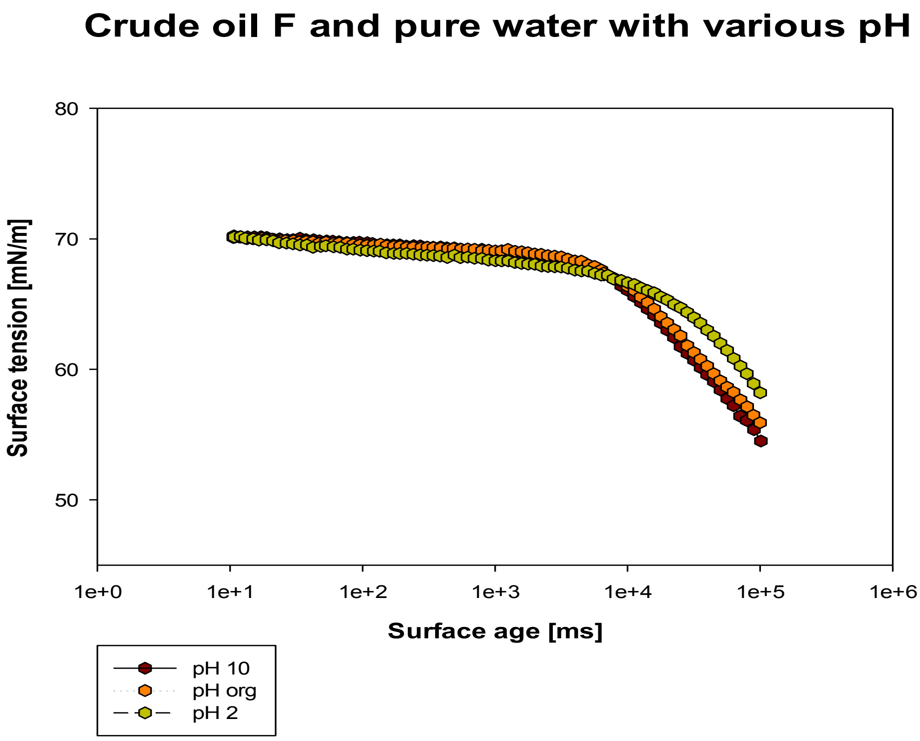

Figure 40: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F and pure water with various pH.

The results in surface tension for crude oil F do not show any obvious trends. Figure 36 shows that pH 10 give most decrease in surface tension, whereas pH 2 give smallest decrease in surface tension in the presence of NaCl. This is in agreement with section 2.4.1 and 2.4.3 which states that at high pH values it is the acidic compounds that govern the surface tension, and in presence of Na^+ ions the dissociation of acids at the surface is promoted which results in reduction of the surface tension. Compared with the other brines, NaCl brine gives more significant changes in surface tension at the different pH values. The results might indicate that different kind of surface active compounds or various amounts of surface active compounds are present at the different pH values.

The other brines, on the other hand, exhibit different behavior for the various pHs. The synthetic brine show very similar surface tension for all pH values. It takes some time before any significant decrease occurs and the decrease is similar for all pHs, see figure 38. Pure water shows the same trend, where all the pH values have similar surface tension at the beginning and after a while the surface tension reduces. The two highest pH values have more decrease than pH 2, but the difference is not very big. See figure 39. This implies that the same kind of surface active compounds or the same concentration of surface active compounds are present in the water phase regardless the pH of the brine.

When $CaCl_2$ brine is present pH 2 has the lowest surface tension, while pH 10 has the highest surface tension. The reason for the high surface tension of pH 10 might be that the Ca^{2+} ions have formed complexes with the dissociated acids and that they might be oil soluble rather than water soluble. However, pH 12 has almost as low surface tension as pH 2 and it is therefore difficult to see any trends for this brine and say something specific about the results. Nevertheless, the differences in surface tension between the pH values are not very big, see figure 37.

5.5.2 The effect of brine composition

Figure 40-42 show how the composition of the brine influences the surface tension of produced water at pH 2, pH original and pH 10 respectively.

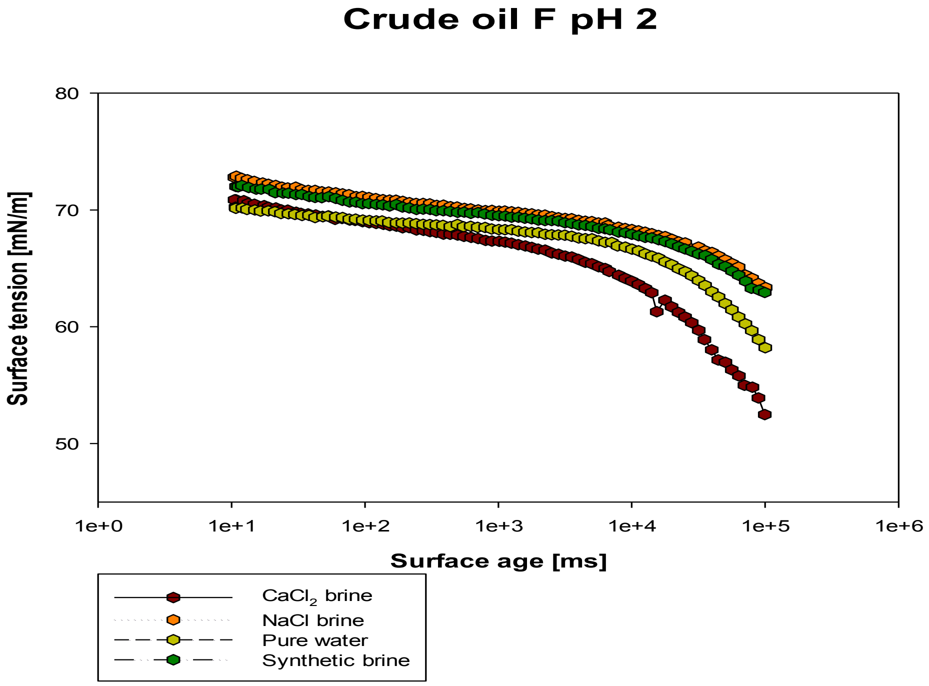

Figure 41: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F, pH 2 and various brine composition.

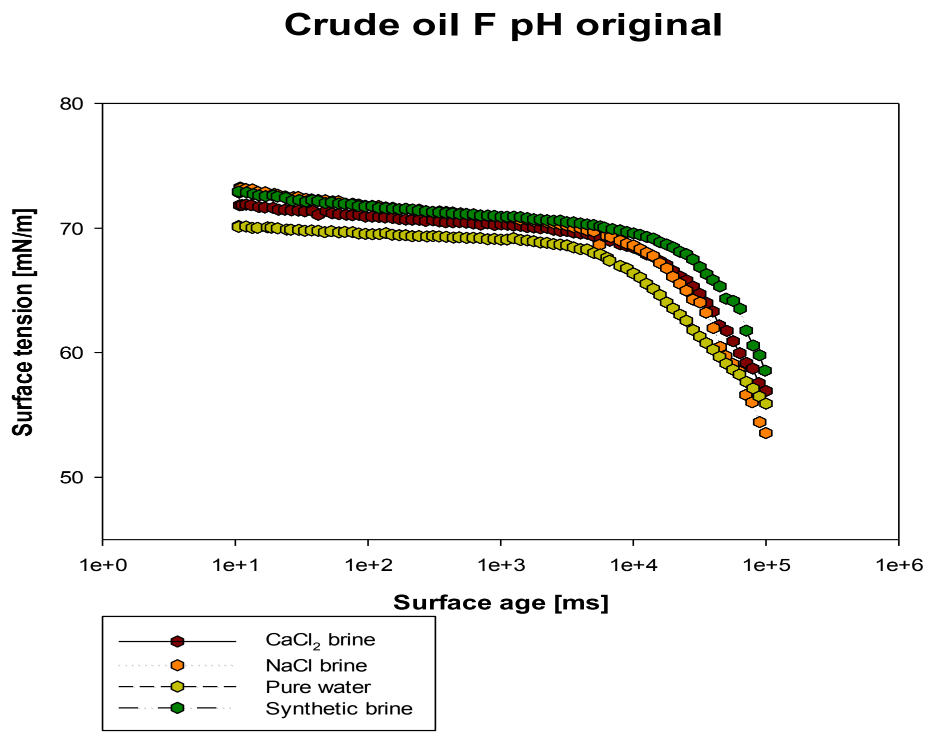

Figure 42: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F, pH original and various brine composition.

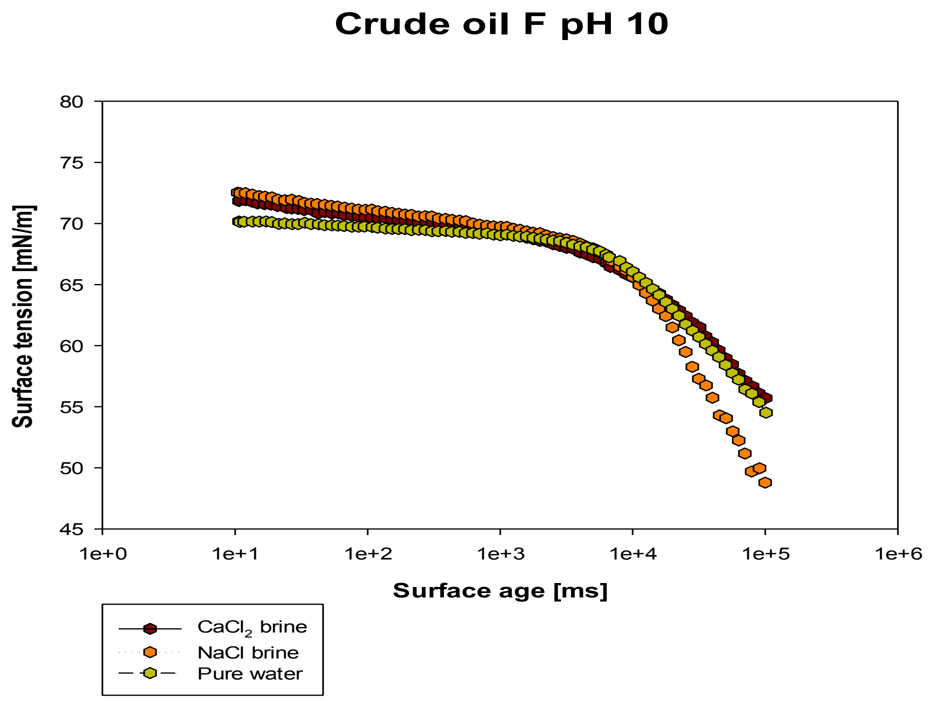

Figure 43: Dynamic surface tension as a function of surface age of produced water samples prepared with crude oil F, pH 10 and various brine composition.

At pH 2, when bases are most likely present, the $CaCl_2$ brine has most decrease in surface tension while NaCl brine and synthetic brine have the highest surface tension and least decrease, see figure 40. As mentioned in section 2.4.3, the surface tension will increase in presence of salts and bases compared to the surface tension of water. In the case of NaCl brine and synthetic brine this correlates, but in the case of $CaCl_2$ it does not. It is difficult to know why the result of $CaCl_2$ brine is like this. It can be that there are some very surface active compounds other than acids and bases that are present in the water phase at pH 2.

Figure 41 and 42 shows that the samples with higher pH values have similar surface tension for all the brines. At pH original pure water give the lowest surface tension and synthetic brine the highest. Nevertheless, the difference is not very big between the various brines, and at the end of the measurement it seems like they are getting more and more similar. Further, pH 10 shows an even more similar trend of the surface tension for the various brines. They have the same curve at the beginning and after some time they show a decrease in surface tension. At the end, NaCl brine show a more rapid decrease than pure water and $CaCl_2$ brine. In general there is no obvious trend regarding the surface tension for the different brines. They are very similar at high pH values, but have more differences at low pH values.

5.5.3. Results of the UV - visible

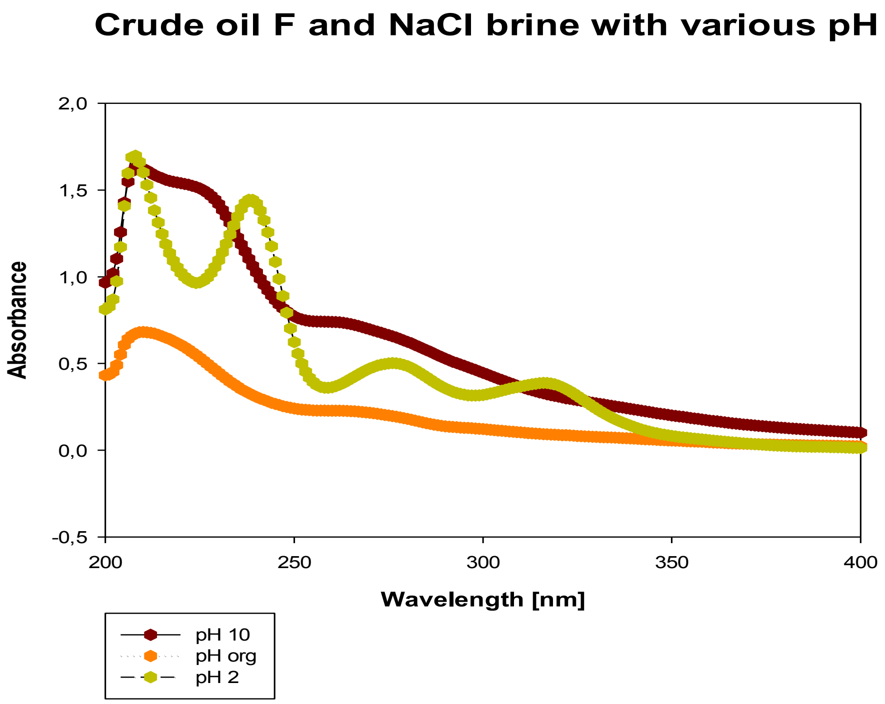

Figure 44: UV measurements of produced water samples prepared with crude oil F and NaCl brine with various pH.

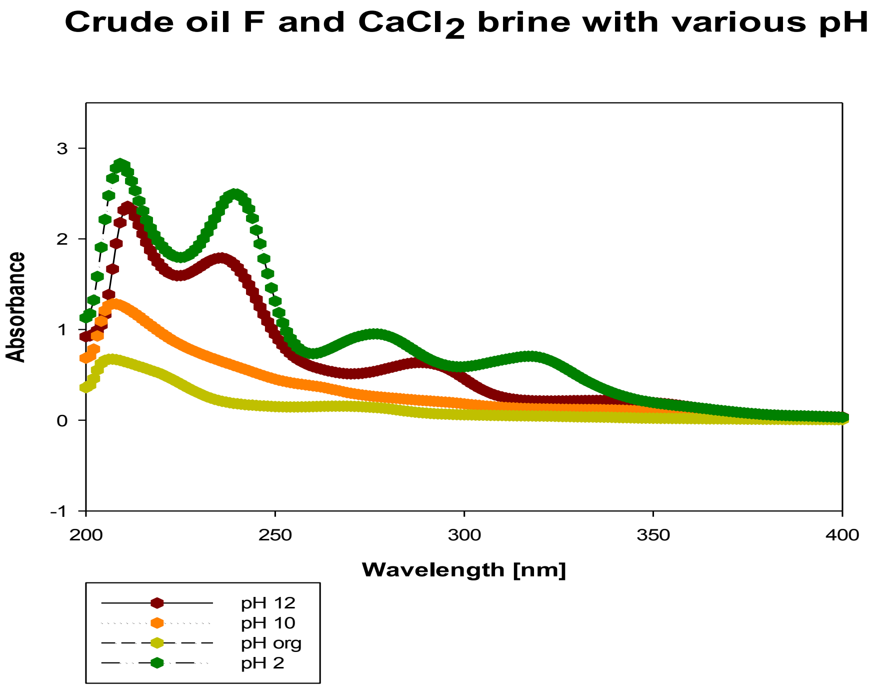

Figure 45: UV measurements of produced water samples prepared with crude oil F and $CaCl_2$ with various pH.

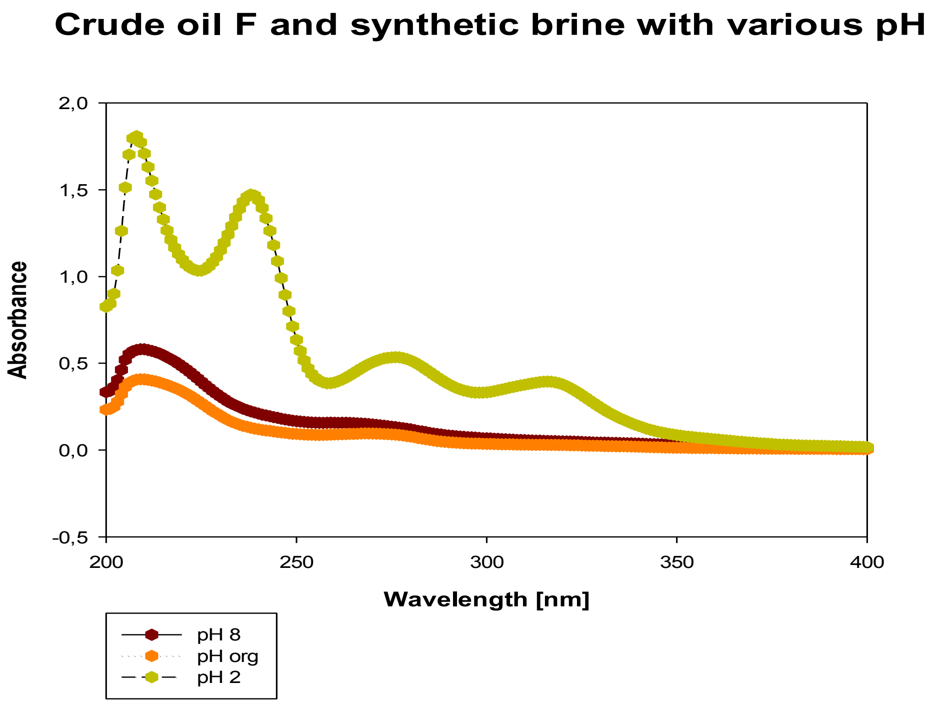

Figure 46: UV measurements of produced water samples prepared with crude oil F and synthetic brine with various pH.

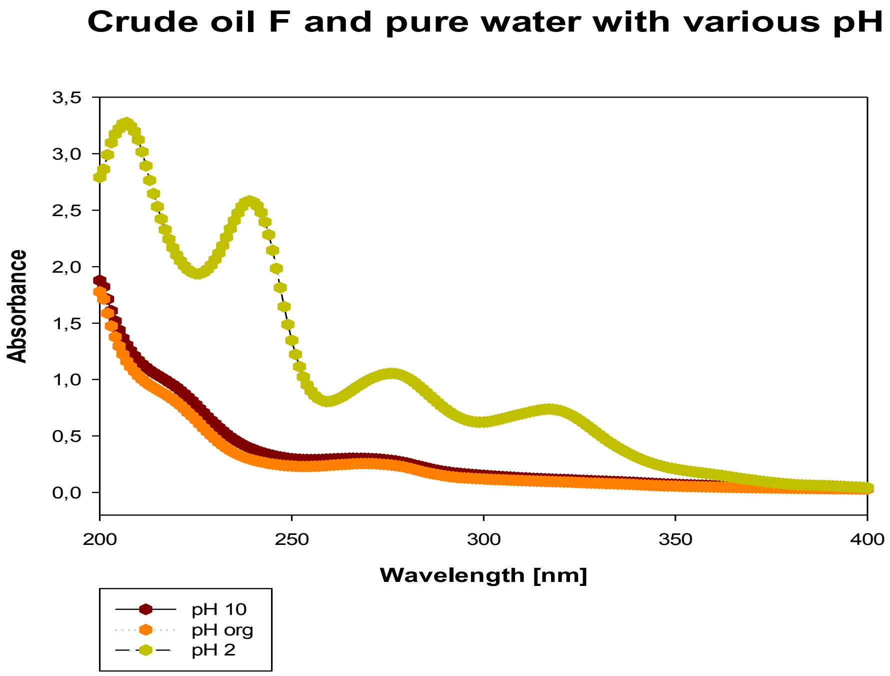

Figure 47: UV measurements of produced water samples prepared with crude oil F and pure water with various pH.

The UV-visible results for crude oil F are given in figure 43-46. There is a clear trend in that the curves which represent the samples of pH 2 show four peaks which are located at approximately 210, 250, 280 and 310 nm. This is similar for all the brines and pure water. It indicates that there are other compounds in the produced water samples for pH 2 than there are in the samples for the higher pH values. The peaks for pH 2 are also the largest ones, which may be due to that the concentration of compounds that absorb at the specific wavelength are high or that the compounds that absorb are large molecules that absorb much light. The surface tension results for pH 2 are quite varying for the different brines and are therefore not in very good agreement with the UV results. However, the absorbed molecules do not necessarily have to be surface active, which means that the molecules absorbing can be other molecules than the molecules that affect the surface tension.

The curves that represent pH 10 in the case of NaCl brine and pH 12 for $CaCl_2$ brine have three peaks, but not in at the same wavelength. For NaCl brine the peaks are more unclear and are located at approximately 210, 220 and 270 nm. For $CaCl_2$ brine the peaks are more pronounced and are located at approximately 210, 250, 290 nm. The absorption for pH 12 for $CaCl_2$ brine and pH 10 for NaCl brine are large, almost equal to pH 2 for the different brines. The result of the surface tension showed that these samples had large decrease in surface tension. This might indicate that the compounds absorbing the light during the UV measurements are compounds that contribute to the large decrease in surface tension. They could either be surface active compounds that do not exist in the samples for other pH values or it may be larger amount of the surface active compounds.

The curves that represent the original pH for all the brines and pH 10 for $CaCl_2$ brine, synthetic brine and pure water have one clear peak at around 210 nm and one very small peak at around 270 nm. This suggests that they contain the same kind of compounds. The absorption for the samples with pH 10 has slightly larger peaks than pH original, which can be because of higher concentration of the molecules that are absorbing. However, the absorption is much lower for these pH values than for pH 2, pH 10 for NaCl brine and pH 12 for $CaCl_2$ brine.

5.6 Surface pressure

The surface pressure, i.e. the change in surface tension from the start to the end of the surface tension measurement for crude oil I, crude oil B and crude oil F are presented in figure 47-49 respectively. These charts summarize all the results and show more clearly how the difference in crude oils, the difference in brine composition and the difference in pH affect the surface tension.

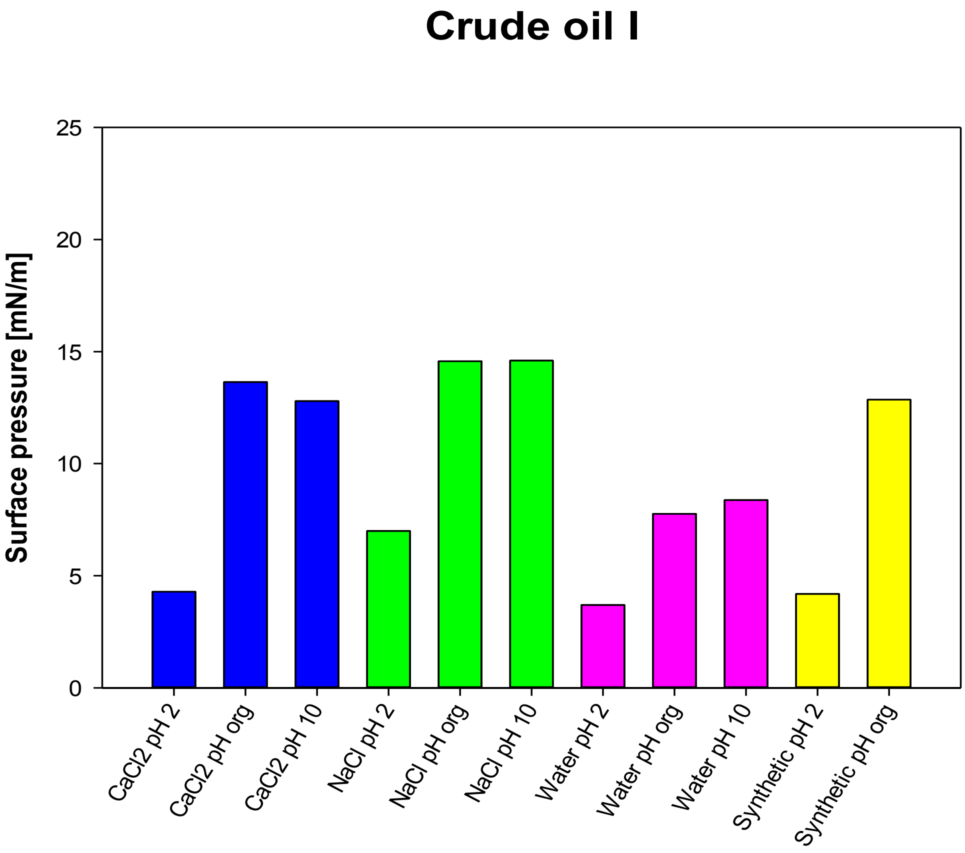

Figure 48: Surface pressure for crude oil I with various brines and pH values.

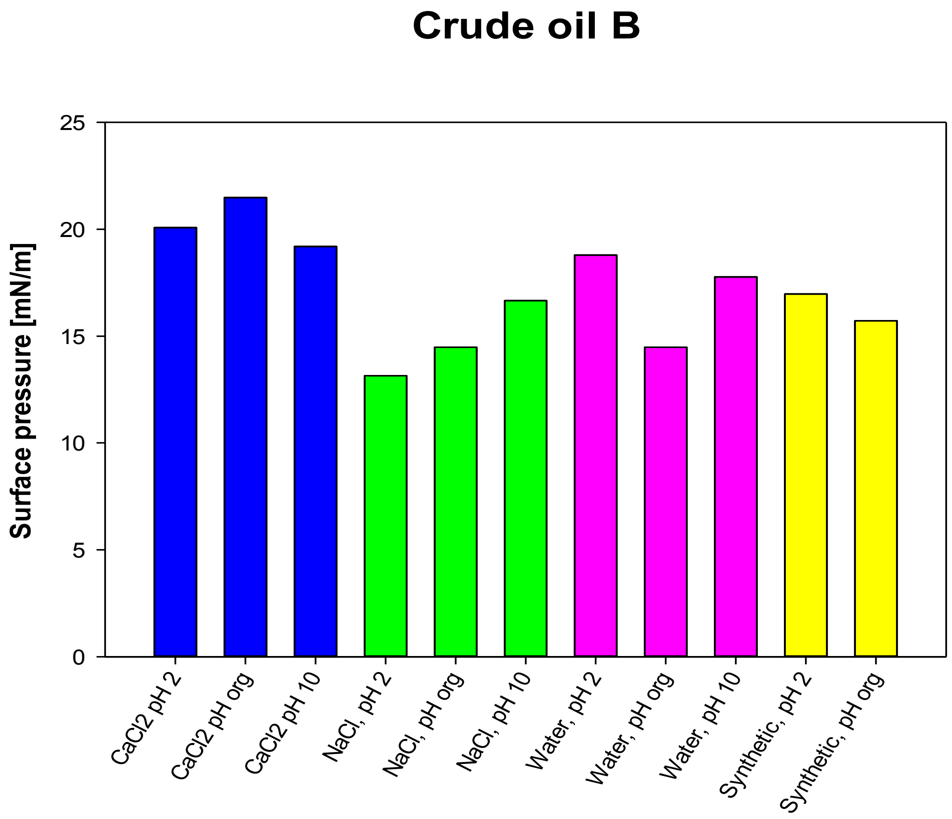

Figure 49: Surface pressure for crude oil B with various brines and pH values.

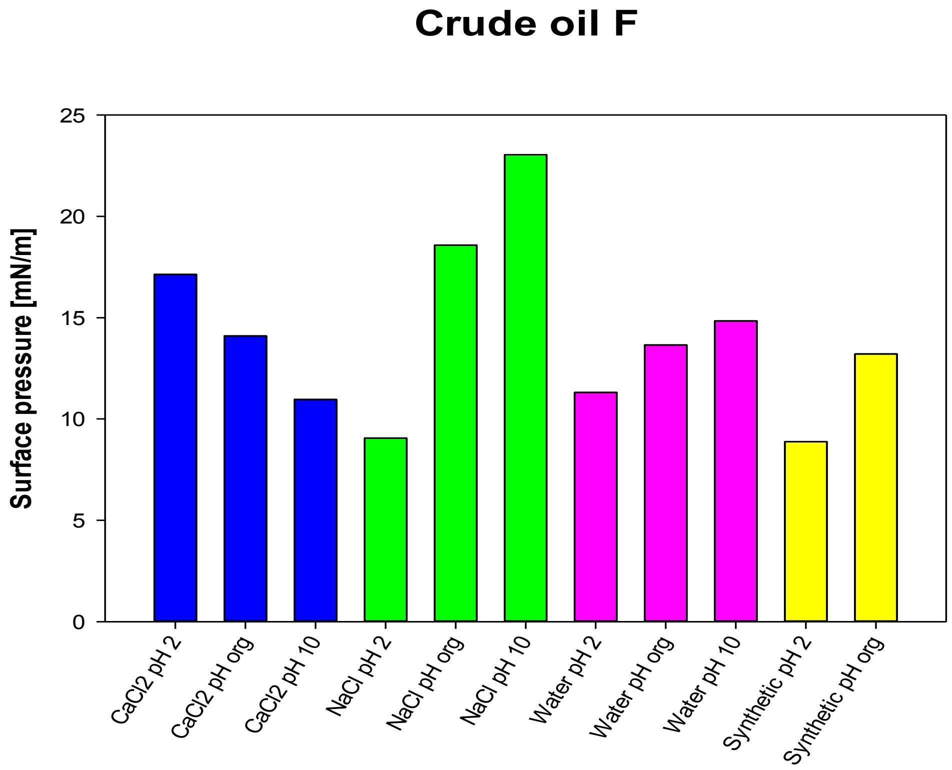

Figure 50: Surface pressure for crude oil F with various brines and various pH values.

For crude oil I the samples with high pH have the largest effect on the surface tension, i.e. they give the largest decrease in surface tension, see figure 47. The various brines show similar decrease in surface tension for the various pH values, but pure water show smaller decrease which indicates that having salts present at high pH values reduce the surface tension, which is in good accordance with section 2.4. For crude oil B the decrease in surface tension is very similar for both the various pH values and the various brine compositions. This implies that there is no significant influence of pH or brine composition on the surface tension of the produced water samples and it can be other compounds than acids and bases that affect the surface tension. Considering crude oil F the samples with low pH have smallest decrease in surface tension, except for $CaCl_2$ brine which shows exactly the opposite. By comparing the different brines it is obvious that NaCl brine with high pH values have the most influence on the surface tension. Another observation is that the samples with synthetic brine have almost the same decrease in surface tension as pure water. In general the results for the samples made with crude oil F give no specific trends and it is not clear why they are like this.

However, one obvious trend for all the crude oils is the behavior of the NaCl brine. For each crude oil, NaCl brine has smallest decrease in surface tension for pH 2 and highest decrease in surface tension for pH 10, which is in good agreement with the theory.

In general the results show that the surface tension of the produced water is largely dependent on the crude oil the brine is mixed with. The physicochemical properties of the crude oils, presented in table 1 in section 4.1.1 can be related to the results. Crude oil I have quite large amounts of acids and bases and also quite large amount of resins. The surface tension results showed a clear trend where the samples with high pH gave larger decrease in surface tension than the samples with low pH. At high pH values the acids are important regarding the surface tension and the results might therefore correlate to the TAN and TBN values. Crude oil B contains the largest amount of acids and bases and the largest amount of resins. As the surface tension results showed, the acids and bases have no influence on the surface tension since changing the pH did not change the surface tension. The large decreases in surface tension are therefore probably due to other polar compounds that are surface active and most likely they come from the large resin fraction. Crude oil F contains the lowest amount of acids and bases and also the lowest amount of resins. However, the samples made with this oil have larger decrease in surface tension than crude oil I and also stands out with the samples containing pure NaCl which have overall largest decrease in surface tension at high pH. It is therefore difficult to relate the results with the properties of the oil.

The results might indicate that it is rather the type of acids and bases than the amount of acids and bases that influence the surface tension. In addition, it can be other surface active compounds than acids and bases in the water phase, such as phenols and BTEXs, that may influence the surface tension of the produced water samples, see section 1.3.

5.8 Result of IR-spectroscopy

The intention of doing the IR analysis was primarily to see if it would work for the produced water samples. Two samples were chosen to being measured, the produced water sample with crude oil B and synthetic brine with pH 4 and the sample with crude oil B and pure water with pH 4. The reason why these samples were chosen was simply because the other samples are needed in case of further analysis using other methods. The results are presented in figure 50- 51.

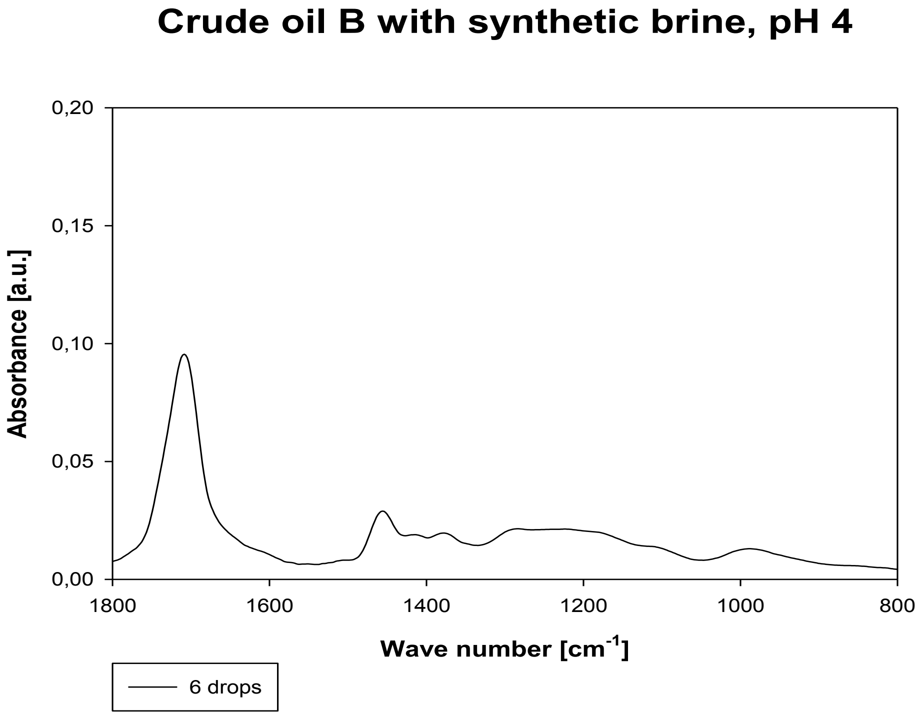

Figure 51: IR spectrum of crude oil B and synthetic brine with pH 4.

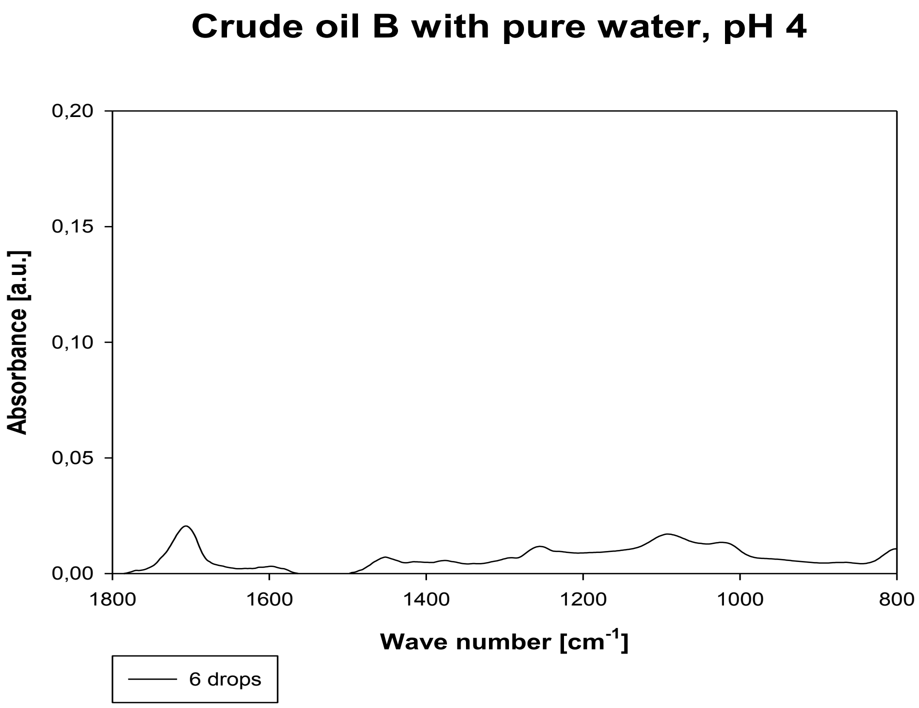

Figure 52: IR spectrum of crude oil B and pure water with pH 4.

Figure 50 shows several peaks in the range of 800 – 1800 cm^{-1} and to identify the peaks Appendix F is used. The largest peak is located around 1700 cm^{-1} and there are several functional groups that absorb at this frequency, among others acids, ketons, aldehydes and amides. The next peak is located around 1500-1450 cm^{-1} which might be due to molecules such as CH_3 or CH_2 bending. Further, there is a peak in the range 1300-1250 cm^{-1} and this peak might suggest that aromatics and esters (C-O stretch) are present in the sample. The last peak is observed at around 1000 cm^{-1} and may be related to absorption of sulfoxide.

Figure 51 have many of the same peaks as figure 49, but the absorption is not as large as for the sample with synthetic brine. According to section 3.3 the intensity of absorption is related to the concentration of the compounds in the sample, which means that the sample with pure water contains smaller amount of the compounds absorbing than the synthetic brine sample.

The IR results indicate that the produced water samples contain many different compounds with various concentrations, and the functional groups mentioned above may have contributed to the surface tension and the UV results.

6. Conclusion

The changes in surface tension of the produced water depended on the crude oil, the composition of the brine and the pH of the brine. In this study, three different crude oils, three different brines and pure water and at least three different pH values for each brine and pure water were used.

The results for crude oil I showed that the high pH values gave the largest decrease in surface tension. At high pH values the surface tension is governed by acids, which dissociates and becomes surface active. The brine composition gave no significant differences between the produced water samples, but the samples with pure water showed smaller decrease in surface tension than the brines. This might be due to that salts reduce the water-solubility of acids and bases and thus reduce the surface tension of the water phase. However, in general the results suggest that the surface tension is more dependent on the pH of the brine than the composition of the brine.

For crude oil B the results show quite similar surface tension for all produced water samples which indicate that the samples contain same amount or same kind of surface active compounds regardless the pH and the composition of the brine. It is most likely other surface active compounds than acids and bases that contribute to the decrease in surface tension and the high amounts of resins imply that it is probably polar molecules from this fraction that do so. The IR results suggest that ketons, aldehydes, esters, sulfoxide, aromatics and amides are present in addition to acids in the samples made with crude oil B and these compounds might have influence on the surface tension.

For crude oil F the results show no trends for the different brines and pH values. In the case of synthetic brine, NaCl brine and pure water it is the high pH values that influence the surface tension the most, but for $CaCl_2$ brine it is the low pH values. As for the brines the NaCl brine with high pH has the largest decrease in surface tension. It is not clear why the results are like this and it is therefore difficult to state any specific explanation.

The reason why the surface tension results differs that much between the crude oils is because the crude oils have different compositions. The various pH conditions and brine compositions might have impact on what kind of compounds that diffuses from the oil phase to the water phase and also the concentration of compounds that will diffuse to the water phase. The change in surface tension depends on the type of compounds, the polarity and the structure of the compounds present in the water phase and it is not only acids and bases that might affect the surface tension but also other surface active compounds.

Further work should include IR analysis of all the produced water samples to get an indication of what kind of compounds the different samples possesses and also total organic carbon (TOC) measurements which would give the total carbon present and the inorganic carbon in the produced water.

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8. Appendices

A The composition of the brines

Table 4: Overview of the composition of the brines with same ionic strength.

Brine	Compound	Weight [g]	Purity [%]	Company
Synthetic brine	NaCl	89,67	99.5	MERCK
	$CaCl_2$ x $2H_2O$	11,958	99	FLUKA
	$MgCl_2$ x $6H_2O$	7,605	99	Analytica
	$NaHCO_3$	0,3004	99.5	MERCK
	Na_2SO_4	0,0665	99	MERCK
	H_2O	890,4		Acros Organics
$CaCl_2$ brine	$CaCl_2$ x $2H_2O$	86,780	99	FLUKA Analytica
NaCl brine	NaCl	117,944	99.5	MERCK

B Determination of ionic strength of the synthetic brine and the mass of $CaCl_2$ and NaCl

To calculate how much $CaCl_2$ that was needed for the $CaCl_2$ brine and how much NaCl that was needed for the NaCl brine, the ionic strength of the original synthetic brine was calculated. The ionic strength was supposed to be the same for all the brines. The total brine solution is assumed to be 1 liter.

Ionic strength is given by,

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

where c_i is the concentration of each ion [mol/l] and z_i is the charge number of each ion. The concentration of the ions, c_i, was found by the number of moles for each salt in the mixed brine and the molar relations. Since the solution is assumed to be 1 liter, the number of moles for each ion will correspond to the concentration c_i. In table 5 the molecular weight, number of moles and the determined concentration of each species in the synthetic brine is given.

Table 5: Overview of the molecular weight, the number of moles and the determined concentration of each species in the synthetic brine.

Compound	**Weight [g]**	**M [g/mol]**	**n [mol]**	**C_i [mol/l]**
NaCl	89,67	58,44	1,5344	1,5344
$CaCl_2$ x $2H_2O$	11,958	128,996	0,0927	0,0927
$MgCl_2$ x $6H_2O$	7,605	113,226	0,0672	0,0672
$NaHCO_3$	0,3004	106,998	0,0028	0,0028
Na_2SO_4	0,0665	142,05	0,0005	0,0005
H_2O	890,4	16,016	49,4227	49,4227

Table 6: Overview of 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	- 1

The ionic strength of the synthetic brine was determined to 2,018. Since the ionic strength of the NaCl brine and the $CaCl_2$ brine was supposed to be the same as for the synthetic brine, the equation for ionic strength given above was used to calculate the mass of NaCl and $CaCl_2$. In 1 liter solution the mass of NaCl was determined to 117,944 g and for $CaCl_2$ x $2H_2O$ the mass was determined to 86,7802 g.

C Detailed procedure of the produced water samples preparation

The procedure for preparation of the produced water samples are described in detail below. It applies for one parallel, but many parallels can be made simultaneously.

1. Clean all equipment with milli – Q water and dry with compressed air.
2. Heat the oil to 60° C and shake it very well before mixing it with brine.
3. Mix oil and brine (35 g or 40 g of each) in a Schott bottle (250 ml).
4. Put the bottle in a shaker at 250 mot/min for 24 hours.
5. Pour the sample in a centrifugal tube and centrifuge at 8000 rpm at 15 min.
6. Use pipettes to remove as much oil as possible and centrifuge again if the amount of water phase is too small.
7. Separate the final water phase from the oil with a separatory funnel in a Schott bottle (50 ml).
8. Measure the density of the sample in order to measure the surface tension at the bubble pressure tensiometer.

D Table of produced water samples that were made

Table 7-9 show the produced water samples that have been made, the pH of the brine, the pH values of the produced water samples after the preparation and before they were measured on the bubble pressure tensiometer (BP 100), and the density of each sample.

Table 7: Produced water samples prepared with crude oil B

Sample	**Brine**	**pH of brine**	**pH of PW after preparation**	**pH of PW before measuring on BP**	**Density [g/cm^3]**
B.Na.2	NaCl brine	2.01	6.40	6.48	1.0789
B.Na.org		5.81	6.63	6.72	1.0788
B.Na.10		9.99	6.62	6.56	1.0774
B.Ca.2	$CaCl_2$ brine	2.05	5.59	5.80	1.0416
B.Ca.org		5.85	6.09	6.08	1.0417
B.Ca.8		7.99	6.06	6.18	1.0455
B.Ca.10		10.00	6.04	6.06	1.0452
B.Ca.12		11.42	8.97	8.55	1.0452
B.SB.2	Synthetic brine	2.03	6.19	6.33	1.0676
B.SB.4		4.23	6.41	6.92	1.0683
B.SB.org		7.10	6.80	6.92	1.0686
B.SB.8		8.00	6.79	7.04	1.0684
B.W.2	Pure water	2.07	5.36	5.40	0.9979
B.W.4		4.00	6.32	6.51	0.9984
B.W.org		5.90	6.31	6.52	0.9984
B.W.10		10.00	6.43	6.31	0.9973

Table 8: Produced water samples made with crude oil F

Sample	**Brine**	**pH of brine**	**pH of PW after preparation**	**pH of PW before measuring on BP**	**Density [g/cm^3]**
F.Na.2	NaCl brine	2.01	2.50	2.48	1.0768
F.Na.org		5.81	7.28	7.26	1.0767
F.Na.10		10.10	7.67	7.72	1.0773
F.Ca.2	$CaCl_2$ brine	2.01	2.05	2.03	1.0446
F.Ca.org		5.60	6.78	6.81	1.0444
F.Ca.10		9.98	6.70	6.70	1.0500
F.Ca.12		11.43	10.48	10.91	1.0449
F.SB.2	Synthetic brine	2.02	2.65	2.65	1.0676
F.SB.org		6.54	7.24	7.24	1.0681
F.SB.8		8.01	7.25	7.20	1.0681
F.W.2	Pure water	2.05	2.23	2.31	0.9826
F.W.org		6.67	7.34	7.24	0.9821
F.W.10		9.99	7.30	7.21	0.9971

Table 9: Produced water samples made with crude oil I

Sample	**Brine**	**pH of brine**	**pH of PW after preparation**	**pH of PW before measuring on BP**	**Density [g/cm^3]**
I.Na.2	NaCl brine	1.99	6.25	6.29	1.0776
I.Na.org		5.81	6.86	6.83	1.0776
I.Na.10		10.00	6.92	6.91	1.0773
I.Ca.2	$CaCl_2$ brine	1.98	4.12	4.12	1.0504
I.Ca.org		6.70	6.36	6.36	1.0504
I.Ca.10		10.05	6.47	6.46	1.0503
I.Ca.12		11.39	7.80	7.80	1.0499
I.SB.2	Synthetic brine	2.01	5.21	5.19	1.0677
I.SB.org		6.53	6.92	6.94	1.0679
I.SB.8		8.00	6.95	7.14	1.0680
I.W.2	Pure water	2.02	2.53	2.59	0.9975
I.W.org		6.80	6.68	6.74	0.9974
I.W.10		9.93	6.77	6.82	0.9974

E The reproducibility of the bubble pressure tensiometer

Figure 52 shows the reproducibility of the bubble pressure tensiometer with the produced water sample made with crude oil B and synthetic brine with pH original (7,10). This illustrates that the bubble pressure tensiometer, BP 100, gives reliable results.

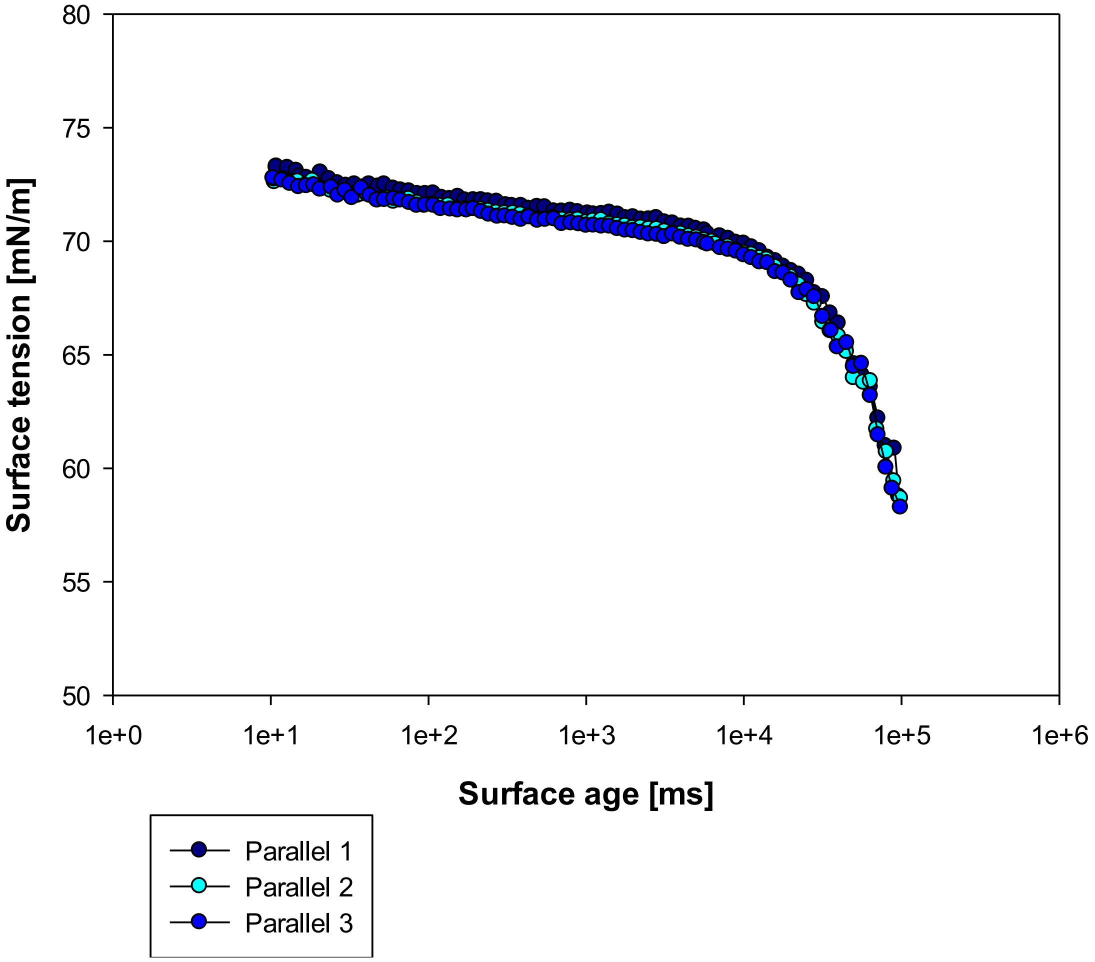

Figure 52: The reproducibility of the measurements of the produced water sample made with crude oil B and synthetic brine with pH original (7,10) with the bubble pressure tensiometer.

F The reproducibility of the UV-visible spectrophotometer

Figure 53 shows the reproducibility of the UV-visible spectrophotometer with the produced water sample made with crude oil B and synthetic brine with pH original (7,10). This illustrates that the UV-visible instrument gives reliable results.

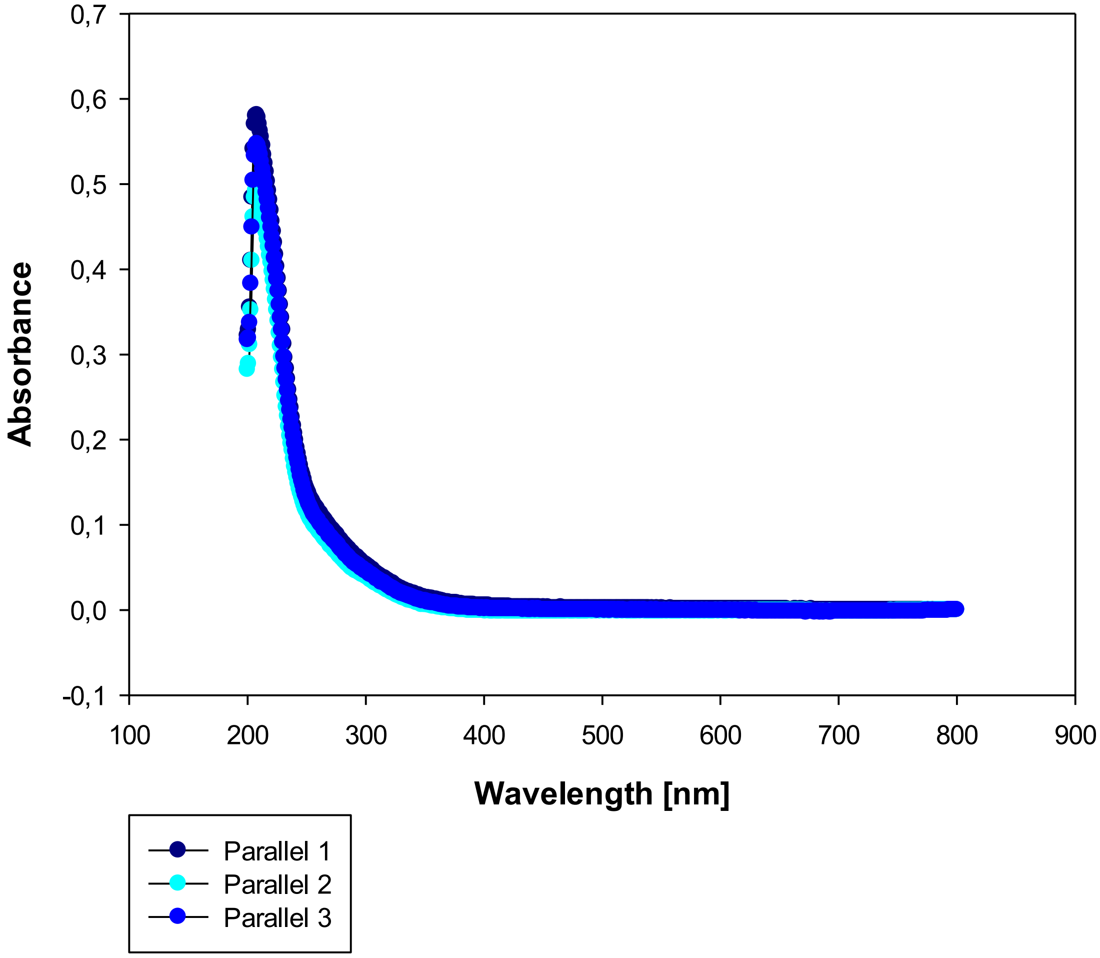

Figure 53: The reproducibility of the measurements of the produced water sample made with crude oil B and synthetic brine with pH original (7,10) with the UV-visible.

G The functional groups and their absorption bands for IR spectra analysis

Functional groups	Absorption bands ($\mathrm{cm^{-1}}$)
Aldehydes (C═O stretch)	1740−1730
Ketons (C═O stretch)	1735−1705
Acid (C═O stretch) R−COOH or Ar−COOH	1760 or 1720
Amide (C═O stretch)	free 1690−1650; associative 1650−1640
C═C conjugated	1650 and 1600
C═C aromatic	1600
$\mathrm{CH_3}$ or $\mathrm{CH_2}$ (bending)	1460
$\mathrm{CH_3}$ (bending)	1379
Ester (C−O stretch)	~1300 and ~1050
Aliphatic	1150−1070
Aromatic	1275−1200
Sulfoxide	1034 (1060−970)
Aromatic C−H (deformation)	
1 adjacent H	900−860
2 adjacent H	860−810
3 adjacent H	800−750
4 adjacent H	750−735
5 adjacent H	770−730 or 710−690
Alkyl chains $(\mathrm{CH_2})_n$; $n \geq 4$	731

Enhet: IKP - Ugelstad laboratory
Dato: 29.10.2012
Deltakere ved kartleggingen (m/ funksjon): Helle Hofstad Trapnes (Student), Gisle Øye (Veileder)
Kort beskrivelse av hovedaktivitet/hovedprosess: Masteroppgave student. Tittel på oppgaven: Dynamisk overflatespenning

ID nr.	Aktivitet/prosess	Ansvarlig	Eksisterende dokumentasjon	Eksisterende sikringstiltak	Lov, forskrift o.l.	Kommentar
1	Prøvepreparering	Helle H. Trapnes	Generelle lab rutiner	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	
2	Målinger med Bubble Pressure Tensiometer	Helle H. Trapnes	Generelle lab rutiner Apparaturkort Instrumentprosedyre/manual	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	
3	Målinger med UV-visible	Helle H. Trapnes	Generelle lab rutiner Apparaturkort Instrumentprosedyre/manual	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven	
4	Vasking av utstyr med toluen, aceton og isopropanol	Helle H. Trapnes	Generelle lab rutinger Kjemikalie dataark	Hansker, briller, labfrakk, avtrekksskap	Arbeidsmiljøloven, Kjemikalieforskriftene	

Enhet: IKP - Ugelstad laboratory **Dato:29-10-2012**
Linjeleder: Gisle Øye
Deltakere ved risikovurderingen (m/ funksjon): Helle Hofstad Trapnes (Student), Gisle Øye (Veileder)
R

	Aktivitet fra kartleggings-skjemaet	**Mulig uønsket hendelse/ belastning**	**Vurdering av sannsyn-lighet**	**Vurdering av konsekvens:**				**Risiko-verdi**	**Kommentarer/status Forslag til tiltak**
ID nr			(1-5)	Menneske (A-E)	Ytre miljø (A-E)	Øk/ materiell (A-E)	Om-dømme (A-E)		
1	Prøvepreparering	Inhalering, olje på hud, søl ved flytting av prøver fra et sted til et annet.	2	D				D2	Vær nøye med å bruke avtrekkskap når man preparer prøver, bytt hansker ofte.
2	Målinger med Bubble Pressure Tensiometer	Søl ved overføring av prøve til glasset som hører til instrumentet	1	B				B1	Bytte hansker etter maks 10 min. Bytte hansker rett etter eventuell søling.
	“	Inhalering ved overføring av prøve til glasset som hører til instrumentet.	2	B				B2	Ha en avtrekkshette over instrumentet.
3	Målinger med UV-visible	Søl ved overføring av prøve til måleglass.	1	B				B1	Bytte hansker rett etter eventuell søling.
	“	Inhalering ved overføring av prøve til måleglass	2	B				B2	Ha en avtrekkshette over instrumentet.
4	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	C				C2	Ha alle prøver og løsemidler i avtrekkskap mens man arbeider. Brukte/forurensede hansker bør byttes regelmessig og legges i avtrekkskapet for fordampning.
	Sannsynlighet	***Konsekvens***	***Risikoverdi (beregnes hver for seg):***						
	1. Svært liten *2. Liten* *3. Middels* *4. Stor* *5. Svært stor*	*A. Svært liten* *B. Liten* *C. Moderat* *D. Alvorlig* *E. Svært alvorlig*	***Menneske = Sannsynlighet x Konsekvens Menneske*** ***Ytre miljø = Sannsynlighet x***						

			Konsekvens Ytre miljø Økonomi/materiell = Sannsynlighet x Konsekvens Øk/matriell Omdømme = Sannsynlighet x Konsekvens Omdømme						

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 < 1uke	Negativ påvirkning på troverdighet og respekt
A Svært liten	Skade som krever førstehjelp	Ubetydelig skade og kort restitusjonstid	Drifts- eller aktivitetsstans < 1dag	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.