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Determination of Mass of Tetrameric Acid at the Air/Water Interface by Combining Langmuir-Schaefer with QCM Measurements

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Preface

This master thesis is a part of the degree of Master of Science at the department of chemical engineering at the Norwegian University of Science and Technology (NTNU). The work is a part of the joint industrial program JIP-2:4 “Prediction of Ca-Naphthenate deposition in water oil systems”, and all the experimental work has been carried out at the Ugelstad Laboratory from January 2013 to June 2013 under the supervision of Dr. Sébastien Simon and Prof. Johan Sjöblom.

I would like to thank Sébastien Simon for all his valuable help with the experimental part and the theoretical aspects of the project and for proofreading my report. I would also like to thank Johan Sjöblom for the supervision during the project time.

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

Abstract

In this work a new analytical method for determination of the mass of tetrameric acids at the liquid/liquid interface has been developed and tested. The method is based on a combination of the Langmuir-Schaefer technique and the quartz crystal micro balance (QCM) technique. The technique allows one to determine the mass of tetrameric acids at the interface as a function of different conditions which again can be used to determine the formation mechanism of calcium naphthenate deposits.

In this work calibration curves at the air/water interface has been made at conditions were tetrameric acid and calcium forms a gelled interface and for condition where there is no gellation. For the experiments the model compound BP-10 has been used to study the relationship between the added amount and the measured amount of BP-10 at the interface at the different conditions. The study showed that the relationship between the added amounts and the measured amounts of BP-10 at the interface showed a linear trend up to a surface coverage of 6 mg/m^2 for the experiments performed at gelling condition and a linear trend up to a surface coverage of 7 mg/m^2 for the experiments performed with non gelling conditions.

The influence of addition of monoacid has also been tested. Two different amounts of monoacid using the model monoacid 4-octylbenzoic acid were added to the interface at pH 7 containing calcium. The tests showed that there was no deposition of monoacid onto the QCM crystal. Experiments with a mixture of BP-10 and monoacid have also been conducted using the same method. The deposition experiments showed that there was deposition onto the crystal, and that the deposition was most likely BP-10.

Content

1. Introduction

Calcium naphthenate deposits are a well known problem in the petroleum industry, and much research has been dedicated to the problem. When the pressure drop during transportation of the oil from the well to the surface, CO_2 is released and the pH in the produced water increases. If the pH increases above the apparent pKa for the naphthenic acids the naphthenic acid deprotonates and naphthenate is formed. The naphthenates are negatively charged and interfacial active and are therefore prone to react with metal ions like calcium in the water phase. This reaction leads to formation of calcium naphthenate deposits.[1-4]

The naphthenic acids in the crude oil are a complex mixture consisting of a carboxylic acid functions with saturated rings connected by aliphatic or hydrocarbon chains.[1, 3, 5, 6] The naphthenic acids are mainly monoacids, however later studies have shown that even if the bulk concentration of naphthenic acids is monoacids the acids responsible for the naphthenate deposits are narrow group of high molecular weight acids. The acids which are often called tetrameric acid or "ARN" acids are 4-protic carboxylic acids with 4-8 unsaturated rings and molecular weight ranging from 1227-1235 g/mole. [1, 3, 4]

It is believed that the formation of calcium naphthenate deposits starts at the oil/water interface. The knowledge of the interfacial composition is therefore of paramount interest to determine the formation mechanism of calcium naphthenate deposits. However there are no techniques available for studies of the interfacial composition.

In this master thesis a new analytical method based on a combination of the Langmuir-Schaefer dipping technique and the quartz crystal micro balance (QCM) has been developed and tested to determine the mass of tetrameric acid at the liquid/liquid interface. Calibration curves at conditions were tetrameric acids and calcium forms a gelled interface and conditions were there is no gellation has been made using the model compound BP-10. BP-10 which has been synthesized at the Ugelstad laboratory has proved to have very similar interfacial activity and film formation properties as the tetrameric acid.[8]

There have also been carried out some experiments to investigate the influence of addition of monoacid to the interface. The experiments were carried out by comparing the QCM-Langmuir result from experiments with only monoacid at the interface, only BP-10 at the interface and a mixture of BP-10 and monoacid at the interface. All experiments were carried out with a sub-phase with pH 7 and calcium present.

2. Goals and Methodology of the Study

The goal for this work has been to develop and test a new method to determine the tetrameric acid amount at the liquid/liquid interface. The method that has been tested is an analytical method based on a combination of the Langmuir-Schaefer technique and the quartz crystal micro balance (QCM) technique. The technique allows one to determine the mass of tetra-acid as a function of different conditions which again can be used to determine the formation mechanism of calcium naphthenate deposits.

A film is formed using the Langmuir trough technique and a part of the interface is deposited onto a QCM crystal using the Langmuir-Schaefer technique. Then the mass deposited onto the crystal is measured using the QCM technique. In order to develop this method the experiments were first started at the air/water interface because it is an easier starting point since one have control over the surface coverage straightforward. At the air/water interface it is also possible to check the validation of the method by looking at the correlation between the spreading amounts and the measured amounts to determine the influence of different parameters. In this work the correlation between the added amounts and measured amounts has been studied at two different conditions. Calibration curves has been made at pH 7 where BP-10 and calcium forms a gelled interface and at pH 5 where there are no gelation occurring.[4]

Later on experiments will be conducted on a liquid/liquid interface for validation by confirming the result from the air/water interface experiments with a few tests. At the end experiments with unknown samples can be conducted at the liquid/liquid interface to study the deposit formation mechanism by determining the influence different parameters has on the mass at the interface.

3. Theory

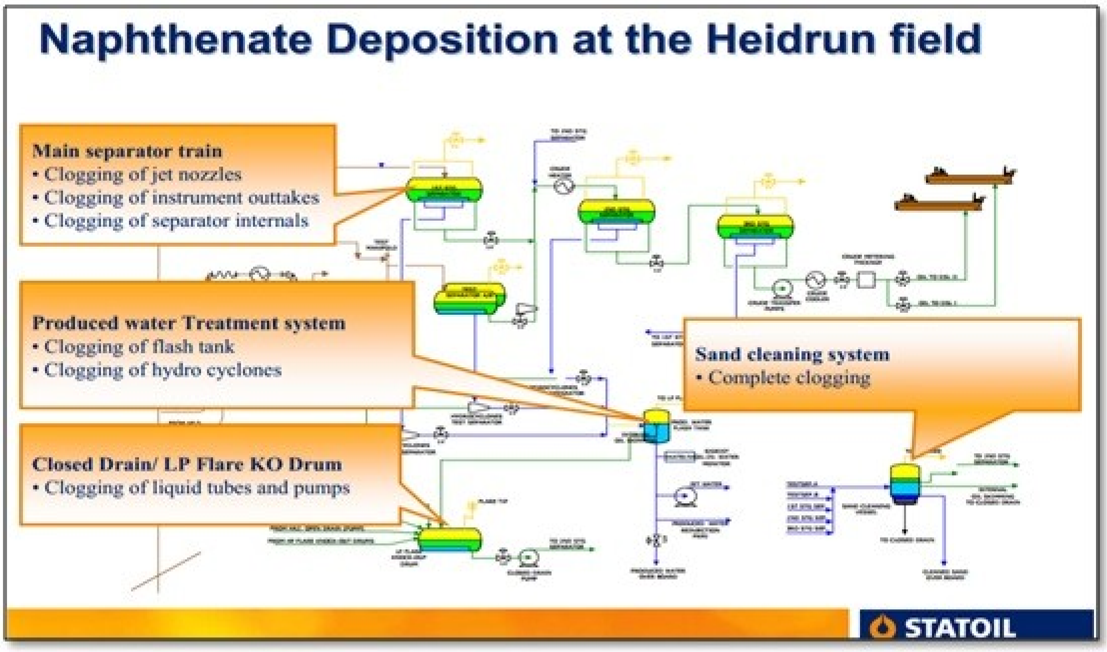
3.1 Deposits

During transportation of the oil from the well to the surface, the pressure drops. This pressure drop leads to degassing of carbon dioxide and hence an increase in pH in the produced water. If the pH increases above the apparent pKa for the naphthenic acids, the naphthenic acids deprotonates and naphthenates are formed. The naphthenates are negatively charged and more interfacial active and are therefore prone to react over the oil water interface with calcium ions in the water phase. These reactions lead to formation of calcium naphthenates. The naphthenates can also react with other metal ions in the produced water, but this chapter will focus mostly on calcium naphthenates. Later discoveries have shown that even if the bulk concentration of naphthenic acids is monoacids, the acids responsible for the calcium deposits are a narrow group of high molecular weight acids. These acids which are often called Arn-acids will be discussed further in chapter 3.3. [2-4, 7]

The calcium naphthenates formed from Arn-acids are insoluble in both the water and the oil phase, and because of that they tend to accumulate at the oil-water interface to form a film.[9] The accumulations can attach them self to process unit surfaces, like oil-water separators and de-salters. Agglomerations in tubes and pipelines are also known to happen. Since the deposits can contain salts, sand scale and other solids, the accumulations are a big problem in many process facilities that process crude oils because of costly shutdown for cleaning.[2, 10-12]

At the Heidrun field process platform the water treatment system is also affected by calcium naphthenate deposits. Problems like accumulation of oil components and naphthenates in the pall rings in the degasser, and clogging of hydro cyclones are some of the systems that are severely affected.[12, 13]

One of the most critical problems is calcium naphthenate formations in the pumps and liquid tubes that control the level in the low pressure knock-out drum. This system operates on intervals and the system is allowed to cool between the operations. Since the naphthenates solidifies when the temperature decreases the pumps are not able to start up again.[11] Figure 1 shows the process systems that are most affected by calcium naphthenate deposits at the Heidrun field process facilities.[12, 13]



Naphthenate Deposition at the Heidrun field

Main separator train
- Clogging of jet nozzles
- Clogging of instrument outtakes
- Clogging of separator internals

Produced water Treatment system
- Clogging of flash tank
- Clogging of hydro cyclones

Closed Drain/ LP Flare KO Drum
- Clogging of liquid tubes and pumps

Sand cleaning system
- Complete clogging

Figure 1: Process systems that are affected by calcium naphthenate deposits at the Heidrun field process facilities[12, 13]

3.2 Naphthenic Acids

To characterize the total acidity of the crude oil one can measure the total acid number (TAN). TAN is the amount of KOH in milligrams needed to neutralize the acid present in one gram of crude oil. If the total acid number of the crude oil exceeds 0.5 mg/g the crude oil is considered acidic. In crude oil an acid called naphthenic acid is mainly, but not alone the reason for acidifying crude oils. [9, 14]

By definition naphthenic acids are a complex mixture consisting of a carboxylic acid function with saturated rings connected by aliphatic or hydrocarbon chains. They are naturally occurring and can have thousands of different structures. In the petroleum industry the term naphthenic acids are generally used as a term for all carboxylic acids present in the crude oil. [5-8] They are present in almost all crude oils, normally in amounts ranging from 0 to 4 wt%. Heavy crude oils from geologically young formations are known to have a higher acid content than lighter paraffinic crude oils. [15]

Naphthenic acids are $C_{10} - C_{50}$ compounds with 0 to 6 fused saturated rings. The number of rings and the distribution of carbon vary from crude oil to crude oil. The carboxylic group is attached to a ring with a short side chain.[6] They have the general formula $C_nH_{2m+z}O_2$, where n indicates the number for carbon atoms and Z is zero for fatty acids, or have a negative value depending on the number of condensed or/and aromatic rings.[9, 15]

Some examples of monoprotic naphthenic acids with different structures and Z values are shown in figure 2.

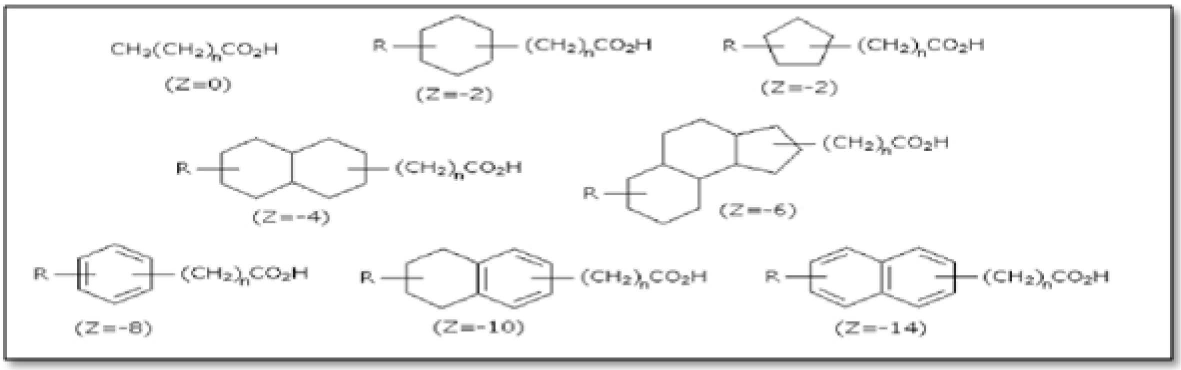


Figure 2:Examples of monoprotic naphthenic acids with different Z values[9, 15]

Naphthenic acids are mainly monoacids, however later discoveries has shown that the bulk of naphthenic acids in calcium naphthenate deposits are four-protic acids.[1, 3, 4] This will be discussed further in the next chapters.

3.3 Tetrameric Acids

As mentioned in the first chapter, calcium naphthenate deposits were becoming a big problem in the oil industry. Instead of looking at the structure of the crude oil scientists from Conoco Phillips and the R&D group at Statoil decided to shift the focus over to the deposit itself, performing thorough analysis of the deposit. The acids were collected and isolated from the deposits by using an Acid-IER method which is a technique that allows one to extract all the acids from a sample. After that several analytical techniques like potentiometric titration, liquid-chromatography combined with mass spectrometry (LC-MS), NMR and vapor phase osometry (VPO) were used to determine the molecular structure.[9]

Even if the bulk concentration of naphthenic acid is monoacids, it turned out that the acids responsible for the calcium naphthenate deposits were a narrow group of high molecular weight acids. The acids are 4-protic carboxylic acids, called tetrameric acids or "ARN" acids, with 4-8 unsaturated rings and molecular weight ranging from 1227-1235 g/mole.[3, 4, 7] Figure 3 shows the structure of the most abundant 6-ring isomer. The structure was found by extensive NMR characterization, performed by Lutnaes and co-workers.[4, 9]

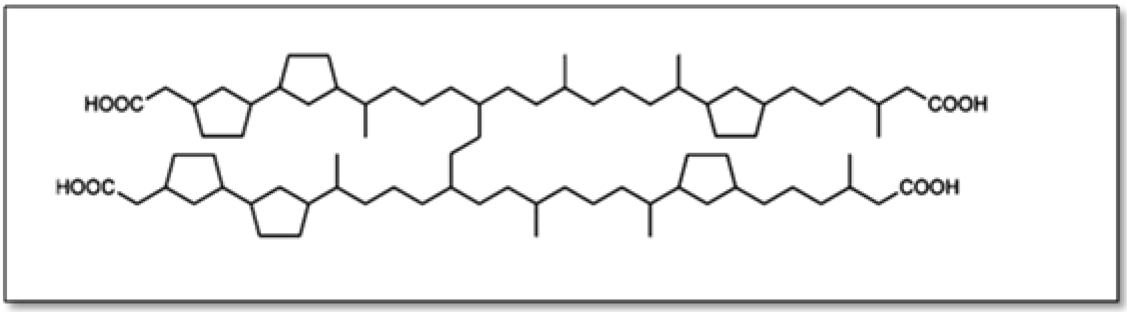


Figure 3: The structure of the most abundant 6-ring isomer of the ARN acids.[4, 9]

The tetrameric acids have a high affinity towards the interface, and if the pH is high enough, at the interface they react with divalent ions in the water phase, especially calcium. Due to the structure of the acid the four acid groups can form cross linked networks with the calcium ions at the interface.[4, 7] The network that is formed has been found to have an elastic character, and the film sort of acts like glue to which sand and other particles can adsorb onto. [3, 4, 9]

As mentioned earlier in this chapter the tetrameric acids are recovered from the deposits by use of an ion-exchange resin (EIR) method. However this method do not provide a sample with a purity that are satisfactory for studying the acids properties. The tetrameric acid also lacks chromophores, and that make the detection of them hard. Because of this a model compound for the tetrameric acid has been synthesized at the Ugelstad laboratory. The model compound that has been given the name BP-10 has shown to have very similar interfacial activity as the C-80 tetrameric acid. The model compound is also UV active and can have fluorescent moieties incorporated in the structure, which makes it easy to detect.[8] Figure 4 shows the molecular structure of the model compound BP-10.

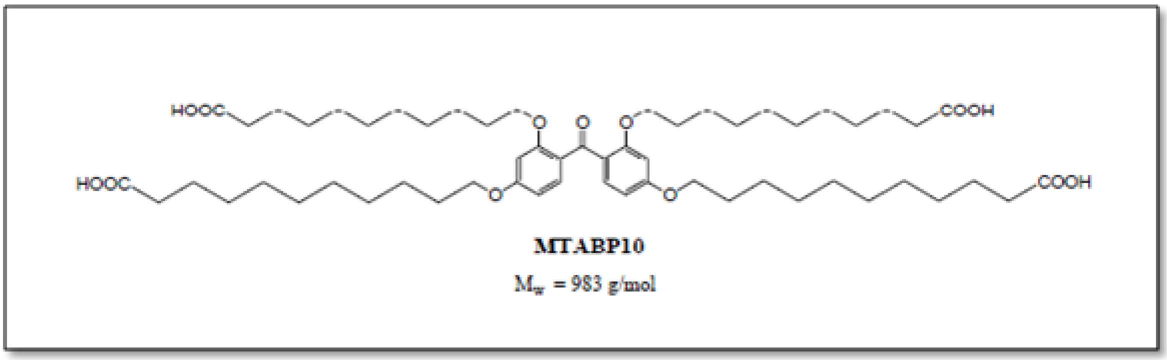


Figure 4: Molecular structure of the model compound BP-10 [8]

3.4 Reaction with Calcium

As mentioned in chapter 3.3 the 4-protic tetrameric acids can cross-link with calcium ions. The reaction product are neither soluble in the oil phase or the water phase, instead it accumulates at the oil/water interface as an elastic interfacial film with solid like behaviour.[3, 4, 9] Figure 5 illustrates how the tetrameric acids can crosslink with calcium at the interface in different conformation. The different conformation is explained later in this chapter.

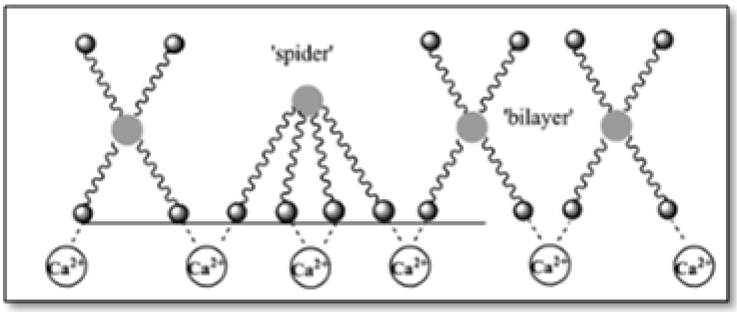


Figure 5: Illustration of the cross-linking between tetrameric acid and calcium in different conformation.[4]

Interfacial shear rheology studies have been used to study the conditions where gelation of calcium naphthenate occurs. The study was conducted using the model compound BP-10 between oil and water, and the studies were carried out as a function of pH, the concentration of calcium and the concentration of monoacid. The experiments that were carried out as a function of pH showed that a pH exceeding 6.2 is crucial for the formation of a gelled interface leading to calcium naphthenate deposits. At lower pH a viscoelastic film was formed after a long aging time. One could say that the film are elastic in nature, but since the hold-up time in a separator are typically 5-15 minutes the results are not relevant from a practical point of view. The pH is also believed to have an influence on the conformation of the acid at the interface.[4]

Langmuir studies have shown that the tetrameric acids have very interesting film properties. When compressing at an air/water interface the molecular structure of the acid have shown to change conformation from having all acid groups aligned towards the water phase in a spider like confirmation, to a bilayer-type conformation with two acid groups facing the water phase and two acid groups facing the air. The same two conformations are also seen in oil/water systems.[3, 4, 9] Figure 6 shows the different conformations of the tetrameric acid upon compressing at an air/water interface with calcium present in the water sub-phase.

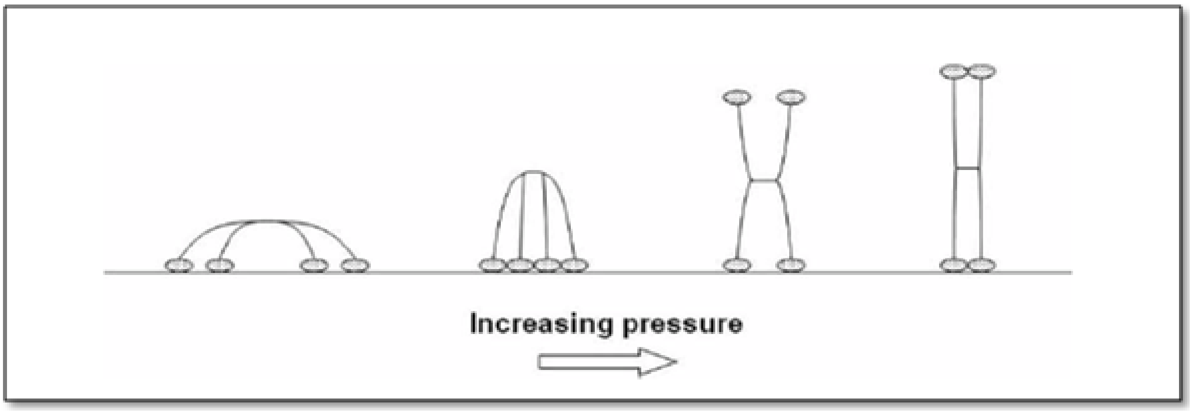


Figure 6: The different conformation of tetrameric acid upon compressing at an air/water interface with calcium present in the water sub-phase.[9]

At an oil/water interface the pH is believed to be the determining factor for the conformation changes. If all four acid groups are dissociated the spider-type conformation is favoured to avoid having any charged carboxylate groups in the oil phase. The bilayer conformation is believed to be most dominant at medium pH values.[4]

If the tetrameric acids are aligned as a bilayer a new polar surface is created. This layer can in principle cross-link or adsorb with more tetrameric acid molecules. Transfer of cations through this layer to stabilize the new interface cannot be ruled out either. If so this arrangement could help forming a thicker layer with stabilization both perpendicular to and along the interfacial plane. If the pH is increased after formation of the bilayer-film more acids will dissociate and direct them self towards the water phase and form the spider-type arrangement. This again will remove the new polar surface and decrease the tendency of film growth. Since the spider arrangement has a molecular area which is almost twice the size of the bilayer-arrangement the tetrameric acid molecules will most likely diffuse away from the interface into the water phase to decrease the number of molecules at the interface. The molecules that diffuse to the water phase can react with calcium in the water phase, and this salt could attach to the interfacial layer from the aqueous side.[4]

The studies also showed that the calcium concentration also play a role when trying to understand the formation of calcium naphthenate deposits. At medium calcium concentrations the divalent cations competes with monovalent cations to have a partially binding to the tetrameric acids instead of forming cross-linked networks. The divalent cations will after some time exchange monovalent cations to gradually build up a network.[4]

It is believed that other acidic species in the crude oil, like monoacids, may act as a natural inhibitor toward naphthenate deposits. Interfacial shear rheology studies with BP-10 showed that the properties of the calcium naphthenate film changed dramatically by addition of monoacid with a concentration similar to what is typical in acidic crude oils. The monoacids are believed to inhibit gelation by placing itself between the tetrameric acids at the interface terminating the cross-linking process. That fact can explain why some acidic tetrameric acid containing crude oils have problems with calcium naphthenate deposits and some not.[4] Figure 7 illustrates the interaction between calcium, monoacid and tetrameric acid at the interface.

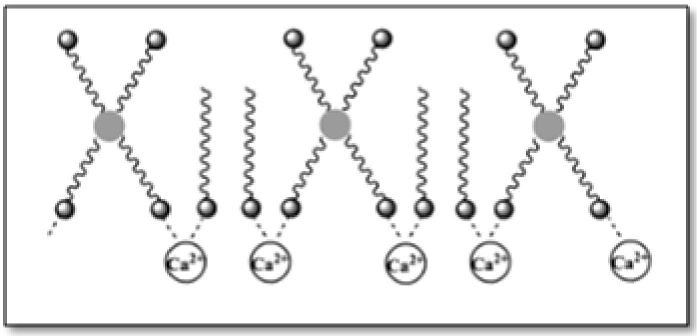


Figure 7: Illustration of how a monoacid can terminate the cross-linking between tetrameric acid and calcium.[4]

4. Experimental Techniques

4.1 Langmuir Trough Technique

The Langmuir technique is used to study film formation and monolayer properties of surface active materials. The technique can give information about how much area each molecule requires, how the molecules interact with each other and how the molecules pack in a monolayer.[15]

To get the film forming material to spread out at the sub-phase it is solubilised in an organic solvent before it is spread onto the sub-phase. The solvent that is being used needs to fulfil several properties. The spreading coefficient of the solvent onto the sub-phase has to be positive so that it spreads spontaneously. The solvent also need to have good ability to spread the film forming molecules so that the amphiphiles are in a monomeric state at the surface. It is also important that the solvent is chemically inert with the respect to the sub-phase and the film forming material in the sample and that it evaporates after a relatively short time.[15]

The instrument consists of a shallow rectangular trough and two moving barriers. The surface pressure is measured with a Wilhelmy paper probe. This probe determines the surface pressure by measuring the force due to surface tension on the probe that is partially immersed in the sub-phase. The dimension of the plate then allows one to convert the force into surface tension (mN/m). Figure 8 shows how the forces are measured by the Wilhelmy- plate method, and the typical experimental setup.[16]

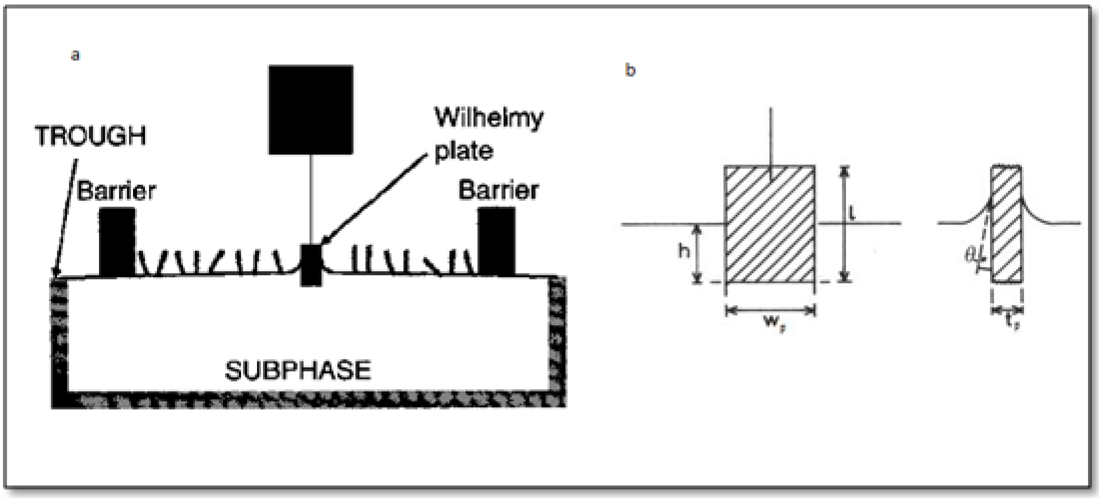


Figure 8: a) Typical experimental setup for the Lanmuir trough.b) Wilhelmy plate partially immersed in a water surface [9, 16]

A typical measurement is carried out by filling up the trough with the water phase. The paper probe is hanged on the balance so that it is partially immersed in the liquid. Then the sample containing the amphiphiles is spread onto the surface. After the solvent has completely evaporated the layer of surfactants are compressed thanks to the barriers.[9, 15] As the compression proceeds the amphiphiles will start to interact with each other, causing an increase in the surface pressure (π) according to equation I,

$$\pi = \gamma_0 - \gamma \qquad \text{(I)}$$

Where γ_0 is the surface tension at a clean surface and γ is the surface pressure in presence of the sample.[9]

At the start of compression the monolayer are in a gaseous phase. This phase has small influence on the surface pressure. As the barriers move and the area gets smaller the molecules gets closer together and they start to exceed a repulsive effect on each other. The interactions lead to an increase in surface pressure and the monolayer forms a liquid phase. A range where the increase in surface pressure is low or a horizontal break indicates a phase transition. During the phase transition the molecules undergo a conformational change of the molecules in the film which causes the surface active molecules to pack closer together. Further compression of the film can lead to a solid phase, where the molecules have reached their optimal packing. Compression after the solid phase will cause the monolayer to collapse into three dimensional structures. The film collapse can be seen as a decrease of the compressibility of the layers. [6, 9, 15, 16] Figure 9 show an example of surface pressure area isotherm. However not all samples can undergo the same phase changes as described in the figure.

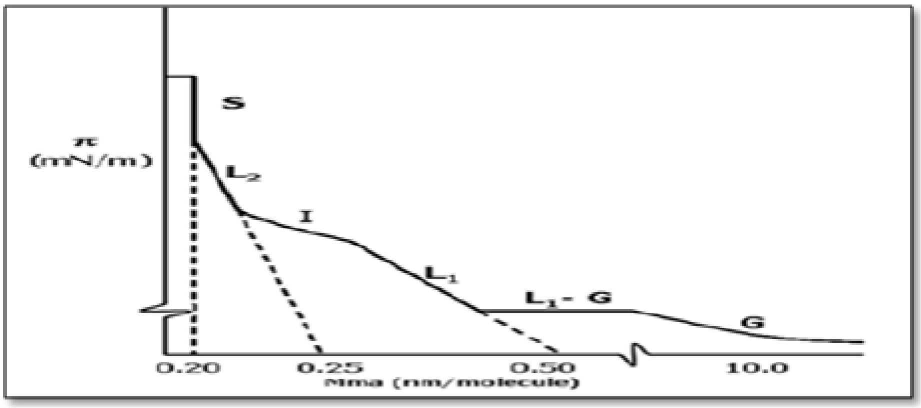


Figure 9: Example of a surface pressure area isotherm [9]

4.2 Langmuir- Schaefer Dipping Technique

The Langmuir technique can also be used to build highly organized multilayers of the amphiphiles that are being used. This is achieved by dipping a solid material onto or down through the monolayer, while keeping the surface pressure constant. The monolayer will then adsorb onto the solid material. In this work a dipping technique called Langmuir-Schaefer has been used.

This technique differs from the other common dipping technique, the Langmuir-Blodgett technique, in which the solid material is dipped horizontally instead of vertically onto the surface. The films that can be made from this technique are ranging from multilayer structures to ultra thin monolayer. In this work the solid material that was used was a silica QCM crystal and the crystal was only dipped onto the surface one time to deposit the material present at the water surface onto the surface of the crystal. More on the crystal and the QCM technique is described in the following chapter. [16, 17] The instrumental setup for the Langmuir-Schaefer technique is illustrated in figure 10.

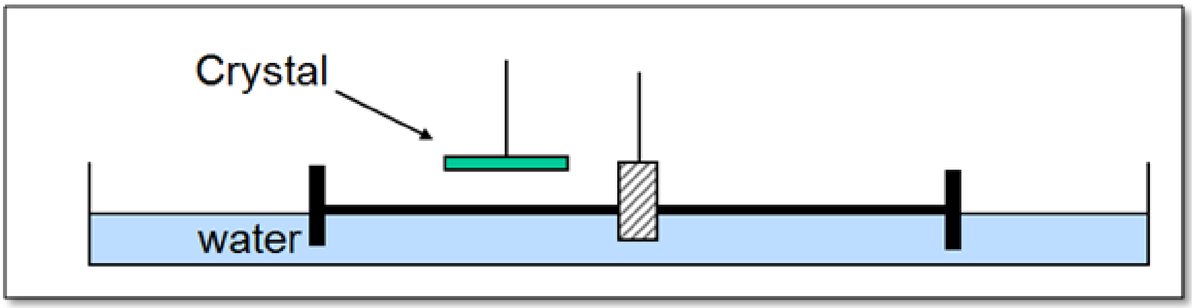


Figure 10: Instrumental setup for the Langmuir-Schaefer dipping technique.

4.3 QCM - Quartz Crystal Microbalance

The quartz crystal micro balance (QCM) is an extremely sensitive mass sensor capable of measuring mass changes down to the nanogram range. The technique is based upon the piezoelectric effect in crystals which was first discovered as early as 1880 by Pierre and Marie Curie.[18, 19]

The piezoelectric effect did not receive a lot of interest until 1917 when more detailed studies were started. In 1921 the first quartz crystal controlled oscillator was described. These oscillators were based on X-cut crystals which are cut so that the plane of the crystal plate is perpendicular to the X crystallographic axis. However, these crystals had a drawback of being very temperature sensitive. The AT-cut crystals where first introduced in 1934.The AT-cut crystals are cut in a way so that the plate contains the X-axis and have an angle of about 35 degrees with the optical axis.[18, 20] The AT-cut crystal had nearly zero frequency drift with temperatures around room temperature, and its findings made the quartz crystal oscillator dominant for all kinds of frequency control applications.[18] Figure 11 illustrates an AT-cut quartz crystal.

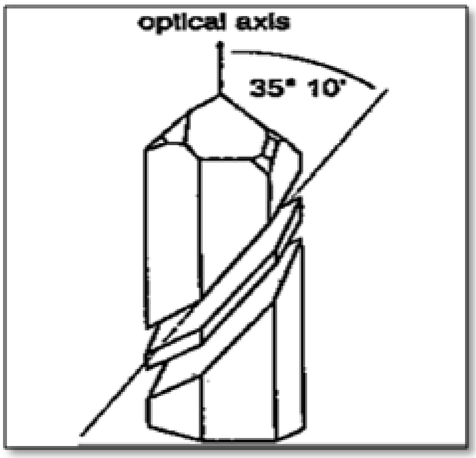


Figure 11: Illustration of an AT-cut quartz crystal.[21]

In 1959 Sauerbrey published a breakthrough paper showing that the frequency shift of a quartz crystal resonator is directly proportional to the added mass. This paper counts as the first step towards the qualitative tool to measure very small masses, the quartz crystal microbalance (QCM).[18, 21]

The heart of the QCM is the piezoelectric AT-cut quartz crystal. When the crystal is placed between a pair of electrodes and the electrodes are connected to an oscillator an AC-voltage is applied over the electrodes.

This effect makes the quartz crystal oscillate at its resonance frequency due to the piezoelectric effect.[18, 21] Figure 12 shows a quartz crystal with its electrodes and deposition area.

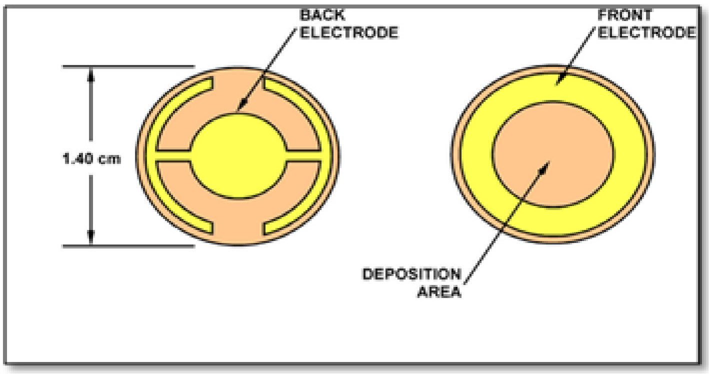


Figure 12: Illustration of the front and the back of a quartz crystal for QCM measurements.[22]

When depositing a mass onto the quartz crystal the resonance frequency will decrease proportionally to the mass of the adsorbed layer according to the Saurbrey equation,

$$\Delta f = -\frac{[2 * f_0^2 * \Delta m]}{[A * (\rho_q * \mu_q)^{1/2}]} \qquad \text{(II)}$$

Where Δf is the measured frequency shift, f_0 is the resonant frequency of the fundamental mode of the crystal, Δm is the mass change pr. unit area (g/cm^2), A is the piezoelectrically active area, and ρ_q and μ_q are the density and shear modulus of quartz.[18, 21]

A simplified version of the equation is obtained by combining all the known components into a constant C.

$$\Delta m_{sp} = -\frac{C\,\Delta f}{n} \qquad \text{(III)}$$

In this work the constant C had a value of 17.7ng Hz^{-1}cm^{-2}, and the overtones, n, used in this work was 1, 3, 5 and 7.

Certain requirements have to be fulfilled for the equations above to be valid. First, the mass adsorbed onto the crystal has to be much smaller than the mass of the crystal its self (< 1%), the adsorbed mass has to be evenly distributed on the crystal, and the adsorbed mass has to be rigidly attached, with no slips or inelastic deformation in added mass due to oscillatory motions.[23, 24]

4.4 Combination of the Langmuir-Schaefer Technique and the QCM Technique

In this thesis a combination of the Langmuir- Schaefer technique and the QCM technique has been used to determine the mass of tetrameric acid at the interface. A Langmuir film was formed using the Langmuir trough technique and then a part of the interface was deposited onto a QCM crystal using the Langmuir-Schaefer technique. Afterwards the amount of acid deposited on the crystal was determined using the QCM. The mass deposited onto the crystal was calculated from the difference in frequency for the clean crystal and the frequency of the crystal after deposition using the Saurbrey equation mentioned in chapter 4.3. As mentioned in the previous chapter the QCM are able to determine the mass down to nanogram range with high accuracy, which makes the method suitable for determining the lowest masses at the interface.

5. Reagents and Solutions

The following chapter gives a short overview over how all the solutions used during the experiments was made.

5.1 BP-10 Solution

The solution was made utilizing the model compound BP-10 that is synthesized at the Ugelstad Laboratory and Chloroform (≥ 99.8 %, Sigma Aldrich). BP-10 (37.5 mg) and chloroform (45 g) were weight up into tall screw cap vial. Afterwards the sample was put into a sonic bath for 1 hour, and then set to shake over night on a shaking table.

5.2 Monoacid Solution

The monoacid solution was made utilizing 4-Octylbenzoic acid (99 %, Acros organic) and Chloroform (≥ 99.8 %, Sigma Aldrich). Monoacid (37.5 mg) and chloroform (45 g) were weight up into a tall screw cap vial and shaken well so that the acid was completely solubilised.

5.3 Monoacid + BP-10 Solution

Monoacid (51.3 mg) and BP-10 (37.5 mg) were weight up into a tall screw cap vial and solubilised with chloroform (45 g). The sample was put into a sonic bath for 1 hour and then set to shake on a shaking table over night.

5.4 Sub-phases for Langmuir Experiments

The sub-phase with calcium at pH 7 was made utilizing 3-(N-Morpholino)propanesulfonic acid, 4-Morpholinepropanesulfonic acid (MOPS) (≥ 95 %, Sigma Aldrich), and Calcium Chloride Dehydrate (Fluka). The Sub-phase with calcium at pH 5 was made utilizing acetic acid (100%, Normapur). For both sub-phases sodium chloride (Emsure) was used.

The sub-phases and their concentration used for the Langmuir experiments are listed in table 1. The pH was adjusted by adding NaOH (0.5M)

Table 1: Sub-phases and their concentrations used for the Langmuir experiments

Solution	Buffer	[Buffer] (mM)	[NaCl] (mM)	[$CaCl_2$, $2H_2O$] (mM)
Sub-phase with calcium pH 7	MOPS	10	20	10
Sub-phase with calcium pH 5	Acetic acid	10	20	10

6. Equipment and Methods

6.1 Equipment

For the Langmuir trough experiments, a Langmuir-Blodgett Mini trough apparatus from KSV Instruments Ltd., Finland with a Teflon trough with an area of 242.25 cm^2 was used. For the Langmuir- Schaefer experiments a dipper-arm from the same brand was used. The QCM apparatus used were a QCM-Z500 delivered from KSV Instruments Ltd., Finland.

6.2 Methods

6.2.1 Crystal Preparation

Before starting the experiments it was very important that the crystals were clean. First the crystal was cleaned with ethanol and Milli-Q water, dried with compressed air and placed in an O_3-bath with the silica facing up, for 10 minutes. After 10 minutes the crystal was cleaned with ethanol and Milli-Q water again before it was placed in SDS 2% washing solution for 30 minutes. After that the crystal was once again washed with ethanol and Milli-Q water, dried with compressed air and put into an O_3-bath for 10 minutes. At last the crystal was put into a heating cabinet at 110°C for 1 hour followed by 30 minutes in a desiccator containing silica-gel.

6.2.2 QCM- Langmuir Experiments

The crystals were cleaned according to procedure described above, and placed in a heating cabinet at 110 °C for 1 hour followed by 30 minutes in a desiccator containing silica-gel. After the desiccator blank analysis was performed to determine the frequency of the clean crystal. Then the Langmuir trough and the dipper was cleaned and prepared for analysis. Desired amounts of BP-10 were injected to the surface and the instrument was set to compress to 125 cm^2 after 10 minutes when the spreading solvent had evaporated. When the compression was done the crystal was collected from the QCM apparatus and attached to the dipper arm. The crystal was then dipped onto the surface in the trough where it was kept for 30 seconds before the crystal was brought up from the surface again and collected. Afterwards the crystal was carefully washed with Milli-Q water before it was placed into an oven for 110 °C for 1 hour and then in a desiccator containing silica-gel for 30 minutes. At the end the crystal was placed back into the QCM apparatus and the analysis was started.

For both the blank analysis and the analysis after deposition, the QCM-experiments were set to run for 10 minutes for each parallel. If the signals were unstable and varied with more than 3Hz during the 10 minutes the experiments were stopped and started again. The mass of BP-10 deposited on the crystal was determined by analyzing the differences in frequency from the blank analysis to the analysis after deposition using the Sauerbrey equation mentioned in chapter 4.3. Figure 13 illustrates the principles for the QCM-Langmuir experiments

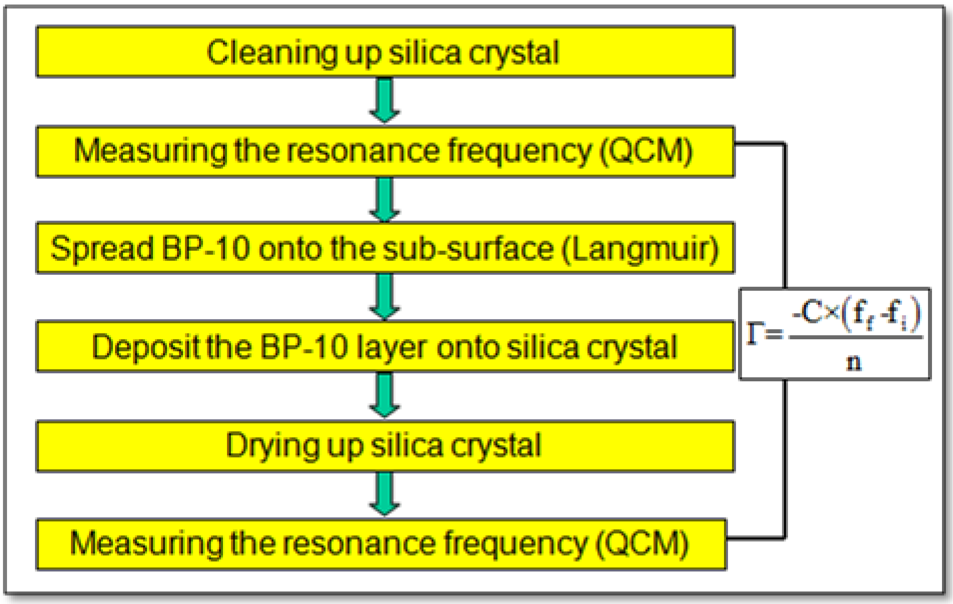


Figure 13: The principles of the QCM-Langmuir experiments

7. Results and Discussion

Calibration curves with BP-10 on sub phases with calcium at pH 5 and pH 7 were made using the method described above in chapter 6.2.2. By compressing to a certain surface area, in this case 125 cm^2, one can from the concentration of the sample, the amount of sample injected to the surface, and the surface area after compression calculate the theoretical surface coverage of the sample. The calibration curves were then made by plotting the results from the analysis against the theoretical surface coverage value.

7.1 Calibration Curve for BP-10 at pH 7 with Calcium Present

First a calibration curve was made at pH 7, which is as mentioned earlier in chapter 3.4 are gel-forming condition. At pH 7 all the acid groups are dissociated so the BP-10 molecule is able crosslink with the calcium ions in the water-phase. Because of that the theoretical surface coverage is calculated based on the assumption that each BP-10 molecule reacts with 2 calcium ions. The calibration curve was made by injecting different amounts of BP-10 to the surface of the sub-phase containing calcium. To ensure good spreading of the BP-10 sample when running the experiments with low surface coverage, the BP-10 sample was diluted so that larger volume of the sample could be spread.

The QCM measurements were conducted at overtone 1, 3, 5 and 7. The signals at overtone 3 have shown to give the most stable result, and because of that these results were used to make the calibration curve. The results obtained in this work at all the different overtones, and the uncertainties of the different experiments are listed in table 10 in appendix 3.

The calibration curve obtained from the experiments is shown in figure 14. Results from previous work are also shown in the figure, however the results from the previous work are not listed in the table in appendix 3.

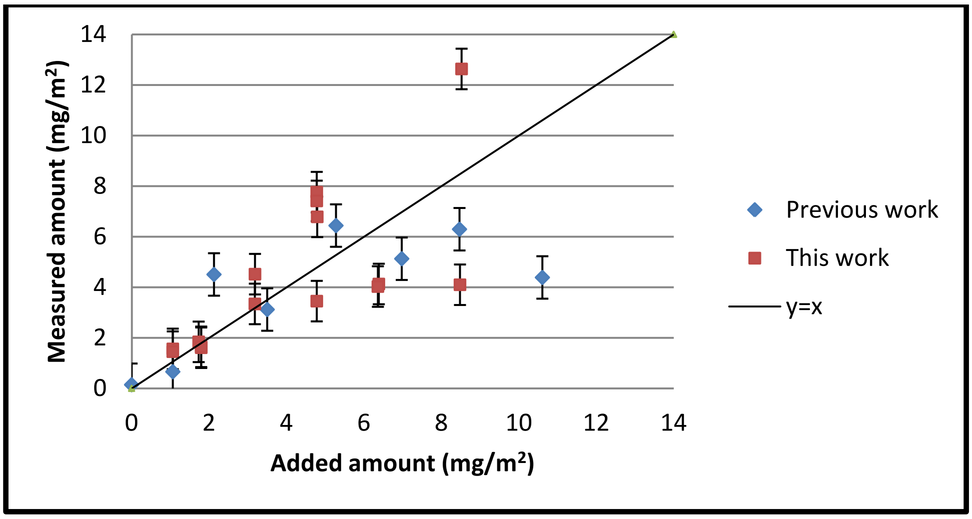


Figure 14: Calibration curve for BP-10 at pH 7 with calcium present

From figure 14 one can see that the relationship between the amounts of BP-10 added and the measured amount showed an almost linear trend up to a surface coverage of 6 mg/m^2. As the spreading amount increased the difference between the measured amount and the added amount was larger.

Figure 15 shows the linear trend at the lower injection amounts. The slope and interception of the curve are shown in the corner of the figure.

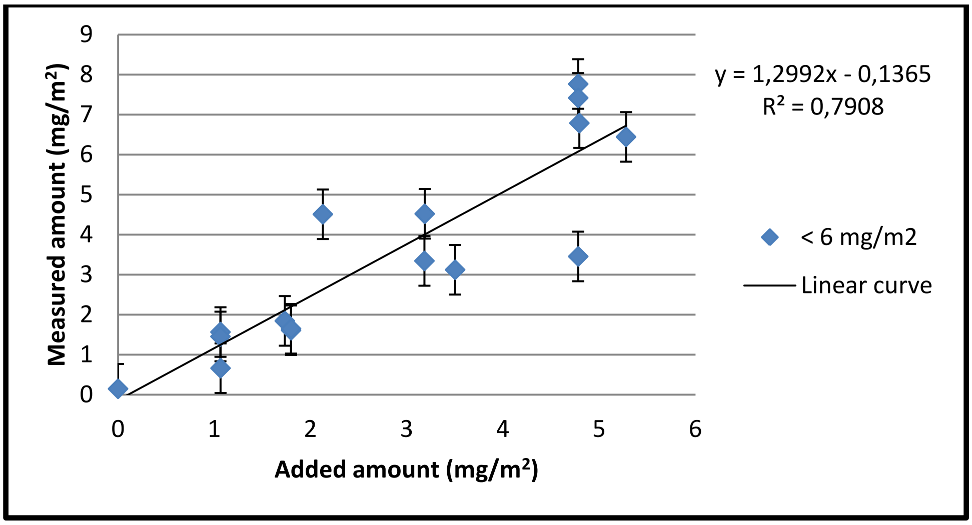


Figure 15: The linear trend for measured amounts smaller than 6 mg/m^2 at pH 7.

The linear curve had a slope of 1.3 and intercepted the y-axis at -0.14 which is very close to the origin. The R^2 value was calculated to 0.79 which means that there is a linear relationship between the measured amounts and the added amounts.

The uncertainties from the QCM measurements were calculated from the standard deviations from the frequencies measured from the blank crystal and the frequencies measured for the crystal after deposition. These standard deviations were then added together and multiplied with the constant C, mentioned in chapter 4.3 and divided by the overtone for which the frequency is measured. Equation IV shows the equation used to calculate the uncertainties.

$$Uncertainties = \left[STD\left(f_{clean\ crystal}\right) * \frac{C}{n}\right] + \left[STD\ \left(f_{crystal\ after\ deposition}\right) * \frac{C}{n}\right] \qquad \text{(IV)}$$

As table 10 in appendix 3 shows, the uncertainties obtained from the QCM measurements were very low, but as figure 14 illustrates, the difference between the measured amounts and added amounts were large in many of the experiments. From that it is clear that the errors is not only due to only the QCM measurements but that it is most likely more errors from other parts of the procedure.

At higher spreading amounts there was no linear trend and the measured amounts were always smaller than the added amount except for one point. Figure 16 shows the calibration curve for higher spreading amounts.

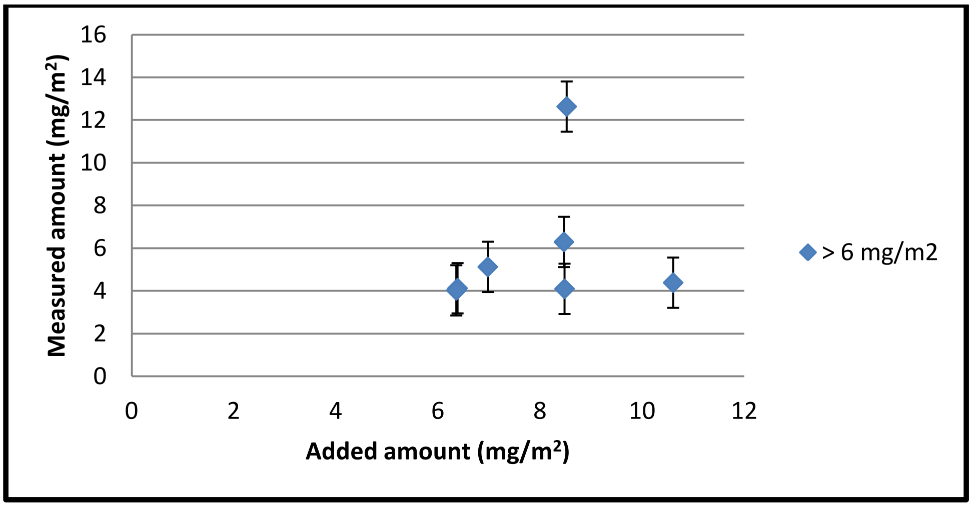


Figure 16: The calibration curve with high spreading amounts at pH 7.

As figure 16 illustrates, the results flattened out at higher spreading amounts and the difference between the measured amounts and the added amounts were large for all the samples. The reason for the poor correlation between the measured amounts and the added amounts can be that there was formation of multilayers at the interface. If that was the case, when dipping the crystal onto the interface only the upper layer would deposit onto the crystal, thus giving a lower measured amount than added amount.

The Langmuir isotherms for each experiment were compared to see if the results could explain the variations in the QCM results. The isotherms showed to have poor reproducibility and there was no clear consistency between the isotherms and the QCM results. All isotherms are listed in appendix 4, but some examples have been chosen to illustrate the poor reproducibility and the lack of consistency in the results.

Figure 17 illustrates the isotherms obtained by spreading 50µl BP-10 (0.26 g/L) onto the sub-phase containing calcium at pH 7. The QCM results for each sample are listed in table 2 beneath the figure.

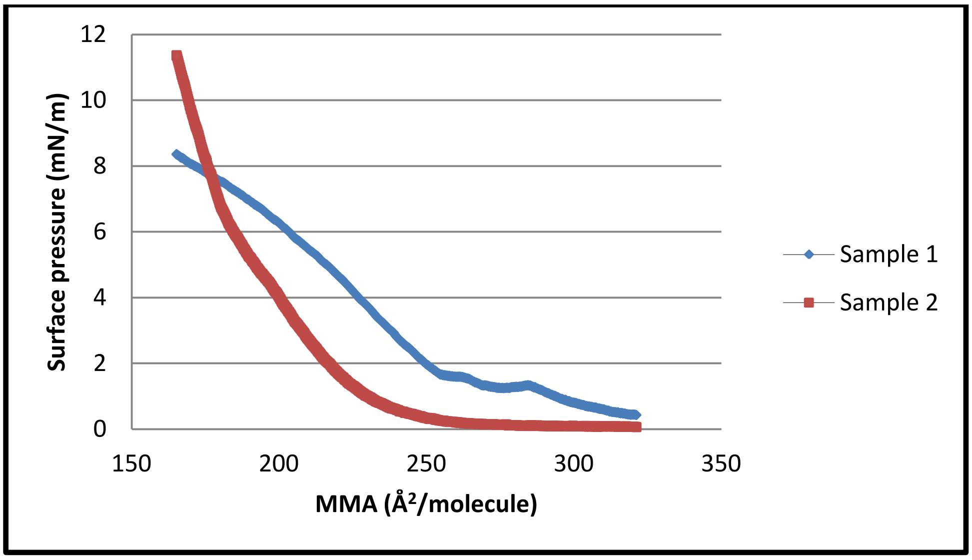


Figure 17: Langmuir isotherms for experiments when spreading 50µl of BP-10 (0.26 g/L) onto a sub-phase at pH 7 and calcium present.

Table 2: QCM results for experiments when spreading 50µl of BP-10 (0.26 g/L) onto a sub-phase with pH 7 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	1.06	1.56
2	1.06	1.45

The experiments were conducted with the same BP-10 sample and the same batch of Sub-phase and hence the added amount was the same. The measured amount of BP-10 for the two samples was also very similar. As figure 17 shows, the Langmuir isotherms obtained did not reflect that. Not only was the shape of the isotherms very different, the surface pressure at the end of compression showed big variations.

The second example shows the isotherms obtained from the experiments with more concentrated solutions of BP-10. In these experiments 45µl of BP-10 (1.23 g/L) were used. The isotherms obtained from the experiments are illustrated in figure 18.

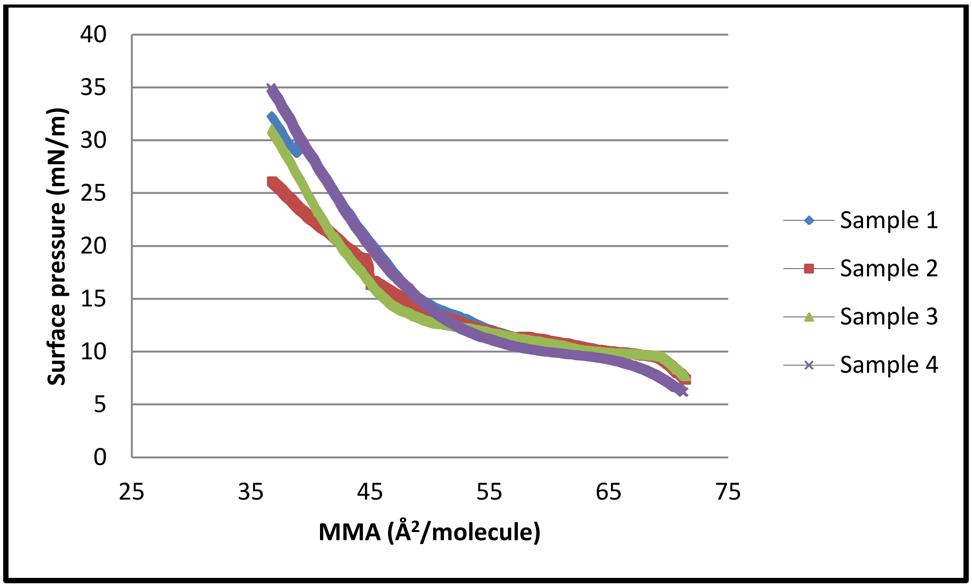


Figure 18: Langmuir isotherms obtained for experiments when spreading 45µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

The QCM results for each of the samples are listed in table 3.

Table 3: QCM result for experiments when spreading 45µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	4.78	3.45
2	4.78	7.76
3	4.78	7.41
4	4.79	6.78

As one can see from figure 18, the isotherms obtained from sample 1, 3 and 4 where quit reproducible, but as table 3 illustrates, the QCM results from these experiments were not.

The isotherm obtained from sample 2 is the isotherm that was most different from the other isotherms, however the QCM result from the experiment with sample 2 were very similar to the QCM results for sample 3 and 4. As illustrated in this example, the reproducibility of the Langmuir experiments were not reflected in the QCM results.

As mentioned earlier the relationship between the added amounts and the measured amounts of BP-10 at the interface showed more variations and no linear trend at higher surface coverage than 6 mg/m^2. The Langmuir isotherms on the other hand had better reproducibility than some of the isotherms obtained with lower injection amount. Figure 19 show the isotherms obtained by spreading 80µl of BP-10 (1.23 g/L) onto the surface.

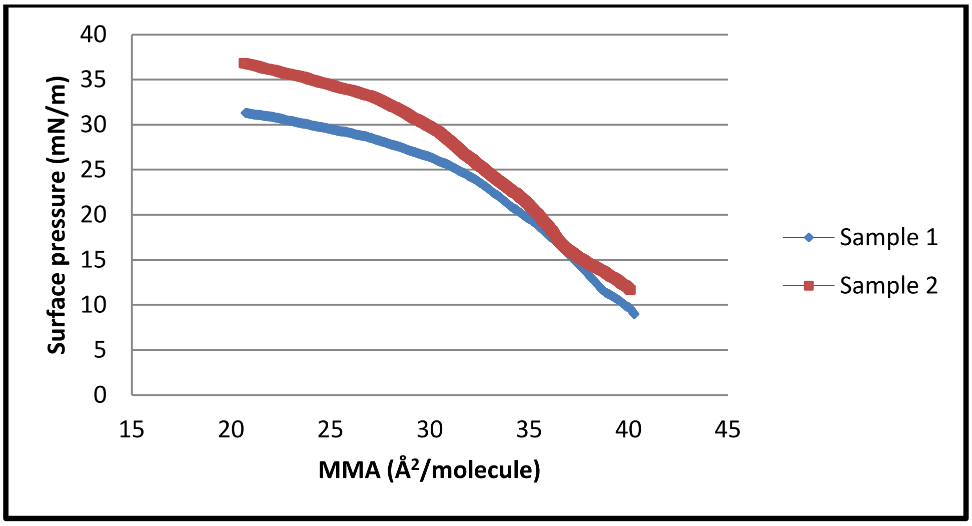


Figure 19: Langmuir isotherms for experiments when spreading 80µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

The QCM results for each sample are listed in table 4.

Table 4: QCM results for experiments when spreading 80µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	8.48	4.10
2	8.52	12.63

From table 4 one can see that the measured amount of BP-10 was very different for the two samples. However the isotherms were very alike with only small differences in surface pressure. In this case a much higher mass at the surface were not reflected in the surface pressure.

From figure 18 and 19 one can see that an almost a doubling of the added BP-10 amount with the same concentration injected to the surface did not affect the surface pressure in any great means. The surface pressure at the end of compression was the same at both experiments. There was also no consistency between the added amounts and the surface pressure obtained. In figure 18 the sample with the highest measured amount of BP-10 at the interface gave the smallest surface pressure at end of the compression. The opposite is seen in figure 19, but the difference was small compared to the huge difference in measured amount of BP-10 at the interface. It is believed that BP-10 forms different conformations during the compression giving different masses at the interface. Formation of multilayers can also be an explanation for the poor correlation between the added amounts and the measured amounts at higher spreading amounts. As the three examples show there was little to no correlation between the reproducibility of the isotherms obtained, but the poor reproducibility did not affect the QCM results.

Studying the Langmuir isotherms also raised questions regarding the shapes of the isotherms. Earlier Langmuir film experiments with BP-10 at pH 7 with calcium present in the sub-phase performed by the author gave isotherms with different shapes than those obtained from these experiments with the same conditions. However, since the isotherms obtained in the earlier experiments were not compressed to the same point, a comparison was difficult to do. And as for the isotherms obtained from this work the isotherms from the previous work also showed poor reproducibility.

7.2 Calibration Curve for BP-10 at pH 5 with Calcium Present

A calibration curve at pH 5 with calcium present in the sub-phase was also made using the same method as for the pH 7 calibration curve. At pH 5 there is no gelation occurring, as the pH is too low to dissociate the acid groups so there is no cross-linking or reaction between BP-10 and calcium. At low pH the theoretical surface coverage is therefore calculated assuming there is no reaction with calcium at the interface. The QCM measurements were performed at overtone 1, 3, 5 and 7, and the results from overtone 3 were used to make the calibration curve. Table 17 in appendix 5 lists the results from each overtone for all the samples. The uncertainties for each experiment are also listed in the table. The calibration curve obtained is shown in figure 20.

Also at pH 5 the results had two different ranges. For injection amounts lower than 7mg/m^2 a linear trend could be seen, for higher injection amounts the measured amounts was always smaller than the added amounts.

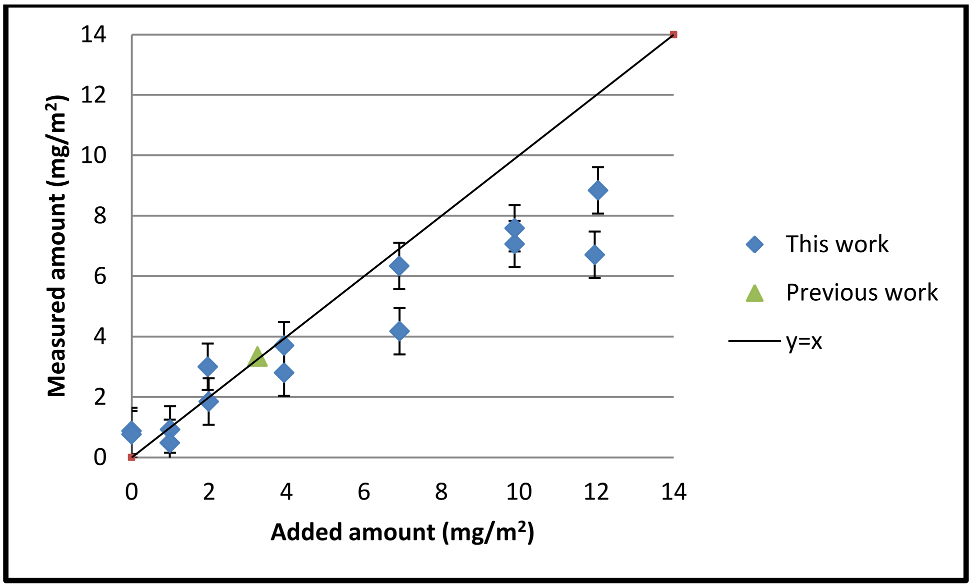


Figure 20: Calibration curve for BP-10 on a sub-phase with pH 5 and calcium present

Figure 21 shows the linear trend for injection amounts lower than 7 mg/m^2. The equation for the linear curve is shown in the corner of the figure.

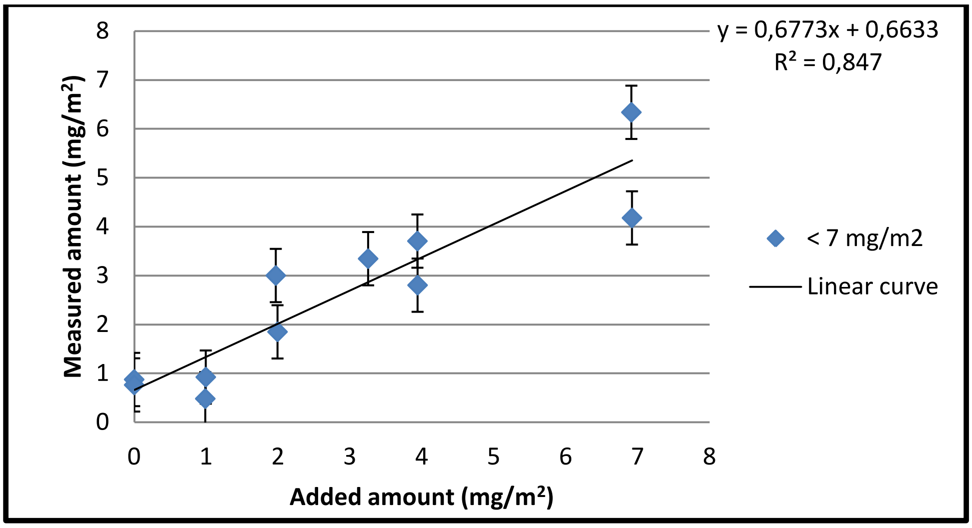


Figure 21: Linear trend for measured amounts lower than 7 mg/m^2 at pH 5.

The linear curve gave an equation with a slope of 0.68 and an interception with the y-axis at 0.66. The R^2 value was calculated to 0.85 which means that there is a linear relationship between the measured amounts and the added amounts.

Above 7 mg/m^2 the results showed more variation. The calibration curve for higher spreading amounts is shown in figure 22.

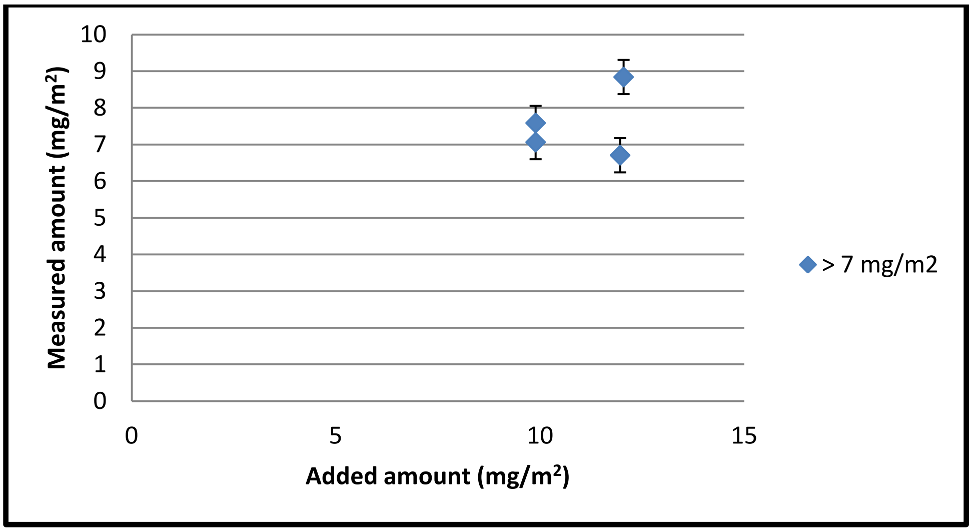


Figure 22: The calibration curve for higher spreading amounts at pH 5.

At higher spreading amounts the results flatted out. The reason could be that the conformation of the BP-10 molecule changed during compression giving a lower mass at the interface.

As for pH 7, the QCM gave stable results and low uncertainties. So error caused by the difference in the measured amounts and the added amounts are most likely caused by errors from other parts of the procedure.

The Langmuir isotherms did not show the same reproducibility and stability as the QCM measurements. Isotherms obtained for each injection amount are listed in appendix 6. Below some examples are shown to illustrate the poor reproducibility.

The isotherms obtained by injecting ~2mg/m^2 onto the sub-phase are illustrated in figure 23. The added amounts and measured amounts for each sample are listed in table 5 beneath the figure. Even if the measured amounts differed some, the isotherms looked completely different. The first sample which had a lower concentration of BP-10 (0.42 g/L) but a higher injection volume (60µl) had a constant surface pressure throughout the compression. For the second sample which had a lower injection volume (50µl) but a higher concentration of BP-10 (0.49 g/L), a good reproducibility was obtained.

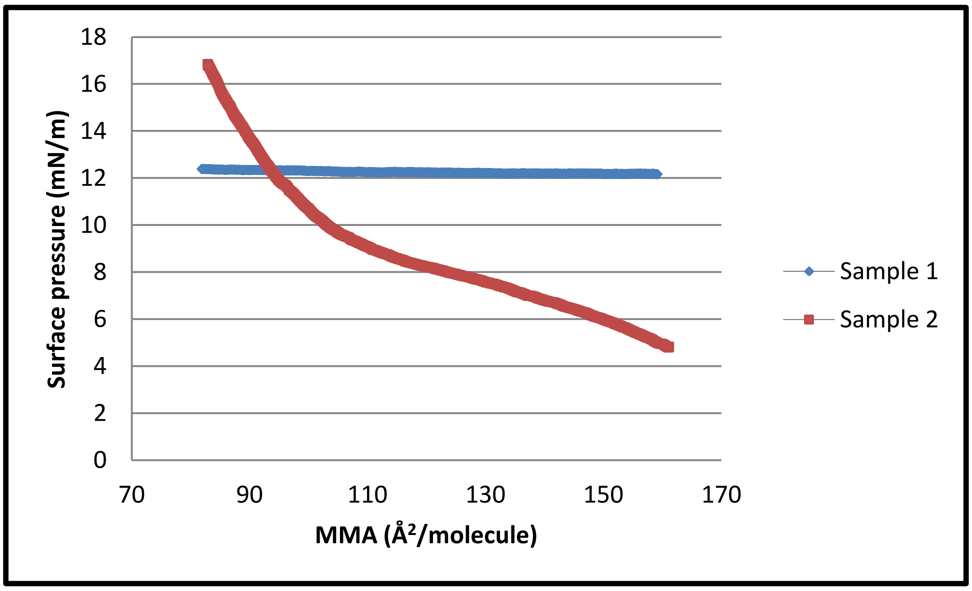


Figure 23: Langmuir isotherm for experiments when spreading for sample 1, 60 µl of BP-10 (0.42 g/L) and for sample 2, 50µl of BP-10 (0.49 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each experiment are listed in table 5.

Table 5: QCM results for experiments when spreading for sample 1, 60 µl of BP-10 (0.42 g/L) and for sample 2, 50µl of BP-10 (0.49 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	1.99	1.85
2	1.97	3.00

The same trend was seen in the isotherms where 40µl of BP-10 (1.23 g/L) was spread onto the surface. Figure 24 shows the isotherms obtained and table 6 shows the added amount and measured amount for each sample. For these experiments the same amount of BP-10 were added to the surface, but the isotherms did not have similar behaviour. Like the first sample in the previous example, the first sample in figure 24 had an almost constant surface pressure throughout the compression. In this case the surface pressure varied with ~1 mN/m. The isotherm obtained from the second sample on the other hand, had a more similar shape as other isotherms obtained at pH 5, see appendix 6.

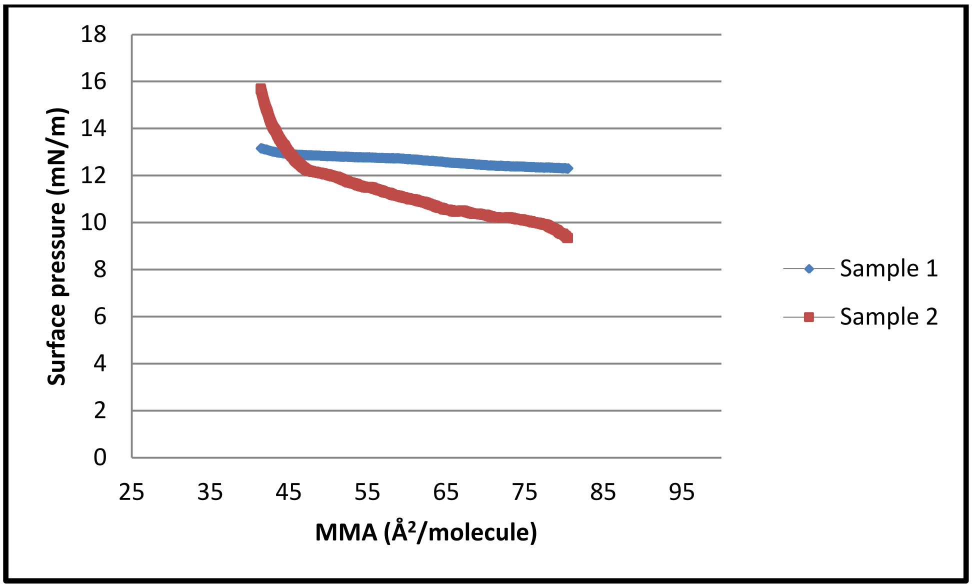


Figure 24: Langmuir isotherms for experiments when spreading 40 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Table 6: QCM results for experiments when spreading 40 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	3.94	3.70
2	3.94	2.80

For both the experiments shown in table 5 and 6 the QCM results varied with almost 1 mg/m^2 from each other. For both experiments the samples which gave isotherms with almost constant surface pressure throughout the compression gave the smallest measured amounts of BP-10 at the interface.

The experiments were performed with different BP-10 solutions and different buffer solutions so error caused by those factors was ruled out. The reason for the difference in the results can be that the spreading of the BP-10 was not good enough for a film to form, or that the acid took different conformation during the compression

Higher surface coverage gave very similar isotherms and good reproducibility for the QCM measurement. However, the measured amount of BP-10 at the interface was significantly different from the spread amount, and the relationship between the added amount and the measured amount did no longer show any linear trend. Figure 25 shows the isotherms obtained by spreading 100µl of BP-10 (1.23 g/L) onto the sub-phase. Beneath the figure the QCM results for each sample are listed in table 7.

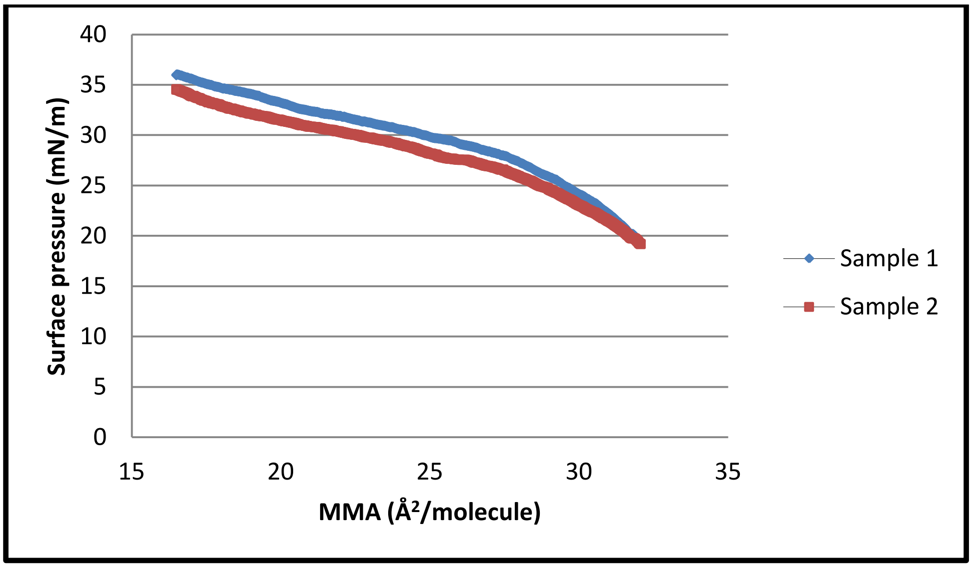


Figure 25: Langmuir isotherms for experiments when spreading 100µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Table 7: QCM results for experiments when spreading 100 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	9.89	7.06
2	9.89	7.59

The example shows that the Langmuir isotherms had good correlation with the QCM results. Sample 2 which had the highest surface pressure at the end of compression, also had the highest measured amount of BP-10 at the interface.

The isotherms showed small differences in both shape and surface pressure, just like the QCM results had small differences in measured amount at the interface. On the other hand the correlation between the measured amount and the added amount was poor. Again the reproducibility of the Langmuir isotherms did not reflect the reproducibility of the QCM results. However, the reproducibility of the Langmuir isotherms did not have any influence on the QCM results.

The results for the experiments at conditions where there is a gelled interface and at conditions where there was no gellation occurring showed the same trends. Both conditions gave a linear relationship between the added amounts and the measured amounts at low spreading amounts, and at higher spreading amounts both conditions gave measured results which were lower than the added amount.

7.3 The Influence of Addition of Monoacid

First two experiments with pure monoacid solution were conducted using the same method as described in chapter 6.2.2. Afterwards the same method was used with a mixed sample of monoacid and BP-10. At the end the results from the experiments with pure monoacid solution, pure BP-10 solution, and the mixed solution were compared to see if the monoacid had any influence on the results.

7.3.1 QCM-Langmuir Experiments with Pure Monoacid Solutions at pH 7 with Calcium Present.

The experiment was performed with a model monoacid in the form of 4 -Octylbenzoic acid (1.23 g/L) at a sub-phase at pH 7 containing calcium. The results that were obtained are shown in figure 26.

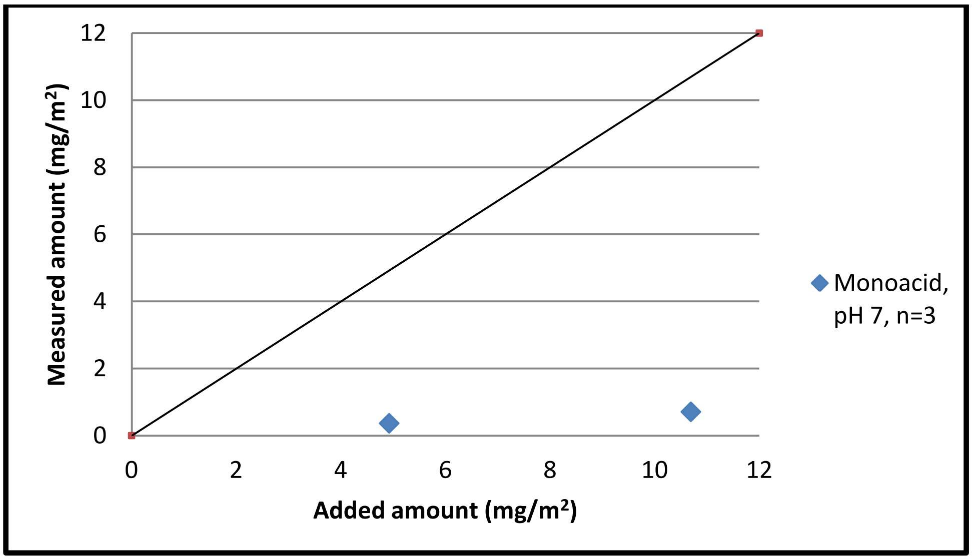


Figure 26: Comparison between the measured amount and added amount for 4-octylbenzoic acid at pH 7 with calcium present.

Table 8 lists the QCM results obtained for each sample.

Table 8: QCM result for monoacid at pH 7 with calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	4.93	0.37
2	10.69	0.71

The first experiment was performed with 45µl of the monoacid sample, the second with 100µl. As figure 26 and table 8 illustrates there was little or no deposition of monoacid onto the crystal for either of the samples, and the measured amount of monoacid at the interface was very similar for the two samples regarding the huge difference in added amounts.

From the results it is believed that the monoacid is unable to form a film at the interface. This is further illustrated in the isotherms obtained from the experiments which are shown in figure 27 and 28.

During the Langmuir experiments it was observed that the behaviour of the monoacid was very different from the BP-10. Unlike BP-10 which spreads out on the sub-phase immediately, the monoacid was harder to spread out as it formed droplet like layers on the interface. The droplets spread out after few seconds. As the monoacid were injected the surface pressure increased fast, but after injection the surface pressure decreased down to zero after a short time. This was the case for both samples. As figure 27 and 28 shows for both samples the surface pressure was nearly zero the whole compression time and only started to rise at the end.

Figure 27 shows the isotherm obtained by spreading 45µl of 4-Octylbenzoic acid (1.23 g/L) the sub-phase at pH 7 containing calcium.

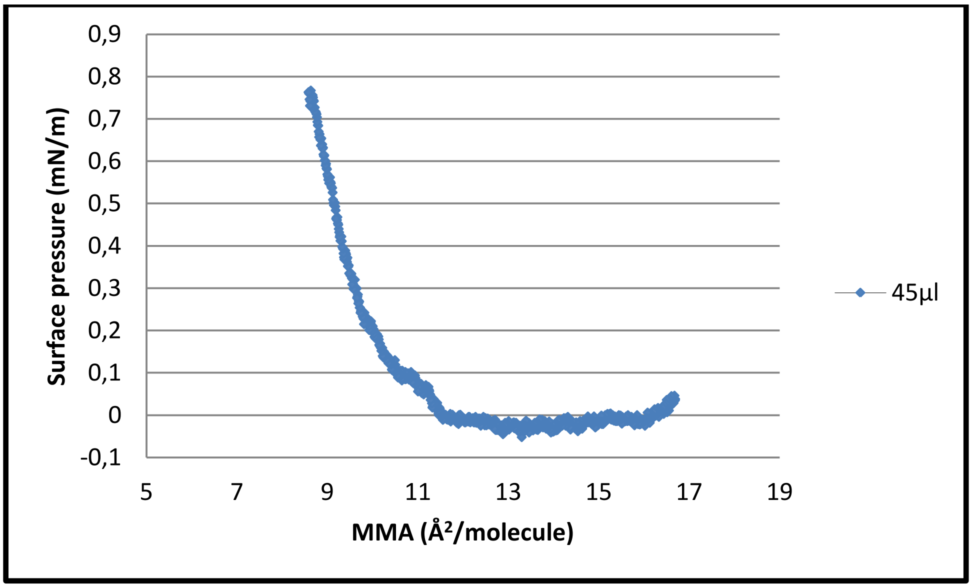


Figure 27: Langmuir isotherm for the experiment when spreading 45µl of 4-octylbenzoic acid (1.23 g/L) onto the sub-phase at pH 7 containing calcium.

Figure 28 shows the isotherm obtained by spreading 100µl of 4-Octylbenzoic acid (1.23 g/L) the sub-phase at pH 7 containing calcium.

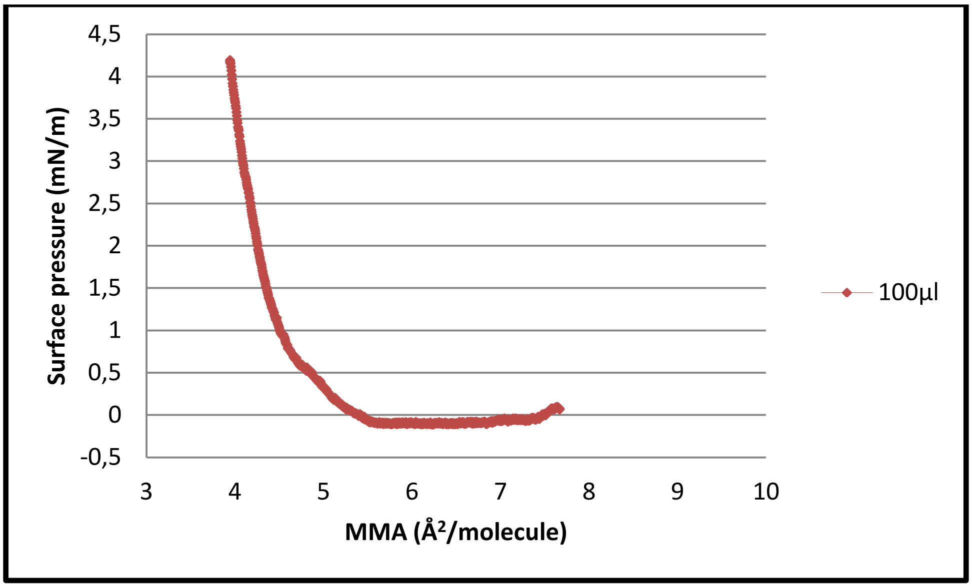


Figure 28: Langmuir isotherm for the experiment when spreading 100µl of 4-octylbenzoic acid (1.23 g/L) onto the sub-phase at pH 7 containing calcium

As expected the sample with the highest surface coverage reached a higher surface pressure at the end of compression, but the behaviour and the shape of the isotherms was the same.

From the results obtained from the experiments with monoacid, it appears that the film that is formed by reaction between 4-octylbenzoic acid and calcium ions at pH 7 are unable to deposit onto the crystal by the Langmuir-Schaefer technique. The reason for that can be that the film that is formed is dispersed in the sub-phase. This would explain the low surface pressure obtained in the Langmuir isotherms and the very low measured mass in the QCM results.

7.3.2QCM-Langmuir Experiment with a Mixture of Monoacid and BP-10 at pH 7 with Calcium Present

In this part the presence of a mixture of BP-10 and a model monoacid (4-Octylbenzoic acid) was investigated on the quantitative aspects of the QCM-Langmuir method. Monoacid (1.67 g/L) and BP-1(1.23 g/L) was mixed together and 45µl of the mixture was injected on to the sub-phase at pH 7 containing calcium. The results obtained are listed in table 9.

Table 9: QCM result for BP-10+ monoacid mix experiments at pH 7 with calcium present.

Sample	Added amount of BP-10 (mg/m^2)	Added amount of Monoacid (mg/m^2)	Measured amount (mg/m^2)
1	4.78	6.56	4.09
2	4.78	6.56	4.15

By comparing the measured amount with the added amount of each component one can determine which component that is deposited on the crystal. As the result in table 9 shows, it is likely that it was BP-10 that deposited onto the crystal. The isotherms obtained from the experiments also reflect that the BP-10 dominated the reaction at the interface. Figure 29 shows the isotherms obtained. The mean molecular area used for the isotherms are based on the BP-10 concentration.

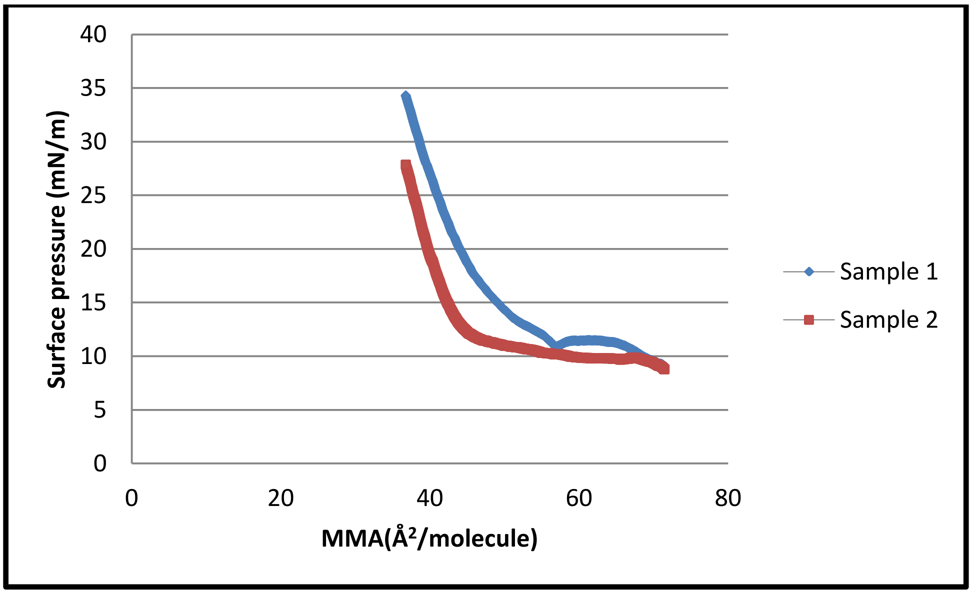


Figure 29: Langmuir isotherms for experiments with BP-10 + monoacid mixture at pH 7.

The reproducibility of the Langmuir experiment was fair, but the QCM results on the other hand showed very good reproducibility. The isotherms obtained from the experiments had similar behaviour as the isotherms with only BP-10 at pH 7. During spreading the samples also had more similar behaviour as for the pure BP-10 solutions. The surface pressure started high when injecting the sample then decreased afterwards but not down to zero as for the pure monoacid samples.

One of the isotherms from the experiment with pure BP-10 solution (1.23 g/L, 45µl), the isotherm for pure monoacid solution (1.23 g/L, 45µl), and one of the isotherms from the experiments with the mixed sample are compared in figure 30. Since there are different solutions involved the isotherms are presented as surface pressure versus trough area instead of mean molecular area.

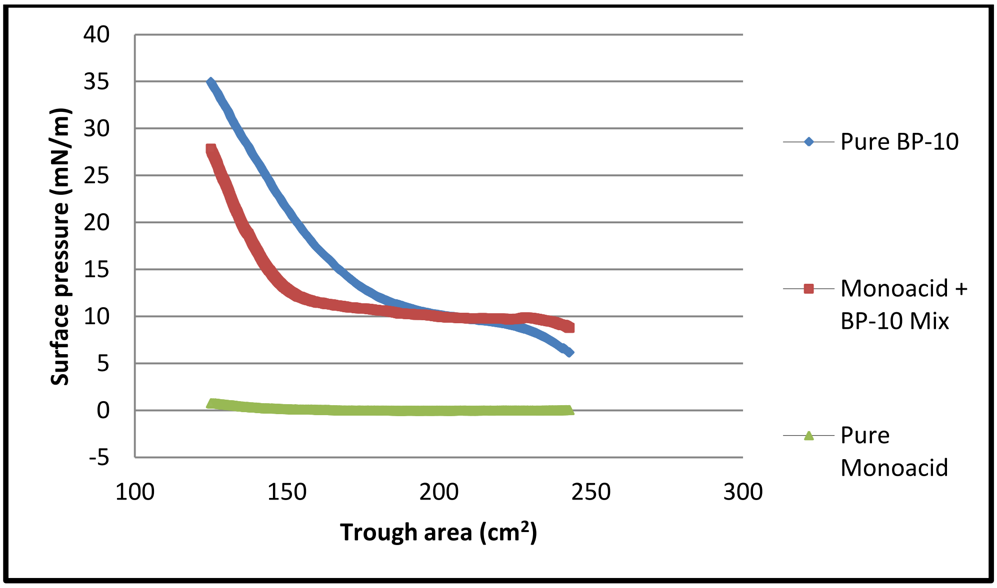


Figure 30: Comparison of Langmuir isotherms obtained for experiments with only BP-10, only monoacid, and BP-10 + monoacid mixture.

The surface pressure increased slower for the mixed sample, and did not reach the same surface pressure at the end of compression as the isotherm for the pure BP-10 solution did. As mentioned previously in chapter 3.4 it is believed that monoacid can work as a natural inhibitor for calcium naphthenate formation. It is believed that the monoacid placed itself between the BP-10 molecules at the interface, slowing down or trying to terminate the cross-linking between the BP-10 and calcium, thus effecting the film formation. From the experiments performed with the mixture of BP-10 and monoacid it was clear that the mixture formed a film at the interface. From the experimental point of view it could look like the monoacid concentration in the sample were too small to terminate the cross-linking.

8. Conclusions

The QCM-Langmuir method showed promising result. The relationship between the measured amounts and the added amounts showed a linear trend for spreading amounts lower than 6 mg/m^2 for the experiments performed at gel forming conditions and for spreading amounts lower than 7 mg/m^2 for non gelling conditions. However, since the results showed large variation between measured amounts and added amounts for higher spreading amounts there is a need for improvement of the method before the method can be used for determination of the mass for unknown samples.

The Langmuir experiments showed poor reproducibility but from the QCM results it is clear that the reproducibility of the Langmuir experiments did not influence the measured surface coverage. The QCM results showed good reproducibility and stable results with low uncertainties. The errors caused by the differences in the added amounts and the measured amounts are therefore most likely from errors from other parts of the procedure and not only form the QCM measurements.

The results obtained from experiments with monoacid showed that the monoacid was unable to deposit onto the crystal. From observations from the Langmuir experiments it seems like the monoacid was dispersed in the water-phase giving low surface pressure during compression and thus no deposition onto the crystal.

Experiments with a mixture of BP-10 and monoacid showed that most likely only BP-10 deposited onto the crystal. The theory is further proved by comparing the Langmuir isotherms obtained from the experiments with pure monoacid solution, pure BP-10 solution and the isotherm obtained from the experiments with the mixed sample.

9. References

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10. Appendices

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Appendix 3: QCM Results for Experiments at pH 7

Table 10: QCM results for each overtone and their uncertainties of the experiments conducted at pH 7

Sample Nr.	Added amount (mg/m^2)	Overtone	Measured amount (mg/m^2)	Uncertainties (mg/m^2)
1	1.06	1	1.107	0.112
		3	1.560	0.069
		5	1.599	0.073
		7	1.611	0.078
2	1.06	1	1.182	0.077
		3	1.450	0.037
		5	1.323	0.049
		7	2.246	0.054
3	2.08	1	1.089	0.108
		3	1.839	0.060
		5	1.942	0.088
		7	1.968	0.076
4	2.16	1	1.005	0.068
		3	1.606	0.047
		5	1.690	0.054
		7	1.683	0.058
5	2.16	1	1.164	0.027
		3	1.643	0.026
		5	1.660	0.012
		7	1.698	0.013

Sample Nr.	**Added amount (mg/m^2)**	**Overtone**	**Measured amount (mg/m^2)**	**Uncertainties (mg/m^2)**
6	3.18	1	3.348	0.114
		3	3.338	0.081
		5	3.386	0.088
		7	3.378	0.074
7	3.19	1	3.853	0.163
		3	4.515	0.088
		5	4.662	0.099
		7	4.700	0.096
8	4.78	1	3.537	0.307
		3	3.450	0.072
		5	3.355	0.096
		7	3.033	0.114
9	4.78	1	7.274	0.347
		3	7.760	0.258
		5	7.894	0.269
		7	7.905	0.258
10	4.80	1	7.457	0.099
		3	6.782	0.069
		5	6.308	0.072
		7	6.309	0.070
11	4.78	1	5.717	0.190
		3	7.412	0.154
		5	8.062	0.174
		7	8.650	0.163
12	6.39	1	3.617	0.152
		3	4.127	0.135
		5	4.138	0.137
		7	4.107	0.134
13	6.36	1	3.424	0.188
		3	4.026	0.120
		5	4.050	0.144
		7	4.044	0.130
14	8.48	1	4.277	0.183
		3	4.097	0.046
		5	4.192	0.045
		7	4.300	0.050
15	8.52	1	15.730	0.188
		3	12.632	0.051
		5	11.355	0.051
		7	10.411	0.052

Appendix 4: Isotherms for Experiments at pH 7

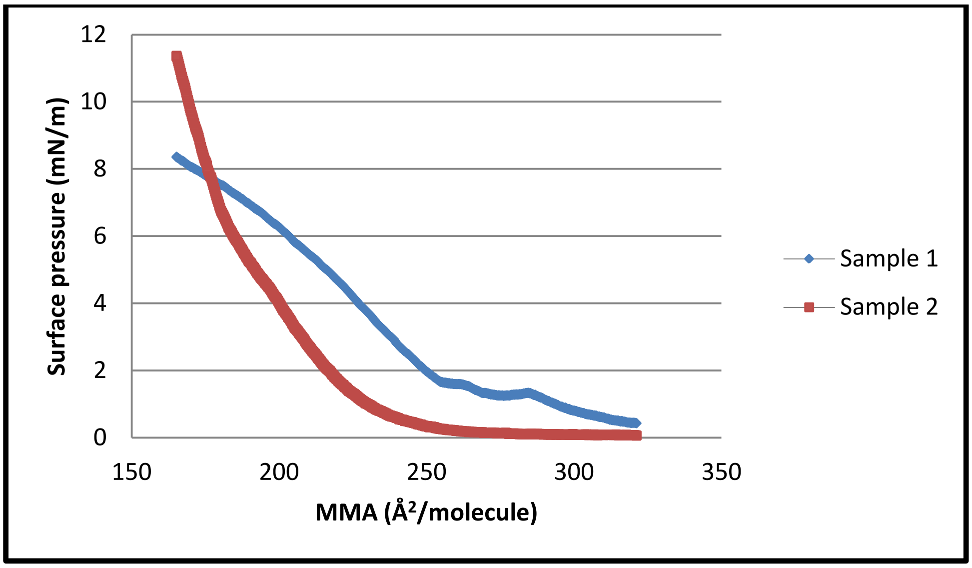


Figure 31: Langmuir isotherms for experiments when spreading 50 µl of BP-10 (0.26 g/L) onto a sub-phase with pH 7 and calcium present.

QCM results for each sample are listed in table 11.

Table 11: QCM results for experiments when spreading 50 µl of BP-10 (0.26 g/L) onto a sub-phase with pH 7 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	1.06	1.56
2	1.06	1.45

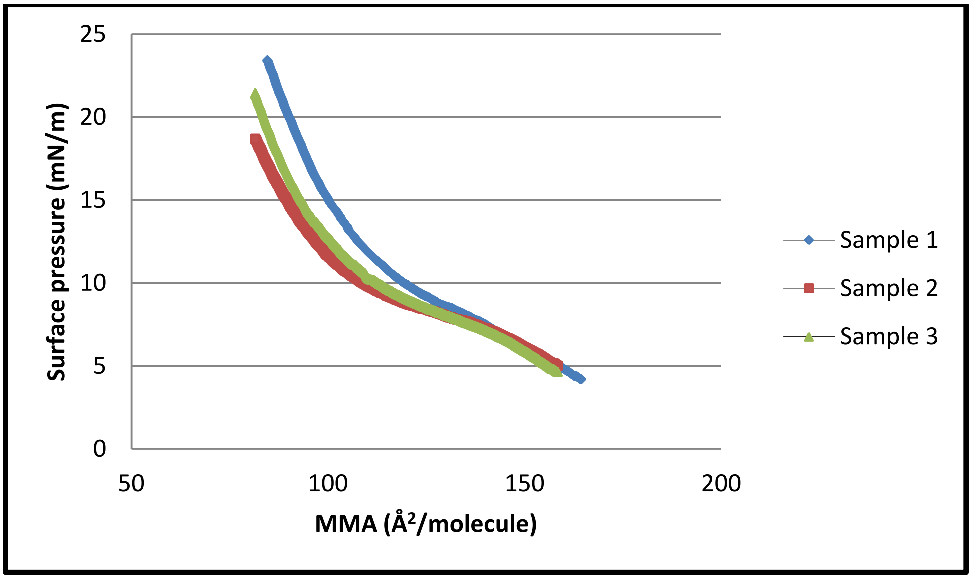


Figure 32: Langmuir isotherms for experiments when spreading 60 µl of BP-10 (0.42 g/L) onto a sub-phase with pH 7 and calcium present.

QCM results for each sample are listed in table 12.

Table 12: QCM results for experiments when spreading 60 µl of BP-10 (0.42 g/L) onto a sub-phase with pH 7 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	2.08	1.84
2	2.16	1.61
3	2.16	1.64

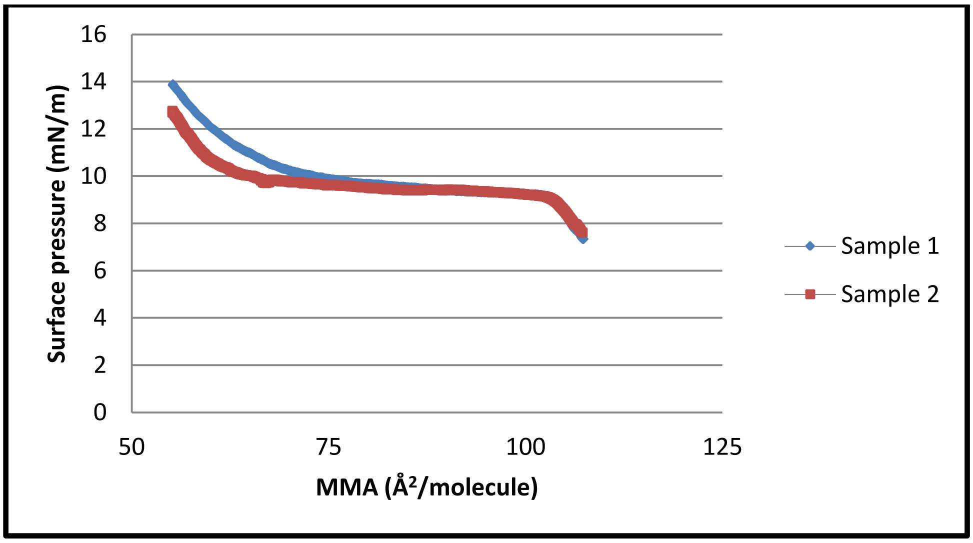


Figure 33: Langmuir isotherms for experiments when spreading 30 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

QCM results for each sample are listed in table 13.

Table 13: QCM results for experiments when spreading 30 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	3.18	3.34
2	3.19	4.52

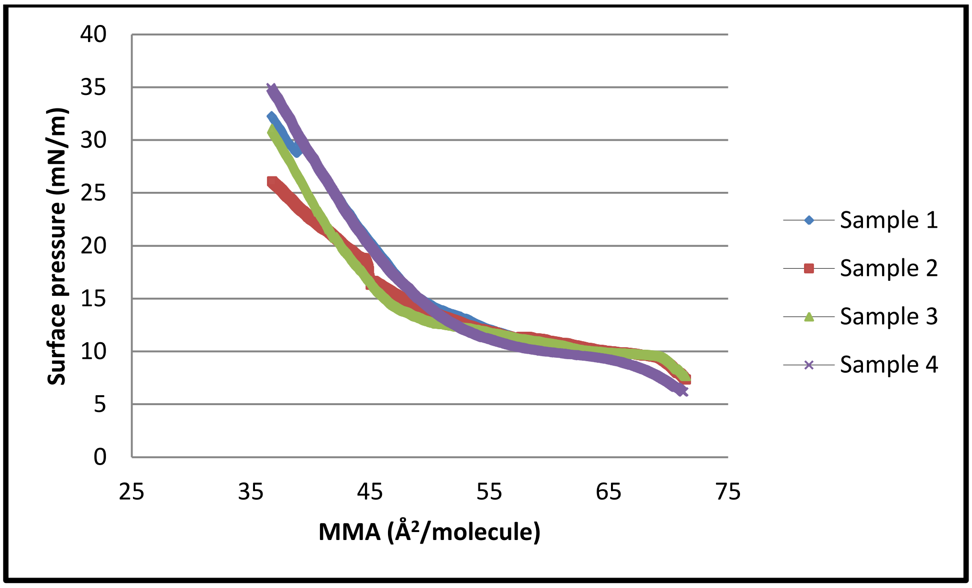


Figure 34: Langmuir isotherms for experiments when spreading 45 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

The QCM results for each sample are listed in table 14.

Table 14: QCM- results for experiments when spreading 45 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present

Sample	**Added amount (mg/m^2)**	**Measured amount (mg/m^2)**
1	4.78	3.45
2	4.78	7.76
3	4.78	7.41
4	4.79	6.78

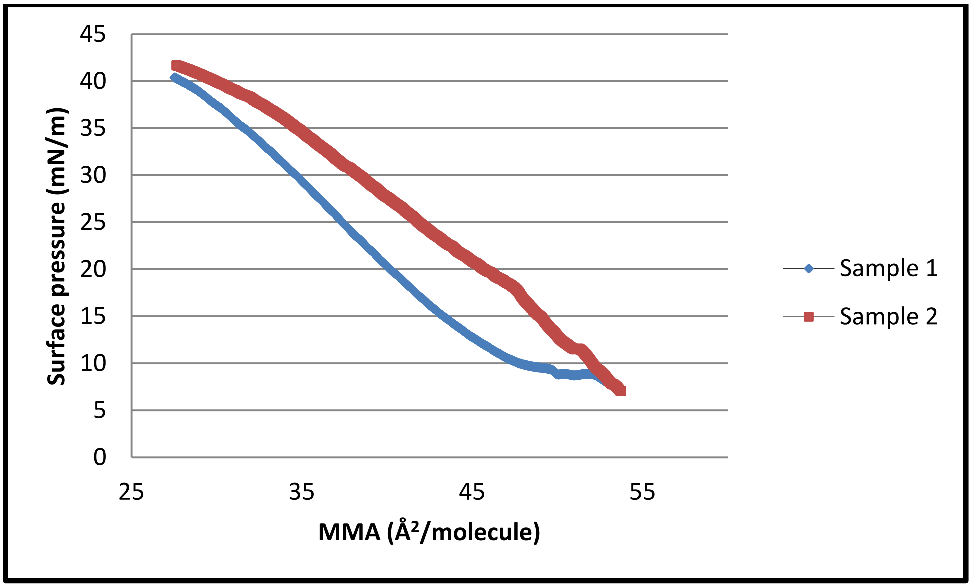


Figure 35: Langmuir isotherms for experiments when spreading 60 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

The QCM results for each sample are listed in table 15.

Table 15: QCM results for experiments when spreading 60 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	6.39	4.13
2	6.36	4.03

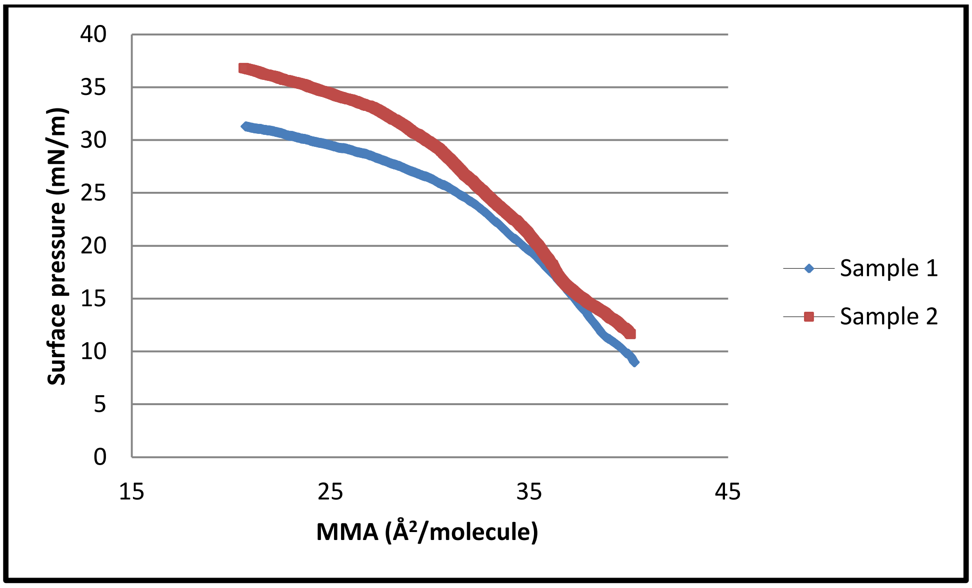


Figure 36: Langmuir isotherms for experiments when spreading 80 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present.

The QCM results for each sample are listed in table 16.

Table 16: QCM results for experiments when spreading 80 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 7 and calcium present

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	8.48	4.10
2	8.52	12.63

Appendix 5: QCM Results for Experiments at pH 5

Table 17: QCM results for each overtone and their uncertainties of the experiments conducted at pH 5

Sample nr.	Added amount (mg/m^2)	Overtone	Measured amount (mg/m^2)	Uncertainties (mg/m^2)
1	0	1	0.60	0.09
		3	0.87	0.05
		5	0.84	0.05
		7	0.88	0.05
2	0	1	0.65	0.11
		3	0.76	0.03
		5	0.71	0.03
		7	0.70	0.04
3	1.0	1	0.55	0.09
		3	0.92	0.03
		5	0.85	0.02
		7	0.90	0.04
4	0.99	1	0.33	0.07
		3	0.48	0.08
		5	0.53	0.10
		7	0.38	0.09
5	1.99	1	1.10	0.15
		3	1.85	0.09
		5	1.80	0.10
		7	1.76	0.09
6	1.97	1	3.03	0.10
		3	3.00	0.04
		5	1.91	0.02
		7	2.84	0.03
7	3.94	1	2.77	0.16
		3	3.70	0.07
		5	3.72	0.07
		7	3.80	0.06
8	3.94	1	2.67	0.12
		3	2.80	0.07
		5	2.71	0.08
		7	2.63	0.07

Sample nr.	**Added amount (mg/m^2)**	**Overtone**	**Measured amount (mg/m^2)**	**Uncertainties (mg/m^2)**
9	6.92	1	3.92	0.10
		3	4.18	0.01
		5	4.14	0.03
		7	4.11	0.03
10	6.91	1	6.91	0.27
		3	6.34	0.09
		5	5.89	0.05
		7	5.28	0.05
11	9.89	1	6.55	0.13
		3	7.06	0.09
		5	7.17	0.09
		7	7.21	0.09
12	9.89	1	7.23	0.09
		3	7.59	0.06
		5	7.45	0.09
		7	7.28	0.08
13	11.96	1	6.73	0.12
		3	6.71	0.07
		5	6.54	0.07
		7	6.59	0.08
14	12.05	1	8.08	0.08
		3	8.84	0.04
		5	8.78	0.04
		7	8.77	0.04

Appendix 6: Isotherms for Experiments at pH 5

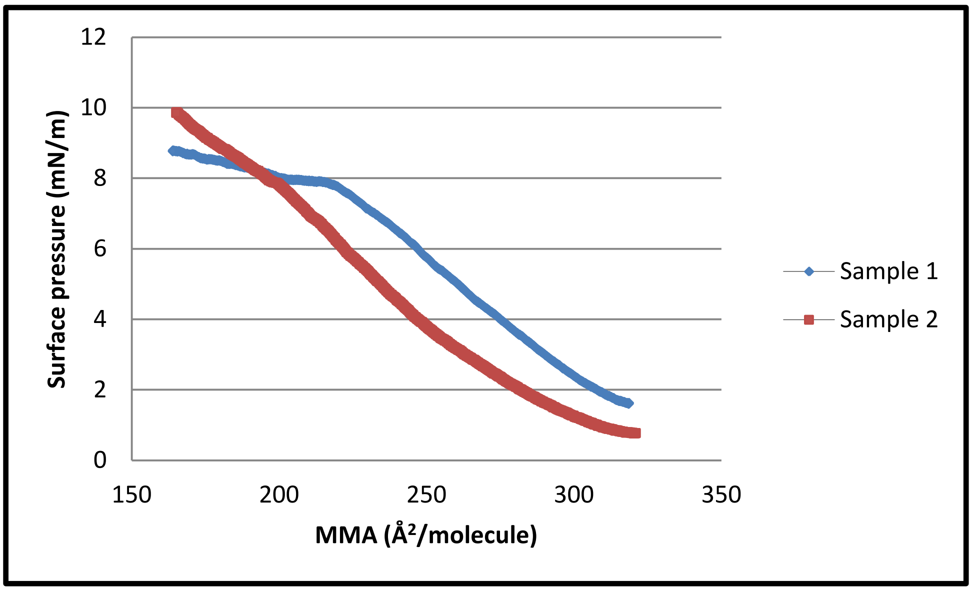


Figure 37: Langmuir isotherms for experiments when spreading 50 µl of BP-10 (0.25 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 18.

Table 18: QCM results for experiments when spreading 50 µl of BP-10 (0.25 g/L) onto a sub-phase with pH 5 and calcium present

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	1.0	0.92
2	0.99	0.48

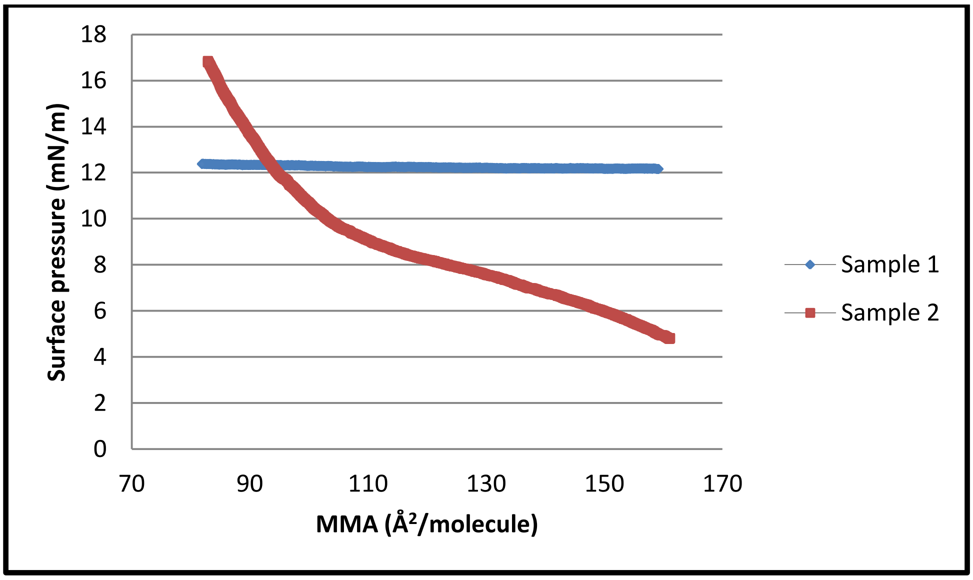


Figure 38: Langmuir isotherm for experiments when spreading for sample 1, 60 µl of BP-10 (0.42 g/L) and for sample 2, 50µl of BP-10 (0.49 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 19.

Table 19: QCM results for experiments when spreading for sample 1, 60 µl of BP-10 (0.42 g/L) and for sample 2, 50µl of BP-10 (0.49 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	**Added amount (mg/m^2)**	**Measured amount (mg/m^2)**
1	1.99	1.85
2	1.97	3.0

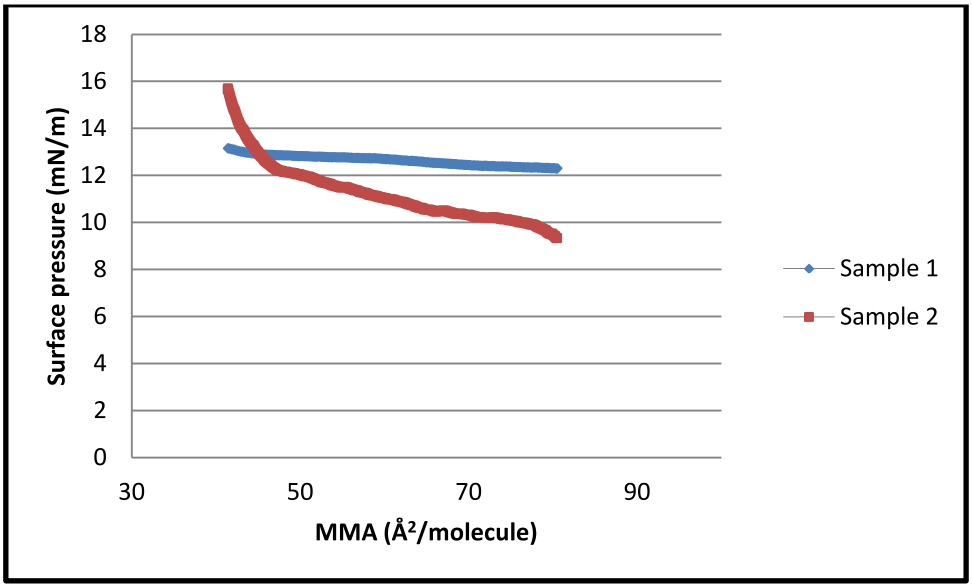


Figure 39: Langmuir isotherm for experiments when spreading 40 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 20.

Table 20: QCM results for experiments when spreading 40 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	3.94	3.70
2	3.94	2.80

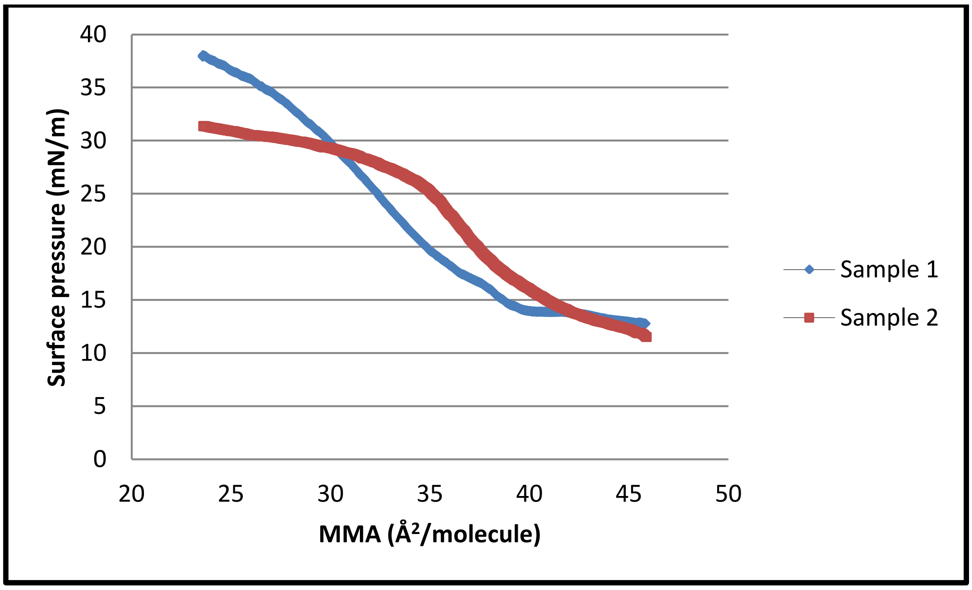


Figure 40: Langmuir isotherms for experiments when spreading 70 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 21.

Table 21: QCM results for experiments when spreading 70 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	6.92	4.18
2	6.91	6.34

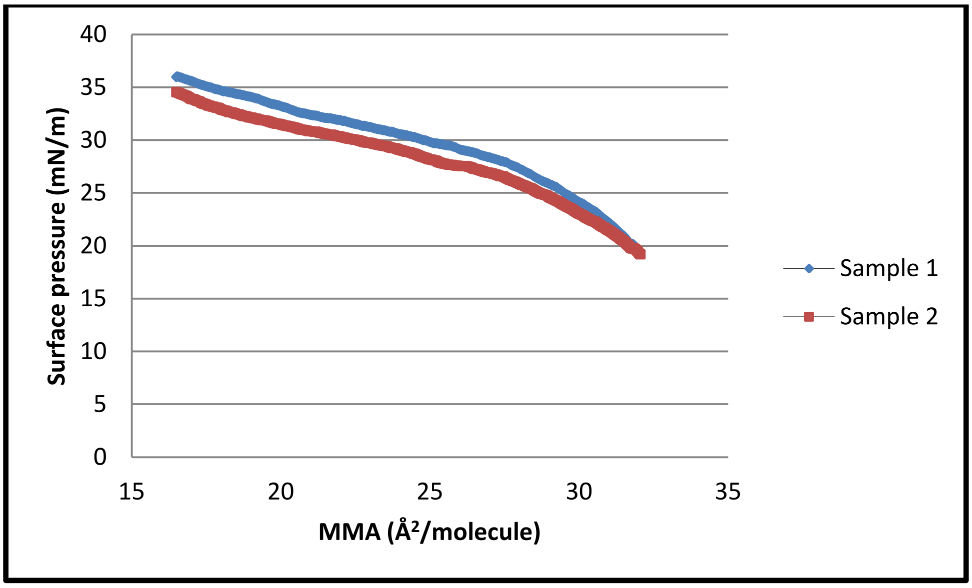


Figure 41: Langmuir isotherms for experiments when spreading 100 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 22.

Table 22: QCM results for experiments when spreading 100 µl of BP-10 (1.23 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	Added amount (mg/m^2)	Measured amount (mg/m^2)
1	9.89	7.06
2	9.89	7.59

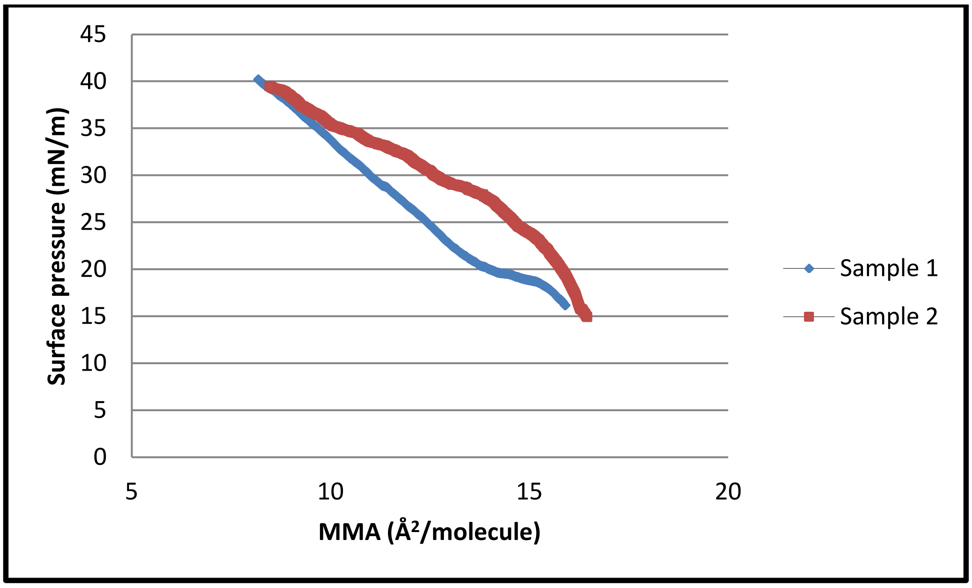


Figure 42: Langmuir isotherms for experiments when spreading for sample 1, 72 µl of BP-10 (2.08 g/L) and for sample 2, 75µl of BP-10 (2.0 g/L) onto a sub-phase with pH 5 and calcium present.

The QCM results for each sample are listed in table 23.

Table 23: QCM results for experiments when spreading for sample 1, 72 µl of BP-10 (2.08 g/L) and for sample 2, 75µl of BP-10 (2.0 g/L) onto a sub-phase with pH 5 and calcium present.

Sample	**Added amount (mg/m^2)**	**Measured amount (mg/m^2)**
1	11.96	6.71
2	12.05	8.84

Appendix 7: QCM Results for Experiments with Pure Monoacid Solution and Experiments with BP-10 + Monoacid Solution

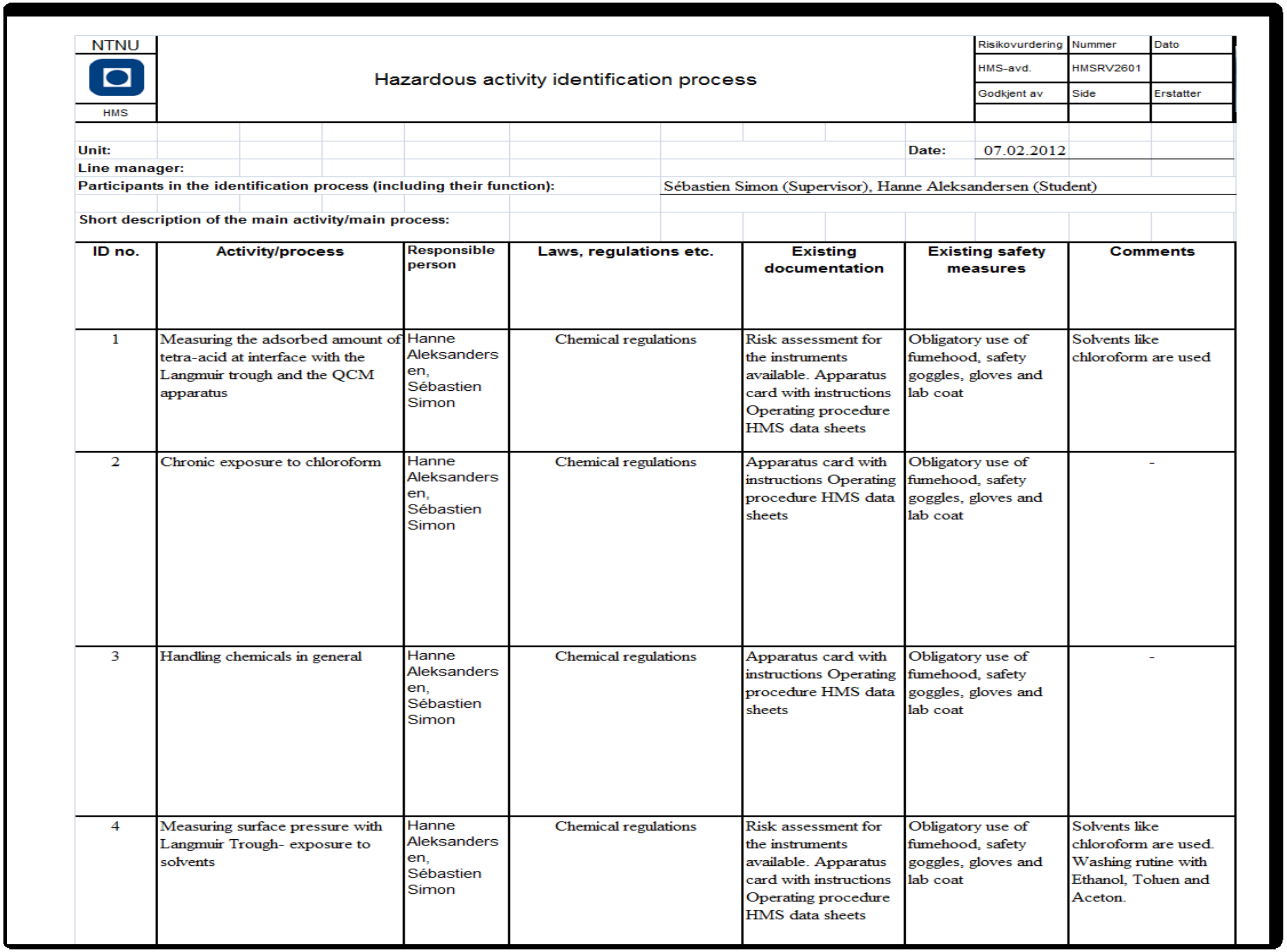
Table 24: QCM results for each overtone and their uncertainties for experiments with pure monoacid solution at pH 7 with calcium present

Sample	Added amount (mg/m^2)	Overtone	Measured amount (mg/m^2)	Uncertainties (mg/m^2)
1	4.93	1	0.57	0.19
		3	0.37	0.04
		5	0.39	0.03
		7	0.39	0.04
2	10.69	1	0.59	0.12
		3	0.71	0.08
		5	0.71	0.07
		7	0.77	0.07

Table 25: QCM results for each overtone and their uncertainties for experiments with BP-10 + monoacid mix at pH 7 with calcium present

Sample	Added amount of BP-10 (mg/m^2)	Added amount of monoacid (mg/m^2)	Overtone	Measured amount (mg/m^2)	Uncertainties (mg/m^2)
1	4.78	6.56	1	3.75	0.10
			3	4.09	0.03
			5	4.07	0.02
			7	4.04	0.03
2	4.78	6.56	1	3.54	0.07
			3	4.15	0.04
			5	3.18	0.05
			7	3.57	0.05

Appendix 8: Risk Assesment



NTNU HMS	Hazardous activity identification process	Risikovurdering HMS-avd. Godkjent av	Nummer HMSRV2601 Side

Dato

Erstatter

Unit:

Date: 07.02.2012

Line manager:

Participants in the identification process (including their function): Sébastien Simon (Supervisor), Hanne Aleksandersen (Student)

Short description of the main activity/main process:

ID no.	Activity/process	Responsible person	Laws, regulations etc.	Existing documentation	Existing safety measures	Comments
1	Measuring the adsorbed amount of tetra-acid at interface with the Langmuir trough and the QCM apparatus	Hanne Aleksandersen, Sébastien Simon	Chemical regulations	Risk assessment for the instruments available. Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	Solvents like chloroform are used
2	Chronic exposure to chloroform	Hanne Aleksandersen, Sébastien Simon	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
3	Handling chemicals in general	Hanne Aleksandersen, Sébastien Simon	Chemical regulations	Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	-
4	Measuring surface pressure with Langmuir Trough- exposure to solvents	Hanne Aleksandersen, Sébastien Simon	Chemical regulations	Risk assessment for the instruments available. Apparatus card with instructions Operating procedure HMS data sheets	Obligatory use of fumehood, safety goggles, gloves and lab coat	Solvents like chloroform are used. Washing rutine with Ethanol, Toluen and Aceton.

NTNU HMS /KS	Risk assessment	Utarbeidet av HMS-avd.	Nummer HMSRV2603	Dato 04.02.2011
		Godkjent av	Side	Erstatter

Unit: **Date:** 20.01.2012

Line manager:

Participants in the identification process (including their function): *Sébastien Simon (Supervisor), Hanne Aleksandersen (Student)*

Signatures:

ID no.	Activity from the identification process form	Potential undesirable incident/strain	Likelihood:	Consequence:				Risk value	Comments/status Suggested measures
			Likelihood (1-5)	Human (A-E)	Environment (A-E)	Economy/ material (A-E)	Reputation (A-E)	Human	
1	Measuring the adsorbed amount of tetra-acid at interface with the Langmuir trough and the QCM apparatus	Exposure to solvents	1	C	B			1C	Portable fumehood is available. Use of labcoat, gloves and goggles is obligatory.
2	Chronic exposure to chloroform	Copied from MSDS-datasheet (Sigma-Aldrich): danger of serious damage to health by prolonged exposure through inhalation and if swallowed. Limited evidence of a carcinogenic effect.	2	C	B			2C	Status: Used in fumehood or below Extraction hood. Obligatory use of nitrile gloves and safety goggles and lab coat. Transport waste in closed container. Ventilation half-mask available (get it from Arne Fossum, basement K5)
3	Handling chemicals in general	Samples without any markings are left behind: Harmful inhalation, skin damage or even explosion when handling waste of unknown origin.	1	C	B			1C	Samples are marked according to special routines: date, name, expiration date, name of chemical, label denoting the toxicity.
4	Measuring surface pressure with Langmuir Trough- exposure to solvents	Exposure to solvents	2	C	B				Avoid spillage